9th International Conference on Gas Geochemistry

Program Proceeding

Taipei, Taiwan 1-8 October, 2007
9th International Conference on Gas Geochemistry

ICGG 9

Taipei, Taiwan
October 1-8, 2007

Organized by
Department of Geosciences, National Taiwan University (NTU)
9th International Conference on Gas Geochemistry
Taiwan, October 1-8, 2007

Organized by Department of Geosciences, National Taiwan University (NTU)

Co-organized by:
- Institute of Earth Sciences, Academia Sinica
- Research Center for Environmental Changes (RCEC), Academia Sinica
- Chinese Petroleum Corporation (CPC)
- National Center for Research on Earthquake Engineering (NCREE), NARL
- Central Geological Survey, MOEA
- Department of Chemistry, National Central University (NCU)
- Department of Earth Sciences, National Chen Kung University (NCKU)
- Geological Society located in Taipei
- Chinese Geoscience Union
- Energy and Environment Research Laboratories, Industrial of Technology Research Institute (ITRI)
- Yangmingshan National Park Headquarters

Sponsored by National Science Council

International Committee:
- Armienta, M.A. (Mexico)
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- Barnet, I. (Czech Republic)
- Baciu, C. (Romania)
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- Chyi, L.L. (USA)
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- Heinicke, J. (Germany)
- Italiano, F. (Italy)
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- Taran, Y. (Mexico)
- Waseda, A. (Japan)
- Woith, H. (Germany)
- Yang, T.F. (Taiwan)
Organizer:

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Local Organizing Committee:

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Edited by

Pei-Chuan Chuang, Wei-Li Hong, Ling Chung, and Tsanyao Frank Yang
General Information

Schedule for 9th ICGG

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**Conference venue**
The College of Engineering Building, NTU.

**Guideline for presentation**

**Oral Presentation**
Except for the first keynote address, the presentation time for each invited speaker is 30 minutes; rest of all speakers is 20 minutes (all including 5 min discussion) for oral sessions. There is only one screen in the conference hall. No overhead projector will be provided. The speakers need to prepare their slides in the format of Microsoft PowerPoint file.

**Poster Presentation**
The frame size for poster display is 150cm (width) x 90cm (height). All presenting authors of poster sessions are requested to present their work briefly for 3-5 minutes at the beginning of scheduled poster sessions before moving to the poster place for further discussion. In addition to the poster, therefore, the authors need to prepare 3-5 slides in the format of Microsoft PowerPoint file too.

To encourage the young scientists to join this society, the organizing committee decided to arrange a special session for young scientists. It will include all enrolled students and young post-doc researchers. The best paper(s) will be selected by referees, and awarded in the general assembly.

**Special issues as conference proceedings**
We are contacting some publishers for potential publication of selected papers as conference volume(s) in international SCI journal(s). The submission deadline of the full papers is December 31, 2007. Detailed requirements for preparation of the manuscripts will be given in future correspondence.
**Registration Desk**

The registration and information desk will open from 08:30 to 17:00 during the conference time (October 1-5) at the conference venue.

**Lunch**

During the conference, lunch boxes will be provided for all participants (10/1-10/5).

**Ice Breaker**

The ICGG9 ice breaker will take place at 18:00-20:30 of Sunday, 30 September, 2007, at the Doutor coffee shop of Lu-ming Hall. Registration desk will open there from 17:00 to 20:30.

**Welcome Reception**

The ICGG9 welcome reception for all participants will be held in the evening of Monday, 1 October, 2007, at the restaurant inside the Lu-ming Hall, NTU.

**Banquet**

All participants are invited to join the ICGG9 Banquet held in the evening of Thursday, 4 October, 2007, at Chinese Dining Room of the Grand Hotel. We will arrange shuttle buses to the restaurant as well as back to the hotel. The buses will leave at 17:40 from the main gate of NTU campus.

**City Tour**

The organizing committee is arranging a half-day city tour for all participants in the afternoon of October 5 to visit some must-go spots in Taipei city. We will visit the most famous Palace Museum, Taipei 101 and Longshan Temple, and will leave some time for you to taste the delicious local food. The buses will leave at 13:10 from the main gate of NTU campus and come back hotels around 21:00.

**Field Excursion**

Following the five-day program (October 1-5, 2007), a three-day field trip (October 6-8, 2007) is organized to visit the hydrothermal areas in northern Taiwan, Petroleum museum of Chinese Petroleum Company, earthquake museum and fault scarps in central Taiwan, and mud volcanoes/seepages along active fault zones in southwestern Taiwan.

October 6 (Saturday): Taipei → Yangmingshan National Park (active hydrothermal areas) → Shihkan Dam (fault scarps) → Earthquake museum and fault carps → stay at Chiayi (southwestern Taiwan)

October 7 (Sunday): Chiayi → Chung-lun mud pool → Sui-ho-tong-yuan everlasting fire on water → Kuan-tze-ling mudding hot springs → Chia-sian carbonate outcrop of cold seep deposits in mudstones → stay at Tainan (southern Taiwan)

October 8 (Monday): Tainan → Wu-shan-ting mud volcano, and nearby mud volcanoes → CPC Taiwan Petroleum Exhibition Hall → arrive Taipei around 18:00.
9th International Conference on Gas Geochemistry
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September 30, 2007 (Sunday)

17:00-20:30 Registration
18:00-20:30 Ice Breaker
9th International Conference on Gas Geochemistry  
Taiwan, October 1-8, 2007  

October 1, 2007 (Monday)

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**Keynote address-1**  
**Chairperson**: Jahn, B. M.  

09:20-10:00: ICGG9A038  
**Ozima, M.**, Yin, Q. Z., Podosek, F. A. and Miura, Y.  
*Earth Evolution Recorded in Noble Gases and Volatiles in the Moon*

10:00-10:40: Group photo-1 and break

**Keynote address-2**  
**Chairperson**: Chen, C. H.  

10:40-11:10: ICGG9A083  
**Marty, B.**, Coltice, N. and Meibom, A.  
*Noble Gas Sources and Fluxes in the Hadean*

11:10-11:40: ICGG9A082  
**Kurz, M. D.** and Curtice, J.  
*Residence Sites of Noble Gases in Basalt Glasses and Peridotites: Implications for Partitioning and Gas Migration*

11:40-12:10: ICGG9A101  
**Huang, W. L.**  
*Oil and Gas Generation and Expulsion: Seeing is Believing*

12:10-13:20: Lunch
Oral session-1
Chairperson: Italiano, F.

Lee, J. K. W.
Using Argon as a Temporal Tracer of Large-Scale Geologic Processes

13:50-14:10 : ICGG9A043
Yang, T. F.
Natural Analogue of Long-term CO$_2$ Storage in the Sedimentary Formation of Western Taiwan

14:10-14:30 : ICGG9A051
Woith, H., Gajewski, C., Steinitz, G., Malik, U. and Piatibratov, O.
Cyclical and Transient Radon Variations at the Tiberias Hot Spring, Israel

14:30-14:50 : ICGG9A093
Soil-Gas Monitoring: A Tool for Fault Delineation Studies along Hsinhua Fault (Tainan), Southern Taiwan

14:50-15:10 : ICGG9A018
Das, N. K., Bhandari, R. K., Sen, P. and Sinha, B.
Scaling and Crossover Phenomena in Anomalous Helium Sequence

15:10-15:30 Break

Oral session-2
Chairperson: Hilton, D.

15:30-16:00 : ICGG9A065 Invited
Taran, Y.
Problems in Interpretation of Nitrogen and Argon Data for Volcanic and Hydrothermal Gases

16:00-16:20 : ICGG9A029
Polyak, B.G.
Mantle Helium Traces around Elbrus and Kazbek Volcanoes (Northern Caucasus)

16:20-16:40 : ICGG9A041
Ohba, T., Sawa, T., Taira, N., Yang, T. F., Lee, H. F., Lan, T. F., Ohwada, M., Morikawa, N. and Kazahaya, K.
CO$_2$/H$_2$O Ratio of Magmatic Gas Estimated from the Analysis of Fumarolic Gas Sampled at Tatun Volcano Group, Taiwan

16:40-17:00 : ICGG9A016
Pflanz, H.
Geogenic CO$_2$-Exhalations and Vegetation – Mofette Plants

18:30-20:00 Welcome Reception
Oral session-3
Chairperson: Notsu, K.

08:30-09:00 : ICGG9A012 Invited
Helium Isotope Studies in Regions of Crustal Unrest: the San Andreas Fault Zone, California and the North Anatolian Fault Zone, Turkey

09:00-09:20 : ICGG9A066
Yuce, G., Streil, T., Nadar, N., Yalcin, T., Yaltirak, C., Oeser, V. and Ugurluoglu, Y. D.
Multi Parameter Hydrogeological Monitoring in Eskisehir Region (Turkey) to Analyze any Precursors Derived from Earthquakes

09:20-09:40 : ICGG9A074
Balderer, W. and Leuenberger, F.
Detection of Sensitive Compounds in Groundwater with Observed Enhanced Fluorescence Spectra from Earthquake Prone Areas: First Results

09:40-10:00 : ICGG9A032
Heinicke, J., Martinelli, G. and Telesca, L.
A 1000 m Water Well as a Test Monitoring System for the Detection of Possible Earthquake Related Anomalies in Fluids

10:00-10:20 : ICGG9A089
Gas Compositions and He-C Isotopic Ratios of Fumarolic Samples from Some Active Volcanoes in Philippines

10:20-10:40 Break
Oral session-4
Chairperson: Balderer, W.

10:40-11:00: ICGG9A002
Kant, K., and Chakarvarti, S. K.
Alpha Active Pollutants as a Precursor of Seismic Activity: A Review

11:00-11:20: ICGG9A039
Chyi, L. L., Quick, T. J., Yang, T. F. and Chen, C. H.
Origin and Detection of Spike-Like Anomalies in Soil Gas Radon Time Series

11:20-11:40: ICGG9A020
Fan, K. C., Kuo, M. C. T., Lin, C. Y., Han, Y. L. and Tsai, C. L.
Anomalous Decreases in Groundwater Radon Precursory to Earthquakes in Eastern Taiwan

11:40-12:00: ICGG9A003
Ramola, R. C.
Subsurface Changes in Radon Concentration Associated with Earthquake Activity in Garhwal Himalaya

12:00-12:20: ICGG9A037
Negarestani, A.
A New Approach Based on Electrical Circuit Model for Using of Time Variation of Radon Concentration in Earth as an Earthquake Precursor

12:20-13:30 Lunch

Oral session-5
Chairperson: Zellme, G.

13:30-14:00: ICGG9A071 Invited
Notsu, K., and Mori, T.
Chemical Monitoring of Volcanic Gas Using Remote FT-IR Spectroscopy at Several Active Volcanoes in Japan

14:00-14:20: ICGG9A011
Singh, R. P., Kumar J. S. and Prasad, A. K.
Satellite Detection of Carbon Monoxide Emission Prior to Earthquakes and Volcanoes

14:20-14:40: ICGG9A080
Sano, Y., Takahata, N. and Yamamoto, J.
High $^3$He Emanation Observed in a Forearc Region of the Kinki district, SW Japan: Revisited
14:40-15:00: ICGG9A004
Koch, U., Heinicke, J., Bräuer, K. and Kämpf, H.
The Gas Flow at Mineral Springs and Mofettes in the Vogtland/NW Bohemia: An Enduring Long-term Uptrend

15:00-15:20: ICGG9A026
Barragán, R. M., Arellano, V. M., Portugal, E. and Segovia, N.
Major $^{222}$Rn Anomalies in Fluids of Los Azufres (México) Geothermal Field

15:20-15:40: Break

Oral session-6
Chairperson: Chalupnik, S.

15:40-16:00: ICGG9A103
Choubey, V. M., Bartarya, S. K. and Ramola, R. C.
Effect of Hydrogeology and Monsoon on Radon Concentrations in Groundwater of Intermountain Basin of Outer Himalaya

16:00-16:20: ICGG9A013
He, J., Bin, X. and Pin, Y.
Migration and Accumulation Characteristics and Potential of Multi-Origin Inorganic CO$_2$ in the Ying-Qiong Basin, the South China Sea

16:20-16:40: ICGG9A088
Lan, T. F., Yang, T. F., Lee, H. F., Fu, C. C. and Sano, Y.
Invasion of Mantle-Derived Fluids into I-Lan Plain, NE Taiwan from Southwest Part of The Okinawa Trough: Evidence of Helium Isotopes In Soil Gases

16:40-17:00: ICGG9A106
Takai, K., Kumagai, H., Suzuki, K., Inagaki, F. and Nakamura, K.
Extremely H$_2$-rich Hydrothermal Fluids Feed a Possible Successor of the Archean Microbial Ecosystem—Ultra-H$^+$ Hypothesis
Oral session-7
Chairperson : Heinicke, J.

08:30-09:00 : ICGG9A068 Invited
Etiope, G., Feyzullaiev, A. and Baciu, C. L.
Methane Seeps and Mud Volcanoes on Land: A Global Perspective of Gas Origin and Advective Fractionation

09:00-09:20 : ICGG9A019
Bräuer, K., Strauch, G. and Kämpf, H.
The Different Degassing Behaviour of Upper Mantle-Derived Fluids in the Western Eger Rift Area (Central Europe)

09:20-09:40 : ICGG9A058
Singh, S., Sharma, D. K., Dhar, S. and Kumar, A.
Tectonic Significance of Radon in the Frontal Himalayan Zones of Nurpur Area District Kangra, Himachal Pradesh, India

09:40-10:00 : ICGG9A086
Hong, W. L. and Yang, T. F.
Methane Flux from Accretionary Prism through Mud Volcano Area in Taiwan- From Present to the Past

10:00-10:20 : ICGG9A063
Geochemistry and Hydrocarbon Potential of Mud Volcanoes in Taiwan

10:20-10:40 Break

Oral session-8
Chairperson : Waseda, A.

10:40-11:10 : ICGG9A079 Invited
Italiano, F., Martinelli, G., Pizzullo, S. and Plescia, P.
Greenhouse Gases Released from the Apennine Chain, Italy: Mechanochemical Production Besides Mantle-Derived Contribution
11:10-11:30 : ICGG9A028
Duan, Z., Zhang, Z., Li, D. and Mao, S.
*Thermodynamic Models of Various Gases and Mixtures Covering a wide Temperature-Pressure-Composition Space*

11:30-11:50 : ICGG9A097
Lin, C. K.
*The Optimum Sequestration Depth for CO₂ Geo-sequestration*

11:50-12:10 : ICGG9A046
Zimmer, M. and Erzinger, J.
*Development and Application of a Gas Membrane Sensor for In-Situ Down Hole Observation of Gases During Geological Storage of Carbon Dioxide*

12:10-13:30     Lunch

*Oral session-9*
*Chairperson : Chi, W. R.*

13:30-13:50 : ICGG9A035
Waseda, A. and Iwano, H.
*Characterization of Natural Gases in Japan Based on Molecular and Carbon Isotope Compositions*

13:50-14:10 : ICGG9A044
Oung, J. N. and Lin, Z. Y.
*Geochemical Characteristics and Genetic Origin of Natural Gas Discovered in Taiwan*

14:10-14:30 : ICGG9A055
Wang, Y., Zhao, C., Wang, Zh., Wang, Ze. and Wang, H.
*Origins of Natural Gases from Marine Strata in Northeastern Sichuan Basin (China) by Molecular and Carbon Isotopic Data*

14:30-14:50 : ICGG9A024
Laier, T. and Nytoft, H. P.
*Gases with Abiogenic Signature in Association with Bitumen in Alkaline Rocks of the Ilimaussaq Intrusion, Greenland*

14:50-15:10 : ICGG9A105
Jean, J. S., Maity, J. P. and Liu, C. C.
*Biogeochemical Characterization of Kuan-Tzu-Ling Hot Spring in Southern Taiwan*

15:10-15:30     Break
15:30-17:10 : Poster session-1
Chairperson : Lin, L. H.

ICGG9A053 : Lu, H. and Ripmeester, J. A.
The Factors Affecting Gas Hydrate Formation in Natural Environment

ICGG9A034 : Wang, Y., Chen, D. F. and Song, Z.
Detecting Surface Oil Slick Related to Gas Hydrate/Petroleum on the Ocean Bed of South China Sea by ENVISAR Radar Data

ICGG9A014 : Song, Z., Zhong, Y. and Wang, C.
Characterizing Organic Matter in the Surface Sediments Associated with Gas Hydrate and Oil Seepage from the Gulf of Mexico

ICGG9A045 : Oung, J. N. and Chen, D. C.
Cutting Gas of Exploration Wells in Taiwan- Geochemical Characteristics and Implications in Hydrocarbon Generation

Occurrences and Isotopic Geochemistry of Natural Gases in Western Taiwan

ICGG9A115 : Yang, T. F., Yeh, G. H., Chuang, P. C., Hong, W. L., Chen, Y. G. and Chen, J. C.
Evolution of Mud volcanoes in the Accretionary Prism of Southern Taiwan: Constraints of Gas and Fluid Geochemistry

ICGG9A116 : Yang, T. F., Fu, C. C., Hong, W. L., Walia, V.
Radioactive Gas Emission from Mud Volcanoes in Taiwan

ICGG9A100 : Liu, T. K., Chen, K. Y., Ou, T. K. and Yang, T. F.
Origin of Methane in Aquifers under two Coastal Plains of Taiwan

REE Signature of Redox Variation and Microbiological Process Preserved in Seep Carbonate at Gas Vent Site

ICGG9A022 : Feng, D., Chen, D. F. and Roberts, H. H.
Sedimentary Fabrics in Seep Carbonates from Bush Hill: Implications for Biogeochemical and Microbiological Processes

18:00-20:00  Business Meeting of International Committee
08:30-10:30 : Young Scientists Poster Presentation-I
Chairpersons : Kies, A., Martinelli, G., Chyi, L. L. and Huang, W. L.

ICGG9A049 : Taira, N. and Hirabayashi, J.
The Effusion Mechanism of Onikobe Geyser (Japan) from Chemical and Isotopic Study

ICGG9A088 : Lan, T. F., Yang, T. F., Lee, H. F., Fu, C. C. and Sano, Y.
Invasion of Mantle-Derived Fluids into I-Lan Plain, NE Taiwan From Southwest Part of the Okinawa Trough: Evidence of Helium Isotopes in Soil Gases

Gas Compositions and He-C Isotopic Ratios of Fumarolic Samples from Some Active Volcanoes in Philippines

Temporal Variations of Gas Compositions of Fumaroles in the Tatun Volcano Group, Northern Taiwan

ICGG9A059 : Kumar, A., Mahajan, S., Bajwa, B. S., Walia, V., Dhar, S., Kochhar, N., Sonkawade R. G. and Singh S.
Geochemical Earthquake Precursor Studies in NW Himalayas, India

Soil Gas Investigation on the Tapingdi Fault in Northern Taiwan and the Continuous Monitoring Results

Evidences Support Nitrogen as Carrier Gas of Helium along Hsincheng Fault, NW Taiwan

Seasonal Variation of Radon Activity in Atmospheric Air - Nowa Ruda Area (Sudety Mts. SW Poland)

ICGG9A027 : Shen, J. C., Sun, C. H., Kuo, C. L., Su, K. H. and Huang, W. L.
Gas from Neogene Coals in the Northwestern Taiwan Region by Hydropyrolysis
ICGG9A084: Chuang, P.C., Yang, T.F., Hong, W.L., Lin, S., Shyu, C.T., Chen, J.C., and Wang, Y.  
Estimation of the Thickness of the Base of Hydrate Stability Zone in Offshore of SW Taiwan Based on Geochemical Data

ICGG9A086: Hong, W. L. and Yang, T. F.  
Methane Flux from Accretionary Prism through Mud Volcano Area in Taiwan- From Present to the Past

ICGG9A042: Maity, J. P., Liu, C. C. and Jean, J. S.  
Gas Biogeochemical Characterizations of Wu-Shan-Ding and Shiao-Kun-Shui Mud Volcanoes in Taiwan

Evaluating the Potential of Anaerobic Methane Oxidation in Terrestrial Mud Volcanoes of Southern Taiwan

Inventory of Metabolic Energy Deduced from Aqueous and Gas Geochemistry of Hot Springs in Northern Taiwan

ICGG9A031: Czuppon, G., Matsumoto, T. and Matsuda, J.  
Helium and Argon Isotopes Measured in Spinel Peridotite Xenoliths from Mt. Quincan, North Queensland, Northeast Australia

$^{40}$Ar/$^{39}$Ar Dating of the Jiali and Gaoligong Shear Zones and its Tectonic Implications to the Crustal Deformation Around the Eastern Himalaya Syntaxis

3-D Plane-fitting Program in $^{40}$Ar/$^{39}$Ar Dating

ICGG9A104: Das, J. P. and Murty, S. V. S.  
Presence of Insoluble Organic Matter in Chondrule Precursors

10:30-10:50 Break

10:50-12:10: Poster Presentation-2  
Chairperson: Baciu, C.

ICGG9A015: Jimsheladze, T., Machaidze, Z., Melikadze, G., Kobzev, G., Martinelli, G., Cenni, N. and Albarello, D.  
Multi-Parametrical Monitoring of Deep Seated Fluids for the Characterization of Medium-Short Term Transients in the Crustal Strain Field

ICGG9A054: Laskar, I., Goswami, A. K., Phukon, P., Chetry, G. and Roy, U. C.  
Correlation between Radon Anomaly with Meteorological Parameters and Earthquake

ICGG9A052: Negarestani, A., Nasari, F., Hashemi, M. S. and Kohestani, A.  
Continuous Radon Monitoring in the Hot Spring of Sirch as an Earthquake Precursor
Submarine Gas Flow Monitoring at Panarea Volcano, Italy

Plant Based Detection of Dry Mofettes – an Example from the Volcanic Laacher See District, Germany

Experimental Investigation of Mechanism of Hydrogen Generation in Hydrothermal Serpentinitization of Ultramafic Rocks

ICGG9A040: Matsumoto, T., Matsuda, J., Pinti, D. L. and Genty, D.  
Noble Gases in Stalagmite Inclusion Fluids: Preliminary results

ICGG9A010: Sato, K., Kumagai, H., Hirose T. and Shimamoto, T.  
Experimental Study for Noble Gas Release and Exchange under High-speed Frictional Melting

ICGG9A050: Flechsig, C., Schütze, C., Bussert, R. and Kämpf, H.  
Geoelectrical Investigation of Magmatic Degassing Zones in the Eger-Rift (Central Europe): A case study of the Hartousov Mofette field

ICGG9A075: Caprai, A., Calvi, E., Doveri, M., Leone, G. and Mussi, M.  
Geochemical Surveillance of Reactive Gas from Pozzuoli Solfatara (Naples, Italy): Chronological Evolution and Local Ground Displacement

ICGG9A070: Solecki, A.T. and Tchorz, D. E.  
Radon Emanation from Coal Ashes

ICGG9A073: Wysocka, M.  
Radon in some Jurassic Caves in Southern Poland

ICGG9A057: Mehra, R., Singh, S. and Singh, K.  
Assessment of the Average Effective Dose from the Analysis of $^{226}$Ra, $^{232}$Th and $^{40}$K in Soil Samples from Punjab, India

ICGG9A008: Bartarva, S. K., Choubey, V.M., Deshpande, R. D. and Ramola, R. C.  
Radon and Helium in Thermal and Natural Water Springs of Upper Bhagirathi, Mandakini and Yamuna Valley, Garhwal Himalaya

ICGG9A060: Mahajan, S., Walia, V., Kumar, A., Yang, T. F., Singh, S., Randhawa, S. S. and Bajwa, B. S.  
Soil Gas Survey in Mandi- Sundernagar Area, NW Himalaya, India: Prospecting in Fault Delineation

Continuous Gas Monitoring at Three Volcanoes
ICGG9A061: Obenholzer, J. H., Parks, J. and Edwards, M.
Arsenic Eaters, Arsenic Drinkers and Arsenic Breathers – Are We Prepared for the Next Big Volcanic Eruption?

ICGG9A009: Reiter, E.
GIS: A New Tool for Volcanic Gases’ Survey – A Case Study at Vulcano Island, Southern Italy

ICGG9A010: Reiter, E.
VolcanoGasML: A New Format for Geochemical Volcanic Gases Data

ICGG9A025: Liu, J. and Song, Z.
Chemical Changes in Rainwater in a Time of Extremely Rapid Urban Development of Guangzhou, China

ICGG9A078: Bayon, F. E. B. and Magro, G.
Differences in Noble Gas Signatures in two Active Geothermal Systems in the Philippines

Tritium as Vapour-Phase Tracer in Leyte Geothermal Production Field: Initial Results

ICGG9A007: Akper, F.
Hydrocarbon Migration and Gas Survey Efficiency in Different Tectonic Settings

ICGG9A001: Ramanathan, A., Chauhan, R. and Adhya, T. K.
Dynamics of CH₄ and N₂O Emission Flux from Bhitarkanika Mangrove Sediments of Eastern Orissa, India

12:10-13:30 Lunch

13:30-14:00 Introduction of Field Excursion

14:00-14:20 Group Photo-2

14:20-17:00 General Assembly

18:30-21:00 Banquet Party
Oral session-10
Chairperson: Solecki, A. T.

08:30-09:00: ICGG9A081 Invited
Diffuse CO₂ Emission and Volcanic Activity

09:00-09:20: ICGG9A062
Vaselli, O., Tassi, F., Nisi, B., Tedesco, D., Capaccioni, B. and Mapendano, M. Y.
Gas Discharges from the Nyiragongo Volcano (D.R. Congo) and Surrounding Areas: Implications for Environmental Impact and CO₂-related Risks from Dry Vents

09:20-09:40: ICGG9A036
Streil, T., Oeser, V. and Ogena, M.
Continuous Measurement of Geochemical Parameters in Aggressive Environment

09:40-10:00: ICGG9A076
Caprai, A.
Methods and Apparatus for Feeding Samples of Gas at Controlled Pressure into Gas Chromatographs (International Patent US 11/718,896 and IT/12.11.04 ITA PI20040083) and its Application in Geochemical Surveillance

10:00-10:20 Break

Oral session-11
Chairperson: Woith, H.

10:20-10:40: ICGG9A102
Kies, A., Tosheva, Z. and Nawrot, A.
Natural Radioactive Isotopes in Glacier Studies

10:40-11:00: ICGG9A069
Baciu, C., Spulber, L., Etiope G. and Cuna, S.
Methane Seepage Hazard for Urban Development Areas – A Case Study
11:00-11:20: ICGG9A056
**Bajwa, B. S.**, Singh, H., Singh, J. and Singh, S.
*Environmental Radioactivity Monitoring around the Tusham Ring Complex, Haryana: A Case Study*

11:20-11:40: ICGG9A072
**Chalupnik, S.**
*Method of Simultaneous Measurements of Radon and Radon Progeny in Air*

11:40-12:00: ICGG9A005
**Shanker, D.**, Singh, H.N., Singh, V. P. and Neelakandan, V. N.
*Geological Evidence of Natural Radioactivity in Southern Tamil Nadu, India - Impact on the Human, Animal Health and Natural Environment*

12:00-13:00: Lunch

13:10-20:00: City Tour
9th International Conference on Gas Geochemistry
Taiwan, October 1-8, 2007

Field Excursion

Saturday (10/6) - Monday (10/8)
Earth Evolution Recorded in Noble Gases and Volatiles in the Moon

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INTRODUCTION

Because of the almost total lack of geological record on the Earth for the time before 4 Ga, the history of the Earth during this period is still enigmatic. We propose that a comparative study of far- and near-side lunar soil would shed new light on this dark age of the Earth history.

Due to a strong dynamic coupling between the Earth and the Moon, theoretical studies of Earth-Moon dynamics have concluded that the Earth has been facing only to the nearside of the Moon since the formation of the Earth-Moon system about 4.5 billion year ago (e.g. Murray and Dermott, 1999). Also, theories have suggested that due to tidal energy dissipation, the Moon has been receding from the Earth. Recent theoretical studies concluded that the distance between the Earth and the Moon was about a half of the present distance about 4 Ga ago (Abe and Ooe, 2001).

From these studies we infer that there may have been substantial interaction between the Earth through the atmosphere and the nearside lunar surface, especially in ancient time, whereas the far side has remained essentially intact to the terrestrial atmospheric influence. Therefore, we suggest that the comparison of the far-side and near-side surface samples may impose unparalleled constraints on the evolution of the Earth such as the onset of the geomagnetic field, the evolution of a biotic oxygen atmosphere, and above all the dynamic evolution of the Earth-Moon system, a long standing fundamental problem, which has been strongly suggested by theoretical studies, but still requires observational confirmation.

OBJECTIVES

By analyzing isotopic ratios and elemental abundances of volatile elements (O, N, light noble gases) implanted on lunar mineral grains (preferably ilmenite grains and metallic particles for higher retentivity of these elements), we may tackle the following fundamental problems.
**When did the geomagnetic field (GMF) first appear?**  Heber et al. (2003) observed anomalous noble gas and nitrogen isotopic compositions in Apollo lunar ilmenites, which are quite different from the generally assumed solar components. Heber et al. (2003) concluded that the anomalous isotopic composition could not be attributed to nuclear processes in the Sun, but was likely to be due to some fractionation during implantation process. However, Ozima et al. (2005) showed that the isotopic compositions were attributable to the mixing of the solar components with terrestrial atmospheric components. They suggested that the terrestrial components have been transported from the Earth and implanted on lunar soils during the period when the Earth had not fully developed the GMF (a non-magnetic Earth). Therefore, if their interpretation were correct, the youngest age of ilmenite grains which show terrestrial isotopic signature in N and light noble gases would impose a crucial constraint on the onset time of the GMF.

**When did the biotic oxygen atmosphere form?**  Recently, Ireland et al. (2006) reported oxygen implanted in lunar metal particles, which were mass-independently positively fractionated relative to the mean terrestrial oxygen. Since the isotopic ratio of this exotic oxygen is very close to oxygen in the terrestrial ozone layer, Ozima et al. (2007) raised the possibility that oxygen fractionated in the Earth’s upper atmosphere was transported to the Moon. The speculation is based on the observation that the oxygen flux escaping from the Earth can account for the amount of the mass-independently fractionated oxygen implanted in the lunar metal particles (Seki H. et al., 2001). Therefore, if the ozone-layer like oxygen (mass independently and positively fractionated) are shown to constitute the major oxygen in the Earth Wind (EW), the oldest record of this exotic oxygen would constrain the onset time of the biotic oxygen earth atmosphere. Currently observations are limited only for minor components such as O$_3$ and CO$_2$ in the middle atmosphere (Boering K. et al., 2004, Thiemens, 2006), and the direct observation of oxygen isotopic composition in the EW is needed to confirm our hypothesis. This issue is also directly relevant to the problem of the origin of life in the Earth.

**Have the day length and Earth-Moon distance changed in geological time?**  If the Moon has been receding from the Earth due to tidal energy dissipation as concluded by an Earth-Moon dynamic theory, we expect that the day length of the Earth should also have changed accordingly. To confirm the day length change in geological time has been a quest of Earth scientists over centuries, but a large number of studies of potential geological records such as the number of growth lines in coral has not so far been conclusive. We suggest that a final answer to this intriguing problems can be reached by examining the following two relevant problems by systematic comparison between far- and near-side lunar soils for terrestrial volatile components: (a) We can identify the time when identical periods of rotation (Earth) and revolution (Moon) had taken place from the last appearance of terrestrial atmospheric components in far-side soils. (b) We would expect a systematic decrease of terrestrial volatile components on the near-side soils, if the Earth-Moon distance has been increasing. Answers to these questions would add observational confirmation to the theory on the Earth-Moon dynamic system for the first time.

**METHODS**

To tackle the above objectives, we need (i) systematic sampling of lunar soils both in the near- and far-side of the Moon, (ii) precise isotopic and elemental analyses of volatile elements such as N, O, light noble gases implanted in lunar soil minerals, and (iii) determination of surface exposure age of an individual mineral grain. We will discuss each issue below.
(i)  Sampling: Sampling of lunar soils in a continuous vertical section of a few meter depths both from far- and near-side sites is required.

(ii)  Elemental and isotopic analyses: The currently available experimental facility such as SIMS, ultra-high vacuum noble gas MS are quite satisfactory to carry out this requirement.

(iii)  Surface exposure age of grains: We have a good reason (Ozima et al., 2005) to believe that the surface exposure time of individual mineral grain is reasonably approximated by the time when a grain was first disintegrated from a bulk host rock. The latter event is very likely to have been caused by major impact event near the sampling site (Dalrymple and Ryder, 1996), and the disintegration time of an ilmenite grain from a host rock may reasonably be assigned to the age of impact melt minerals at the site. Therefore, by $^{40}$Ar-$^{39}$Ar dating of impact melt minerals at or near a sampling site, we may infer the surface exposure time of an ilmenite grain. In addition to this method, the direct application of $^{40}$Ar-$^{39}$Ar dating to an ilmenite grain with a very carefully controlled step-heating procedure may enable us to resolve the disintegration time of ilmenite grains from their host rock.

CONCLUSION

Comparative study of lunar soils from near- and far-side of the moon will yield new insight on some of the most fundamental problems in Earth and planetary sciences such as the first appearance of the geomagnetic field, the evolution of oxygen in the atmosphere, and the dynamical evolution of the Earth-Moon system. Apart from the sampling from the far-side, all the objectives can be carried out with currently available experimental techniques.

REFERENCES


Noble Gas Sources and Fluxes in the Hadean

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ABSTRACT

The rock record begins around 3.9Ga ago. Before, very little observations exist for what is called the Hadean eon. Our knowledge of mantle dynamics in the early Earth comes from small zircons found at Jack Hills (Australia) and Acasta (Canada) which can be as old as 4.2-4.4Ga, and from the composition of mantle derived rocks in isotopes coming from extinct radioactivities. It has been suggested, from geochemical studies on the Hadean zircons, that the Earth is already close to modern by 4.4Ga, having large continents, liquid oceans and potentially plate tectonics. The present work confronts this hypothesis to modeling of Xe isotopes coming from extinct radioactivities. We show that the transition from the Hadean to the Archean corresponds to a change in the thermal and mechanical regime of the Earth's mantle: the transition from magmatic to modern solid-state mantle convection.

The Lunar cratering record is consistent with the occurrence of a late heavy bombardment (LHB), which marked the end of terrestrial planet accretion 3.8 billion years ago. However, clear evidence of a LHB on Earth has not yet been identified. Here it is shown that the LHB did indeed occur on Earth and that we are breathing its aftermaths. The terrestrial atmosphere and hydrosphere is enriched in noble gases relative to the abundance of volatiles in the mantle. This enrichment is consistent with the mass delivered to Earth during the LHB only if this material consisted of ~0.5% Kuiper-belt objects mixed in with a population of largely chondritic (i.e. asteroidal) impactors. This places strong constraints on dynamical models for early Solar System evolution.
Residence Sites of Noble Gases in Basalt Glasses and Peridotites: Implications for Partitioning and Gas Migration

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**ABSTRACT**

Models for the evolution of noble gases in the earth’s mantle and crust are critically dependant on an understanding of both isotopic compositions and abundances. The residence sites of noble gases within the mantle and mantle-derived rocks and minerals are therefore crucial. An understanding of partitioning and residence sites is also crucial to minimizing the effects of air contamination and fractionation for mantle derived samples. Coupled vacuum crushing and melting studies of submarine basalt glasses from the Galapagos archipelago show that crushing releases more atmospheric neon contamination than melting of the associated glasses. This suggests that atmospheric contamination is introduced after eruption on the seafloor, possibly via air migration into vesicles. In order to test this idea, we have developed a new sampling method which involves collection of seafloor glasses without exposure to air, on the ship or in the laboratory. Preliminary tests of the new procedure, at Loihi seamount, suggest that air contamination can be reduced, and that gas migration into vesicles may be an important mechanism of air contamination of seafloor basalts. Dredged peridotites provide important insights into mantle noble gas geochemistry, but have not been extensively studied for noble gases. New helium and neon data from St. Paul’s Rocks and Southwest Indian Ridge abyssal peridotites, also using coupled vacuum crushing and melting, shows that most of the helium and neon within abyssal peridotites is contained in the mineral matrices rather than fluid or melt inclusions. Mylonites and ultramylonites have high helium concentrations, up to $4.4 \times 10^{-7}$ cc STP/gram, suggesting a relationship between metamorphic texture and noble gas abundance, and that mylonitization can introduce mantle helium into mineral matrices. The most likely mechanism is trapping within defects at pressure in the mantle. The $^{3}\text{He}/^{4}\text{He}$ ratios in the peridotites are similar to the associated basalts, suggesting that peridotites reflect the source mantle isotopic compositions. The relationships between texture and helium abundances in peridotites show that these samples should not be viewed as simple residua of partial melting, and that metamorphism is a potentially a very important control on noble gases. The possibility that noble gases are controlled by defect distribution may explain different noble gas partitioning results obtained by different laboratories. The results demonstrate the utility of noble gas partitioning site data in solid samples; these data are also potentially useful for understanding gas migration in continental crust and tectonically active areas.
Oil and Gas Generation and Expulsion: Seeing is Believing

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ABSTRACT

Petroleum (oil and gas) was thermally generated from organic matter (kerogens) within deeply buried organic-rich sedimentary rocks (source rocks). An innovative pyrolysis technique using Diamond Anvil Cell (DAC) has been developed in order to visualize real-time petroleum generation and expulsion from source rocks (Huang, 1996). The observations from experiments heated at programmed rates were VCR recorded in real-time. The visualization experiments provide direct observations and estimation of the temperature (or timing) and yields of oil and gas generation at a variety of experimental conditions. The technique can also be used to study the effect of a variety of geological parameters such as the pressure, the chemical openness and the presence of water, gases or catalysts on the behavior and kinetics of kerogen transformation. This study reviews the technique and presents results from new experiments which were conducted using a variety of source rocks and coals worldwide.

The visualization enables to determine oil maturation window, discern oil-prone from gas-prone kerogens or coals and estimate the physical properties of generative oils. In general, the temperatures (or timing) of petroleum generation from the study kerogens visually determined are consistent with those measured indirectly using conventional pyrolysis methods (Weng et al., 2003). The visual observation confirms the previous findings that the transformation temperatures (or maturity) vary significantly with the diverse types of kerogens, for instance, sulfur-rich kerogens generated petroleum at maturity much lower than other oil-prone source rocks (Lewan and Ruble, 2002). The visual observation furthermore enables to discrete the timing of oil from gas generation, estimate the oil/gas ratio, and identify oil-prone kerogens and coals. For instance, an India’s lignite was shown to generate significant amount of oil by this technique, although most lignites were commonly considered as gas-prone (Ramaswamy, 2005.). Similarly, some non-perhydrous vitrinite unexpectedly generated large amounts of visible oil although the oil is darker and thicker than that from liptinite (Mo et al., 2007).

The experiments have also revealed some visual characteristics of the generation/expel processes of oil and gas, which otherwise may be ignored using conventional pyrolysis techniques. Oil generation from kerogen was found to take place episodically, in contrast to the progressive reactions conventionally assumed for modeling petroleum generation. The visual observations also show that some kerogens can absorb significant amount of generative oil before expulsion. The absorbed oil was expelled episodically whenever kerogen was supersaturated with oil. The previously proposed expulsion model of petroleum from source rocks, in some cases, may need to be modified by including the episodic expulsion of petroleum from the kerogen in addition to the episodic expulsion accompanied by the release of pore pressure. The expelling of generative petroleum from the kerogens
was observed to be enhanced by the axial anvil pressures and openness of the system, implying that they may play important roles in petroleum expulsion from source rocks. Differential lithologic stress commonly occurred in geological environments may accelerate primary migration of oil from source rocks.

The deposition of pyrobitumen during kerogen transformation has been visually observed. Kerogen produces much more pyrobitumen in closed system than semi-open system. In contrast to the anhydrous system, the deposition of significant amount of pyrobitumen at the end of experiment was observed in the closed hydrous system. The yield and timing of pyrobitumen formation, therefore, is a function of kerogen type, the openness of the system, and the amounts of water. The dissolution of neoformed oil in aqueous fluid in closed hydrous system depends on experimental temperature and pressure. The observation confirms that the solubility of oil in hydrothermal water decreases significantly with increasing pressure (Price, 1981). The some dissolved oil can survive from cracking into gas at higher temperatures than the free immiscible oil. However, the results show that the rate of kerogen transformation was not significantly retarded by higher water pressure.

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Using Argon as a Temporal Tracer of Large-Scale Geologic Processes

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ABSTRACT

Argon (Ar) has proven to be one of the most useful elements in understanding the timing and duration of a variety of geological processes. Because of its chemical and physical properties, Ar is a particularly sensitive indicator of temperature variations resulting from geological events. Coupled with the fact that it occurs in many common rock-forming minerals (i.e. \(^{40}\)Ar is the radiogenic daughter product of radioactive \(^{40}\)K), Ar has been used as a temporal tracer to understand a wide variety of geological phenomena, including the origin and evolution of the earth’s atmosphere, thermochronology, and the duration of large-scale tectonic events. The development of the \(^{40}\)Ar/\(^{39}\)Ar dating technique in combination with detailed knowledge of the diffusional behaviour of Ar has proven to be a powerful research tool in elucidating many large-scale earth-system processes.

INTRODUCTION

Since its discovery by Lord Rayleigh and Sir William Ramsay in 1894 (Rayleigh and Ramsay 1895), argon (Ar) has proven to be one of the most useful noble gases in studying the earth and the solar system. As the first noble gas ever discovered, its name comes from the Greek word argo as derived from “argos”, which means idle, lazy, or inactive, reflecting its non-reactivity with other chemical elements. Argon has three stable naturally-occurring isotopes – \(^{36}\)Ar, \(^{38}\)Ar, and \(^{40}\)Ar, with respective natural relative abundances of 0.337%, 0.063%, and 99.6% (Nier 1950). In addition, Ar isotopes such as \(^{36}\)Ar, \(^{37}\)Ar, \(^{38}\)Ar, \(^{39}\)Ar, \(^{40}\)Ar, and \(^{42}\)Ar can also be created by cosmic-ray spallation reactions (e.g. Regnier 1979, Lal 1988), although production rates for these isotopes are orders of magnitude smaller than corresponding absolute terrestrial abundances (e.g. Lal 1991, Leya et al. 2004) and some of these isotopes (e.g. \(^{37}\)Ar, \(^{39}\)Ar, and \(^{42}\)Ar) are radioactive. As a natural component of the earth’s atmosphere, Ar comprises 0.937% by volume of dry air (Kellas 1895).

By its very nature and abundance, argon has proven to be an ideal tracer which can be used to understand a variety of geological processes. As a gas, Ar tends to be much more mobile than other elements, and is therefore much more sensitive to the effects of temperature; this is particularly useful when attempting to understand the thermal history of rocks and geologic terranes. As a noble element, Ar forms only very weak van der Waals-type chemical bonds with other elements; this means that its mobility in rocks and minerals is essentially independent of chemical bonding, and it exhibits much simpler, near-ideal, diffusive behaviour. As with all noble gases, Ar is a scarce element in the earth; this scarcity makes it easy to detect “anomalous” concentrations of argon which can result from a variety of geological phenomena. Finally, Ar is relatively easy to measure accurately and precisely; its
relatively low mass number means that high mass-resolution mass spectrometers are not required to clearly separate and measure all of the Ar isotopes. Indeed, Ar was one of the first noble gases whose isotopic composition was measured by a gas mass spectrometer.

The initial use of Ar as a temporal tracer of geological processes primarily came about through the development of the K-Ar geochronological method. Based on the decay of $^{40}$K to $^{40}$Ar, the K-Ar dating technique was the first geochronological method to be applied to a wide variety of rock types. Its more modern variant, the $^{40}$Ar/$^{39}$Ar dating technique, is now one of the most widely used geochronological methods and is an integral part of many geologic, tectonic, structural, and economic-geology studies. In recent times, the utility of Ar as an effective temporal tracer of earth-system processes has been exhibited in several diverse applications; a few are highlighted below.

MODERN APPLICATIONS

*Origin and Evolution of the Earth’s Atmosphere*

The earth’s atmosphere may be considered to be the product of two large-scale processes: (1) the earth’s accretion during its formation, and (2) continuous degassing of the solid earth through time. Because of its inert chemical nature, Ar is not chemically bound to any minerals and is typically free to diffuse under appropriate temperature and Ar partial-pressure boundary conditions. Simple considerations of the total $^{40}$Ar budget for the Earth suggest that over half of the radiogenic $^{40}$Ar from the mantle has been degassed and now resides in the Earth’s atmosphere (Ozima and Podosek 2002). As a result, understanding the origin and evolution of the atmosphere can provide key insights into the formation and evolution of the earth itself.

Early models suggested that the earth’s atmosphere could have been primary, i.e. derived from the condensing solar nebula during planetary accretion. However, Ozima and Podosek (1983) have shown that the atmospheric abundances of noble gases in the earth’s atmosphere are less than their corresponding solar abundances by at least 6 orders of magnitude, thus indicating that most of the earth’s atmosphere must be secondary, i.e. derived after its accretion. Several quantitative models using Ar as a tracer have been proposed to explain the evolution of this secondary atmosphere through geologic time (Ozima and Podosek 1983, 2002). Of these, there have been three main theories: (1) continuous degassing, (2) catastrophic degassing, and (3) mass transfer. Rubey (1951) suggested that because the composition of the earth’s atmosphere is similar to that of volcanic gases, it could have resulted from continuous degassing of the earth’s interior (e.g. the mantle) via volcanic activity over geologic time. Fanale (1971), however, proposed that the elevated temperatures of the early earth must have resulted in catastrophic degassing shortly after accretion. This has been supported by observations of the $^{40}$Ar/$^{39}$Ar ratios in the upper mantle (> 30,000) versus air (295.5), which are consistent with the notion that stable isotopes such as $^{36}$Ar would have degassed from the mantle during the earth’s earliest history, whereas radiogenic $^{40}$Ar would continue to accumulate through time. Support for catastrophic degassing has also come from studies of excess $^{129}$Xe/$^{130}$Xe in mantle-derived minerals, which indicate that the formation of the earth’s early atmosphere must have formed within a few tens of Ma (from the half-life of parent $^{129}$I) of accretion (Ozima and Podosek 2002). Further calculations using $^{40}$Ar global inventories also indicate that the upper mantle must be almost entirely degassed. Nevertheless, radiogenic $^{40}$Ar production from the earth’s interior is continuous and several more recent models have invoked mass transfer via magma generation and emplacement to explain ongoing mantle degassing throughout time (e.g. Allegre et al. 1987, Porcelli and Wasserburg 1995).
Despite the high degree of research interest in the 1980’s and 1990’s, further work using today’s modern techniques and technological advances is needed and would be timely.

$^{40}\text{Ar}/^{39}\text{Ar}$ Thermochronology

Since its early beginnings in the 1960’s, the $^{40}\text{Ar}/^{39}\text{Ar}$ dating technique has become one of the premier geochronological methods today has several advantages over the conventional K-Ar method on which it is derived. Unlike K-Ar dating, where separate aliquots of sample must be used to measure K and Ar, all Ar isotopes can be measured from the same sample using the same equipment. This makes sample analysis much more convenient and reduces problems from sample inhomogeneities and machine calibrations. Furthermore, because all Ar isotopes can be measured on the same mass spectrometer at the same time, only ratios (e.g. $^{40}\text{Ar}/^{39}\text{Ar}$) as opposed to absolute values (e.g. ppm K and cm$^3$/g $^{40}\text{Ar}$) need to be measured; this means $^{40}\text{Ar}/^{39}\text{Ar}$ dates have significantly improved precision over K-Ar dates. $^{40}\text{Ar}/^{39}\text{Ar}$ sample sizes are also much smaller than K-Ar aliquots, such that single grains can be analysed routinely. Finally, there are a variety of analytical techniques which can be used in $^{40}\text{Ar}/^{39}\text{Ar}$ dating (total fusion, step-heating, laser spot-dating) which greatly expand the versatility of the method.

Ar is one of the few geochronometers which can record a large portion of the thermal history of a geologic terrane. Due to its gaseous nature and inert chemical behaviour, Ar has enhanced mobility with respect to most other geochronologically important radiogenic isotopes, diffusing readily in response to elevated temperatures. Using solid-state diffusion theory, Dodson (1973) quantitatively developed closure-temperature theory, which has revolutionized thermochronology by allowing the temperature of slowly cooling systems to be directly correlated with the cooling ages of minerals. Thermochronological techniques are the most highly developed in the $^{40}\text{Ar}/^{39}\text{Ar}$ system, where the Ar diffusivity in various common rock-forming minerals (K-feldspar, micas, amphiboles) has been tightly constrained through detailed laboratory experiments. $^{40}\text{Ar}/^{39}\text{Ar}$ thermochronology is now one of the most powerful techniques in elucidating geological thermal histories and has been applied widely to geological, tectonic, structural, sedimentary-basin, paleomagnetic, and petrologic studies (see various references in McDougall and Harrison, 1999).

Duration of an Orogenic Cycle

The durations of geological processes that shape the earth have always been the subject of vigorous debate. Using $^{40}\text{Ar}/^{39}\text{Ar}$ laser-spot dating coupled with solid-state diffusion theory, Camacho et al. (2005) were able to constrain quantitatively for the first time, using a single isotopic system, the complete duration of an orogenic cycle (subduction of crust followed by its exhumation), and show that it is much shorter than previously thought (~13 Myr). Combined with geological evidence and thermal modelling, the $^{40}\text{Ar}/^{39}\text{Ar}$ age data and calculations show that in continental-collision zones, the subducted crust remains cool (400-500°C) because is at depth for very short periods of time (~2 Myr) and is only heated locally through multiple pulses of hot fluids. This fundamentally different interpretation contrasts with many conventional views held in earth science, but neatly explains several enigmatic geological observations from the lower crust in a coherent framework. The research has not only resulted in the development of a new technique based on diffusion theory to estimate the duration of thermal pulses, but has significant implications for global mountain-building processes.

CONCLUSIONS

Argon has proven to be an extremely useful tracer of large-scale geological processes throughout the
earth’s history; as a noble gas found in many common rock-forming minerals, its chemical and physical properties have been vital in its utility as a temporal probe. Through diverse applications in studies of the origin and history of the earth’s atmosphere, thermochronological investigations, and estimating the duration of finite geological events, Ar will continue to play a key role in elucidating earth-system processes.

ACKNOWLEDGMENTS

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REFERENCES


Natural Analogue of Long-term CO₂ Storage in the Sedimentary Formation of Western Taiwan

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ABSTRACT

CO₂ geo-sequestration is considered as the feasible method for the mitigation of CO₂ emission. It is usually very huge amount of natural carbon dioxide being stored in the substrata. There are many sources for natural carbon dioxide, including: magma related source, decomposition of carbonates in metamorphosed rocks, releasing of CO₂ dissolved fluids, and oxidation of organic matters, etc. Recent studies revealed that the storage time of natural carbon dioxides in the strata can be a wide range from very short time to up to several million years. It will be helpful to better understand the safety parameters of CO₂ injecting into the strata for storage, if we can study more natural analogue cases and know better about the residence time and the condition of CO₂ storage in natural cases.

Many CO₂ natural gases occur along active faults and/or drilling wells in western Taiwan, where does not have any signature of recent magma activity. However, elevated helium isotopic ratios (up to 6 Ra), carbon isotopes ($\delta^{13}$C = -7 ~ -4‰) and high CO₂/$^3$He ratios ($2\times10^{-9} ~ 10^{10}$) of the natural gases strongly indicate that they were magmatic source in origin. Considering that the latest magmatic event occurred in Miocene (ca. 8 Ma), I propose that the CO₂ gases were degassing with the Miocene magmatism and consequently, they have been trapped in the strata until recent. We can reasonably assume that the original Miocene magmatic gas with helium isotopic composition of 6.5 Ra did not experience any lose of $^3$He and $^4$He, and was increasing the amount of $^3$He from the radiogenic nuclei of host rocks through time. Then, the mass balance calculation of helium isotopic composition support that the gases could be stored in the strata up to 5 million years. Those “old” magmatic CO₂ gases were able to migrate to surface through the fault zones due to recent crust activity. It demonstrates that the CO₂ gas could be long-term stored in the strata safely under certain conditions.
ABSTRACT

Radon is continuously being monitored at the hot spring of Tiberias, Israel since 2000. The radon signal contains periodic daily and non-periodic multi-day variations as well as periodic seasonal variation patterns. Additionally, a remarkable drop in the average radon concentration occurred in the year 2003.

Tidal effects (O1 and M2 constituents) are absent from the spectra. Spectral analysis shows diurnal (24-hour; S1) and semidiurnal (12-hour; S2) periodic constituents. The amplitudes of these constituents exhibit regular temporal variation having a long-term seasonal pattern. On a seasonal scale radon is negatively correlated with air temperature and positively correlated with the air pressure. We tentatively present a mathematical procedure to remove the influence of air temperature and air pressure from the radon time series. Seasonal radon maxima occur during the rainy winter time. The hot spring waters of Tiberias are a mixture of shallow and deep water components: shallow groundwaters are recharged in the west, flow eastward and emerge to the surface along sub-vertical border faults, where they mix with saline fluids characterized by high temperatures. Rain fall should increase the hydraulic pressure in these conduits and thus should increase the flow velocity. Increased flow means less time for radon to decay and thus a positive correlation between flow rate and radon – at least qualitatively explaining the winter maxima.

Until spring 2003 the average radon concentration was ca. 700 cps (counts per second), whereas thereafter the average radon concentration dropped to 450 cps. The drop of the radon level in 2003 was accompanied by a significant increase of the seasonal radon amplitude – it doubled from ± 60 cps to ± 120 cps. What happened in 2003? We may rule out rain fall (measured at Tiberias and kindly provided by Mekorot Ltd.), because the amount of winter rains did not change significantly over time. At this stage we suspect the level of the Tiberias lake (the distance between the monitoring station and the lake shore is ca. 50 m) as the driving force for the radon drop in 2003. Until 2003 the lake level hovered around -214 m ± 1 m seasonal variation. In spring 2003 the lake level has risen to -210 ± 1.2 m corresponding to the long-term Kinneret lake level (1927-1986). A tentative hydrogeological mixing model will be presented.
Soil-Gas Monitoring: A Tool for Fault Delineation Studies along Hsinhua Fault (Tainan), Southern Taiwan

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ABSTRACT

To investigate active tectonic structures, soil-gas composition has been vastly used in recent past. Soil gases in fault zones therefore appear as a suitable tool for studying spatial and temporal patterns. Gas geo-chemical profiling along 13 traverses was performed across the Hsinhua fault located Southern Taiwan, to find out the regional activity of this fault system. More than 250 samples were collected for He, Rn, CO$_2$, CH$_4$, Ar, O$_2$ and N$_2$ etc. from around 110 sampling locations across the fault system. Data analysis clearly reveals anomalous values for each gas at specific location along the traverses. Before selecting a monitoring site, the occurrence of deeper gas emanation is investigated by the soil-gas surveys followed by continuous monitoring of some selected sites with respect to tectonic activity to check the sensitivity of the sites. One site is selected for long term monitoring on the basis of coexistence of high concentration of helium, radon and carrier gases and sensitivity towards the tectonic activity in the region. A continuous monitoring station was established in October, 2006 at the selected site. Preliminary results of the monitoring station show that the site is suitable for earthquake monitoring as the soil-gas variations have shown good correlation with impending earthquakes of 26th December, 2006 having local intensity of 4. Geochemical monitoring at the established earthquake monitoring station along the Hsincheng fault has shown potential precursory signals for some earthquakes that occurred in the region.
Scaling and Crossover Phenomena in Anomalous Helium Sequence

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ABSTRACT

Investigations concerning detection and analysis of anomalous signatures of crustal phenomena like early degassing of the volatiles from the depth of the earth emerge to be an important subject especially after the occurrence of devastating Tsunami on December 26, 2004. The deep seated hydrothermal systems are considered to be potential channel for carrying information from the earth’s bowels to the surface. In this perspective we have set up a laboratory to study the time dependent emission of helium and radon from a deep seated and perennial thermal spring located at Bakreswar (23°52’30”N ; 87°02’30”E), Birbhum, West Bengal. The spring appears through the intersections of intensive faults and fissures and turns out to be highly sensitive to seismo-tectonic activity. The system constitutes a two phase fluid flow and characterized by the significant presence of deep seated fluids. The gas bubbles emerging out of the spring vents are trapped under water with an inverted funnel and fed to the equipments (radon monitor and gas chromatograph) after passing through the gas driers. During the past few years we have observed and reported several typical fluctuations of radon and helium time series ahead of some major quakes. The observed anomalies in gas concentrations of spring emanations could be the result of stress-strain evolutionary mechanism within the solid earth during the earthquake preparatory phase. The stress-strain episode also brings about greater interactions of the reservoir fluid with the adjacent rock matrix causing excessive release of gaseous elements. Aside from the studies on temporal anomaly of the helium signal, nonlinear analysis was carried out with the field data to extract the scaling behaviour of the helium time series. The method called Detrended Fluctuation Analysis (DFA) was used on temporal helium data including the anomalous peaks for seven months (September, 2006 – March, 2007). The analysis captures the signature of crossover phenomenon distinguishing two scaling regions. Presence of crossover point could be the precursor of the crustal instability in the earthquake nucleation stage. The scaling exponent at higher time scale expresses the persistent long range correlation while that at shorter time scale resembles somewhat brown noise. Our findings suggest the possibility of trade off between precursory anomalies and the alteration processes within the crust occurring in the earthquake initiation phase.
Problems in Interpretation of Nitrogen and Argon Data for Volcanic and Hydrothermal Gases

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ABSTRACT

There are not too many large volcanic gas data sets with simultaneous analyses of N₂, Ar, He and only two sets with \(^{40}\text{Ar}/^{36}\text{Ar}\) in same samples. The best are for Italian volcanoes and hydrothermal systems, the good ones for a few Japanese volcanoes and the data of workshops of the IAVCEI Commission of the Chemistry of Volcanic Gases (CCVG). Analysis of these data revealed some regularities which seem to have importance when we try to distinguish sources and estimate their contributions.

INTRODUCTION

Nitrogen, argon and other air components are inevitably recycled from the subducting oceanic slab to the surface by magmatism and accompanying volcanic and hydrothermal activity. A part of N and Ar are of the “old” atmosphere origin, and a significant fraction of N can be derived from the subducted organic-rich sediments, appearing as “excess nitrogen” in volcanic and geothermal gases. However, excess nitrogen can be released also from the continental sedimentary organics or metamorphic rocks, with the same isotopic characteristics ($\delta^{15}\text{N} \geq +5\%$) and the same high N₂/Ar ratio in the gas discharge. On the other hand, gas with the N₂/Ar ratio close to the air and ASW (air-saturated water) values (40-80), $\delta^{15}\text{N} \sim 0$ and \(^{40}\text{Ar}/^{36}\text{Ar} \sim 296\) can be released also from altered basalts of the subducted oceanic plate and is common in minerals of arc-related magmatic rocks. A complex interplay between $\delta^{15}\text{N}$, \(^{40}\text{Ar}/^{36}\text{Ar}$, N₂/Ar and absolute concentration of N₂ and Ar in a surface thermal manifestation has different issues for the volcanic and hydrothermal vents within different tectonic and geologic settings.

SOURCES OF NITROGEN

- Nitrogen is relatively stable and its behavior is often similar to that of noble gases. However, its reduced partners, NH₃ and NH₄⁺ are abundant in the crust and not only in organic sediments and derived rocks, but in metamorphic rocks, in low-temperature minerals. The relationship between N₂ and NH₃ is similar to those as for CO₂ and CH₄. Similar to carbon, nitrogen has a geochemical cycle coupled with life and the Earth’s organic matter.

- The mantle source of N, though exists, is very poor. According to Marty and Dauphas (2003), the depleted mantle contains on average not more than 0.5 ppm of N. Similar values have been reported for the enriched mantle and for altered ocean basalts. The depleted mantle CO₂/N₂ is near 500. The
solubility of N\textsubscript{2} in basaltic melts is one order of magnitude lower than that of CO\textsubscript{2}. It is important to know, that in depleted mantle the N\textsubscript{2}/Ar is close to the atmospheric value (70-100), however, this argon has $^{40}\text{Ar}/^{36}\text{Ar} > 20,000$.

-Nitrogen in the crust can be produced from sedimentary organics by oxidation, bio- and thermo-degradation. Thus, this non-atmospheric nitrogen is the reason for high N\textsubscript{2}/Ar ratios in natural gases, because there is no Ar in bioorganic sediments. Old and deep metamorphic rocks also release non-atmospheric N\textsubscript{2} with high N\textsubscript{2}/Ar ratio (KTB well). High N\textsubscript{2}/Ar is characteristic also for volcanic gases of subduction zones. This is attributed to the release of biogenic N\textsubscript{2} from subducted oceanic sediments together with other gases and water to the magma generation zones and then to the surface by magmatism.

-Therefore, volcano-hydrothermal nitrogen, except of pure atmospheric, may have crustal and magmatic origin. In turn, magmatic nitrogen can be a mixture of recycled N from subducting oceanic slab and mantle nitrogen. The problem is to distinguish between these sources in a sample of volcanic or hydrothermal gas. The problem cannot be resolved simply by applying stable isotope techniques, because the same positive $\delta^{15}\text{N}$ have crustal non-atmospheric nitrogen and the volcanic N from subduction zones and, as was suggested by Marty and Dauphas (2003), the enriched mantle of mantle plumes. Moreover, the negative $\delta^{15}\text{N}$ is usual not only for the MORB nitrogen, but also for crustal natural gases. It should be noted also, that the natural isotopic fractionation of N, though poorly understood, but seems to be an effective mechanism to produce negative $\delta^{15}\text{N}$ in N\textsubscript{2} in contact with NO\textsubscript{3}, NH\textsubscript{3} or NH\textsubscript{4}\textsuperscript{+}.

-The main part of hydrothermal fluids is meteoric water (ASW) or seawater (ASSW) saturated initially with air.

**METEORIC-SEAWATER HYDROTHERMAL SYSTEMS WITH NO NON-ATMOSPHERIC NITROGEN** (too low to be detected)

Nitrogen and argon in ASW and ASSW have initial concentrations ~12 ppm and ~0.3 ppm (mole fractions) and N\textsubscript{2}/Ar ~ 40. Because of high values of distribution coefficients between water and steam, steam is enriched in N\textsubscript{2} and Ar. Concentrations of gases and isotopic composition of steam and water, can be connected through steam fraction Y in a two-phase aquifer (Taran, 1988):

$$Y = x_o/x; \quad Y = (\delta_o - \delta_v)/\Delta D; \quad \delta_v D= \delta_o D- \Delta D(x_o/x)$$

(1)

These expressions can be used for plotting data on N\textsubscript{2} (Ar) concentrations and $\delta$D of hydrothermal steam vents. An example is shown in Fig. 1 for Nysiros volcano (Chiodini et al., unpublished) where hydrothermal fluid is formed of meteoric and seawater with a low contribution of magmatic fluid.
ENDMEMBER CHARACTERISTICS FOR NON-ATMOSPHERIC NITROGEN

A simple plot “Ar/N₂ vs Ar” may be used for the estimation of the N₂/Ar ratio in the non-atmospheric source of N₂ by extrapolation of Ar/N₂ to zero Ar concentration. Figure 2 illustrates such an extrapolation for the (Campi Flegrei, Italy). Unpublished very large set of data from INGV OV (Chiodini et al.) and published data by Tedesco and Scarsi (1999) give very comparable results for this endmember. A negative correlation between Ar and CH₄ observed by Tedesco and Scarsi is a strong evidence for the crustal source of the non-atmospheric N₂ for Solfatara.

**Figure 1.** A δD-N₂ diagram for Nissiros hydrothermal fumaroles with a mixed ASW+ASSW source of water (boiling at 100°C). The fraction of seawater as well as the steam fraction can be estimated from this diagram (unpublished data of Chiodini et al., INGV, Osservatorio Vesuviano).

**Figure 2.** Data for Solfatara (unpublished, OV INGV, Italy). The “zero-Ar” endmember is characterized by N₂ ~ 350 ppm and N₂/Ar ~ 4000
CONTROL BY $^{40}\text{Ar}/^{36}\text{Ar}$ (VULCANO AND SOLFATARA)

At least for Italian volcanoes (Vulcano and Solfatara) non-atmospheric sources of $\text{N}_2$ contain very low amount of Ar with high $^{40}\text{Ar}/^{36}\text{Ar}$ (Magro and Pennisi, 1991; Tedesco and Scarsi, 1999).

![Figure 3](image.png)

Figure 3. $^{40}\text{Ar}/^{36}\text{Ar}$ in gases from Solfatara (Tedesco & Scarsi, 1999) and Vulcano (Magro & Pennisi, 1999). The low-Ar endmember is enriched in radiogenic Ar. In Solfatara gases same endmember is enriched in CH$_4$ indicating a crustal, not magmatic, source.

CONCLUSIONS

Both the high $\text{N}_2$/Ar ratio and positive $\delta^{15}\text{N}$ do not indicate an unambiguous “subducted” (magmatic) nitrogen in volcanic gases but rather a mixture between magmatic and crustal sources. Because of inevitable contamination of these gases by air and ASW, large data sets are needed and more components should be involved (CH$_4$, $\delta$D, He, $^3\text{He}/^4\text{He}$) for unrevealing the source problem in geochemistry of volcanic and hydrothermal gases.

REFERENCES


Mantle Helium Traces around Elbrus and Kazbek Volcanoes (Northern Caucasus)

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ABSTRACT

The Northern Caucasus region includes the alpine Greater Caucasus orogen and the epi-Hercynian Scythian plate. The central segment of the orogen was re-activated by N_{2}-Q volcanism. The brightest manifestations of this activity are the Elbrus and Kazbek volcanoes. The last one was active in Quaternary, the Mt. Elbrus erupted in I-II centuries AD (Bogatikov et al., 1998).

Study of $^{3}$He/$^{4}$He in subsurface fluids of the region carried on in 1993-2003 by GIN RAS team revealed in the orogen the $^{3}$He/$^{4}$He ratio values exceeding those typical of the Scythian plate where the mean $^{3}$He/$^{4}$He $\sim 1 \times 10^{-7}$. The values of $^{3}$He/$^{4}$He $(0.6-0.9) \times 10^{-5}$ surround the Mt. Elbrus and gradually decrease with distance from the volcano. The halo is extended in NW direction into the plate for a distance $\sim 300$ km and at the same time $^{3}$He/$^{4}$He ratio values decline to $(2-3) \times 10^{-7}$. The halo of high $^{3}$He/$^{4}$He ratios in the vicinity of the Elbrus Volcano correlates with positive anomaly in temperatures of CO$_{2}$-rich spring waters. Hydrodynamic modelling of the halo formation showed that it can not be explained only by discharge of mantle fluids through the feeder of the volcano and their following lateral migration accompanying with contamination by radiogenic He. The halo reflects additional supply of mantle derivatives into subsurface waters due to degassing of other young magmatic foci.

Another halo of enhanced $^{3}$He/$^{4}$He ratios up to $-0.8 \times 10^{-5}$ surrounds the Kazbek Volcano being active in Quaternary. This anomaly degenerates to the north much more rapidly than the Elbrus halo. CO$_{2}$-rich Upper Karmadon Spr. and N$_{2}$-CH$_{4}$ Lower Karmadon Spr. discharging in northern foothills of the Mt. Kazbek at a distance of $\sim 6$ and $\sim 14$ km from its summit show decreasing $^{3}$He/$^{4}$He ratio from of $1.9 \times 10^{-6}$ to $2.7 \times 10^{-7}$, respectively. The segment between these springs is also marked by sharp changes in geophysical characteristics. Toward the volcano a negative gravimetric anomaly up to -25 mGal manifests itself (Arbuzkin et al., 2004). It was interpreted as sign of shallow magma chamber. The MT-sounding in the same segment revealed an object with anomalously low values of the electric resistance $(0.6-3.0$ Om·m) at the depths of 6-8 km (Kopaev and Gurbanov, 2004).

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CO₂/H₂O Ratio of Magmatic Gas Estimated from the Analysis of Fumarolic Gas Sampled at Tatun Volcano Group, Taiwan

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INTRODUCTION

The activity of Tatun volcano group of Taiwan have been regarded to be extinct, because of the historical no eruption (Song et al., 2000). However, a hydrothermal system is now well developed along Chinshan fault, one of the significant faults in northern Taiwan. Yang et al. (1999) detected He in fumarolic gases sampled at Tatun volcano group, the ³He/⁴He ratio of which suggested their mantle origin. Chen and Lin (2002) revealed the existence of eruptive activity younger than 20ka at Tatun volcano group based on the ¹⁴C dating of charcoal buried in Taipei basin. Considering the above evidences and the recent discussion on the definition of active volcano (Szakacs, 1994), the eruptive potential of Tatun volcano group should not be neglected in spite of the dormancy.

The evaluation of the eruptive potential for a dormant volcano is important on the point of view for mitigation of volcanic disaster over long term. The potential of eruptive activity would be related to the content of volatile in magma. However, there is no way to evaluate the amount of volatile in magma directly. The concentration of volatile in magma deduced by melt inclusion analysis is only the concentration of magma responsible for the last eruptions. A stagnant magma would emit a gas, the CO₂/H₂O ratio of which decrease along the progress of degassing, because CO₂ gas has the solubility in magma much lower than H₂O (e.g., Newman and Lowenstern, 2002). The CO₂/H₂O ratio of magmatic gas could be a useful information on the potential of magmatic activity.

The gas emitted from a degassing magma is included in a hydrothermal system developed beneath volcanic body. The high temperature gas is mixed with a deep circulation ground water resulting in a formation of hydrothermal fluid. The hydrothermal fluid ascends to shallow depth, then, boils. The vapor phase generated at the boiling will be discharged as fumarolic gas. Near the surface, the vapor phase again interacts with a shallow ground water, and the vapor could be partially condensed (Ohwada et al., 2003, Sawa et al., 2006).

In this study, we intend to elucidate the complicated process between magmatic gas and meteoric ground water in hydrothermal system developed at Tatun volcano group. The process is understood
based on the chemical composition, H$_2$O isotopic ratio and rare gas content in fumarolic gas. As a result, the CO$_2$/H$_2$O ratio of the magmatic gas is estimated.

**SAMPLING AND ANALYSIS**

Fumarolic gases were sampled in 2006 at Hiao-you-keng (HYK), Gung-tze-ping (GTP) and She-huang-ping (SHP) geothermal areas located between Chinshan and Kanchiao faults (Fig.1). Evacuated glass bottles containing KOH solution (Giggenbach, 1975) were used for the sampling. The gas phase in the head space of bottle was used for the determination of $^{36}$Ar concentrations. The CO$_2$ and H$_2$O amount in gas was determined by the analysis of solution in the bottle. The D/H and $^{18}$O/$^{16}$O ratio of gas was determined by the analysis of the fumarolic gas condensate, which was sampled in addition to the evacuated bottle samples. The temperature, chemical composition and isotope ratios of sampled gases are listed in Table 1.

**RESULT AND DISCUSSION**

The isotope ratios of H$_2$O in fumarolic gas are plotted on the δD vs. δ$^{18}$O plain (Fig.2). Some of them look like the mixture of the typical andesitic water (Giggenbach, 1992) (MV in Fig.2) and the local meteoric water characteristic to Taipei basin (Wang and Peng, 2001) (MW in Fig.2). However, the simple mixing between those end members is inappropriate to the interpretation of gas composition, because,

1) the fumarolic gases contains HCl and SO$_2$ with limited concentrations,
2) the fumarolic gases is composed of mainly H$_2$O, CO$_2$ and H$_2$S,
3) the R$_H$ {=log$_{10}$(H$_2$/H$_2$O)} is -7.3 to -4.4 consistent to the vapor phase in volcanic hydrothermal system (Giggenbach, 1987).

The most acceptable explanation for the origin of fumarolic gas is the “primary steam” (Giggenbach and Stewart, 1982). The primary steam is the vapor phase evolved after the mixing between magmatic gas and meteoric underground water. The chemical composition and isotope ratio of primary steam is given by the following equations.

$$E_{MV} f + E_{MW} (1 - f) = E_{PS} g + E_{PL} (1 - g)$$  \hspace{1cm} (1)

$$\delta_{MV} f + \delta_{MW} (1 - f) = \delta_{PS} g + \delta_{PL} (1 - g)$$  \hspace{1cm} (2)

$$R_{MV} f + R_{MW} (1 - f) = R_{PS} g + R_{PL} (1 - g)$$  \hspace{1cm} (3)

$$\alpha = \frac{\delta_{PL} + 1000}{\delta_{PS} + 1000}$$  \hspace{1cm} (4)

$$\beta = \frac{R_{PL}}{R_{PS}}$$  \hspace{1cm} (5)

In the above equations, $f$ is the fraction of magmatic gas when it mixes with meteoric water. The $g$ is the fraction of primary steam evolved after the mixing. The $E$, $R$ and $\delta$ is the enthalpy, molar ratio and isotope ratio in delta notation of H$_2$O, respectively. The $\alpha$ and $\beta$ is the isotopic fractionation factor and distribution coefficient between H$_2$O liquid and vapor. The subscripts, PS and PL indicate the primary steam and “primary liquid”, a conjugated liquid phase equilibrated with PS in terms of isotope exchange and CO$_2$ and $^{36}$Ar distribution. The chemical composition and isotope ratios of primary steam is calculated by using the parameters listed in Table 2. Allowing the degree of freedom in $f$ value, the composition of primary steam is expressed as line on the δD vs δ$^{18}$O plane (Fig.2), as curve in the correlation between δ$^{18}$O
and $^{36}$Ar/H$_2$O ratio (Fig.3) as also a curve in the correlation between $\delta^{18}$O and CO$_2$/H$_2$O ratio (Fig.4).

In Fig.3, HYK-2, 3 and GTP-1,2 are plotted close to the primary steam curve, which is also common in Fig.4. In Fig.4, the primary steam curve is drawn with assuming the CO$_2$/H$_2$O ratio is 0.03. The CO$_2$/H$_2$O ratio has been adjusted so that the HYK-2 and 3 is approaching to the PS curve. The points for HYK-1, GTP-3 and SHP is plotted far from the PS curve in Fig.3 and 4, which could be due to a contamination of vapor phase generated from local meteoric water (Vm in Figs.).

The CO$_2$/H$_2$O ratio of MV is estimated to be about 0.006 at Mt.Kusatsu-Shirane and Mt.Hakone in Japan with the similar method in this study. The five times larger value for Tatun volcano group suggests a richness of volatile in magma beneath Tatun volcano group. A stagnant magma in crust will be depleted in CO$_2$ quickly if no injection of volatile rich magma brought by a much deeper magma source. The CO$_2$/H$_2$O ratio of magmatic gas in Tatun volcano group may indicate a living magma plumbing system.

Fig.1: Sampling points of fumarolic gas (closed circles, triangles and rectangle). CF and KF is the Chinshan and Kanchiao fault, respectively.
Fig. 2: Isotope ratios of H$_2$O in fumarolic gases. The symbols are common to those in Fig. 1. MV, MW, PS and Vm is the magmatic gas, the local meteoric water, primary steam and vapor evolved from MW at 100°C, respectively.

Fig. 3: $\delta^{18}$O and $^{36}$Ar/H$_2$O ratio of fumarolic gas Fig. 4: $\delta^{18}$O and CO$_2$/H$_2$O ratio of fumarolic gas

Table 1: Isotopic ratios and chemical composition of fumarolic gas from Tatun volcano group

<table>
<thead>
<tr>
<th>Location</th>
<th>Date</th>
<th>Temp. °C</th>
<th>$\delta$D$_{SMOW}$ (%)</th>
<th>$\delta^{18}$O$_{SMOW}$ (%)</th>
<th>CO$_2$/H$_2$O</th>
<th>$^{36}$Ar/H$_2$O</th>
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<tr>
<td>HYK1</td>
<td>2006/6/21</td>
<td>96.5</td>
<td>-49</td>
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<td>2006/6/21</td>
<td>106.5</td>
<td>-21</td>
<td>1.0</td>
<td>0.0207</td>
<td>4.78E-10</td>
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<tr>
<td>HYK3</td>
<td>2006/6/21</td>
<td>119.5</td>
<td>-19</td>
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<td>0.0196</td>
<td>5.01E-10</td>
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<tr>
<td>GTP1</td>
<td>2006/6/22</td>
<td>110.4</td>
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<td>GTP3</td>
<td>2006/6/22</td>
<td>97.7</td>
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<tr>
<td>SHP</td>
<td>2006/6/22</td>
<td>97.7</td>
<td>-27</td>
<td>-4.3</td>
<td>0.0179</td>
<td>9.25E-10</td>
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Table 2: Parameters for the calculation of primary steam

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<th>Enthalpy</th>
<th>f, g</th>
<th>(\delta^{18}O_{GMOW})</th>
<th>(\delta^{18}O_{GMOW})</th>
<th>(\text{CO}_2/\text{H}_2\text{O})</th>
<th>(^{36}\text{Ar}/\text{H}_2\text{O})</th>
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<tr>
<td>MV</td>
<td>900</td>
<td>4391</td>
<td>0.200</td>
<td>~0.612</td>
<td>-5</td>
<td>8</td>
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<tr>
<td>MW</td>
<td>10</td>
<td>44</td>
<td>0.088</td>
<td>~0.999</td>
<td>-33</td>
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<td></td>
<td></td>
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<td>8.5E-10</td>
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<tr>
<td>PL</td>
<td>120</td>
<td>503</td>
<td></td>
<td></td>
<td></td>
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<td></td>
</tr>
</tbody>
</table>

\(\alpha(D/H)\) \(\alpha(^{18}O/^{16}O)\) \(\beta(\text{CO}_2/\text{H}_2\text{O})\) \(\beta(^{36}\text{Ar}/\text{H}_2\text{O})\)

1.02103 1.00438 3.6E-04 3.2E-06

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Geogenic CO$_2$-Exhalations and Vegetation – Mofette Plants

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ABSTRACT

Mofettes (or natural CO$_2$ springs, NCDS) are geogenic CO$_2$-emissions consisting of pure gaseous carbon dioxide sometimes contaminated with traces of CO, CH$_4$ or even H$_2$S. Independent of the origin of the CO$_2$ (which may be earth mantle or crust) the emitted gas influences organismic life on the earth surface. After leaving the soil medium, the gas is either immediately diluted by winds and therefore has no direct consequences for life, or, as CO$_2$ is heavier than air, it forms transient gas lakes (depending on surface morphology) greatly influencing life in the surroundings of the vents. Above concentrations of 8-10% CO$_2$ irritates animals leading to a loss in consciousness and to death because of anoxia or acidosis if concentrations exceed 15-20%. Plants are not that sensitive and some species are able to tolerate CO$_2$ concentrations as high as 100% for a certain period. Several distinct plant species are indicative for mofette fields and for changes within the emission regime. Sometimes mofettes can therefore be distinguished from their surroundings due to their specific “azonal” vegetation regime. In some special mofettes, plants form concentric rings around the CO$_2$ vents which correlate with the CO$_2$ concentration within the rooting zone. Aside from changes in species composition, plants occurring within mofettes reveal differences in habitus and growth. The closer the plants grow to the emitting CO$_2$ vents the smaller they get. Growth reduction is often accompanied by a slight chlorosis. Plants also react physiologically to changes in atmospheric/geogenic CO$_2$. At concentrations between 0 and 3000 ppm plants increase photosynthesis with increasing CO$_2$. Yet, when CO$_2$ concentrations reach the percentage range (5-10%) photosynthesis gets reduced. A further increase in carbon dioxide may lead to a total (but mostly transient) loss of photosynthesis. This is the case in and around mofettes where CO$_2$ concentrations may far exceed 90%.

CONCLUSIONS

Plants can thus react in two main ways to CO$_2$ extremes: (i) with fast physiological/biochemical reactions e.g. photosynthesis or respiration; reactions that are obvious and can be monitored within a few minutes to hours using special equipment and (ii) with slow reactions like chlorosis or changes in growth; reactions that will be evident after days/weeks or months. There is some evidence in E-Germany (Vogtland) and NW-Czech Republic (Cheb basin) that pre-earthquake events may change the geogenic gas composition and the overall CO$_2$ gas flux to the atmosphere. If this change would be large enough, vegetation could be used to monitor or indicate earthquake related reactions.
REFERENCES


Helium Isotope Studies in Regions of Crustal Unrest: The San Andreas Fault Zone, California and the North Anatolian Fault Zone, Turkey

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ABSTRACT

We present new He data from groundwaters, geothermal fluids and/or submarine cold seeps sited close to two of the world’s great fault systems: the North Anatolian Fault Zone (NAFZ), Turkey and the San Andreas Fault (SAF), California. Our aim is to assess the sensitivity of He isotopes and related gas and fluid chemistries to respond to periods of crustal unrest along these tectonically-active plate boundaries. In both regions, $^{3}$He/$^{4}$He ratios are significantly greater than crustal production values indicating that leakage of mantle-derived He – albeit heavily diluted by crustal He – is closely associated with faulting in both areas. In the case of the NAFZ, the most sensitive tracer to crustal perturbations over our monitoring period (2002-2004) appears to be carbon dioxide with large variations in the CO$_2$/$^{3}$He ratio at different localities. At the level of seismicity experienced over the monitoring period, $^{3}$He/$^{4}$He values along the NAFZ were nearly constant. In contrast, we observed marked changes in $^{3}$He/$^{4}$He ratios at Monterey Bay, California during month-long deployments of our new flow meter designed to capture a temporal record of cold seep fluid chemistries. Although seismicity remained low throughout the deployment period, other factors – e.g. those related to tidal pumping – are seen to play an important role in controlling subsurface mixing between mantle and crustal He components.

INTRODUCTION

Helium isotopes have great potential in studies related to seismic or magmatic activity. Their utility stems from the wide range in isotopic ratios between mantle-derived He ($^{3}$He/$^{4}$He ~8R$_A$, where R$_A$ = air He) and He produced in crustal lithologies by radiogenic decay (0.02R$_A$). Consequently, changes in crustal properties (e.g., permeability) or instances of magma movement, related to either seismic or magmatic unrest, can upset the balance in He inputs from mantle and crustal endmembers resulting in easily-perceived variations in $^{3}$He/$^{4}$He ratios in crustal fluids such as groundwaters and geothermal waters. We report, here, new He isotope data from 2 regions characterised by significant, on-going seismic activity to further evaluate controls on, and effects of, the interaction between volatiles of
mantle and crustal origin.

THE NORTH ANATOLIAN FAULT ZONE, TURKEY

We report new helium and carbon abundance and isotope results from nine geothermal locations situated along an 800-km transect of the North Anatolian Fault Zone (NAFZ). During the period November 2001 to November 2004, geothermal waters were collected every 3 to 6 months. At the nine sample locations, the helium isotope ratios range from 0.24 to 2.3 $R_A$, $\delta^{13}C$ values range from $-4.5$ to $+5.8^{\%}$, and $CO_2/He$ ratios range from $5 \times 10^9$ to $5 \times 10^{14}$. The results are illustrated in the following ternary plot.

We note the following geochemical observations: (1) At each of the nine sample locations, the $^3He/He$ ratios are generally constant; however, $CO_2/He$ ratios and helium contents both show one order of magnitude variability, and $\delta^{13}C$ values show $\sim 4^{\%}$ variability at each sample location; and (2) At each of the sampling locations, $\delta^{13}C$ values show positive correlations with $CO_2$ contents. Analyses of the geochemical results indicate that at least three processes are necessary to explain the geochemical variations: (1) Binary mixing between crustal and mantle-derived volatiles can explain the general characteristics of $^3He/He$ ratios, $\delta^{13}C$ values, and $CO_2/He$ ratios; however (2) Preferential degassing of helium from the geothermal waters is responsible for temporal variations in $CO_2/He$ values and $CO_2$ and helium contents at each sample location; and (3) $CO_2$ dissolution followed by calcite precipitation contributes to temporal variations in $CO_2$ contents and $\delta^{13}C$ values at most locations.

In respect He-isotopes, anomalies in the temporal record are defined by values that fall outside two standard deviations of average geochemical values at each specific location. Geochemical anomalies that may be related to seismic activity along the NAFZ are recorded on 6/28/2004 at Yalova, where a M4.2 earthquake occurred at 15 km distance from the sample location 43 days earlier, and on 4/7/2003 at Efteni, where a M4.0 earthquake occurred at 12 km distance 44 days later. In both cases, the sampling periods containing geochemical anomalies were preceded by an increase in $M \geq 3$ earthquakes within 60 days and 40 km distance.

There are numerous factors that could influence whether He-isotopes respond to crustal disturbances, e.g. magnitude of seismic/magmatic event, distance between event and sampling point, hydrologic controls on fluid mixing, etc: however, one variable which is clearly important for recording changes in $^3He/He$ values is frequency of sampling. For example, the study of [Italiano and Martinelli, 2001]
adopted a weekly sampling regime and was able to catch a He-isotope perturbation following the Umbria-Marche seismic crises in 1997-98 prior to $^3\text{He}/^4\text{He}$ ratios returning to normal background values within 2 months. Not all He-isotope anomalies are so short-lived, however: [Sano et al., 1995] estimated a time-constant for return to pre-seismic He-isotope values of ~15 years following volcanic activity at Izu-oshima, Japan. It is unknown if the 3-monthly sampling frequency adopted at Long Valley [Hilton, 1996] and the NAFZ missed any short-lived He perturbations: sampling/analysis frequency in each of these cases was limited to 4-times per year.

SAN ANDREAS FAULT, CALIFORNIA

If He-isotopes are to realize their full potential as a precursory tracer of crustal unrest then a new approach is required that is capable of producing a near-continuous record of He-isotope changes in a natural system without recourse to high frequency (and expensive) sampling. In effect, what is required is an approach that utilizes continuous sampling together with preservation of fluids - to enable specific times of interest (e.g. immediately prior to and/or following a crustal event) to be targeted for detailed, follow-up analytical work. In this way, it should be possible to recognize any anomalous He-isotope signals over a monitoring period irrespective of their duration.

We have developed such a system for deployment on natural cold seeps in the submarine environment. The device consists of a modified CAT-meter (Chemical Aqueous Transport meter; see figure below and description by [Tryon et al., 2001]. The modification involves the addition of a second osmotic pump, high pressure valves, and copper sample coils to collect and store a temporally-resolved continuous water record for later dissolved He (+ other gases) analysis. The plastic sample coils are used to collect fluids for non-gas aqueous chemistry and to enable calculation of fluid flow rates. The major ion and flow rate record assist in identifying periods of interest for the more expensive and time consuming gas analyses.

We have deployed the modified CAT-meters at the Extrovert Cliffs site in Monterey Bay, California. The area is situated close to several active strike-slip faults, including the Monterey and San Gregorio fault zones, and it has many cold seeps located at ~1000m depth. Deployments took place in 2004 and were of ~ 1-3 months duration. Copper coils were processed for both helium and CO$_2$ (isotopes and abundances) using conventional laboratory methods [Fueri et al., 2005]. All samples are supersaturated with respect to seawater in helium and carbon dioxide indicating addition of extraneous CO$_2$ and He. The main feature of the He isotope results is that they vary between ~ 1R$_A$ and 3.4 R$_A$, i.e., between values expected for mantle-derived He (8 R$_A$) and radiogenic He produced in crust and/or
sediments (0.02Ra). Using a simple 2-component mixing model for He, up to ~25% of the total He is mantle-derived.

Perhaps the most significant result of our deployments, however, is the record of the temporal variation of the He concentration and isotopic composition preserved in the coils. The data demonstrate remarkable temporal variation over days/weeks in the volatile content of the cold seep fluids:

Using a new inlet line interfaced directly with the mass spectrometer preparation line, we can process small fluid samples (< 1cm³). In the above plot, we show a total of 11 He isotope analyses which cover a total time period of 1 day (i.e. sampling was achieved with a frequency of ~2.5 hours). Corrected ³He/⁴He ratios vary between 1.4 and 3.4 Ra over a single day and appear to correlate with tide height.

CONCLUSIONS

The Monterey results show an unprecedented level of sampling frequency for He-isotopes. The results offer the exciting prospect that geothermal fluids can be collected on an almost continuous basis, with storage for later He analysis at a frequency determined by the seismic or volcanic record. We are presently evaluating the Monterey results with the aim of understanding the processes regulating the inputs (earthquakes, tidal influences, etc.). The next challenge is to adapt the CAT-meters so that they can be used on groundwater wells and subaerial cold and hot springs.

REFERENCES


Multi Parameter Hydrogeological Monitoring in Eskisehir Region (Turkey) to Analyze Any Precursors Derived from Earthquakes

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ABSTRACT

Earthquakes are the most destructive natural disaster in the nature. Turkey is one of the major earthquake areas in the world. Earthquake prediction is therefore a priority. The objective of this project is the investigation of geochemical and hydrogeological effects related to earthquakes, particularly in the seismically active areas of Turkey. Multi-parameter stations for the continuous recording of the suitable parameters were installed in selected sites of Turkey and the gathered data are used in this investigation.

Eskisehir region is selected as study area and five multi parameter hydrogeological monitoring systems are installed in the area. Motivations to select Eskisehir region for this research are;

- Thrace-Eskisehir fault zone has normal fault segments component during the Pliocene to recent. The sedimentation of Pliocene to recent sediments in the region and NW-SE directed fault blocks indicate the activity of the fault zone at least since Pliocene. Additionally in 20th century 15 earthquakes over M=4 have occurred in the region. The greatest earthquake (February 20, 1956 M=6.4) had taken place on WNW – ESE directed segment 10 km in length.
Thermal springs within the city and thermal water wells in the region indicate the tectonic activity of the region and should be taken under observation.

The plain area is covered by new alluvium (max 8-10m) and old alluvium (max 80-90m) and the occurrence of permeable and porous environment. The shallow depth of groundwater reaching from 3 to 5 m and occurrence of silt and the fine sand triggers the possibility of liquefaction as a risk during the earthquakes.

The availability of the water level observations of 19-drilled wells from mid of 1999 encourages the selection of Eskisehir as the central point of investigations (journals.tubitak.gov.tr/earth/issues/yer-05-14-3/yer-14-3-3-0510-5.pdf.)

The Thrace-Eskisehir Fault Zone (TEFZ), an older right-lateral strike-slip fault, is now an active normal fault. It strikes NW-SE through the Marmara region and has been displaced by the three strands of the North Anatolian Fault Zone (NAFZ). At present, the different parts of this fault are characterized by low seismic activity and normal character, presumably due to dextral shear strain of the NAFZ. Yaltirak et. al. (2005) model is based on the relationship between seismogenic normal faults produced by angular stress vectors conformable with seismogenic faults. For instance, stress reaches a maximum prior to earthquakes in the NW-SE oriented low activity basins located at 45° to the E-W dextral strike-slip seismogenic faults, such as the NAFZ. Poro-elastic changes in loose sediments surrounding the shallow wells show anomalies due to maximum stress prior to earthquakes.

Based on the obtained data in the project, some suspicious anomalies several days before an earthquake in the geochemical parameters and the radon concentration of the water in the aquifers are precursors before an earthquake occurs. Using these precursors exist the possibility to warn the first responders and reduce the losses of life and health.

The measured parameters in waters are radon and CO$_2$ concentration, redox potential, conductivity, pH value, water level, water temperature and the climatic parameters. The data collected from five measuring stations now date more than one year. The data are analyzed against seismic activity occurred during measurement period. Small probable anomalies are found in connection with earthquakes. In Station no. 3, named Uyuzhamam mineral borehole, redox potential decreases while pH increases with seismic events. The Station no.4 (Uyuzhamam thermal spring), that is in the closer vicinity of the Station no. 3, radon and CO$_2$ fluctuated with same seismic events. In Station no.8, named Kandilli borehole, CO$_2$ and redox potential are changed with seismic events. Additionally, according to long-term observations in the project, well water level change is very sensitive parameter to the seismic events in the area. Because it comprises naturally filtered anomalies, reflecting only changes due to earthquakes. During installing and operating these stations, some major difficulties are encountered. In this paper, these difficulties are also storied to share experiences gained in the project.
Detection of Sensitive Compounds in Groundwater with Observed Enhanced Fluorescence Spectra from Earthquake Prone Areas: First Results

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ABSTRACT

This publication is based on observations of fluorescence intensities revealed by using the Synchrosan technique to assess fluorescent intensity made on normal groundwater, thermal- and mineral waters before and after large earthquakes of M >5.

Since the most plausible explanation for this phenomenon appears to be an enhancement of the natural fluorescent substances contained in groundwater samples, the need to further characterize these substances was deemed necessary. In a first step, the waters were investigated by means of liquid chromatography combined with an on-line fast synchronous spectral scanning fluorescence detector. This was followed, in a second step, by their analyses using HPLC coupled to an ion trap mass spectrometer.

INTRODUCTION

The main topic of this project is the investigation of changes in the fluorescence spectra of groundwater components based on observations of groundwater (springs and boreholes) before and after strong to moderate earthquakes.

The changes in the fluorescence spectra, as opposed from normal groundwater and thermal and mineral waters of western Turkey, was first observed in samples taken before and after after the strong 17.8.1999 Izmit M = 7.6 earthquake. Variations in the fluorescent properties of groundwater emerged during the routine tests of the waters with our commercially available fluorescence detector HP LS-50 in “Synchrosan-mode”, used for the rapid screening of water. Previously, for the same earthquake, changes in the chemical and isotopic composition of the water were observed (Balderer, et al., 2006, Balderer et al., 2004). A further opportunity to investigate this singular phenomenon was made possible after an earthquake of moderate intensity happened in Northern Italy in November 2004 (Richter scale M>5). At the thermal spring of Waldkirch/ Oberbergen, which originates from a carbonatite rock within the mid-Tertiary (Oligocene to Miocene) volcanic complex of Kaisersstuhl at the edge of the Rhine Graben in the Black Forest, Germany (Schmassmann et al, 1984), small weak earthquakes of M ≈ 2 to 3 were also reflected in the resulting fluorescence spectra, of the spring water sampled at 2 days intervals (Balderer and Leuenberger, 2006, 2007).
STATE OF THE PRESENT WORK

In this publication the first results achieved towards the identification of molecular signatures observed by the fluorescence spectra in groundwater will be presented. Furthermore, an outline of the additional work towards the systematic characterization of occurring fluorescence peaks in groundwater using HPLC coupled to on-line synchronous scanning spectrometer in parallel to an Ion-trap mass-spectrometer will be given.

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A 1000 m Water Well as a Test Monitoring System for The Detection of Possible Earthquake Related Anomalies in Fluids

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ABSTRACT

The Miano monitoring water well is located in a seismically active area of Northern Apennines (NW-Italy) close to Parma river. A local monitoring station record water temperature, gas and water flow rate measured on a two-phase fluid system (CH₄ and H₂O) out flowing from a 1000 m well drilled in 1905 for hydrocarbon researches. The fluid is a mixture of thermal water (38°C) and methane and is originated from a calcareous highly fracturated rock aquifer. The water discharge is of 4 liter/sec and the gas discharge around 5 liter/sec. The record of gas and water flow as well as water temperature begun on November 2004 and was disturbed by some gaps due to different technical problems. Some significant anomalies were detected in gas flow rate, water flow rate and temperature. In particular temperature anomalies of 0.1 up to 0.4°C characterized by duration of 6 - 15 hours were detected. The evaluation of recorded anomalies is possible be means of comparison with the contemporary recorded ambient temperature.

The statistical evaluation of recorded data show significant anomalies which could have been triggered by an increased warm water supply from the deep aquifer due to a pore pressure variation induced by local crustal strain. Crustal deformative processes along the N-S trending Parma faulted area could be responsible for recorded geophysical variations observed in monitored fluids.
Gas Compositions and He-C Isotopic Ratios of Fumarolic Samples from Some Active Volcanoes in Philippines

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ABSTRACT

Taal volcanic is located on the southwestern of Luzon Island in the Philippines. It is hazardous because of its high level of activity and proximity to Manila. Kanlaon volcano is located in Negros Island, central Philippines. It is also an active volcano. They are related to subduction system of Manila trench and Negros trench, respectively. Fumarolic gas and bubbling gas of hot spring samples were collected in February 2007 from these two volcanoes to compare their compositions with others in the world.

Preliminary results of gas analysis for these samples show a similar composition of low-temperature fumaroles in the world, i.e., temperature <200°C, and dominant with CO₂ and H₂S/SO₂ >1. H₂O is the major species of gas samples from both volcanoes; and CO₂ is the dominant component after de-watering. Minor components include H₂S, N₂ and H₂. Kanlaon samples show similar compositions with those from Taal volcano, however, exhibit more CH₄ than H₂. The gas composition of most of these samples falls in the range of affinity with convergent plate gases based on the plot of N₂-He-Ar. The high ³He/⁴He ratios of those samples indicate a mantle-derived degassing ource in origin.

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Alpha Active Pollutants as a Precursor of Seismic Activity: A Review

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ABSTRACT

Radon, an alpha active air pollutant is ubiquitously present in the atmosphere. There are various reports, where a critical analysis of the data reflects a correlation between radon levels and seismicity and radon has been used as a precursor in the prediction of earthquakes, volcanic activity, fault mapping and characterization of geothermal sources. Anomalous radon changes in ground water and soil gas have been reported for several earthquakes at favorably selected monitoring stations located at distances of several hundred kilometers from their respective epicenters and the release of large amount of radon depends to a larger extent on the tectonic disturbance of the host materials.

In the present paper, various techniques for measurement of radon have been discussed and the origin and mechanism of observed anomalies in concentration of radon and their relationship to earthquakes have been reviewed.
Origin and Detection of Spike-Like Anomalies in Soil Gas Radon Time Series

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ABSTRACT

Soil gas radon as recorded in a time series have two origins. One source is radon of deeper origin that is migrating upward as a continuous flux with other soil gases. Radon of this source can fluctuate up and down gradually but has no sudden changes. Radon variation of this source is likely to relate to the movement of plates, and secular variation of heat flow. This type of radon can be observed easily when counting at a site with numerous vertical fractures such as an active fault zone. The \( ^3\text{He}/^4\text{He} \) ratios as studied by Yang et al. (2003) suggested that there is significant amount of mantle origin soil gas at Taiwan 1 site. The first monitoring station, Taiwan 1, was established in October of year 2000. It is located on a gravelly sandy river terrace within a fault zone created by six active faults. This fault zone is very wide and has a large lateral extension of approximately 600 m. As a result, the deep source radon counts are high (Chyi et al., 2002). The second monitoring station was established in the same area inside a mud volcano pond but was abandoned due to moisture condensation problems in the radon detector system. The third station, Taiwan 3, was established in a mud volcano area found within Chishan fault zone with a smaller lateral extension of about 60 m. The station started to function in March of 2004 (Chyi et al., 2005). The radon of deeper origin is not as high as Taiwan 1 because of the low permeability nature of the soil. Both Taiwan 1 and 3 are located in southeastern Taiwan. Taiwan 4 is located within Chishang fault zone with ??? lateral extension in east central Taiwan. It was established in March of 2007. The site is covered by a debris flow with a large amount of mud and thus has a low soil permeability. The deep source radon appears to be low as observed by the low counts in our initial observation.

The other source is the desorbed radon off the surface of soil and mineral particles when there is a passing of stress force, a perturbation of groundwater table, or a change of static charges in the vicinity related to a stress. It is possible that all these processes are in progress and thus result in a sudden change of pH conditions in the near surface soil environment and result in a sudden release of absorbed radon as a burst. If this is the case, then the timing of the radon desorption should of special significance in indicating the stress of the terrain reaching a given level (Chyi et al., 2007). Desorption of radon is of short duration and that is usually accomplished in less than one minute based on our binary event counting in 2000 to 2001 with a 16 second interval (Chyi et al., 2002). It can be demonstrated that the spike-like anomaly become essentially not detectable if the counting interval is longer than a day. As this absorbed radon is quickly released, the surface of soil and mineral particles
are depleted of radon gas molecules. Continue counting of radon with a given time interval can thus register radon count as a spike-like anomaly in a time series. Counting soil gas radon count in intervals longer than a day will, therefore, gives dubious results. Only continue counting of radon in real time with a counting interval a few hours or less is capable of catching these spike-like anomalies (Chyi, 2006).

The size of the anomaly is related to the stress induced geologic processes that affect radon desorption off mineral and soil particles. The magnitude of the stress should have been related to the magnitude and distance to the origin of the stress. If stress is propagated outward from the center of stress, or hypocenter, and decays logarithmically, then the timing of the arrival of the stress at a given site as indicated by this radon spike-like anomaly can be used to calculate the distance to the origin of the stress. A small impending earthquake close-by can induce similar magnitude of stress to a much larger earthquake farther away. The size of the anomaly thus cannot be a good indicator to the magnitude of earthquake. But with multiple monitoring stations, location, timing, and magnitude of the inducing earthquake can be calculated.

The monitoring station to detection of significant spike-like anomalies must meet the following requirements (Chyi, 2007). The monitoring site must be sensitive to tectonic changes such as the passing of stress force. The current choice is an known active fault zone. The station must be able to provide reliable soil gas radon counts without environmental and human interferences. The current choice is a specific ditch and housing design (Chyi, 2006). The station must not be inundated and must have a large soil gas receiving zone (Chyi, 2006). The detector system must be able to provide radon level recording at a time interval short enough to catch the anomaly and the recording must be continuous (Chyi, 2006). Without considering these factors, the soil gas radon recording must be considered dubious and thus insignificant in forecasting earthquakes. If all these considerations are followed; soil gas radon can be a very sensitive indicator of incoming earthquake.

REFERENCE


Anomalous Decreases in Groundwater Radon Precursory to Earthquakes in Eastern Taiwan

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ABSTRACT

We began to accumulate data on groundwater radon concentration at the Antung hot spring in eastern Taiwan in July 2003. One anomalous minimum in the concentration of groundwater radon at 326 ± 9 pCi/L was observed to precede the earthquake of magnitude M_W 6.8 that occurred on December 10, 2003 located 20 km from the Antung radon-monitoring station. Another anomalous minimum in the concentration of groundwater radon at 371 ± 9 pCi/L was observed to precede the earthquakes of magnitude M_W 6.2, and M_W 5.9 that occurred on April 1 and 15, 2006, 2006 located 52 km from the Antung radon-monitoring station. The anomalous minima in radon concentration repeatedly observed at the Antung hot spring suggest that the groundwater radon, when observed at suitable sites, can be a sensitive tracer for strain changes in crust associated with earthquake occurrences.

INTRODUCTION

Variations in radon (Rn-222) content in groundwater have been observed prior to some earthquakes (Hauksson 1981; Igarashi et al. 1995; Liu et al. 1985; Noguchi. & Wakita 1977; Silver & Wakita, 1996; Teng, 1980; Wakita et al., 1980). Most of the radon anomalies from these observations indicate a radon increase prior to the earthquake. However, precursory radon declines are also known to exist. For example, Wakita et al. (Wakita et al., 1980) observed a sudden drop followed by an increase in the radon concentration that occurred prior to the 1978 Izu-Oshima-kinkai earthquake of magnitude 7.0. Unfortunately, observations like these are generally irreproducible (Roeloffs, 1999). Radon anomalies, generally at isolated locations, have been noted in several parts of the world, but this research is the first example of three anomalies occurring at the same location – and all in a period of less than four years. We have monitored groundwater radon since July 2003 at the Antung hot spring that is located near the Chihshang fault – part of the eastern boundary of the present-day plate suture between the Eurasia and the Philippine Sea plates. This paper reports evidence of the recurrent groundwater radon anomalies observed at the Antung hot spring in eastern Taiwan, located about 3 km southeast of the Chihshang fault, since July 2003 (Fig. 1). The Chihshang fault ruptured (Hsu 1962) during two 1951 earthquakes of magnitudes (M) 6.2 and (M) 7.0. The annual survey of geodetic and GPS measurements has consistently revealed the active creep of the Chihshang fault that is moving at a rapid steady rate of about 2-3 cm/yr during the past 20 years (Angelier et al. 2000; Lee et al. 2003; Yu & Kuo 2001 ). Since July 2003, recurrent anomalous minima in radon concentration were observed to precede the earthquakes of magnitude M_W 6.8, M_W 6.2, and M_W 5.9 that occurred on December 10,
2003, April 1 and 15, 2006 with epicenters located 20 km, 52 km, and 47 km, respectively, from the Antung radon-monitoring station. Geological conditions near the Antung hot spring may explain the radon anomalous decreases.

MATERIALS AND METHODS

We initiated monitoring groundwater radon in July 2003 at a well (D1) located at the Antung hot spring (Fig. 1). The observation well (D1) is located approximately 20 km north of the epicenter of the magnitude M\textsubscript{w} 6.8 earthquake that occurred at 4:38 am on December 10, 2003 (UT). Discrete samples of geothermal water have been collected from a well at the Antung hot spring for analysis of radon (Rn-222) content. The production interval ranges from 167 m to 187 m below ground surface. The well was pumped more or less continuously. The liquid scintillation method was adopted to determine the activity concentration of radon-222 in groundwater (Noguchi 1964). For a count time of 50 min and background less than 6 cpm, a detection limit below 18 pCi/L was achieved using the sample volume of 15 ml.

RESULTS AND DISCUSSION

Recurrent groundwater radon anomalies were observed to precede the earthquakes of magnitude M\textsubscript{w} 6.8, M\textsubscript{w} 6.2, and M\textsubscript{w} 5.9 that occurred on December 10, 2003, April 1 and 15, 2006 near Chengkung in eastern Taiwan. Fig. 2 shows the radon concentration data since July 2003 at the monitoring well (D1) in the Antung hot spring. The box-and-whisker plot is used on the left-hand side in Fig. 2. It shows the median (50\textsuperscript{th} percentile, 724 pCi/L) as a center bar, and the quartiles (25\textsuperscript{th} and 75\textsuperscript{th} percentiles, 599 pCi/L and 769 pCi/L) as a box. The whiskers (371 pCi/L and 952 pCi/L) cover all but the most extreme values in the data set. The recurrent anomalous minima in radon concentration observed at the Antung hot spring are as follows: (1) a minimum value of 326 ± 9 pCi/L that occurred on November 20, 2003 before the December 10, 2003 earthquake; and (2) a minimum value of 371 ± 9 pCi/L that occurred on March 16, 2006 before the April 1 and 15, 2006 earthquakes. Records of temperature and rainfall were examined to check if the radon anomalies could be attributed to these environmental factors. The temperature of the groundwater was very stable, and its variation was less than 0.2 °C during the observation period. There was no heavy rainfall responsible for the radon anomaly. It is also difficult to explain such a large radon decrease by mixing of groundwater. Two earthquakes, with magnitudes (M\textsubscript{w}) of 5.2 and 6.2, occurred on January 1, 2004 and May 19, 2004. Based upon their magnitudes and locations, we consider these as aftershocks of the Chengkung earthquake of December 10, 2003.

Some of the characteristics of the radon concentrations observed for the Chengkung quake of Taiwan can be compared to those of the Izu-Oshima-kinkai tremor of Japan. For example, the distance from the epicenter to the radon monitoring station for the 2003 M\textsubscript{w} 6.8 Chengkung earthquake was about 20 kilometers; this distance is quite similar to the epicenter–station distance of 25 kilometers for the 1978 (M) 7.0 Izu-Oshima-kinkai earthquake of Japan. The observed radon anomaly precursory to the 2003 Chengkung earthquake (Kuo et al. 2006) also behaved similarly to that observed precursory to the 1978 Izu-Oshima-kinkai earthquake (Wakita et al. 1980). Sixty-five days before the 2003 Chengkung earthquake (Fig. 2), the radon concentration of ground water started to decrease. Similarly, about seventy-five days before the 1978 Izu-Oshima-kinkai earthquake, the radon concentration started to decrease. The radon concentration recovered to the previous background level just before the earthquakes. All the three recurrent anomalous decreases observed at Antung follow the same
v-shaped progression and are marked with green inverted triangles in Fig. 2. According to a worldwide survey (Hauksson 1981), most radon (Rn-222) anomalies showed increases in radon content of groundwater. Contrarily, few anomalies manifested decreases in radon content of groundwater (Wakita et al. 1980; Kuo et al. 2006).

CONCLUSIONS

Although the Japanese earthquake mentioned earlier recorded a similar decrease in radon concentration prior to a large earthquake (Wakita et al. 1980), the significance of our research is that it is the first documented case of recurrent (recorded by the same groundwater monitoring station) precursory decreases in radon anomalies associated with large magnitude earthquakes.

ACKNOWLEDGEMENTS

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**FIGURES**

Fig. 1: (a) Tectonic setting of Taiwan (study area: location of b). (b) Map of the epicenters of the earthquakes near Chengkung (The open stars labeled with 1, 2, and 3 are the epicenters of the earthquakes that occurred on December 10, 2003, and April 1 and 15, 2006, respectively; filled stars are 1951 mainshocks; filled triangle is radon-monitoring station).

Fig. 2: Radon concentration data at the monitoring well (D1) in the Antung hot spring (open inverted triangles: anomalous radon minima; long arrows: mainshocks; short arrows: aftershocks; earthquake magnitude Mw shown beside arrows).
Subsurface Changes in Radon Concentration Associated with Earthquake Activity in Garhwal Himalaya

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ABSTRACT

Research on earthquake related radon monitoring has received enormous attention in recent past. Anomalous behaviour of radon in soil and groundwater can be used as a reliable precursor for an impending earthquake. While earthquake prediction may not yet be possible, earthquake prediction research has greatly increased our understanding of earthquake source mechanisms, the structural the structural complexities of fault zones, and the earthquake recurrence interval, expected at a given location. This paper presents some results of continuous monitoring of radon levels in soil-gas and spring water in Garhwal Himalaya, India. Sudden increases in radon concentration in soil-gas and spring water were observed before during and after the earthquakes occurred in the area. The variations in radon concentrations in soil-gas and spring water are found to be correlated with the seismic activities in the Garhwal Himalaya. A significant correlation was also observed between water discharge rate and seismic activity in the area. Based on the recorded data, it was observed that the continuous measurements of various parameters viz. radon, helium, earth’s conductivity and resistivity, groundwater level and temperature, water discharge rate from spring, ULF/VLF measurements and land deformation study at several sites in a grid pattern is necessary for making successful prediction of an earthquake in future. The role and usefulness of some earthquake precursors are discussed in this paper.
A New Approach Based on Electrical Circuit Model for Using of Time Variation of Radon Concentration in Earth as an Earthquake Precursor

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ABSTRACT

A new model based on electric circuit theory has been introduced to simulate radon behavior in the earth. This model simulates the radon generation in earth as a voltage source, migration to a closed area as a conductivity and radon concentration in the closed area as the voltage across a capacitor. This simulation considers the migration of radon through the earth by diffusion–advection mechanism and in one dimension geometry. The measured data at Roselend tunnel, in the French Alps have been used to simulate the behavior of radon in the atmosphere of the inner room at this tunnel.
Chemical Monitoring of Volcanic Gas Using Remote FT-IR Spectroscopy at Several Active Volcanoes in Japan

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ABSTRACT

Chemical composition of volcanic gases of seven Japanese active volcanoes (Usu, Asama, Miyakejima, Aso, Unzen, Sakurajima and Satuma-iwojima volcanoes) have been monitored using an FT-IR spectrometer from a distant safe place. In the absorption measurement, infrared light source behind volcanic gas emission is essential in the volcanic environment. Hot lava dome, hot ground and scattered solar infrared light were available for the light source. Until now, eight species, \( \text{SO}_2 \), \( \text{HCl} \), \( \text{HF} \), \( \text{CO} \), \( \text{CO}_2 \), \( \text{COS} \), \( \text{SiF}_4 \) and \( \text{H}_2\text{O} \) have been measured with this method and significant variations in observed chemical data associated with volcanic activity were obtained at Aso and Asama volcanoes.

INTRODUCTION

Since Mori et al. (1993) first determined HCl and \( \text{SO}_2 \) in volcanic gas from a distant place using an FT-IR spectrometer, several groups of volcanologists have applied this method for monitoring active volcanoes in the world (Oppenheimer et al., 1998, Burton et al., 2000, Allard et al. 2005). The great advantage of the remote FT-IR technique is its ability to measure chemical composition of volcanic gas emitting from inaccessible vents during erupting events from less hazardous places. In this paper, we summarize recent advances in this method and monitoring studies on Japanese active volcanoes since the beginning of 1990’s using this new method.

METHODOLOGY AND OBSERVATION

Chemical species of volcanic gas, such as \( \text{CO}_2 \), \( \text{SO}_2 \), \( \text{H}_2\text{S} \), HCl, have absorption features in infrared region. In case that infrared light source is available behind the volcanic gas emission, absorption spectra of these species can be measured from a distant place. The infrared light sources we have utilized are hot lava dome, hot ground surface with abundant fumaroles and solar infrared light scattered by higher clouds or plumes. The source infrared light, after absorbed by some chemical species constituting volcanic gases, is gathered with a Cassegrarian telescope with a diameter of 30 cm and a field of view of 5 mrad and is introduced into an FT-IR radiometer (BOMEN, MB-100). Its spectral resolution is 1 cm\(^{-1}\), and a MCT detector or an InSb detector is used depending on the range of wavelength used to detect the target volcanic gas species. Recorded row spectrum is retrieved to column amount of each species, with a sophisticated spectral analyses developed by ourselves. Until now, eight species, \( \text{SO}_2 \), \( \text{HCl} \), \( \text{HF} \), \( \text{CO} \), \( \text{CO}_2 \), \( \text{COS} \), \( \text{SiF}_4 \) and \( \text{H}_2\text{O} \) have been measured with this method. We tried to apply this method to seven volcanoes in Japan (Fig. 1), starting the first attempt at Unzen volcano (Mori et al., 1993).
CASE STUDY

(1) Unzen volcano (Mori et al., 1993)
Unzen volcano started to erupt on the summit area in November 1990, and dacite lava domes were built accompanied with a pyroclastic flows from the middle of May 1991. Since the summit area with intense volcanic gas emission was extremely hazardous, we tried to apply a remote FT-IR measurement 4 times from in March 1992 to July 1994. Infrared emission from hot lava dome was used as a light source and absorption spectra of volcanic gas released from the dome was observed at a safe site 1.3 km far from the volcanic gas. The $\text{SO}_2$/HCl ratio did not change significantly between 0.7 and 1.8 from March to December 1993, but the decrease in source infrared emission due to the decrease in surface temperature of lava domes related to the drop of lava effusion rate resulted in the absence of absorption spectrum of HCl in July 1994.

(2) Usu volcano volcano (Mori et al., 1995)
After the 1977-1978 eruptions, high temperature volcanic gas has been releasing intensely from fumaroles around I crater in the summit caldera of Usu volcano. In 1995, we tried to measure infrared
absorption spectra of the volcanic gas at a site 900 m from it, using hot ground surface with abundant fumaroles (~500°C) as light source. But, we could observe only very weak absorption feature of SO₂.

(3) Aso volcano (Mori and Notsu, 1997, 2007)
Aso volcano has several central cones in a large caldera with about 20 km in diameter. One of the central cones, Nakadake, has seven summit craters and the bottom of the First crater is filled with hot acid water, with intense fumarolic activities on the southern wall. Remote FT-IR observations were carried out, viewing down volcanic gas 200m far and 150m below from the crater rim and using hot ground as an IR source, in 1996, 1997, 1998, 2001, 2002 and 2003. We could determine 7 components: HCl, SO₂, CO₂, CO, COS, HF and SiF₄. Gas temperature in the depth of Nakadake, estimated from CO/CO₂ ratios, kept constant with more than 700°C during the period 1996-2003. Temporal variation in volcanic gas data showed that selective scrubbing of HCl by hydrothermal interaction occurred in 1998, when a total supply of volcanic gas from the depth decreased.

(4) Satsuma-iwojima volcano (Mori et al, 2002)
Since the latest eruption about 1200 years ago, Iwodake of Satsuma-iwojima volcano has probably been intensely degassing. In the summit crater of Iwodake, fumarolic activities up to 880°C are observed. We carried out in October 1996 remote FT-IR observations, viewing down fumarolic areas 250m far, and detected four species, SO₂, HCl, HF and SiF₄. Measured SO₂/HCl ratio (= ~4) was higher than high-temperature volcanic gas, possible caused by sulfur combustion. The SiF₄ flux was measured about 13 ton/day, the highest in the world. Measured SiF₄/HF ratio cannot be explained in terms of thermodynamic calculations of high temperature volcanic gas composition.

(5) Sakurajima volcano (Mori and Notsu, 2003)
Sakurajima volcano has been frequently erupting since 1995 and was continuously emitting 1000-2000 ton/day of SO₂. We tried to use solar scattered light as an infrared source first in April 1999 and four species, SO₂, HCl, HF and SiF₄, were detected. Repeated observations were done in 2001 and 2002.

(6) Miyakejima volcano (Notsu et al., 2002)
Miyakejima volcano started to erupt in June 2000, and after the collapse to form a big summit caldera with 1.6 km in diameter and 450m in depth, huge amount of volcanic gas has continued to emit, with a maximum monthly SO₂ flux of 54 kt/day in December 2000 (Kazahaya et al., 2004). We carried out remote FT-IR measurements of volcanic gases using solar scattered light as a light source in December 2000 and March 2001. Measured HCl/SO₂ ratios were 0.05-0.08 for dense volcanic gas with white color, and 0.09-0.12 for transparent to pale-colored volcanic gas.

(7) Asama volcano (Mori and Notsu, 2005)
Asama volcano erupted on 1 September 2004 after 21 years’ quiescence. Since we have already observed IR absorption spectrum of SO₂, HCl and HF in volcanic gas using solar scattered light as a light source in 2000 and 2001, we continued the same observations four times (15 and 16 September 2004, 1 October 2004 and 10 March 2005) after the eruptions. Measured HCl/SO₂ ratios after eruptions (0.17~0.20) were slightly higher than those before eruptions (0.11~0.15). Measured HF/HCl ratios grew higher over 0.19 during the high activity period from mid-September to October 2004.
SUMMARY

Remote FT-IR spectroscopy was first applied to detect HCl and SO$_2$ in volcanic gases at Unzen volcano, Japan, in 1992. Then this technique was improved to measure more species and now absorption spectra of eight species, SO$_2$, HCl, HF, CO, CO$_2$, COS, SiF$_4$ and H$_2$O can be obtained with this method using IR emission from hot lava dome, hot ground surface or solar scattered light as a light source. Repeated observations over several years at Asama and Aso volcanoes show chemical changes in volcanic gases related to volcanic activities.

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Satellite Detection of Carbon Monoxide Emission Prior to Earthquakes and Volcanoes

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ABSTRACT

The recent satellite advancement has capability in providing information about various gases. Changes in land, ocean and atmospheric parameters from the satellite observations have been observed in the epicentral and surroundings regions of several earthquakes occurred in the ocean and on the land. The satellite observations have revealed strong coupling between land-ocean-atmosphere-ionosphere associated with earthquakes of magnitudes more than 5.5 with focal regions within 35 km. In the present paper, detailed analysis of MOPITT, SSM/I satellites together with metrological observations will be presented. The MOPITT data provide information about the carbon monoxide. MOPITT CO data available at different pressure levels at 22 km horizontal resolution. We have used level 3, \(1^\circ \times 1^\circ\) resolution MOPITT CO profile and CO total column over a dozen of earthquakes occurred on the land. MOPITT CO (carbon monoxide) data have been analyzed for earthquake precursor signal detection. The rise in CO before the earthquake event has been observed at different pressure levels. Most of the event signal observed at 100hpa, 200hpa and 350hpa pressure levels, at some events the significant changes have been observed at 1000hpa pressure level. We have also carried out analysis of several other parameters measured from satellites e.g. brightness temperature, water vapor and meteorological parameters. These parameters also show complementary behavior with the carbon monoxide emission prior to the earthquakes. The detailed analysis of satellite data from seismically active Koyna region in India, Kashmir, Gujarat, and Sumatra earthquakes will be presented. Satellite parameters show a great potential in providing information about early information about earthquakes. Further, we have found anomalous CO anomaly associated with the activities of Taal volcano (121E, 14N) located 60 km south of Manila, Philippines. This anomalous CO shows one to one relation with the activities of Tall volcanic activities.
High $^3$He Emanation Observed in a Forearc Region of the Kinki District, SW Japan: Revisited

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ABSTRACT

The Japanese Islands are divided into two major blocks, Northeastern (NE) Japan and Southwestern (SW) Japan by Itoigawa-Shizuoka tectonic line. NE Japan is considered as a well-defined island arc system with a deep trench, a frontal arc, a volcanic arc, and a back arc region with a marginal sea. Perpendicular to the trench axis, geophysical data such as terrestrial heat flow, gravity anomaly and seismic velocity vary significantly across the island arc. There is a clear contrast of $^3$He/$^4$He ratios perpendicular to the trench axis, low-$Ra$ in the frontal arc and high-$Ra$ in the volcanic arc. This may reflect the presence or absence of magma with high-$Ra$ in the shallow crust. As a carrier of primordial helium, source melt may be generated in low-V zone of the wedge mantle by dehydration of Pacific slab at about 150 km deep and may flow upward sub-parallel to the slab, which is well constrained by S-wave velocity perturbation.

In SW Japan a well-defined island arc system features has not developed. The volcanic front is not as clear as in NE Japan except for Kyushu and heat flow values are relatively high in the trench region. These features are generally attributable to the subduction of the young and warm lithosphere of the Philippine Sea plate beneath the Eurasian plate. In addition the Pacific plate descends from east beneath the Philippine Sea and Eurasian plates. This has resulted in a complicated surface geology and lateral heterogeneity in the upper mantle structure of SW Japan. However in the Chugoku and Shikoku districts of SW Japan, there is a geographical contrast of $Ra$ similar to NE Japan except for the region at about 100 km from the volcanic front where medium-$Ra$ was found. High-$Ra$ observed in volcanic arc of the Chugoku district may be attributable to the mantle helium derived from the magma source generated below the Philippine Sea slab. Medium-$Ra$ in the Shikoku district is explained by dehydration of the young slab with a moderate aging effect.

In the Kinki district of SW Japan, anomalously high-$Ra$ was observed in the frontal arc region that was called “Kinki Spot”. Again the high-$Ra$ cannot be attributable to dehydration of the young slab. Since the high-$Ra$ is located at much wider region from the volcanic front when compared with NE Japan and the Chugoku and Shikoku districts, the melt generated below the Philippine Sea slab may penetrate into the fissure of the slab tear and may arrive at the shallow crust by upwelling flow. In order to verify the hypothesis, we collect several gas and water samples in the Kinki district. We will measure the $^3$He/$^4$He ratios of these samples and present data at the conference.
The Gas Flow at Mineral Springs and Mofettes in the Vogtland/NW Bohemia: An Enduring Long-term Uptrend

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ABSTRACT

Since 1993, an increase of the $^3$He/$^4$He ratios at gas emission sites in Vogtland and the Cheb basin (NW Bohemia) was observed. The highest values up to 6.2 Ra were measured at the mofette Bublák (CZ). This rise of the upper mantle-derived helium in the upstreaming gases signalises an active magmatic process beneath the Cheb basin.

Overlapping this, continuous high-resolution CO$_2$ gas flow records (dt =10 min) at mineral springs of Bad Brambach ('Eisen-' and 'Schillerquelle' since 1998, 'Wettinquelle' since 2000) as well as at mofettes in NW Bohemia (Nature Park Soos and Bublák since 2001 and 2004, respectively) show a significant and presently enduring increase of the gas flow rate. The uptrend of the average yearly gas flow amounts between 1.6 % at the 'Schillerquelle' and 36 % per year at Soos. Thereby, the influences of temporary periodical variations of meteorological parameters on the gas flow may be neglected because they are levelled due to the long-term averaging (months, years).

For a characterisation of the gas flow pathways, the ratios of the effective cross-sectional areas for the free gas flow were estimated at three springs and two mofettes by means of a simplified model calculation. As a result, a matrix of cross-sectional area ratios was established which allows to compare the gas vents among themselves. Applying this to the spring 'Wettinquelle' (W) and the mofette Soos (S), a ratio of the effective cross-sectional areas of $A_S/A_W = 13.2$ is obtained. That parameter may be considered as a measure for the different dimensions of the gas-bearing fissures and cracks between both locations, without knowing fluid-relevant rock parameters. Using the continuous-ness equation for fluids, a respective matrix of the gas flow velocity ratios between the springs and mofettes could be calculated as well. From 2001 to 2006, the average yearly gas flow velocities increased by the factor 1.12 at the mineral spring 'Wettinquelle' and 2.82 at the mofette Soos.
The comparison between the monthly fluctuations of free gas flow and dissolved CO$_2$ at the 'Wetinquelle' shows an inverse dependence of both parameters. However, the concentration of dissolved CO$_2$ does not show any long-term trend as observed in the case of free gas flow. This indicates that the mineral water body acts as a kind of (mostly saturated) CO$_2$ buffer being degassed more or less strongly, depending on the flow rate of the ascending free gas. At mofettes, such an effect is not expected since the emitted gas volume is there extremely large, compared to the permeated water phase.

The results give hints for an increased activity of the magmatic reservoir below the Cheb Basin, not only from the qualitative ($^{3}$He/$^{4}$He) but also from the quantitative point of view.
Major $^{222}\text{Rn}$ Anomalies in Fluids of Los Azufres (México) Geothermal Field

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ABSTRACT

A new interpretation of the $^{222}\text{Rn}$ anomalies occurred at the time of the September 1985 M8.1 Michoacan, Mexico, earthquake in fluids from Los Azufres, Mexico, geothermal field wells is given. $^{222}\text{Rn}$ data was correlated to the thermodynamic conditions of wells at bottom conditions (enthalpy, pressure and steam/water ratio) and the results suggested that $^{222}\text{Rn}$ behavior was due to the changes occurred in such variables. At least two processes seemed to occur previous to the earthquake, when samples were collected, which were different in every zone of the field. A compression process occurred at the southern zone of the field, where most of the steam wells are located, while an expansion process took place at the northern zone where two-phase wells occur. At the south, in steam wells, due to the pressure increase, a small fraction of liquid phase was formed, causing the increase in $^{222}\text{Rn}$, since it remained in the steam. In contrast, at the north, the expansion process increased the enthalpy of the mixture (evaporating some liquid) which caused the decrease in $^{222}\text{Rn}$, since it was already in the steam phase and the evaporated liquid was almost $^{222}\text{Rn}$ depleted. This interpretation explains both variations: the $^{222}\text{Rn}$ increase observed in steam wells and the $^{222}\text{Rn}$ decrease, observed in two-phase wells of the field.

INTRODUCTION

Important $^{222}\text{Rn}$ anomalies were observed in fluids from the Los Azufres, Mexico, geothermal field wells in September 1985 one week before the occurrence of the (Ms = 8.1) earthquake, with an epicenter in the Michoacán Coast and related to the subduction of the Coco’s Plate. Such anomalies were then well documented, since $^{222}\text{Rn}$ is a useful precursor of seismic activity, (Nieva et al., 1987; Santoyo et al., 1991). Segovia et al., (1989) also found $^{222}\text{Rn}$ variations in the soil at the Los Azufres geothermal field related to the seismic event. In 2005 a study was carried out to investigate the thermodynamic conditions of Los Azufres fluids at bottom-hole conditions by using production data (Arellano et al., 2005; Barragán et al., 2006) and the results provided a more comprehensive explanation of the $^{222}\text{Rn}$ behavior.

The objective of this work is to correlate $^{222}\text{Rn}$ data of Los Azufres geothermal field wells to variations in well-bottom conditions (enthalpy, pressure and steam/water ratio) to better understand the $^{222}\text{Rn}$ behavior observed in September 1985.
METHODOLOGY

$^{222}$Rn collection and analytical technique methods were given by Santoyo et al., (1991). The thermodynamic well-bottom conditions of fluids were obtained by using the WELFLO program (Arellano et al., 2005) which is a simulator of heat and mass flows in geothermal wells and use production data as input. The results include: well bottom pressure, enthalpy, temperature, steam/water ratio, among other. The studied wells are shown in Figure 1. Wells AZ-6, 16AD and 17 produce steam and are located at the southern zone of the field and wells AZ-5 and 13 produce two-phase fluids and are located in the north.

RESULTS

Figure 2 shows the $^{222}$Rn data over time, for wells AZ-6, AZ-16AD, AZ-17, AZ-5 and AZ-13. In this work, results for wells AZ-17 and 5 are discussed. Figure 3 shows the pressure versus the enthalpy in a semi-log plot, where the solid curve corresponds to saturated water data from steam tables. The dates for the points are also given. Arrows indicate the direction of the trends. This diagram is useful to illustrate the behavior of the thermodynamic well bottom parameters (pressure and enthalpy) obtained for September 1985 data. Simulation results indicate the transitory tectonic-related effects in thermodynamic deep well parameters, (pressure, enthalpy and steam/water ratio) as is discussed below.

![Fig.1: Location of wells at Los Azufres geothermal field](image-url)
Fig. 2: Time series for $^{222}$Rn in some Los Azufres wells.

**WELL AZ-17**

Production data history of well AZ-17 indicates that saturated steam occurs at the bottom of the well, (Figure 3, May and November 1985 data) where the well bottom pressure and the enthalpy are located on the saturation curve. However, well bottom data for September 4-6, 1985 indicate a small pressure decrease and enthalpy increase regarding the baseline points. These changes moved the location of well bottom conditions to the “superheated steam region” and were probably “first signal” precursors of the 19 September earthquake. Subsequently, the point for September 12, 1985 shows a compression process (pressure increase and enthalpy decrease) with the formation of a small fraction of liquid phase at the well bottom. $^{222}$Rn sample was taken in September 9-13, 1985, when probably this process was dominant in the well. Two values for $^{222}$Rn were recorded in 1983-1984 which were 50 and 40 nC/kg. The large increase in $^{222}$Rn concentration (~ 90 nC/kg) found for September 1985 was then due to the change in the well bottom steam/water ratio occurred as a result of the compression process. In this process, part of the steam became liquid (well bottom enthalpy decreased) which is depleted in $^{222}$Rn and in other volatile species. The $^{222}$Rn content in the original steam, before it changed phase, ($y = 1$) remained in the new fraction of steam ($y = 0.9$) at the well bottom. This caused an increase in $^{222}$Rn concentration in the sample. The $^{222}$Rn concentration stabilized (Figure 2, November 1985 data) and a new baseline seems to appear with qualitative lower $^{222}$Rn values (~ 25 nC/kg) than those recorded before the earthquake (~ 50 nC/kg).

**WELL AZ-5**

Simulation results of the well AZ-5 provided the well bottom thermodynamic conditions which were plotted in Figure 3. In this well a decrease in total discharge $^{222}$Rn was found in September 1985 regarding measurements recorded in 1983-1984, (11 and 8 nC/kg respectively). Anomalously lower values for $^{222}$Rn were found in September 12, 1985: 2.5 and 3.5 nC/kg. This decrease in the total discharge is explained considering the thermodynamic well bottom conditions as follows. As the $^{222}$Rn decrease was observed in total discharge values which depend on enthalpy (which depends on steam/water ratio) the variations in enthalpy produce variations in calculated species concentrations. When dealing with volatile species (as $^{222}$Rn) which strongly partition into steam phase, a reliable
estimation of the steam/water ratio is needed to obtain reliable values of species concentrations in the total discharge fluid. As seen in Figure 3, the well bottom conditions of well AZ-5 since 1984 and before September 17, 1985 indicate a small decrease in pressure and an increase in enthalpy. As production data for September 17, 1985 were collected to different hours during the day, important changes are seen in well bottom conditions: increases in pressure, enthalpy and steam/water ratio which are considered “precursors” of the earthquake. The $^{222}$Rn sample was collected in September 12, 1985, when the dominant effect was an expansion process: pressure decrease and enthalpy increase. The pressure drop caused that some portion of liquid at the bottom of the well to be evaporated causing the decrease in $^{222}$Rn, since the mass of liquid before being evaporated was almost $^{222}$Rn depleted and the $^{222}$Rn content of the steam was diluted in a greater amount of steam: that existing at the bottom of the well plus the new formed by the evaporated liquid. As the increase in enthalpy (caused by the increase in well bottom steam fraction from 0.5 to ~ 0.6) was not considered in the calculation of $^{222}$Rn total discharge concentration, (Santoyo et al., 1991), such decrease in $^{222}$Rn concentration was more difficult to explain than the $^{222}$Rn increase observed in steam wells. After the anomalously low values found for September 1985, total discharge $^{222}$Rn concentrations in well AZ-5 showed a tendency to decrease, the last value recorded was 4 nC/kg (Figure 2).

**CONCLUSIONS**

A comprehensive interpretation of the $^{222}$Rn anomalies observed in fluids from two wells of the Los Azufres geothermal field, precursors of the (Ms=8.1) September 19, 1985 earthquake was provided. This relies on the thermodynamic well bottom conditions obtained by the analysis of production data and explains both the $^{222}$Rn increase observed in some steam wells and the $^{222}$Rn decrease observed in some two phase wells. Previous to the earthquake, tectonic-related changes occurred in well bottom pressure, enthalpy and steam/water ratio at Los Azufres reservoir which probably caused the changes observed in total discharge $^{222}$Rn concentration.

Fig. 3: Pressure vs enthalpy diagram.
REFERENCES


Effect of Hydrogeology and Monsoon on Radon Concentrations in Groundwater of Intermountain Basin of Outer Himalaya

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ABSTRACT

Groundwater in intermountain basin of Dun valley in outer Himalaya is present in multi-tier aquifer under unconfined conditions. The source of recharge to these aquifers is monsoonal rains that occur between July and September. The water table in these aquifers shows fluctuation with monsoonal recharge. Radon concentrations were measured in post-monsoon season in 60 samples of groundwater drawn from tubewell and borewell (handpumps) in intermountain Dun Valley. The depth of these tubewell and handpumps varies from 8 to 193 meters. Radon concentrations in groundwater vary from 15 Bq/L to 110 Bq/L in premonsoon and from 11 Bq/L to 93 Bq/L in post monsoon. The data were compared with the pre monsoon data to understand the effects of monsoonal recharge and hydrogeological characteristics on the radon concentrations.

Radon concentrations showed no relationship with depth of the tubewells and handpumps when taken together for the whole valley indicating mixing of groundwater from different aquifers and probably heterogenous nature of aquifer. However, radon concentrations showed significant relationship when Dun Valley aquifer was divided in several sub- aquifers or hydrogeologic units depending upon the aquifer characteristics, flow path, geomorphic features and lithological composition of the aquifer. The relationship was better in post monsoon data set. This suggests that the aquifer in Dun Valley is not uniform and rather consists of several hydrogeological units, having different composition, and probably formed at different time.

A comparison of post monsoon with pre monsoon data showed slight dilution in radon concentration by recharge or changes in groundwater contributing areas of the aquifer. The filling of pore spaces of aquifer by infiltrated water during monsoon has probably reduced the supply of radon in water thus resulting in decreased radon concentration in post monsoon samples.
Migration and Accumulation Characteristics and Potential of Multi-Origin Inorganic CO$_2$ in the Ying-Qiong Basin, the South China Sea

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ABSTRACT

There are three types of inorganic CO$_2$ reservoirs (i.e., crust derived type, mantle-crust derived type and volcanic-mantle derived types) in the Ying-Qiong Basin of the northern South China Sea. The crust-derived CO$_2$ and crust-mantle derived CO$_2$ reservoirs are chiefly distributed in the shallow structures (about 1100-2380m depth) of the mud diapir zones in the Yinggehai Basin, and the volcanic-mantle derived CO$_2$ mainly accumulate in the No. II Fault Zone of the eastern Qiongdongdan Basin and adjacent areas of the Songdong-Baodao Sag.

INTRODUCTION

CO$_2$, a common non-hydrocarbon component in natural gas, has not only huge negative effects on the global environment and ecosystem, but tremendous market economical values used for industrial and agricultural production. Therefore, to reasonably utilize the CO$_2$ resources is a great challenge for our human being.

Ying-Qiong Basin (Yinggehai Basin and Qiongdongnan Basin), a Cenozoic basin complex, is located in the northwest of the northern margin of the South China Sea. The northern margin of the South China Sea features quasi-passive continental margin setting affected by the interplays of Eurasia, Indo-Australia and Pacific Plates. Due to complex tectonic movements and deep dynamic activities, the Ying-Qiong Basin has formed various geological phenomena, which are mainly characterized by faulted-subsidence rift in its early phase and thermal subsidence depression with rapid subsidence and sedimentary infilling in the late phase, by high temperature and high pressure conditions, by frequent mud diapiric and heat fluid piercing activities, and by plentiful CO$_2$ resources. Analogous to other continental rift basins in eastern China, the Cenozoic Ying-Qiong Basin consists of distinctly double tiers structure, i.e., the lower terrestrial Paleogene infilling and the upper widespread marine Neogene-Quaternary onlapping strata. Differently, Yinggehai Basin developed with thin Paleogene infilling but thick Neogene-Quaternary sediments with the maximal thickness of 17 Km, in contrast, the neighboring Qiongdongnan basin developed with thick Paleogene infilling (e.g. thick Eogene Yacheng Formation and Oligocene Lingshui Formation of alluvial) and the overlying thick Neogene-Quaternary developed as a whole monocline stratum towards deep sea (Xie et al., 2006).

Several hydrocarbon and CO$_2$ pools have been found in this area since the petroleum exploration in the 1960s. It is important to study the origins of these CO$_2$ and their characteristics during the process of their migration and accumulation.
THE CLASSIFICATION OF INORGANIC CO$_2$ IN THE YING-QIONG BASIN

According to the features of carbon isotope of the CO$_2$ and the accompanying helium isotope, all these CO$_2$ are regarded as inorganic source, and can be subdivided into three types (He et al., 2003; He and Liu, 2004). The first type is the crust-derived CO$_2$, which occurs in the shallow and medium-deep strata of mud-diapir zones in the Yinggehai Basin. Especially in the shallow strata of mud-diapir zones, the content of CO$_2$ is as high as 28.5% to 88.9% with the maximal value of 93%, both the values of carbon isotope of the CO$_2$ ($\delta^{13}C_{CO2}$) and of the ethane ($\delta^{13}C_{ethane}$) are high, and the ratios of $^3$He/$^4$He and R/Ra are low as 0.39–6.9×10$^{-7}$ and lower than 0.6, respectively. The second type is the crust-mantle derived CO$_2$, which occurs mainly in the Ledong-1 structure area in the diapir zones of the Yinggehai Basin. The relative high ratios of $^3$He/$^4$He (8.4–21.9×10$^{-7}$) and R/Ra (1–1.56) are the most important geochemical features. The content of CO$_2$ (39–79%) is also high analogous to that of the crust-derived CO$_2$. The third type is volcanic-mantle derived CO$_2$, which are accumulated around the No. II Fault Zone in the Qiongdangnan Basin. This type shows highest ratios of $^3$He/$^4$He (41.4–87.5×10$^{-7}$) and R/Ra (2–6.3), and the highest content of CO$_2$ (80–97.6%). (Table 1).

Table 1 Various origins of inorganic CO$_2$ in Ying-Qiong Basin of the South China Sea

<table>
<thead>
<tr>
<th>Origin</th>
<th>Structur e and gas section</th>
<th>Fm .</th>
<th>Depth (m)</th>
<th>Composition of gas</th>
<th>Delay. coef.</th>
<th>Carbon Isotope $\delta^{13}$C(‰)</th>
<th>R/Ra</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>CO$_2$</td>
<td>N$_2$</td>
<td>C$_1$</td>
<td>C$_2$</td>
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<tr>
<td>Crust derived</td>
<td></td>
<td></td>
<td></td>
<td>1331-136</td>
<td>64.70</td>
<td>5.8</td>
<td>27.97</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1493-166</td>
<td>80.13</td>
<td>6.2</td>
<td>13.30</td>
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<td></td>
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<td></td>
<td></td>
<td>1832-184</td>
<td>88.91</td>
<td>5.4</td>
<td>5.26</td>
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<tr>
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<td>Ny</td>
<td></td>
<td>2200-222</td>
<td>75.17</td>
<td>4.1</td>
<td>18.70</td>
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</tr>
<tr>
<td></td>
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<td></td>
<td>1553-156</td>
<td>83.97</td>
<td>6.6</td>
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<td></td>
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<td>80.42</td>
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<td>7.10</td>
<td>1.3</td>
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<td>Ny</td>
<td></td>
<td>3789-381</td>
<td>8.54</td>
<td>1.0</td>
<td>83.22</td>
<td>7.2</td>
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<tr>
<td></td>
<td>Ny</td>
<td></td>
<td>3021.5</td>
<td>6.54</td>
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<td>342-352</td>
<td>78.90</td>
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<td>39.29</td>
<td>3.4</td>
<td>55.65</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1245-126</td>
<td>59.74</td>
<td>3.9</td>
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<td></td>
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<td>1723-173</td>
<td>71.20</td>
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<tr>
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<td>59.74</td>
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<td>71.20</td>
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<td></td>
<td></td>
<td>2267.5</td>
<td>97.64</td>
<td>0.4</td>
<td>1.80</td>
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</tr>
</tbody>
</table>

Note: R = the $^3$He/$^4$He values of samples, Ra = the $^3$He/$^4$He values of standard air.
THE CHARACTERISTICS OF MIGRATION AND ACCUMULATION

As dated above, crust-derived CO$_2$ and crust-mantle derived CO$_2$ accumulates mainly in the shallow structures (about 1100-2380m depth) of the mud diapir zones in the Yinggehai Basin. These CO$_2$ pools generally show zonal migration and accumulation features, and are controlled by the intrusion of hot fluid into the mud diapirs and the physical-chemical reaction of thick marine calcic elastic rocks (Xie et al., 2001). The inorganic CO$_2$, mainly rich in the shallow layers of the Yinggehai Basin, has also been found in the deeper layers by drilling but with comparatively low concentration (generally no more than 7%) in the natural gas (He and Chen, 1998). In the basin, the reservoirs-formation laws of these inorganic CO$_2$ is layer-controlled vertically and block-controlled in plane. Dongfang Blocks is a representative example. For DF1-1 gas field in the plane, west block is rich in hydrocarbon gas but poor in CO$_2$ (<1%), while the east and north blocks are rich in non-hydrocarbon gas including abundant crust-derived CO$_2$. there is an obvious stratificational and zonal feature vertically, hydrocarbon gas and crust-derived CO$_2$ are chiefly rich in the strata with a depth less than 1900m, whereas hydrocarbon gas with small amount of crust-origin CO$_2$ (<7%) occur below this depth, except several small layer section with rich crust-derived CO$_2$. Additionally, this basin features episodic infilling and migration of crust-derived CO$_2$ or hydrocarbon gas with low CO$_2$ content, according to analysis of fluid inclusion and carbon isotope data, there are at least 3-4 episodes of hydrocarbon-infilling and migration (He et al., 2003).

The volcanic-mantle derived CO$_2$ reservoirs mainly distributed in the No. II Fault Zone of the eastern Qiongdongdan Basin and adjacent areas of the Songdong-Baodao Sag, and are controlled by the effective configuration of the mantle derived gas gushing activities and of the migration systems of big-deep fault. this area is located in the extension zone of two Tertiary-Quaternary NWW-trending basalt belts developed from onshore the southeast China, as well as in the extension zone of Tan-Lu Fault running from South China into the continental shelf (Ten et al., 2004), it shares the similar tectonic setting and the fault systems with the faulted and depressed terrestrial basins in East China. In addition, volcanism is fluent in the basin. Therefore, the area was provided with basic migration and accumulation conditions for the development of mantle derived CO$_2$ reservoirs. The distribution of CO$_2$ reservoirs and hydrocarbon gas reservoirs with high CO$_2$ content are chiefly rich in these local strata which have close connection with big-deep fault and can be effected by the mantle derived volcanism intensively, and the CO$_2$ reservoir has single source that is the primitive CO$_2$ emerged from mantle volcanism (Dai et al., 1997). Obviously, the mantle derived CO$_2$ have simple migration and accumulation conditions relative to the crust derived CO$_2$ and crust-mantle mixed derived CO$_2$.

POTENTIAL OF MULTIORIGIN NON-BIOLOGY (INORGANIC) CO$_2$

So far, according to incomplete statistics to the shallow layer of the mud diapir in Yinggehai Basin and area of No. 2 Fault belt in the northern of Qiongdongnan Basin, the proven inorganic CO$_2$ reserve of various origins in total is about 300 billions m$^3$. Anyhow, natural gas exploration and drilling proved the huge amount of the non-biology CO$_2$ resource in Ying-Qiong Basin, and, especially the huge potential of crust-origin CO$_2$ in Yinggehai Basin in the northern of the South China Sea. It will be a great challenge to develop and exploit these CO$_2$ reservoirs.
REFERENCES


He, J., Wang, Z. and Pei, Q. (2003) Genesis and migration and accumulation features of CO₂ in the Ying-Qiong Basin and in the west of the Pearl River Estuary Basin. *China Offshore Oil and Gas (Geology)*, 17(5), 293–297.


Invasion of Mantle-Derived Fluids into I-Lan Plain in NE Taiwan from Southwest Part of the Okinawa Trough: Evidence of Helium Isotopes in Soil Gases

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ABSTRACT

The I-Lan Plain is located in northeastern Taiwan and is famous for its hot and cold springs. With subsidence rate of 126 mm/y, the I-Lan Plain is considered to be the westward extension of the Okinawa Trough on land. An active volcanic islet, Kueishantao, is located at the most southwestern part of the Okinawa Trough and only ca. 10 km east to the Plain. The helium isotopic ratios of bubbling gases from submarine hot springs around Kueishantao are up to 8.3 Ra, where Ra is the \(^{3}\text{He}/^{4}\text{He}\) ratio of air. It implies that a primordial mantle component is degassing in the region. Moreover, elevated \(^{3}\text{He}/^{4}\text{He}\) ratio can also be found in the gas and fluid samples from hot/cold springs in the Plain. In order to better understand the distribution/migration of possible mantle fluids in this region, we systematically conducted the soil gas survey in the Plain. Helium and carbon isotopes were also analyzed to examine their gas sources. The results show that most samples exhibit both excess \(^{3}\text{He}\) and \(^{4}\text{He}\) and progressively decrease from east toward west of the Plain. It infers that the mantle-derived fluids may have invaded into the I-Lan Plain through the westward extension of the Okinawa Trough. Furthermore, the distribution of excess helium isotopes can be helpful to delineate the surface trace of possible deep faulted-structure in central part of the Plain.

INTRODUCTION

The I-Lan Plain, a deltaic triangular plain situated at northeastern Taiwan, is believed to be the onshore propagation of the Okinawa Trough (Ho, 1986; Tsai, 1986). The back-arc basin of Ryukyu subduction began to open just past million years ago (Teng, 1996; Teng et al., 2000), and many active submarine volcanoes and vigorous hydrothermal activities had been identified in the mid-Okinawa Trough (Ishibashi et al., 1995; Konno et al., 2006). Some of the highest helium isotopic ratios among the west Pacific volcanic region were found near the Kueishantao islet (Yang et al., 2005), which is only 10 kilometers east of the I-Lan Plain. Moreover, according to the \(V_p\) and \(V_s\) velocity structures and tomography, the sausage-like body would perhaps refer to water-rich component and/or melt from the narrow conduits in Okinawa Trough back arc. This phenomenon might be the reason for high...
mantle signatures in helium isotopes and phenomenal hydrothermal activities near Kueishantao (Lin et al., 2004a, 2004b). Since this small young and hydrothermal-brisk volcanic islet is so close to Taiwan, it draws our attention to understand the spatial distribution of mantle fluids in the nearest on-land area, the I-Lan Plain.

Noble gases have been widely exploited as geochemical tracers, especially helium. With properties of high mobility and chemical inertness, helium fails to react with other species under almost all circumstances (Hilton and Porcelli, 2003). The major consequence of this inertness is that helium passes easily into the gas phase, and is efficiently lost from the solid Earth. Scientists have adopted these great properties to elucidate the sources and the evolution history of fluids for several decades.

In this study, helium isotopes in soil gases were chosen as a tool to differentiate the sources of fluids in the I-Lan Plain. We systematically sampled soil gas in the plain and developed a spatial statistical model to constrain the diffuse behavior of soil gas.

METHOD

We conducted grid sampling about every 1 ~ 2 km all over the I-Lan Plain. A stainless steel probe (1 m in length, 1 cm of diameter) was inserted into soil around 1 m depth, and then we pumped soil gas into pre-evacuated low-permeability sample bottles and sample bags for isotopic and composition analysis.

Soil gas compositions were analyzed by a gas chromatograph (GC, SRI 8610C), with two thermal conductivity detectors (TCDs) and one flame ionic detector (FID). Analysis of soil gas composition was utilized the same method (Lee et al., 2005). Concentration and isotopic ratio of helium, neon and other noble gas were analyzed by a high-precision noble gas mass spectrometer (Micromass 5400) from the potassium-glass sample bottles with high-vacuum stopcocks at both ends. Observed $^{3}\text{He}/^{4}\text{He}$ ratios were calibrated against atmospheric standard gas and were expressed in the $R_A$, where $R_A$ is the air $^{3}\text{He}/^{4}\text{He}$ ratio of $1.39 \times 10^{-6}$. After purification of soil gas samples by traps held at liquid N$_2$ and ethanol-dry ice temperature, carbon dioxide for carbon isotopic was analyzed using a Finnigan MAT mass spectrometer. Measured $^{13}\text{C}/^{12}\text{C}$ ratios are expressed in the delta ($\delta$) notation, as parts per thousand ($\permil$) from the international standard, PDB.

RESULTS AND CONCLUDING REMARKS

Due to severe air-contamination in soil gas, we separately discuss the abundance of $^{3}\text{He}$ and $^{4}\text{He}$ normalized to that in air as “excess $^{3}\text{He}$ ($\Delta^{3}\text{He}$) and excess $^{4}\text{He}$ ($\Delta^{4}\text{He}$)”.

$$\Delta^{3}\text{He} = \left( {^{3}\text{He}_\text{sample} - ^{3}\text{He}_\text{air}} / {^{3}\text{He}_\text{air}} \right)$$  \hfill (1)

$$\Delta^{4}\text{He} = \left( {^{4}\text{He}_\text{sample} - ^{4}\text{He}_\text{air}} / {^{4}\text{He}_\text{air}} \right)$$  \hfill (2)

Geographical distribution of $\Delta^{3}\text{He}$ and $\Delta^{4}\text{He}$ shows the decrease of mantle-derived signatures from east to west in the I-Lan Plain. It indicates the mantle-derived fluids have invaded into I-Lan Plain, and the extent of $\Delta^{3}\text{He}$ and $\Delta^{4}\text{He}$ could be up to 23% and 51% respectively. Notably, in the center of the plain, a higher zone of $\Delta^{3}\text{He}$ could be identified, which is consistent with a deep fault from the Lang-Yang River mouth to the Chin-Sui geothermal area (Tsai, 1975). The fault becomes a good channel for soil gas to carry magmatic $^{3}\text{He}$ to surface. Thus, $^{3}\text{He}$ not only marks magmatic signals but also depicts the surface location of deep structures. On the other hand, $^{4}\text{He}$ in the crust is produced by
radioactive decay of U and Th. With the extension of the Okinawa Trough, more paths for soil gas were gradually generated through time. Not as sensitive to fault traces as $^3$He, spatial distribution of $^4$He is likely related to the progressive opening of the I-Lan Plain.

The foregoing results can be summarized as follows: 1) most samples in the I-Lan Plain exhibit both excess $^3$He and $^4$He. 2) Magmatic signatures progressively decrease in certain direction imply that the mantle-derived fluids might have invaded into the I-Lan Plain through the westward extension of the Okinawa Trough. 3) The distribution of excess helium isotopes can also be useful to locate the surface trace of possible deep faulted-structure in central part of the Plain.

REFERENCES


Extremely $\text{H}_2$-rich Hydrothermal Fluids Feed a Possible Successor of the Archean Microbial Ecosystem – Ultra-$\text{H}_3$ Hypothesis

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ABSTRACT

A lithoautotrophic microbial community, completely independent from the photosynthesis, is one of the possible candidates of the earliest established ecosystem on Earth. In present Earth, such communities are found beneath the seafloor hydrothermal field escaping from oxidizing atmosphere. To explain the occurrence of such communities, a working hypothesis, “Ultra-$\text{H}_3$ linkage,” has been investigated. It stands on the hydrogenesis associated with the serpentinization of ultramafic rocks. Most of the case seems to be explained by the hypothesis, however, some of the hydrothermal systems may be out of the framework.

INTRODUCTION: THE Ultra-$\text{H}_3$ LINKAGE

Based on the consideration of possible and sustainable redox couple for microbial metabolism in the Archean Earth, we propose that $\text{H}_2$-based hyperthermophilic lithoautotrophic microorganisms were the primary producer in the reductive environment of pre-photosynthetic world. Such hyperthermophilic microorganisms are found around the abyssal hydrothermal field in the present Earth as the possible successor of the Archean microbial ecosystems. Some of them choose their habitat beneath the seafloor avoid the current oxidizing atmosphere even in the abyss (Figure 1). Based on their community, consumer of generated methane and much higher trophic levels could be maintained, which eventually makes the ecosystem independent from photosynthesis. We call such an ecosystem as HyperSLiME: Hyperthermophilic Subsurface Lithoautotrophic Microbial Ecosystem (Takai et al., 2006b).

To understand volcano-tectonic environment for such a microbial ecosystems independent from the photosynthesis, we propose a working hypothesis, named as “Ultra-$\text{H}_3$ linkage,” to investigate. Among the various hydrogen-generating process in nature, we choose the serpentinization of ultramafic rocks.
to the hydrogenesis reaction beneath the present sea floor. Because serpentinized ultramafic mantle rocks were widely corrected from the fracture zone or distinguishing topographic feature, called as Oceanic Core Complex (OCC), mainly near the slow spreading Mid-Ocean Ridges (Ildefonse et al., 2007). The reaction is described schematically,

\[
\text{Olivine + Water } \rightarrow \text{ Serpentine + Magnetite + “Hydrogen”}
\]

(1)

Fig. 1: Schematic model of the HyperSLiME at present Earth (modified from Takai et al., 2006)

**LIMITED EXISTENCE OF HyperSLiMEs**

The first example of the HyperSLiME was found beneath the Kairei hydrothermal field (KHF), one of the Indian Ocean ones (Takai et al., 2004). To date, very limited number of HyperSLiME community has been found within numbers of seafloor hydrothermal field. The occurrence of HyperSLiME seems to correlate with the concentration of hydrogen in the hydrothermal vent fluid (Table 1). Also, the HyperSLiME sites are commonly surrounded by the ultramafic exposures near their recharge zone.

At least two hydrothermal fields, the complete linkages have been proved. In the case that KHF, where the HyperSLiME was firstly found, exposure of the serpentinized ultramafic rock on the seafloor has been found on the eastern flank of the 25°S OCC (Kumagai et al., 2006). The typical H₂-based lithoautotrophic archaea have been identified in Rainbow hydrothermal field (Takai et al., 2006a).

In contrast to these two near-ridge ultramafic-related hydrothermal fields, the Lost City field (LCF)
did not show any sign of the existence of HyperSLiME. It may due to the alkaline signature of vent fluid of LCF (pH 9-11), which may be explainable by the little input of magmatic acidic volatiles at the segment end condition.

Table 1: Hydrogen concentration and existence of HyperSLiME of hydrothermal fields.

<table>
<thead>
<tr>
<th>Hydrothermal Field</th>
<th>Lithology</th>
<th>Hydrogen</th>
<th>HyperSLiME</th>
<th>References of $[H_2]$</th>
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<tbody>
<tr>
<td>Rainbow (MAR)</td>
<td>Ultramafics</td>
<td>16</td>
<td>Proven</td>
<td>Charlo et al. (2002)</td>
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<tr>
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<td>Positive</td>
<td>ditto</td>
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<td>Denied</td>
<td>Kelley et al. (2005)</td>
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<td>- 8.9</td>
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<td>Kairei (CIR, Indian)</td>
<td>Ultramafics + Ol-rich gabbro</td>
<td>2.5 - 8.5</td>
<td>Proven</td>
<td>Van Dover et al. (2001)</td>
</tr>
<tr>
<td>Edmond (CIR, Indian)</td>
<td>Basalt</td>
<td>0.2</td>
<td>Denied</td>
<td>ditto</td>
</tr>
<tr>
<td>Endeavour(JdFR)</td>
<td>Basalt + sediment</td>
<td>0.16 – 0.42</td>
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<td>Kelley et al. (2001)</td>
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<td>Typical MAR</td>
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<td>-</td>
<td>ditto</td>
</tr>
<tr>
<td>21°N EPR</td>
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<td>0.23 -1.7</td>
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</tr>
<tr>
<td>Okinawa Trough</td>
<td>Andesite + sediment</td>
<td>&lt; 0.1</td>
<td>Denied</td>
<td>unpublished</td>
</tr>
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9°50′N-EPR: NOT IN THE CASE OF UltraH₃-LINKAGE

The UltraH₃ linkage seems to well explain the occurrence of HyperSLiME, even one more factor, magmatic input may be required. However, in terms of the geological aspect of the linkage, “Ultramafics-Hydrothermalism-Hydrogenesis,” there is at least one exception. One of the four hydrothermal activity that show higher hydrogen concentration than that of KHF, 9°50′N field of EPR seems to be hardly explained by the ultramafic-hosted activity. Because the spreading rate of EPR 9°50′N reaches 120mm/yr as full rate (MacDonald et al., 1988), vigorous magma supply inhibits the any exposure of the ultramafic mantle rocks. All the known ultramafic exposure on the seafloor, Oceanic Core Complexes, is limited in the slow to intermediate spreading ridge axis. It is impressive that another hydrothermal activity having relatively high concentration of hydrogen associate with the nearby on-island H₂-rich hot-spring activity at Soccoro Island (Taran et al., 2002). In terms of Soccoro island, the occurrence of a kind of Fe-rich rhyolitic lava, pantellerite, seem to be a key to understand the high concentration of hydrogen in the volcanic fumarole (Bryan, 1966).

CONCLUSIONS

Based on the field observation, a lithoautotrophic microbial community completely independent from the production of photosynthesis has been found beneath the seafloor hydrothermal field. The tectono-geologic environment for the community is mostly explained by the UltraH₃ linkage hypothesis. Some other H₂-rich hydrothermal field, that potential habitat of HyperSLiME, may require another mechanism to be explained.

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Methane Seeps and Mud Volcanoes on Land: a Global Perspective of Gas Origin and Advective Fractionation

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ABSTRACT

A global data-base of gas composition and methane stable isotopes from terrestrial gas seeps shows that whereas dry seep gas generally maintains the reservoir C1/(C2+C3) “Bernard” ratio, most mud volcanoes are shifted towards higher C1/(C2+C3) ratios, suggesting a molecular fractionation during advective fluid migration; so the “Bernard” parameter can be misleading when applied to mud volcanoes as it does not reflect the original gas composition. A mud volcano behaves like a “natural refinery” and the origin of gas with δ13C(CH4)<50‰ and C1/(C2+C3)>500 should be attributed to a thermogenic phase, rather than oxidation of biogenic gas.

INTRODUCTION

Natural gas seeps are the result of vertical migration of light hydrocarbons generated in source rocks and trapped in reservoirs. The seeps, including mud volcanoes, dry seeps and CH4-rich springs, have historically been important indicators of subsurface hydrocarbon accumulations driving global petroleum exploration (Link, 1952). Offshore and onshore seepage, including microseepage, have been estimated to be the second natural source of atmospheric methane, after wetlands (Etiope, 2004). Understanding the seep gas (methane) origin may contribute to tectonic, structural and petroleum geology studies (depth of gas-bearing faults; definition of the Petroleum Seepage System, gas hydrate formation), assist hydrocarbon exploitation (assessment of geochemical and pressure variations during fluid extraction) and support environmental impact studies (aquifer contamination, underground gas storage ability). The interpretation of methane origin starts with conventional diagrams widely used for reservoir gas, i.e. δ13CCH4 vs δDCH4 (Schoell, 1983) and δ13CCH4 vs C1/(C2+C3) (Bernard et al., 1978). The application of such parameters to surface gas seeps can be, however, misleading in case of alteration due to secondary post-genetic processes, such as oxidation of biogenic gas or molecular separation during migration. For this reason, the origin of methane from mud volcanoes has been sometimes uncertain (e.g., Grassa et al. 2004).

In this work we show for the first time a global data-base of gas seep composition and methane stable isotopes (13C and 2H), including terrestrial mud volcano and dry seep data from the main 12 countries hosting mud volcanoes and other macro-seeps. Some seeps have been compared with the...
corresponding reservoir gas. This exercise straightens the global gas origin of seeps, the difference between mud volcano gas and dry-seep gas, and the occurrence of gas fractionations.

THE GLOBAL “SCHOELL” AND “BERNARD” DIAGRAMS FOR MACRO-SEEPS

Alkane composition (methane, ethane, propane) and methane stable isotopes (\(^{13}\)C and \(^2\)H) from more than 160 mud volcanoes and other macro-seeps of Azerbaijan, Georgia, Greece, Italy, New Zealand, Pakistan, Papua New Guinea, Romania, Russia (Taman), Trinidad, Turkmenistan and Ukraine (Valyaev et al., 1985; Baylis et al., 1997; Delisle et al., 2002; Deville et al 2003; Etiope et al., 2006; 2007; Etiope and Baciu, unpublished data) have been examined and plotted in the “Schoell” and “Bernard” diagrams, i.e. \(\delta^{13}\)C\(_{\text{CH}_4}\) vs \(\delta\)D\(_{\text{CH}_4}\) (Schoell, 1983) and \(\delta^{13}\)C\(_{\text{CH}_4}\) vs \(C_1/(C_2+C_3)\) (Bernard et al., 1978). We name “dry seeps” those manifestations independent from mud volcanism, showing only gas-phase, without bubbling and water discharge. Mud volcano samples, instead, refer to gas + aqueous mud (+sediment) emissions (craters, gryphons, salses, bubbling pools).

The \(\delta^{13}\)C\(_{\text{CH}_4}\) vs \(\delta\)D\(_{\text{CH}_4}\) diagram shows that most seeps fall in or close to the thermogenic field. The \(\delta^{13}\)C\(_{\text{CH}_4}\) vs \(C_1/(C_2+C_3)\) diagram (Fig. 1) shows that all dry seeps fall in the thermogenic field but most mud volcanoes fall in an ambiguous sector, geometrically above the thermogenic field and to the right of the biogenic area (\(\delta^{13}\)C\(_{\text{CH}_4}\) <50‰ and \(C_1/(C_2+C_3)\) >500); such a sector should indicate alteration due to secondary post-genetic processes, oxidation of biogenic gas or molecular separation during migration. More than 80% of mud volcanoes are in this sector or clearly in the thermogenic field. Less than 20% of mud volcanoes fall within the biogenic-thermogenic mixing trend or in the biogenic field. Some seep gas data of Azerbaijan, Greece, Italy, Romania and Trinidad have been compared with the corresponding reservoir gas, where borehole data are available (a specific work has been made to localize the reservoir below the mud volcano or seep and to find at least its alkane composition data). All reservoirs examined were thermogenic. It is evident that all mud volcanoes are shifted towards lighter \(C_1/(C_2+C_3)\) ratios, falling also outside the thermogenic field, i.e., mud volcanoes gas is lighter than its reservoir gas (an example of such a shift is shown in Fig.1). In contrast, dry seep gas always maintains the reservoir \(C_1/(C_2+C_3)\) ratio.

This picture suggests that a molecular fractionation occurs in the mud volcano gas. No significant isotopic fractionation is observed. Basically it is clear a difference between “dry” seepage (only gas phase) and the typical MV multi-phase seepage (gas, water, mud).

Such a fractionation, however, cannot be explained by diffusion, as generally done in the studies of early fractionation of gas, from source rock to reservoir and among multi-level reservoir gas, because the seep is rather the result of a rapid ascent of gas by advection driven by pressure and density gradients (in different forms, including microbubbles, bubbles and slugs). In this case we should consider that during the advective bubble ascent there may be a segregation process or “chromatographic effect” during migration to the surface related to differential adsorption on the solid grains of the mud, and solubility processes, so that seeping gas is dryer than reservoir gas. This phenomenon was also observed in many geochemical prospections for petroleum exploration in US. In dry-seeps the gas ascent mechanism is different (mainly one-phase system) and less influenced by water.
So, a mud volcano behaves like a “natural refinery” and the origin of gas samples falling in the “ambiguous” sector of the Bernard diagram must be attributed to a thermogenic phase, rather than oxidation of biogenic gas. Indeed, also some data falling within the biogenic field could be explained by molecular fractionation of mixed gas. Basically, more than 80% of terrestrial mud volcanoes release purely thermogenic methane and the biogenic contribution is extremely low. The mechanisms of the molecular advective segregation, however, should be studied quantitatively by specific models and experiments.

REFERENCES


The Different Degassing Behaviour of Upper Mantle-derived Fluids in the Western Eger Rift Area (Central Europe)

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ABSTRACT

Fluids are involved in most active geological processes and play an important role for the understanding of complex geodynamic processes in the earth’s lithosphere which are hitherto largely unknown. The Vogtland, the Oberpfalz and NW Bohemia are part of the European Cenozoic rift system and are characterised by Quaternary volcanism, CO₂-rich mineral springs and mofettes, and the occurrence of swarm earthquakes, which are a common feature in areas with active volcanism.

Since about fifteen years, studies on these mantle-related fluids have been carried out to contributing to light upon the origin of the fluids (Bräuer et al., 2004), the possible location of the fluid sources
(Geissler et al., 2005) as well as the role of fluids as a triggering mechanism for earthquake swarms in the Vogtland and NW Bohemia (Bräuer et al., 2003, 2007).

In April 2005 we have started with the monthly monitoring of the gas and isotope compositions of three locations marked by a high $^{3}$He/$^{4}$He level and located closed to the Nový Kostel focal zone. The mineral spring U Mostku (~5.5Ra) and the Bublák mofette (~6.0Ra) are located within the Počátky-Plesná fault zone (PPZ, Bankwitz et al., 2003), south of the Nový Kostel epicentral area (Fig. 1). The Kopanina mineral spring (~4.5Ra) is located in the Nový Kostel epicentral area at the intersection between Počátky-Plesná fault zone and the Mariánské Lázně fault zone (MLF).

Micro-swarm activity has been occurred in the Nový Kostel epicentral area in June 2005. The time series of the helium isotope ratios of the monitoring locations show changing portions of upper mantle derived helium. The decrease of the $^{3}$He/$^{4}$He ratios after the micro-swarm indicates the seismically triggered release of crustal-derived helium (Bräuer et al., 2003, Bräuer et al., 2007). In contrast to that in spring 2006 at the locations Bublák and U Mostku a clear increase of the $^{3}$He/$^{4}$He ratios were found. This contemporaneous increase of mantle-derived helium may be an indication of a small magmatic (dyke) intrusion at the Počátky-Plesná fault zone from uppermost mantle into the lower crust. Only small fluctuations were observed at the Kopanina degassing place which is located in the Nový Kostel epicentral area.

The observation of the regional trends in respect of the driving forces of the Eger rift geodynamic traced by long-time studies of the isotope signature of the upper mantle-derived fluids have been continued. Based on the results of the regional distribution studies of the fluid signatures between 1992 and 1994, at several gas-rich locations of the Cheb basin and of the Mariánské Lázně degassing centre the sampling was repeated in 2000-03, 2005 and 2006, respectively. These studies result in the observation that the $^{3}$He/$^{4}$He ratios in the Cheb basin are still higher than between 1992 and 1994. Besides that a further clear increase of $^{3}$He/$^{4}$He ratios at the mofettes Dolní Častkov and Hartoušov in the eastern part of the Cheb basin was noticed between 2005 and 2006. In contrast to that the $^{3}$He/$^{4}$He ratios of locations from the degassing centre Mariánské Lázně are still nearly the same as between 1992 and 1994, respectively. The highest values were found at the mofettes along the Počátky-Plesná fault between Hartoušov and Milhostov (Fig. 1). Unfortunately, the long-time behaviour of the U Mostku spring can not be evaluated because this location was sampled the first time in 2001 but the monitoring data fit well in this scenario. The $^{3}$He/$^{4}$He ratios of these degassing locations cover the sub-continental mantle range confirmed by noble gas xenolith studies worldwide (Dunai and Porcelli, 2002). The increase of the $^{3}$He/$^{4}$He ratios at locations of the eastern part of the Cheb basin has been interpreted as an indication of presently arising magma beneath this area (Bräuer et al. 2005) which may be responsible for the recurrence of swarm earthquakes in this region.

The continuous migration of magma-derived CO$_{2}$ seems to be the key for fluid-triggered geodynamic processes in the continental lithosphere. Possibly, there is a progressive ascent of magma from the upper mantle at sub-Moho depth into the lower crust. But the time scaling of these active magmatic processes is unknown. The studies give evidence of the infrequent chance to trace presently ongoing active geodynamic process in the lithosphere and prove the western Eger rift area as exceptional natural laboratory in the European Cenozoic rift system.
REFERENCE


Tectonic Significance of Radon in the Frontal Himalayan Zones of Nurpur Area District Kangra, Himachal Pradesh, India.

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ABSTRACT

The paper reports tectonic significance of radon in water from the Frontal Himalayan region of Nurpur area district Kangra, Himachal Pradesh. The study was based on using remote sensing data, toposheets and ground truth of the area under study. The study area has deciphered lineaments trends of significant nature which are either longitudinal to the trends of Himalayas or transverse to this direction (Dhar et.al; 2002). Further neo-tectonic activity is usually seen to be controlled by lineaments and faults and has resulted in the contemporary morphological re-adjustments in the region. Water samples were taken to observe radon concentration along the zones comprising:

I) Regional Longitudinal thrust plane
II) Transverse Lineaments
III) Lineaments of local nature

Radon concentration deciphers higher trends along the zone traversed by transverse lineaments at an average value of 12.6 Bq/l. While the zone-I and zone-III shows average value at 7.27 and 7.52 Bq/l respectively. Highly fractured rocks possibly increase ratio of rocks surface area to water volume as a result of which emanation efficiency of radon increases (Lawrence et.al; 1991). Further the water get enriched by dissolving radon, which emanates from the deeper part of crust through deep seated thrust and faults (Chobey and Ramola; 1997). The paper also reports the tectonic significance of radon along the areas comprising thrust /lineaments and its lower proportion in the regions comprising predominantly of alluvium and other recent deposits, which could possibly be attributed to the high water carrying capacity, high porosity and permeability of the litho units as encountered in the area under investigation.
Methane Flux from Accretionary Prism through Mud Volcano Area in Taiwan- From Present to the Past

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ABSTRACT

Methane is the most abundant organic trace gas in the atmosphere. It plays an important role chemically in troposphere and stratosphere and it is also a very important greenhouse gas. Several hypothesis claimed that sudden and large release of methane may be one of the causes of PETM (Paleocene Eocene Thermal Maximum) and the Quaternary climate change. Although methane is of much importance to our climate system, its source and sink flux, especially the geological source, is seldom clearly quantified.

Taiwan Island itself is an accretionary prism which was formed when South China Sea oceanic crust subducted beneath Philippine Sea plate from Manila trench. During the accretion, a lot of organic matters accumulated. Along with the high temperature gradient, accretionary prism is a terrific nursery for methane to generate. The collision between Eurasia plate and Philippine Sea plate uplifted this accretionary prism and resulted in forming a lot of deep faults and fractures which served as the pathway for methane to migrate and also formed a lot of mud volcanoes. Our aim is to find an estimation of methane generated from the accretionary prism and to know how much of these were released during the orogeny from mud volcano area present and in the past.

In this study, the present day microseepage methane flux from mud volcanoes was measured by close chamber method (Norman et al. 1997). The gas inside the chamber was sampled by syringes and analyzed by GC (Gas Chromatography) with FID (Flame Ionization Detector). Our results show that the microseepage flux is about $10^2$ g/m$^2$/day which is comparable to other studies worldwide ($10^2$ to $10^6$ mg/m$^2$/day, Etiope et al., 2002; 2004a; 2004b). Together with the vent flux (Yang et al., 2004), the overall methane release from mud volcano area was about 135 tons/year which is significant and couldn’t be neglected. The past methane output from accretionary prism was estimated numerically. By knowing the matured sediment volume of accretionary prism and the related petroleum system parameters (total organic carbon content, hydrogen index, etc); the amount of methane generated from these sediments could be estimated. If we assumed that all of these methane will be released out during Taiwan orogeny, then the methane output in the past could be estimated. Comparing the present output with the past value, the conclusion could be made as follow: the methane flux in the past must higher than present day or the distribution of mud volcanoes on the Taiwan Island must be denser in the past.
REFERENCES


Geochemistry and Hydrocarbon Potential of Mud Volcanoes in Taiwan

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ABSTRACT

Mud volcanoes are the exposure of potential subsurface hydrocarbon reservoirs, and many have been observed in Taiwan (Fig. 1a). Most mud volcanoes in southwestern Taiwan are distributed along active faults or near the axial zones of anticlines in the Western Foothills, yet their occurrences are not restricted to the foothill area. Sparse activities are also found on the Costal Plains without apparent connection to geological linearity. Most gases exhaled from the mud volcanoes show methane-dominated nature, a general composition of natural gas; while two other distinctive gas types are also identified. The Chu-Ko Fault is the northernmost province of mud volcano in southwestern Taiwan. Gases along Chu-Ko Fault exhibit a CO$_2$-dominated composition, in which CO$_2$ can be as high as 83% and the $\delta^{13}$C$_{CO2}$ falls between $-8 \sim +1$‰ (vs. V-PDB) at the period of this study. Another anomalous group of mud volcanoes occur on the Coastal Range of east Taiwan. Their occurrence is associated with hot spring and exhibits nitrogen-excess nature in gas composition. Chemical and carbon and hydrogen isotopic analyses (Fig. 1b) show that hydrocarbon gases along Chu-Ko Fault, Chi-Shan Fault, and east of Chi-Shan Fault are thermogenic and have been derived from various extents of maturation of organic matter, ranging from mature to post-mature. Mud volcanoes located on the Ku-Tin-Ken Mudstone predominantly exhale methane. The erupted methane is most likely generated from early mature source rocks or early mature sources mixed with bacterial gas. Although the hydrocarbon gases of mud volcanoes developed on the Costal Range are of thermogenic origin, their sedimentary environments and tectonic setting have hindered any possible correlation with their counterparts on the southwestern side of the island. A preliminary evaluation based on the calculated maturation degree of methane, $\,$, and other geochemical parameters suggests that mud volcano gases along Chi-Shan Fault and on the east side of the fault might be originated from Pliocene strata, including Nan-Shih-Lun Sandstone and the strata below. However, deeper origins (e.g. Miocene and pre-Miocene strata) are possible for those post-mature gases. The Chi-Shan Fault and its affiliated shear zones have provided the pathways, allowing those gases to be uncovered. The Ku-Tin-Ken Mudstone might have served as the source rocks for both gas and associated mud, although the origin of the mud might span a wide range of sedimentary interval from Pliocene to Pleistocene. The Costal Range is an accretionary wedge consisted of pyroclastic deposits, orogenic sediments and subduction-collision complex. As a result, the hydrocarbon potential in this terrace may be limited by the nature of dispersive organic richness of source rocks. The geochemical characteristics of their source rocks need to be determined.
Fig. 1: (a) Location map of mud volcanoes in Taiwan; (b) carbon and hydrogen isotopic compositions of methane exhaled from mud volcanoes, Taiwan. The boundaries of gas type refer to Whiticar (1999).

REFERENCE

Greenhouse Gases Released From the Apennine Chain, Italy: Mechanochemical Production besides Mantle-Derived Contribution

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ABSTRACT

The evidence that a large amount of CO$_2$ and CH$_4$ are released in the absence of a clear contribution from the mantle or from mantle-derived fluids, leads to the hypothesis that an additional energy source can be considered to account for the origin of the released greenhouse gases. The CO$_2$-dominated gases released along the Thyrrhenian sector of the Apennine chain come from both geothermal and seismic areas. Although in some cases (mainly in gases from Tuscany region) a mantle-derived contribution is evident, most of them are marked by $^{3}$He/$^{4}$He ratios in the range of 0.01-0.1 Ra of typical radiogenic signature. Other evidences, such as the large presence of deep-located CO$_2$ reservoirs with high helium concentration and low, crustal-driven, R/Ra values, the CH$_4$ content sometimes close to 1%, or temperatures as low as 100-120°C measured in the reservoir at a depth of more than 4000 m, require an additional source for CO$_2$ and CH$_4$ production besides the already proposed “deep” origin where “deep” was intended for “mantle-derived”. Laboratory experiments carried out by a ring mill demonstrate that stress application on sedimentary rocks produce CO$_2$ and CH$_4$ and, even though the experimental approach cannot be compared to a natural system, it shows a way to model the processes occurring on fault planes where mineralogical phases are involved and modified with the total reorganization of the crystalline lattice and the contemporary production of a gas phase. The evidence that the mechanochemical production of CO$_2$ and CH$_4$ plays an important role over the entire Apennine chain leads to the consideration that similar greenhouse gas production has to be evaluated on a global scale.
Thermodynamic Models of Various Gases and Mixtures Covering a Wide Temperature-Pressure-Composition Space

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ABSTRACT

Thousands of experimental data for the thermodynamic properties (liquid-vapor solubilities, gas solubilities, PVT properties, activities, fugacities, enthalpy ect.) have been published. However, all these data only cover a limited temperature-pressure-composition space, far from sufficient to meet the needs of geochemists to do quantitative calculations. Through molecular level simulation and equation of state, we have developed extensive thermodynamic models for water and pure gases (H$_2$O, CO$_2$, CH$_4$, N$_2$, H$_2$S, O$_2$, H$_2$), binaries(H$_2$O-CO$_2$, H$_2$O-CH$_4$, H$_2$O-H$_2$S, H$_2$O-H$_2$H$_6$, H$_2$O-N$_2$), ternaries(H$_2$O-CO$_2$-NaCl, H$_2$O-CH$_4$-NaCl, H$_2$O-H$_2$S-NaCl, H$_2$O-N$_2$-NaCl etc.), and seawater-gas systems, up to high temperatures and pressures. These models have been programmed and online calculations are made available on www.geochem-model.org/models.htm.
The Optimum Sequestration Depth for CO₂ Geo-sequestration

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ABSTRACT
A conceptual model is proposed to determine the optimum sequestration depth for CO₂ geo-sequestration that is defined as the depth has the maximum profit per unit rock volume in this study. Simulation result shows that the optimum sequestration depth is around 1100 m depth for a hypothetical case.

INTRODUCTION
CO₂ geo-sequestration, putting CO₂ back underground, is currently recognized as the most feasible concept for the mitigation of CO₂ emission because of its technological maturity and large storage capacity. Depleted oil and gas reservoirs, un-minable coal beds, and deep saline formations are three different types of underground formations proposed for CO₂ geo-sequestration (IPCC, 2005). CO₂ can be sequestrated physically by structure and residual-gas trapping mechanisms, and sequestrated chemically by solubility and mineralization trapping mechanisms while CO₂ be injected into the underground formation (Bachu et al., 2007).

The higher density of the sequestrated CO₂, the more CO₂ mass can be sequestrated in the void volume of rock formation. CO₂ density will increase abruptly when CO₂ be compressed from its gas phase into supercritical phase isothermally. So, typically, CO₂ should be compressed up to its supercritical phase before injection in order to increase the CO₂ sequestration density. A substance with temperature and pressure higher than its critical temperature and critical pressure is said to be in its supercritical phase. The critical temperature of CO₂ is 304.12 K, and the critical pressure of CO₂ is 73.74 bar (Poling et al., 2001). If the groundwater pressure is the only pressure barrier for CO₂ injection, and the groundwater pressure gradient is 0.1 bar/m, then the sequestration depth must be deeper than 737.4 m in order for CO₂ to be sequestrated in a supercritical phase.

CO₂ density will increase when its pressure increase but will decrease when temperature increase. Typically, both groundwater pressure and temperature will increase when depth increase. Although this is usually true, without any theoretical assessment, it is not appropriate to say that the density of the sequestrated CO₂ will increase when the sequestration depth increases.

The higher fugacity of the sequestrated CO₂, the higher solubility of CO₂ is dissolved into the groundwater. Fugacity is the product of the pressure and the fugacity coefficient that describes the non-ideality away from the ideal gas behavior. Fugacity increases when pressure increases isothermally, but it is not a linear function of pressure.
CO₂ geo-sequestration could mitigate global warming, but it is not a free process. The injection of CO₂ requires compression energy and operation cost. Deeper sequestration depth needs higher injection pressure which increases the cost of sequestration. Typically, the charge/offset/compensation per unit mass of CO₂ sequestration is a constant value (e.g. 500 NT$/tonCO₂). That is, the depth increase will suppress the net income per ton of CO₂ sequestration, therefore, a limitation for injection depth must be determined if the CO₂ sequestration is needed to be operated under profitable condition. A conceptual model (Fig. 1) is proposed to determine the optimum sequestration depth for CO₂ geo-sequestration that is defined as the depth has the maximum profit per unit rock volume in this study.

STUDY METHOD AND ASSUMPTIONS

Peng-Robinson equation of state is used to determine the density and fugacity coefficient of CO₂, and the theoretical one-stage adiabatic compression energy required for CO₂ compression (Walas, 1985). CO₂ solubility is calculated by the GWB® (The Geochemist’s Workbench) (Bethke, 1996). Major assumptions for the hypothetical case used in this study are as follows:

1. Rock porosity decrease from 0.3 at surface to 0.1 at 7000 m depth, and is constrained by an exponential decay curve; porosity = 0.3 * exp [(-1.5*depth)/(depth+2000)].
2. Underground temperature gradient is assumed equal to 0.03 °C/m.
3. Groundwater pressure gradient is assumed equal to 0.1 bar/m.
4. Chemical composition of groundwater is assumed same as seawater (Faure, 1991) in all depth before sequestration. CO₂ sequestration under seabed sedimentation rock is recognized as a feasible option in Taiwan.
5. The overhead pressure for injection is ignored and the injection pressure is assumed equal to the groundwater pressure.
6. CO₂ is presumably trapped physically in (1-SW) volume fraction of rock porosity. SW is the saturation degree of groundwater and is assumed equal to 0.9 in all depth.
7. Mineralization trapping is ignored due to its slow speed with respect to the other trapping mechanisms.
8. 2 NT$ for 1 kWh compression energy, and 500 NT$ per ton of CO₂ for sequestration compensation are used to determine the profit from the operation of CO₂ geo-sequestration.

RESULTS

Based on the assumptions used in this study, simulation result (Fig. 2 and Fig. 3) shows that:

1. The CO₂ sequestration density will not exceed 650 kg/m³.
2. The ratio of fugacity to solubility of CO₂ in groundwater is roughly equal to 100 bar/molal.
3. The pH value of groundwater is in the range of 3 to 6 without consideration of the buffering effects from rock’s minerals.
4. The compression cost for CO₂ injection down to 1000, 2000, 3000, and 7000 m depth are 237, 295, 333, and 427 NTS/tonCO₂.
5. The optimum sequestration depth is around 1100 m depth that has a maximum profit value around 3.5 NT$ per cubic meter of rock formation.
Sequestration Depth

Injection pressure

Underground temperature

GW chemical composition

Mineral composition

Rock porosity

GW saturation degree (SW)

Equation of State

CO2 Fugacity

CO2 Density

CO2 Compression Energy

Chemical Trapping (CTrap)

Physical Trapping (PTrap)

Sequestration Capacity, (ton CO2/m³) (TTrap = CTrap + PTrap)

NetIncome, (NT$/tonCO2) (NetIncome = Income – Cost)

Optimum Sequestration Depth (depth with the maximum profit per unit rock volume, [NT$/m³])

(TTrap = CTrap + PTrap)

NetIncome, (NT$/m³)

Optimum Sequestration Depth

(depth with the maximum profit per unit rock volume)

Assumptions and notations:

(1) Temperature gradient = 0.03 °C/m
(2) Pressure (groundwater) gradient = 0.1 bar/m
(3) Porosity = 0.3 * exp[(-1.5*Depth)/(Depth+2000)]
(4) Fugacity and density of CO2 calculated by Peng-Robinson EOS
(5) Chemical composition of GW in all depth = constant = ~ seawater
(6) CO2 Solubility and pH of GW calculated by the GWB

Fig. 1: Conceptual model for determining the optimum sequestration depth

Fig. 2: Simulation result for CO2 density, fugacity and solubility

Fig. 3: Simulation result for the optimum sequestration depth
CONCLUSIONS

The optimum sequestration depth is determinable if the underground information is available, and the following items are identified for improving the simulation result in the future:
1. Capital cost (compressor, drilling, etc.) is needed to be included in the calculation. Capital cost for 1 MtonCO$_2$/year injection capacity is around 3.2 billion NT$ (2.7 billion NT$ for compressor train) (Torp and Brown, 2004), and is not an ignorable cost.
2. The procedure used to calculate the compression energy ought to be improved. Commercial process is usually operated as multi-stage compression for saving energy.
3. Emission of CO$_2$ from electricity generation must be considered in the calculation. A 500 MW coal-fired power plant will emit ~3 MtonCO$_2$/year (MIT, 2007).
4. Algorithm for predicting the saturation degree (SW) of groundwater is needs to be developed. SW is recognized as the most important factor by this author for determining the sequestration capacity and optimum sequestration depth.

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REFERENCES

Development and Application of a Gas Membrane Sensor for In-Situ Down Hole Observation of Gases During Geological Storage of Carbon Dioxide

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ABSTRACT

The geological storage of carbon dioxide (CO₂) in deep permeable reservoir rocks is regarded as one of the most promising technologies for a considerable reduction of greenhouse gases entering the atmosphere from stationary point sources such as large fossil fuel power plants. However, comprehensive research is essential to characterize and map the geological storage structures and to better understand the behaviour of CO₂ during storage. Therefore we aim to develop and apply a new, innovative geochemical monitoring tool for the real time and in-situ observation of CO₂ and additional physical parameters during geological sequestration.

The method uses a phase separating silicone membrane, permeable for gases, in order to extract the gases dissolved in borehole fluids, water and brines and a carrier gas to conduct the gathered gas through capillaries to the earth surface. At the surface, the gas phase is analyzed directly, e.g. in real-time with a mass spectrometer allowing for the determination of all permanent gases, and can be sampled for more detailed investigations in the laboratory.

The permeation rates of the used membrane for CO₂ at given concentrations and temperatures (bore hole conditions) have been determined in a specially developed calibration device and a formula was created to calculate the dissolved gas concentrations.

The concept for on-line determination of gases dissolved in brines with the gas membrane sensor technique was proved successful during a test at the site of the German Continental Scientific Drilling Program, KTB.
Characterization of Natural Gases in Japan 
Based on Molecular and Carbon Isotope Compositions

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ABSTRACT

Origin, maturity, migration, biodegradation and mixing of natural gases in Japan are interpreted by the molecular and carbon isotope compositions. No indication of abiogenic gases has been found. Gases are classified into microbial or thermogenic. However, secondary alteration (mixing, migration, biodegradation) sometimes largely affects the compositions of natural gases. Biodegradation especially alters both molecular and isotopic signatures. Thus, although the prime order of isotopic and molecular fractionation in gases is due to genetic phenomena, secondary effects must be taken into account by putting together various pieces of information. If the secondary alteration is small, carbon isotope compositions of thermogenic hydrocarbons are largely controlled by the maturity. An isotope model developed by Berner and Faber (1996) was successfully applied to natural gases in Northeast Japan. Besides the maturity estimation, the application of the model enables detection of biodegradation, mixing between microbial and thermogenic gases, and mixing among gases with different maturities.

INTRODUCTION

Genetic characterization and maturity assessment for natural gases have been proposed using the molecular and isotope compositions (e.g. Schoell, 1983; Berner and Faber, 1996). Commercial gas reservoirs in Japan are distributed in Tertiary-Quaternary sedimentary basins. In this study, we investigated carbon isotope compositions and molecular compositions for natural gases in Japan in order to reveal their genetic origin and secondary alteration.

SAMPLES AND ANALYSIS

Over 500 gas samples are collected from oil/gas fields, surface seeps and coal mines in Japan (Fig. 1). The molecular compositions of hydrocarbon gases were determined on a Shimazu GC-7A or Agilent 6890 gas chromatograph. The stable carbon and hydrogen isotope compositions were measured using a VG Isotech Sira Series II or GVI IsoPrime mass spectrometer.

ORIGIN AND MIGRATION

The relationships between $C_1/(C_2+C_3)$ ratios and carbon isotope composition of methane ($\delta^{13}C_1$) are shown in Fig. 2. $\delta^{13}C_1$ values range between -75 and -25‰. Abiogenic (inorganic) gases generally have $\delta^{13}C_1$ values heavier than -20‰ and their carbon isotope compositions decrease with increasing carbon number ($\delta^{13}C_1 > \delta^{13}C_2 > \delta^{13}C_3$). No gases show such isotope data, suggesting all gases are
biogenic (microbial or thermogenic decomposition of organic matter).

Based on the classification in Fig. 2, most gases from oil/gas fields are genetically classified into thermogenic or mixture of thermogenic and microbial gases, except for some microbial water-dissolved gases and gas-hydrate-dissociated gases. Gases in deeper reservoirs tend to show heavier carbon isotope compositions. Most gas seeps are classified into thermogenic based on the $\delta^{13}C$ values, while the $C_1/(C_2+C_3)$ ratios are generally high. This suggests that gas migration to surface through sediments caused fractionation only for the molecular compositions, and not for the isotope compositions.

Fig. 1: Location map of oil/gas fields and sedimentary basins where gas samples are collected

Fig. 2: Genetic characterization of natural gases in Japan
MATURITY, BIODEGRADATION AND MIXING

Berner and Faber (1996) developed isotope/maturity models for methane, ethane and propane based on open-system dry pyrolysis experiments and instantaneous kinetic models. If the δ13C value of the source kerogen for gases is known, the Ro (vitrinite reflectance) equivalent maturity can be estimated. In the case of the Akita/Yamagata and Niigata Basins, the source rocks for oil and gas are inferred to be the middle Miocene shales and the δ13C value of the kerogen can be estimated to be -22.3‰. Using this kerogen isotope composition, the gas maturity model for Type II kerogen was successfully applied to natural gases in Akita/Yamagata and Niigata Basin (Fig. 3). The samples show wide ranges of maturity from less than 0.6 to more than 2.0% Ro equivalent values. The estimated maturities of gases in the Niigata Basin are generally higher than those in the Akita-Yamagata Basin.

Most gases from the Akita/Yamagata Basin show relatively heavy δ13C3 values and plot away from the maturity line. This could be due to selective biodegradation of propane. Abnormally high C2/C3 and i-C4/n-C4 ratios for the gases with heavy δ13C3 values also suggest that the gases should be biodegraded.

As shown above, mixing of different origin (thermogenic and microbial) are inferred based on the C3/(C2+C3) ratios and δ13C3 values. On the other hand, a different mode of mixing is possible. Most gases from the Niigata Basin plot lower right side of the maturity line in Fig. 3. As mentioned above, the maturity line is based on instantaneous gas generation from kerogen. If the gases with different maturities mixed together, the δ13C of ethane and propane should plot on the lower right side of the line, since the molecular composition change with maturity (higher hydrocarbons decrease with increasing maturity). Thus, most gases in the Niigata Basin are interpreted to be mixtures of gases generated at different maturity levels or cumulative gases generated in wide range of maturity.

![Fig. 3: Relationship between ethane and propane carbon isotope composition.](image-url)
CONCLUSIONS

Molecular and carbon isotope compositions provide valuable information on genetic origin and secondary alteration for natural gases in Japan.

1. Microbial and thermogenic origin can be differentiated, mainly based on the $\delta^{13}$C$_1$ value.
2. Migration can be assessed based on the relationship between the $\delta^{13}$C$_1$ value and C$_1$/(C$_2$+C$_3$) ratio.
3. Maturity can be estimated using the $\delta^{13}$C values of C$_2$, C$_3$ and source kerogen.
4. Abnormally heavy $\delta^{13}$C$_3$ value and high C$_2$/C$_3$ and i-C$_4$/n-C$_4$ ratios suggest that the gas is biodegraded.
5. Mixing between microbial and thermogenic can be inferred, mainly based on the $\delta^{13}$C$_1$ and $\delta^{13}$C$_2$ values.
6. Mixing among gases with different maturities can be inferred based on the relationship between $\delta^{13}$C$_2$ and the $\delta^{13}$C$_3$ values.

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Geochemical Characteristics and Genetic Origin of Natural Gas Discovered in Taiwan

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ABSTRACT

Oil exploration has been carried out in Taiwan for more than 60 years. Natural gas with a small amount of condensates has been discovered in the Tertiary Taihsi-Taichung (TT) and Tainan basins. Several gas fields in the TT basin onshore and offshore northwestern Taiwan have been developed into production and one gas discovery in the Tainan Basin offshore southwestern Taiwan is going to be developed. Geochemical characteristics, including chemical and isotopic composition of natural gas from major gas fields and discoveries are investigated for the purpose to understand the natural gas genetic origin and to guide the hydrocarbon exploration.

Natural gas discovered in both the TT basin and Tainan basin is of thermogenic origin and generated from terrestrial organic matters. Geochemical characteristics are highly related to the genetic origin including organic matter type and maturation level. All natural gas is dominated with C1 to C4 hydrocarbons. A small amount of light hydrocarbons (C5-C8) is detected and bears significant geochemical significances.

Natural gas from the TT basin shows C2+ content increasing basinward, i.e. from offshore toward onshore area. Horizontal variation of maturity and organic source results in the variation in chemical composition of natural gas from different gas fields. Partially vertical migration is indicated. Natural gas discovered in the Tainan basin is of moderately mature judged from the C2+ content. Stable carbon isotope of methane is lighter compared to that of the gas of the TT basin, probably resulting from the organic matters different from that of the TT basin.

Nonhydrocarbons in natural gas including CO₂ and H₂S are surveyed. H₂S is present usually only in a trace amount in all natural gas samples, consistent to the implication of nonmarine source origin of the natural gas. Natural gas with a high amount of CO₂ occurs in deep reservoirs in several gas fields in the TT basin. Stable carbon isotopic composition is determined for the CO₂ and shows a variation ranging from -3‰ to -20‰, inferring that the CO₂ is related to the magma activities. A small amount of CO₂ attributed to organic origin and some of thermal decay of limestone is not excluded. The CO₂ content in the Tainan basin is ranging from 2% to 11%, with higher content in natural gas from deeper reservoirs. Stable carbon isotopic value of the CO₂ is measured as -3.5‰, inferring inorganic origin from marine limestone.

In addition to these thermogenic natural gas, several biogenic gas discoveries, mainly methane with very light carbon isotopic composition, occur in the northern offshore Taiwan and in southwestern onshore Taiwan.
Origins of Natural Gases from Marine Strata in Northeastern Sichuan Basin (China) by Molecular and Carbon Isotopic Data

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INTRODUCTION

Sichuan Basin is the largest basin with the highest natural gas reserves and production in China, especially in the marine strata in the northeastern areas. It is widely accepted that the natural gases are originated from the secondary cracking of the oil formed previously. Analysis of the molecular and carbon isotopic to the gas samples indicates that most natural gases from Carboniferous and Triassic experienced serious mixing process. Besides the oil cracking, highly maturated residual kerogen is another very important source of the natural gases in Carboniferous strata in Eastern areas and TSR (Thermal Sulfate Reduction) is very important reason for the formation of highly maturated methane in Triassic strata in Northeastern areas. In this study, gas filed of Wubaiti and Wolonghe in eastern Sichuan area and Liujiazhai, Tieshanpo and Dukouhe in northeastern Sichuan area were chosen for sampling. The molecular and carbon isotope were analyzed in laboratory by gas chromatograph (GC) and gas chromatograph isotope ratio mass-spectrometer (GC-IRMS). Some molecular and isotopic diagrams were used to identify the origins of the natural gases.

RESULTS AND CONCLUSIONS

For determining the gas maturity, the isotopic composition of the individual gas components was used, which is a function of thermal maturity, the isotopic composition of the source rock kerogen, and the gas alteration history. In this study, an isotope-maturity model developed by Berner and Faber (1996) was used to estimate the type and maturity of the precursor (source) material. The modeled carbon isotopic ratios of methane, ethane, and propane are expressed with source rock maturities represented by vitrinite reflectance. In this model, a selection mode allows the user to calibrate the maturity lines for a terrestrial and and/or for a marine (sapropelic) source rock, respectively, choosing the carbon isotope ratio for each precursor material.

According to the model, carbon isotope ratios of corresponding methane against ethane or ethane against propane (Fig. 1) should plot on or near the maturity line if both gases derive from one terrestrial or marine source rock (Berner and Faber, 1996). In our case, all samples for C₁-C₃ diagram clearly plot above the projected maturity line indicating an admixture of heavy (₁³C-enriched) methane to the lower maturated ethane, especially for the Triassic gas samples. The scattering of the δ₁³C ethane values might represent source variations. Comparatively, all samples from Carboniferous strata
for C₂-C₃ diagram clearly plot alone the projected maturity line indicating that ethane and propane have the same source and maturities while samples from Triassic strata for C₂-C₃ diagram plot somehow above the projected maturity line indicating an admixture of heavy ethane to the propane. But the mixing degree is not serious. Also, the scattering of the δ¹³C propane values might represent source variations. According to these plots, the maturities of methane, ethane and propane can be estimated. The maturities of ethane and propane from Carboniferous strata are estimated about 0.9-2.0%Ro and 0.8-2.2%Ro respectively.

Fig. 1: Isotopic composition of methane against ethane and ethane against propane in natural gases of the northeastern Sichuan Basin. The maturity line is according to Berner and Faber (1996). Diamond and square data points indicate Carboniferous and Triassic gas samples, respectively. Numbers on the line of marine organic matter indicate the maturity of the source rock in %Ro

Fig. 2: Molecular ratios of gases of our case using ln(C₁/C₂) versus ln(C₂/C₃) diagram proposed by Prinzhofer (1995), differentiation of gases generated by primary cracking of kerogen (sub- horizontal trend) from gases generated by secondary cracking of oils (sub- vertical trend).
For the gas formation mechanism, we used the model of genetic fractionation for thermogenic gases expressed with the \( \ln(C_1/C_2) \) versus \( \ln(C_2/C_3) \) diagram proposed by Prinzhofer (1995), allowing differentiation of gases generated by primary cracking of kerogen (sub-vertical trend) from gases generated by secondary cracking of oils (sub-horizontal trend). The diagram for our case is shown in Fig. 2. It can be found that all samples of Carboniferous gases and low-\( \text{H}_2\text{S} \) gases are plotted along the secondary gases of oil, which indicates that the gases in these two areas were mainly formed through secondary cracking of the oil. The high-\( \text{H}_2\text{S} \) gases are plotted deflecting from the vertical line to the direction of \( \ln(C_1/C_2) \) increasing while \( \ln(C_2/C_3) \) keep steady, which indicates the obvious increasing of the methane and the decreasing of the ethane. Considering the increasing of \( \text{H}_2\text{S} \), the results clearly reflect the TSR (Thermal Sulfate Reduction) process, which promote the cracking of heavy hydrocarbons including ethane cracked into methane.

For further understanding the mixtures of our case, Chung’s model was used and the results are plotted in Fig. 3. Chung et al. (1988) proposed a model to differentiate natural gases that are derived from a single source from gases that are mixtures derived from two or more sources. The method is based on plotting the isotopic composition of methane through pentane as a function of the reciprocal carbon number of the hydrocarbon (Fig. 3). A linear fit to the data supports a co-genetic origin for the gas species, whereas a non-linear fit suggests that the gas accumulation is a mixture of gases, a chemically altered gas or a gas derived from a structurally heterogeneous carbon source. This model is commonly referred to as the natural gas plot.

![Fig. 3: An example of a natural gas plot using Chung (1988)’s method.](image)

The \( \delta^{13}\text{C} \) values for the gas components \( \delta^{13}\text{C}_n (n = 1 \text{ to } 3) \) are plotted as a function of \( 1/n \), where \( n \) is the number of carbon atoms in the molecule. The lines are extended to the intercept, which corresponds to the \( \delta^{13}\text{C} \) values for the gas-producing groups in the kerogen. One sample obviously does not follow the linear trend: a mixture of source inputs, or heterogeneity in the source, would cause this deviation.
In Fig. 3, three marine precursors of gases including in-reservoir oil, in-source oil and residual kerogen were used and the isotopic compositions from methane to propane were plotted against the reciprocal carbon numbers and the results of Triassic and Carboniferous gases were also plotted in Fig. 3. It can be found that there existed mixing of the gas sources. The ethane and propane of both Carboniferous and Triassic gases are mainly from the in-source oil cracking. As the maturities are not very high (Fig. 1), they may not from the in-reservoir oil cracking. However, the maturities of methane are obviously higher than ones of ethane and propane. For the source of methane, it can be deduced that the methane of Carboniferous gases may be from the high-matured residual kerogen and the methane of Triassic gases may be from both the high-matured residual kerogen and the TSR-induced oil cracking. Combining the geological characteristics of the study area, it is deduced that the residual kerogen from Ordovician marine shale and the palaeo oil reservoirs are main sources of the Carboniferous gases in Eastern Sichuan Basin, and the residual kerogen from Ordovician and Permian marine rocks and the palaeo oil reservoirs in Permian are main sources of the Triassic gases in Northeastern Sichuan Basin.

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Gases with Abiogenic Signature in Association with Bitumen in Alkaline Rocks of the Ilimaussaq Intrusion, Greenland

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ABSTRACT

Hydrocarbon gases released from the crystalline rocks of the Ilimaussaq intrusion either by crushing or acid digestion show an abiogenic isotopic signature, $\delta^{13}C$ of methane and ethane ranging from $-1.6$ to $-5.0\%_{oo}$ and $-9.2$ to $-12.5\%_{oo}$ respectively. Propane of one of the samples gave an isotopic value of $-16.5\%_{oo}$. The bitumen extracted from various rock samples, on the other hand showed a hydrocarbon distribution pointing to thermal maturation of a marine type of source rock.

GASES

Numerous gas inclusions, mostly less than 10 $\mu$m, are present in the various rocks of the Ilimaussaq intrusion. The gas released by crushing consisted of 90 percent hydrocarbons (C$_1$-C$_5$) and 10 percent inorganic gases, mostly hydrogen (Petersilie and Sørensen, 1970; Konnerup-Madsen et al., 1979). By reaction with warm hydrochloric acid larger yields of hydrocarbons were obtained, up to 65 mg of methane per kg of rock, compared to the crushing method (Laier and Nytoft, 1995). The composition of the gas released by the two different methods was similar with respect to both chemical and isotopic composition (Konnerup-Madsen et al., 1988), and do not fit any known origin (Fig. 1).

Fig. 1: Gas released by acid from the Ilimaussaq rocks plotted in a $\delta^{13}C_1$ vs. $C_1/(C_2+C_3)$ diagram. Names attached to the data points refer to different rock types.
The gas was therefore considered to be of abiogenic origin (Petersilie and Sørensen, 1970; Konnerup-Madsen et al., 1988).

**BITUMEN**

Dispersed bitumen present in the various rock types, up to 300 mg HC per kg of rock, was extracted and analyzed either by IR spectroscopy (Petersilie and Sørensen, 1970) or GC and GC-MS (Laier and Nytoft, 1995). The results of latter point to hydrocarbons generated by thermal maturation of a marine type of source rock (Fig. 2), and not to an abiogenic origin as had previously been suggested by Petersillie and Sørensen (1970). Stable carbon isotopic analyses of different extracts of bitumen gave $\delta^{13}C$ values in the range -17 to -24 ‰ (Konnerup-Madsen et al., 1988) thereby confirming its organic origin, and the authors therefore suggested that methane and bitumen were of different origin.

Fig. 2: Chromatograms of aliphatic fraction from dichloromethane extract of kakortokite rocks of the Ilimaussaq intrusion.
Studies of bitumen in thin sections of the various rocks under UV light, show that it exist along grain boundaries, as well as in fluid inclusions along with gas inclusions. Therefore, it is more likely that both gaseous and liquid hydrocarbons entered the magma at some stage due to hydrothermal convection. Bitumen having $\delta^{13}C = -19.5 \%$ were also found in the sandstone formation into which the magma intruded c. 1100 m.y. ago (Konnerup-Madsen et al., 1988). No potential source rock exist presently in the vicinity of the Ilimaussaq intrusion, however 1800 - 2000 m.y. old organic rich rocks, containing thermally mature bitumen, are found less than 100 km north of the area. Therefore organic rich rocks expelling petroleum into the sandstones intruded by the magma may have been present.

DISCUSSION AND CONCLUSION

Formation of layered kakortokites from the magma has been explained by consecutive crystallization in response to loss of volatiles from individual layers (Larsen and Sørensen, 1987). If loss of gas occurred by diffusion an enrichment of the $^{13}C$ content of the gas remaining would have resulted. This enrichment would be greatest for the component with the lowest molecular weight, i.e. methane, which is what is observed for the Ilimaussaq gases. Therefore, the most likely explanation for heavy isotopic signature of the Ilimaussaq gas is loss of part of the original hydrocarbon gas by diffusion. Thus, a common organic origin for both methane and higher hydrocarbons can be assumed.

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Biogeochemical Characterization of Kuan-Tzu-Ling Hot Spring in Southern Taiwan

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ABSTRACT

Hot springs are unique features in tectonically compressed area like Taiwan. This is an important natural source of the greenhouse gas methane to the hydrosphere and atmosphere. Kuan-Tzu-Ling is one of Taiwan's best-known hot springs, which was developed during the Japanese Colonial Period (1895-1945). The importance of the hot spring is that when fluid erupted from an erupted point, some gases and muds also came out mixed with liquid. The samples were collected from two different eruption points of Kuan-Tzu-Ling hot spring like KTL-1 (N23° 28.3′ and E120° 29’ 45.4′) and KTL-2 (N23° 20′ 23″ and E120° 29′ 47.8″) during March 2007. The temperature of the KTL-2 hot spring (65.3 °C) was found higher than that of the KTL-1 (60.6 °C). The pH, conductivity, salinity, and dissolved oxygen level was observed at the maximum in the KTL-2 point with respect to the KTL-1. However, KTL-1 exhibited higher redox potential relatively to KTL-2. Gases isolated from two eruption points were found significantly predominated in SO₂ (>10.2 ppm), H₂S (>50 ppm), CH₄ (>70%), and CO₂ (>300 ppm). In fluids of both eruption points, the ionic concentrations of Na⁺ and Cl⁻ were observed very high relative to other ions like K⁺, Mg²⁺, Ca²⁺, NO₂⁻, and SO₄²⁻ which suggest a marine origin from actively de-watering sedimentary pore waters along major structures on land. Also, KTL-1 reflected maximum amounts of Na⁺, K⁺, Mg²⁺, Ca²⁺, NO₂⁻, and SO₄²⁻ ions, except Cl⁻ ions in contrast to KTL-2. The Ca²⁺ concentration was found 2-fold higher in KTL-1 than in KTL-2. The elemental concentrations (V, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Se, Rb, Sr, Mo, Cd and Ba) of KTL-1 and KTL-2 were estimated qualitatively and quantitatively using ICP-MS. Significant variations (p≤0.05) in different elements in the fluids and sediments of this hot spring area were noted to be different at different eruption points, revealing that the elemental compositions and their release mechanism may be different in different places. The concentrations of V, Cr, Mn, Fe, Ni, and Zn were found significantly higher in the sediment, whereas the concentrations of Cu, As, Se, Rb, Sr, and Ba were found significantly higher in the fluid sample, which indicates that more electronegative elements were released into the fluid. The As concentration was found at the maximum in the fluid of KTL-1 in contrast to its sediment, which can signify the release of As under low redox conditions. The Co, Mo and Cd were not found from both eruption points. The humic acid was extracted from sediments of hot spring and then analyzed by Fourier Transform Infrared (FT-IR). The FTIR spectra showed the presence of possible functional group of secondary amines, ureas, urethanes (amide) and silicon. Also, the results of present study also significantly reflected that the Kuan-Tzu-Ling hot spring contain sulfate-reducing bacteria that grew well in sulfate-reducing medium.
The Factors Affecting Gas Hydrate Formation in Natural Environment

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ABSTRACT

The factors that possibly affect the formation of gas hydrate in natural environment are discussed in this paper, which include gas availability, space availability, pressure-temperature condition, time, etc. It has been found that saturation level of gas hydrate in sediment is closely related to sediment type, high in sand but very low in fine clay-rich sediments.

INTRODUCTION

Natural gas hydrate forms in a complex system in which many factors are involved. With the recognition of great potential as a kind of energy resources, natural gas hydrates have been investigated worldwide. Through the continuous efforts of DSDP (Deep Sea Drilling Project), ODP (Ocean Drilling Program) and IODP (Integrated Ocean Drilling Program), and several high-profile national gas hydrate programs in US, Japan, India, et al., huge amount of data have been accumulated. Based on these results, a synthetic analysis about what factors affect the formation of gas hydrate in natural environment and how they work has been possible. Here we present the results of our studies in this field.

FACTORS AFFECTING GAS HYDRATE FORMATION IN NATURAL ENVIRONMENT

In laboratory-based studies on gas hydrate, the materials, suitable P-T condition, space, and time, are among the important factors affecting hydrate formation. Similarly, these factors are among those affecting the formation of natural gas hydrate as well, although these may well appear in different ways.

In natural environments, gas hydrate formation mainly involves two kinds of materials – water and gas. Natural gas hydrate generally exists in sediments, so the source of water is the aqueous solution in sediment pores. According to ODP investigations, pore water content can be as much as about 20 % even at a depth of 1000 m below seafloor, so water is always available for hydrate formation. Two origins of the hydrate-forming gas have been proposed – biogenic and thermogenic, as based on composition and isotope analyses of gas from natural gas hydrate. Biogenic gas is thought to originate from the bacterial degeneration of organic matter in sediments, which generally supplies gas for in-situ hydrate formation. Thermogenic gas originates from the decomposition of organic matter by heat at a depth much greater than where hydrates form, so it has to migrate upwards into the hydrate stability zone. Although the composition and isotope results for the hydrated gases suggest that most natural gas hydrates are composed of biogenic gas, the nature of organic matter in sediment does not support
this. For example, TOC in Nankai Trough offshore Japan is generally less than 1.0%, which means that the sediment can have a hydrate saturation level of ~20% if all the organic matter is converted to methane gas at the same time. It is clear that there is not enough biogenic gas produced in-situ to fill the pores to about 80% as estimated from pore water chemistry and geophysical logging results. Furthermore, all of the organic matter in sediment cannot be expected to degrade at the same time. Moreover, ODP investigations also suggest that organic matter in sediment degrades gradually with depth of burial but this does not happen over a short period of time. Thus migrated gas from deeper sediments should be considered as a main source for hydrate formation.

As limited by stability conditions, natural gas hydrate can form only in an environment where pressure and temperature conditions will stabilize gas hydrate. Thus natural gas hydrates have been found mainly under the permafrost and on the continental slope in a certain range of depths. The depth range for marine gas hydrate formation depends on water temperature and the composition of available gases. With water temperature control, methane hydrate can be expected to form at a depth greater than about 500 m below sea level, however shallower depths are possible if thermogenic gases such as ethane, propane, etc are available.

Gas hydrate generally forms in sediment pores that range from several nm to several mm. When faults or fractures are present, much larger void space can be expected in sediment sections. Most pores occurring in sizes ranging from several nm to about 1000 nm are much larger than the size of the unit cell of sI gas hydrate (~ 12 Å for methane hydrate), so enough space is usually available for hydrate formation (note that there need to be a minimum number of contiguous unit cells to give a volume that will scatter X-rays and give the characteristic diffraction pattern). However, pore size can affect hydrate formation by reducing its stability range when it becomes smaller than ~ 50 nm. Field investigation and experimental results also indicate that the saturation level of gas hydrate in sediment is affected by sediment type: it is high in sand but low in clay rich sediments.

The time required for the initiation of hydrate formation, denoted as the induction time in laboratory-based experiments, in is rather small in natural environments (minutes, hours to several days) on a geological time scale (several tens thousand years or much longer) and can be ignored. However the concept of time is important in another way in natural environments. The saturation of pore water with gas is the basic necessity for hydrate nucleation. It is easy to have water saturated with gas in the laboratory, however this can take time in natural environments. The length of the time needed for pore water to become saturated with gas depends mainly on the gas flux from the deeper portion of sedimentary sections, it can be very short when the flux is large.

Sediment controls on the occurrences of natural gas hydrate have been documented in the studies conducted in Alaska, Blake Ridge, Nankai Trough and Mallik. Investigations on natural and synthesized gas hydrate samples indicate that the saturation level of gas hydrate can be over 80% of pore space in sand but generally less than 3% in clay or clayey silt.
Detecting Surface Oil Slick Related to Gas Hydrate/Petroleum on the Ocean Bed of South China Sea by ENVI/ASAR Radar Data

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INTRODUCTION

As highly concentrated methane (Contains >160 times CH₄ volume in standard TP state and more organic carbon than all other forms of fossil fuels combined), Gas hydrate is important both as an energy resource and as a factor in global climate change. Gas hydrate could provide a clean and tremendous energy source in the future if it could be found and would cause global climate changes if releasing or not properly used. Till to now, gas hydrate is found in sub-oceanic sediments in the Polar Regions (shallow water) and in continental slope sediments (deep water), where pressure and temperature conditions combine to make it stable.

To present, methods effectively for finding gas hydrate include laboratory simulation (stable area), geophysical method (seismic data and model, sonar, etc.), Ocean Drilling Program (ODP), deep sea survey (camera/sampling/in situ measuring) and remote sensing (UV/visible/IR/Thermal IR/Radar bands). Radar remote sensing is an indirect way for detecting gas hydrate. The key for radar remote sensing detecting of gas hydrate is the gas/oil seepage from the gas hydrate to ocean surface. Previous studies demonstrate that there exist many styles of gas venting at natural seeps. Results in the Gulf of Mexico indicate that bubbles of gas, which are often contaminated with oily coatings, escape from a shallow deposit of gas hydrate at 570m water depth, single large bubble of gas can rise from a pool of brine on a small mud volcano and the diameter of crater is about 25 cm (Macdonald et al, 2002; Beukelaer, et al, 2003).

SAR (Synthetic Aperture Radar) technology was widely used to detect the oil slick on ocean surface. SAR recognizes object as the radar pass over an object the echo is Doppler shifted due to the satellites motion relative to the object. The backscatter from an ocean is usually very large due to the constructive interference of waves, thus the ocean appears bright. If there is a slick on the water surface the radiation is reflected, the sea surface acts as a mirror. Consequently almost no echo signal returns to the radar and the area appears dark.

The objectives of this paper include: (1) Try to detect the oil slick on the ocean surface of some potential areas in South China Sea; (2) Map the oil slick from anomaly area in radar image; (3) Validate the oil slick (gas hydrate/ free oil/oil spill contaminants); (3) Probe the possibility of ENVI/ASAR for detecting oil slicks and radar image processing way for extracting the anomaly signals related to oil slick inducing oil/gas seeps.
STUDY AREA, DATA AND METHODS

The South China Sea has been believed a potential area for the occurrence of gas hydrate. The previous studies have found very good BSR (Bottom-simulating reflectors) in this area. BSR are observed commonly at a depth of several hundred meters below the seafloor in continental margin sedimentary sections such as Qiongdongnan Basin, Pearl River Mouth Basin and Taixi-Dongsha areas, which have undergone recent tectonic consolidation or rapid accumulation. They are believed to correspond to the deepest level at which methane hydrate is stable. The possible distributions of gas hydrate stable zone in Qiongdongnan Basin of South China Sea have been circled through the laboratory simulation and kinetic calculation. This study will detect and track the oil slicks in these sections of South China Sea by using the ENVI/ASAR data and try to validate the result by integrating the in-situ sampling and geochemical analysis.

ENVIsat Advanced Synthetic Aperture Radar (ENVI/ASAR) is built up on the experience gained with the ERS-1/2 active microwave instrument (AMI) to continue and extend Earth observation with SAR. ENVIsat is a satellite launched by ESA (European Space Agency) in 2002. The main features of ENVI/ASAR include: (1) selection of different swaths (up to 400 km scanning mode); (2) alterable image mode/wave mode, including alternation of polarization mode (HH/VV/HV) and incidence angles; (3) high resolution images PRI, SLC, and GEC (10-25m); and (4) global monitoring /programming receiving data. The ENVISAT, the big “last dinosaur” with all together 10 instruments will serve many purposes. Operational systems have been developed for mapping, sea ice- and oil slick monitoring, and ship detection. ASAR is an all-weather, day or night radar imaging instrument with different polarization opportunities. Important new capabilities of ASAR include beam steering for acquiring images with different incidence angles, dual polarization and wide swath coverage. Users have access to a variety of beam selections that can image swaths from 56 to 405 kilometers in width, with resolutions from 30 to 150 meters and at incidence angles from 15 to 45 degrees. The data we used in this study is shown in Table 1.

Table 1 Data used in this study

<table>
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<th>Date</th>
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</table>

The general method flow of this study includes: (1) potential area selection: geology, BSR, laboratory simulation; (2) data selection: preparing of ENVI/ASAR data: date, location, mode, polarization, angle, resolution…; (3) ENVI/ASAR image processing: sparkle removal, Lee filter, low pass filter, density segmentation, false color…; (4) anomaly extraction: robust method, statistics; (5) validation of the anomaly: sampling, geochemical analyzing; (6) comprehensive evaluation: analysis with geophysical results, laboratory kinetic simulating results, in-situ geochemical analyzing results through GIS (Geographic Information System).
RESULTS AND DISCUSSIONS

The detected oil slick on ocean surface in Qiongdongnan Basin, South China Sea by ENVI/ASAR data is shown in Fig. 1, whereas the false composite image of the radar data is in the left (VV(Red), VV(Green), VH(Blue), and the false indexed color map of the image is shown in the right. It can be found that there are three near-shore oil slicks in the southeastern Hainan Island and four offshore oil slicks in the eastern area of Qingdongnan Basin. From the indexed color map, it can be found that the intensity of the near-shore oil slicks is stronger than that of off-shore slicks, and among four offshore anomalies, the one in the northern (E111.35-111.52, N19.15-19.30) in the strongest one.

Fig. 1: Map of surface oil slick in Qiongdongnan Basin, South China Sea by ENVI/ASAR data

The detected oil slick on ocean surface in Dongsha-Taixi area, South China Sea by ENVI/ASAR data is shown in Fig. 2. Just as in Fig. 1, the grey-scale image of the radar data is shown in the left, and the false indexed color map of the image is shown in the right. It can be found that there are four oil slicks in this area and they are all very strong.

Fig. 2: Map of surface oil slick in Dongsha-Taixi area South China Sea by ENVI/ASAR data
For validating the results, two sites were designed for gathering water samples and four samples were gathered in different depths including surface, 25m, 50m and 200m. The oils were extracted using organic solvent in laboratory and analyzed by using Gas Chromatograph (GC). The chromatograms of oils in the designed site of surface slicks are shown in Fig. 3. It can be found the biomarker carbon numbers of the oil cover the whole range of 12-35, which demonstrates a typical composition of oil rather than ocean microbial origins. The organic composition of the oil in different depth exhibits a quite similar distribution of carbon numbers, which indicates the source of the ocean surface oil is originated from the seepages of petroleum in deep area rather than the contrived oil spills. The autogenetic carbonate samples with very negative carbon isotopic composition were found in the bottom samples from the same site, which also supported the results of radar data. Another technique we used is to extract the oil slicks by using multi-temporal data of the same area. The results from the ENVI/ASAR data of 2004 are coincided with those from the ERS-1/ASAR data of 1999, which confirm the effectiveness of our results in another ways.

ACKNOWLEDGEMENTS

The authors would like to thank CAS for the financial supports (Grant No. KZCX2-YW-108, KZCX3-SW-224).

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Characterizing Organic Matter in the Surface Sediments Associated with Gas Hydrate and Oil Seepage from the Gulf of Mexico

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ABSTRACT

The abundance, hydrocarbon composition and distribution of organic matter in six seafloor sediments collected from the sites of Gulf of Mexico associated with oil-seeps, gas venting and gas hydrates are studied. The results indicate that the abundance and hydrocarbon composition vary significantly among these samples, S-1, S-7 and S-9 samples show the characteristics of modern organic matter and microbiodegradation, while aliphatic hydrocarbon composition and distribution in S-8, S-10 and S-11 are indicative of petroleum contamination as well as related sterane and hopane ratios. Also, the lack of normal alkanes in S-8 and S-11 samples is clearly signature of severe biodegradation. Furthermore, a group of 2,6,10,15,19-pentamethylicosienes (PMIΔ) containing 1—5 unsaturated double bonds has been identified in S-1 sample that was collected Green Canyon 238 site of the Gulf of Mexico. These PMIΔ compounds are distributed between nC22 and nC34 on the mass chromatogram of aliphatic fraction with very much depleted δ13C value ranged from -86.7‰ to -115.5‰, whereas the δ13C values of companion n-alkanes range from -28.4‰ to -34.6‰. These unsaturated PMIΔ compounds are typical biomarkers derived from the anaerobic oxidation of methane mediated by methane-oxidizing archaeal bacteria and indicative of the gas seeps or even the occurrence of gas hydrates in the deep sea sediments. The characteristics of organic matter suggest that the sampling site of the S-1 sample is likely associated with gas hydrates or gas venting system.
Cutting Gas of Exploration Wells in Taiwan-Geochemical Characteristics and Implications in Hydrocarbon Generation

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ABSTRACT

Gas indigenous to drilling cuttings of exploration wells (so-called cutting gas) bears geochemical information concerning hydrocarbon genetic origin in the encountered strata and therefore valuable for petroleum exploration. In this study, fresh cutting samples collected on well site of several exploration wells, onshore and offshore Taiwan, were analyzed by using headspace gas analysis technique for hydrocarbons with molecular range from C1 to C6, and from C6 to C8 for samples from some wells.

It is found that the hydrocarbon content and chemical composition vary vertically and related to the organic matter and maturation level. Geochemical parameters based on the chemical composition were applied to investigate the natural gas generation and to evaluate the hydrocarbon potential of the encountered strata in the exploration area. The results indicate that the Lower Miocene coal-bearing formations in northwestern offshore and onshore area show high content of hydrocarbon gases, inferring their potential for natural gas generation. The threshold of the thermogenic natural gas generation is at the maturity equivalent to Ro 0.4-0.5% based on the occurrence of C2+ hydrocarbons. Cutting gas of thermogenic origin found in the shallow immature strata may be attributed to vertical migration of mature gas from deep strata. Major organic matter in most encountered Tertiary formations is gas-prone, judged from the low C5+ content in the cutting gas. Enhancement of maturation and therefore gas generation caused by volcanic intrusion is observed in a well offshore northern to Taiwan. Such a maturation effect is restricted to a small interval of depth.
Occurrences and Isotopic Geochemistry of Natural Gases in Western Taiwan


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ABSTRACT

The onshore hydrocarbon reservoirs of Taiwan found over the years are mainly located in the Neogene sequences which consist of Miocene to early Pleistocene shallow marine to shelf clastic sediments and are widely distributed over western Taiwan from Western Foothills and costal plain and terraces. These Neogene strata are characterized by Type III source rocks, indicating a gas-prone potential. Of the explored structures in northwestern Taiwan, Ching-Tsao-Hu (CTH), Yung-Ho-Shan (YHS), Chin-Shui (CS), Pai-Sha-Tun (PST), Chu-Huang-Keng (CHK) and Tie-Chen-Shan (TCS) gas fields (Fig. 1) have proven economic gas accumulation. These gases are generally produced along with various amounts of associated condensate. The $\delta^{13}C$ (-41.1 ~ -29.9‰ vs. V-PDB) and $\deltaD$ (-213 ~ -164‰ vs. V-SMOW) of methane in the gases of these Neogene reservoirs suggest thermogenic origin (Fig. 2) and have been inferred to have local Miocene source rocks. Partially revered order of $\delta^{13}C$ values of hydrocarbon gases (i.e. $\delta^{13}C_1 <$ $\delta^{13}C_2 <$ $\delta^{13}C_3 > \delta^{13}C_4$) is common in these gases. In the region of southwestern Taiwan, three gas fields, namely Pa-Chang-Chi (PCC), Hsin-Ying (HSY), and Long-Ten (LT), have been discovered. The gas in the PCC gas filed is derived from thermogenic origin, but the associated condensate might have undergone severe biodegradation. Hydrocarbon exploration in the island has been preferentially focused on anticlines and affiliated structures, and the strategy has succeeded in northwestern Taiwan. While, other reservoir types should not be neglected. The Neogene strata in western Taiwan gradually thicken from north to south and turn more shaly and muddy in the south. Although, in terms of reservoir quality, the lithofacies in the north surpass their equivalents synchronically deposited in the south, local pinched and lenticular sand bodies resulted from paleo channel fills (Fuh et al., 2006) in young Pleistocene strata may have served as excellent reservoirs in costal plain and terraces of southwestern Taiwan. The discovery of gases in HSY and LT fields proved the presence of shallow reservoirs in the form of stratigraphic trap. Gases from these Pleistocene pools are methane-dominated and have $\delta^{13}C$ and $\deltaD$ values of -65.2 ~ -59.3‰ and -204 ~ -197‰, respectively, suggesting a bacterial origin.
Fig. 1: (a) Location map of gas fields in Taiwan. CTH = Ching-Tsao-Hu; YHS = Yung-Ho-Shan; CS = Chin-Shui; PST = Pai-Sha-Tun; CHK = Chu-Huang-Keng; TCS = Tie-Chen-Shan; PCC = Pa-Chang-Chi; HSY = Hsin-Ying; LT = Long-Ten.
Fig. 2: Carbon and hydrogen isotopic compositions of methane from gas fields in western Taiwan. The use of the fields of natural gases types and their abbreviations follow Schoell (1983). B = bacterial, T = thermogenic associated; TT(m) = non-associated gases from liptinitc sapropelic organic matter; TT(h) = non-associated gases from humic organic matter; M=mixed gases; To = gases associated with petroleum; Tc = gases associated with condensates. Data for TCS refer to Lu & Lin (1984).

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Evolution of Mud volcanoes in the Accretionary Prism of Southern Taiwan: Constraints of Gas and Fluid Geochemistry

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ABSTRACT

Taiwan is located at the plate boundary between Eurasian plate and West Philippine plate. Mud volcanoes, which are believed to be the products of accretionary prism due to collision, are commonly found in on-land of SW Taiwan. According to available seismic data, many active mud volcanoes were also observed in offshore SW Taiwan. Meanwhile, many bottom simulating reflectors (BSR) can also be recognized, which indicates potential submarine gas hydrate deposits may exist in this area. Since the diapiric structures can be continuously extended from offshore towards on-land in SW Taiwan, local geologists suggested that on-land mud volcanoes may be genetically related to offshore mud volcanoes and gas hydrate deposits.

For better understanding their relationship, fluid samples of representative mud volcanoes in SW Taiwan were collected for geochemical analyses. According to the data of chlorine concentrations and oxygen isotopes, some of on-land mud volcanoes exhibit compositions which fall in the mixing trend between published compositions of gas-hydrate waters and seawater. This indicates that on-land mud volcanoes are genetically related to offshore gas hydrate deposits. Furthermore, some of them exhibit higher $\delta^{18}O$ value than the mixing line. It implies that these fluids may be derived from the deeper sources which have been experienced serious water-rock interaction during diagenesis processes.

We suggested that the relationship between gas hydrates with mud volcanoes on-land and offshore SW Taiwan can be considered as an accretionary prism conveyor belt. Therefore, a four-stage genetic model is proposed to explain the evolution of mud volcanoes from offshore toward on-land in southwest Taiwan. In the passive margin, where is away from the accretionary prism, the gas hydrates was produced and well-preserved (stage I). While the accretionary prism accreted and collided, the gas hydrates would be partially dissociated due to the intruded thermal fluids via the fractures/faults and then may mix with sedimentary pore water. Consequently, this pressured fluid can migrate to the surface, and then produce mud volcanoes in submarine (stage II). In stage III, offshore mud volcanoes became on-land mud volcanoes following the continuous accretion. Finally, some dehydrated clay fluids were involved in the genesis of mud volcanoes through the deep faults (stage IV).
Radioactive Gas Emission from Mud Volcanoes in Taiwan

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ABSTRACT

Many mud volcanoes are distributed along the tectonic sutures in southern Taiwan and can be divided into five zones based on their relative positions in different tectonic domains. Most active mud volcanoes are exhaling methane-dominated gases. Nevertheless, some mud volcanoes show unusual carbon dioxide-dominated compositions in western Taiwan and nitrogen-excess compositions in eastern Taiwan. This implies that there are multiple sources for the gas compositions of mud volcanoes in Taiwan. Radioactive gas, mainly radon, continuously emissions from these mud volcanoes accompanied with other major gases, for examples, CH\textsubscript{4} and CO\textsubscript{2}. Recently, Yang et al. (2003) concluded that the carrier gases (CO\textsubscript{2} and CH\textsubscript{4}) play a dominant role in controlling transport and redistribution of radon gases towards the Earth’s surface via a fault/fracture zone. To better understand the controlling factors for the radon emission from mud volcanoes, we systematically measured the radon concentration of bubbling gases from mud volcanoes in Taiwan.

A wide range of radon concentration, 0.1 to 16 kBq/m\textsuperscript{3}, in mud volcano gases are obtained. They can be divided into three groups: (1) High radon concentration (9-16 kBq/m\textsuperscript{3}), with high CO\textsubscript{2} contents at deep faulted zone in western Taiwan; (2) low radon concentration (0.1-2.0 kBq/m\textsuperscript{3}), with high CH\textsubscript{4} contents in southern Taiwan; (3) medium radon concentration (3.8-5.0 kBq/m\textsuperscript{3}), with excess N\textsubscript{2} contents in eastern Taiwan. It is consistent with previous results that the bubbling gases accompany with higher flux of carrier gases at deep fault/fractures zones usually exhibit much higher radon concentrations.

It is interesting to find that the radon concentrations in bubbling gas of mud volcanoes are always lower than the soil radon around mud volcano areas in Taiwan. Non-aqueous phase-Liquids (NAPLs), which exhibit very high partition coefficient for radon between air and NAPLs, are considered to play an important role to affect the radon concentration of bubbling gases with hydrocarbon-rich compositions. It can explain those methane dominated mud volcanoes exhibit much lower radon concentration than those with high CO\textsubscript{2} content and excess N\textsubscript{2}.
Origin of Methane in Aquifers under two Coastal Plains of Taiwan

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ABSTRACT

Dissolved methane is abundant in groundwater drawn from the confined aquifers in the Chianan and Lanyang coastal plains in Taiwan. Serious endemic “blackfoot disease” occurred in the Chianan plain, especially during A.D. 1950-1970, has been demonstrated to arise from drinking the highly reducing groundwater. In order to characterize the origin of methane, stable carbon isotope ratios ($\delta^{13}C$) and $^{14}C$ ages for methane, dissolved inorganic carbon (DIC) and sediments were determined. Composition of gases and $\delta^2H$ of methane from groundwater were also analyzed. Several major conclusions can be made from the analytical results obtained. (1) The $\delta^{13}C_{\text{DIC}}$ ($-65$ to $-75\%o$) and $\delta^2H_{\text{methane}}$ ($-211.8\%o$) values indicate that, except the sample of thermocatalytic origin from the Lanyang plain, all the other methane samples were produced via microbially mediated CO$_2$ reduction. (2) The $^{14}C$ ages of methane from all shallow wells ($<60$ m depth) and some from deeper wells are remarkably greater than the $^{14}C$ ages of coexisting DIC and organic sediments, suggesting the presence of methane migrated from the deeper aquifers. (3) The $^{14}C$ ages of methane, DIC, and deposition of sediments of individual well are generally equal for many groundwater samples from the upper confined aquifer, suggesting in-situ generation of methane and sluggishness of groundwater flow. (4) Several $\delta^{13}C_{\text{DIC}}$ values are as high as 3–9 $\%o$, representing the occurrence of Rayleigh enrichment during CO$_2$ reduction.
REE Signature of Redox Variation and Microbiological Process Preserved in Seep Carbonate at Gas Vent Site

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ABSTRACT

At cold vent site, venting gas is precipitated as hydrate in the subsurface within the gas hydrate stable zone, and is oxidized to carbon dioxide by the combined metabolism of methane oxidizing archaea (MOA) and sulphate reducing bacteria (SRB), to deposit carbonate with seawater calcium near the seafloor (Valentine and Reeburgh, 2000). The microbiological process of this methane oxidation induces a change of redox condition near the seafloor. Up to now, it is difficult to trace this variation of bacterial process and redox condition during gas venting at recent and ancient seep sites. The Ce anomaly of authigenic sediment deposited at seafloor is an effective indicator of the sedimentary redox variation (McArthur and Walsh 1984; Wright et al. 1987; German and Elderfield 1990; Chen et al., 2003; Shields et al., 2004). The aim of this study is to trace the variation of redox condition near the seafloor at gas vent site by using the Ce anomaly of seep carbonate.

Modern seep carbonate analyzed in this paper was recovered from two active gas vent sites, Hydrate Hole of Congo Fan, and Bush Hill of Gulf of Mexico. The Hydrate Hole (HH) seep carbonate was sampled from Hydrate Hole, an active seep site ~3113m water depth, at the Southwest African continental margin by using the TV-Grab during the R/V Meteor M56-B Cruise. The Hydrate Hole seep carbonate mainly consists of Mg-calcite and aragonite. The Bush Hill (BH) seep carbonate was collected from the Bush Hill gas vent site, ~540m water depth, at Gulf of Mexico using a clamshell sampler at the end of the robot arm of Johnson-Sea-Link-I submersible. The Bush Hill seep carbonate mainly consists of bioclasts and matrix cement of microcrystalline aragonite. There is fossilized tube warm, foraminifer, and bivalve shell. Ancient seep carbonate was sampled from the Oxfordian Formation at Beauvoisin in southeastern France, and from the Miocene Formation at Monferrato hills, east of Torino in northern Italy (Peckmann et al., 1999).
Sample powder of seep carbonate was treated with 50 ml of 5% HNO$_3$ in a centrifuge tube for 2-3 hours to separate the carbonate mineral phase and residue phase, then 2500ng of Rhodium was added as an internal standard for calculating the concentration of the Rare Earth Elements (REE) in the 5% HNO$_3$ dissolved-solution of carbonate mineral phase. Five milliliters of this solution was diluted 10 times for the analysis of the REE by using Finnigan MAT ELEMENT high resolution ICP-MS (Chen et al., 2005; Qi et al., 2005). Shale-normalized REE pattern is against the standard Post Archean Australian Shale (McLennan, 1989).

**Hydrate Hole seep carbonate:** The total REE content of HH seep carbonate samples is 14.36 - 42.54ppm. The shale-normalized REE patterns all display positive Ce anomaly (Fig.1a), showing that seep carbonate was deposited in anoxic environment, suggested that the HH seep carbonate was precipitated in an anaerobic zone of methane oxidization induced by MOA and SRB activity at/near the seafloor.

**Bush Hill seep carbonate:** The total REE content of BH seep carbonate samples is 1.85 - 26.57ppm. The shale-normalized REE pattern of a bivalve shell shows a profound negative Ce anomaly (Fig.1c), similar to that of normal seawater. One microcrystalline aragonite sample and two micritic aragonite samples show negative Ce anomaly (Fig.1c), but other three micritic samples have no Ce anomaly (Fig.1b). These complex Ce anomalies of BH seep carbonate suggest that redox condition was varied at/near the seafloor at Bush Hill gas vent site, and might be controlled by the activity of MOA and SRB processes.

**Beauvoisin seep carbonate:** the Beauvoisin seep carbonates were collected from the Oxfordian (J$_3$) Formation in southeastern France. The shale-normalized REE patterns of the Beauvoisin seep carbonates have no Ce anomaly (Fig.1d), indicated these ancient seep carbonates were deposited in reducing environment at/near the seafloor.

**Marmorito seep carbonate:** the Marmorito seep carbonates were collected from the Miocene Formation at Monferrato hills, east of Torino in northern Italy. The shale-normalized REE patterns show obviously negative Ce anomaly, suggested that the Marmorito seep carbonate was precipitated in oxic zone.

In conclusion, both modern and ancient seep carbonates have variable Ce anomaly. The Hydrate Hole seep carbonate has positive Ce anomaly showing anoxic environment. Bivalve shell and microcrystalline aragonite of the BH seep carbonate show negative Ce anomaly induced by oxic condition, and micritic aragonite has no or negative Ce anomaly, showing anoxic or oxic condition. Ancient Beauvoisin seep carbonate has no Ce anomaly, while Marmorito seep carbonate has obviously negative Ce anomaly, indicated their redox conditions are different. In a word, the redox condition at cold vent site is very complex.

**ACKNOWLEDGEMENT**

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Bush Hill seep carbonate samples are obtained on the cruises sponsored by the Mineral Management Service, and other seep carbonate samples are from Research Center for Ocean Margins, University of Bremen.

Fig. 1: Shale-normalized REE patterns of modern and ancient seep carbonate at seep site (a) is the HH seep carbonate showing positive Ce anomaly; (b) and (c) is the BH seep carbonate showing complex Ce anomaly, (b) is the dark micritic part of the BH seep carbonate, black dot in (c) represents bivalve shell, black diamond in (c) represents microcrystalline part of seep carbonate, and cycle and square in (c) represent dark micritic part; d is ancient seep carbonate, the Beauvoisin seep carbonate (dot line) shows no Ce anomaly, while the Marmorito (solid line) seep carbonate shows negative Ce anomaly.

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Sedimentary Fabrics in Seep Carbonates from Bush Hill: Implications for Biogeochemical and Microbiological Processes

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ABSTRACT

Submarine gas seepages, releasing vast amounts of hydrocarbons are well known from various sites in the world. Associated to gas vent site gas hydrate and carbonate accumulations are frequently observed on the slope. It is generally believed that carbonate precipitation in gas vent site is closely related to the microbial methane oxidation that is achieved through the combined metabolism of methane oxidizing archaea (MOA) and sulphate reducing bacteria (SRB) (Valentine and Reeburgh, 2000).

Bush Hill is a typical site of gas venting and hydrate occurrence as well as seep carbonate accumulation. It is located near the boundary of CC184 and GC185 (27º46’N; 91º30’W), Gulf of Mexico (GOM), where the bottom water temperature is ~7ºC, and water depth is ~540 m. We report sedimentary fabrics preserved in seep carbonate recovered from Bush Hill gas vent site by Johnson-Sea-Link I submersible in 1997 and 1998. Mineralogical analysis (XRD) showed that seep carbonate is primarily composed of aragonite (89%–99 wt. %, average 94%, n=7) with minor calcite and dolomite. The stable carbon isotopic value of seep carbonate varies from -15‰ to -29‰ (versus PDB). The aim in this paper is to understand the origin of sedimentary fabrics developed in seep carbonates. These typical sedimentary fabrics in seep carbonates are as:

Framboidal pyrite: pyrite framboids about 3-20 µm in diameter (average ~ 5µm) are dispersed within the carbonates, and are composed of numerous smaller spherical particles about 0.5µm in diameter (Fig. 1). Pyrite particles usually show cubic or pentagonal dodecahedron crystals (Fig. 1C and D). Pyrite framboids occur as layered structure (Fig. 1A), similar to living collaborating colonies of MOA and SRB (Boetius et al., 2000). The pyrite framboids also occur within the foraminifer chambers (arrows in Fig.1B). These pyrite framboids in seep carbonates are considered to be biogenic origin (Boetius et al., 2000; Chen et al., 2006; 2007; Popa et al., 2004).

Clotted microfabric: this fabric is the aggregates of irregular microcrystalline clots about 100µm in diameter or smaller (Fig. 2A-C), commonly showing intense fluorescence. Previous work demonstrates that clotted microfabric in seep deposit is caused by microbial metabolism (Peckmann and Thiel, 2004).
Botryoidal aragonite: botryoidal aragonite, consisted of fibrous aragonite, commonly occurs as isopachous layers or filling voids with intense fluorescence in seep carbonates (Fig. 2, B, D to G), and shows multiple stages of mineral growth. Fibrous aragonite sometimes aggregates as a rosette-like morphology (Fig. 2H). The botryoidal aragonite in seep carbonates was considered to be induced by microbial activity (Roberts et al., 1993; Goedert et al., 2000). This hypothesis is also in agreement with the negative stable carbon isotope values (as low as -29 ‰, PDB).

Microfilament: microfilament is tree-like growth and curly appearance ~1µm in diameter or smaller, always attaches to the surface of the aragonite and pyrite crystals (Fig. 2I). The tree-like microfilaments are considered to be fossilized bacteria (Peckmann et al., 2001; Chen et al., 2007).

In conclusion, all the sedimentary fabrics mentioned above in seep carbonates are an indicator of biologically controlled fabrics produced during methane oxidation and sulphate reduction by MOA and SRB. The result of the light microscope and scanning electron microscope observation shows that microbes are involved in the precipitation of authigenic carbonates at Bush Hill gas vent site, GC 185, GOM. Thus, the distinctive biogenic fabrics might be diagnostic markers of biogeochemical and microbiological processes at gas vent and hydrate sites.

Fig. 1: Framboidal pyrites from Bush Hill seep carbonate. (A) is reflected light microscope images, showing that pyrite framboids occur as layered structure, composed of numerous small pyrite (white) and aragonite (black) grains. (B) is transmitted light microscope image showing that framboidal pyrites (arrows) occur within a foraminifer chambers. (C) and (D) are SEM images showing cubic or pentagonal dodecahedron pyrite crystals, respectively.
Fig. 2: Aragonite from Bush Hill seep carbonate. (A) is light microscope images and shows clotted microfabric. (B) is SEM image of fibrous aragonite and clotted microfabric (right down corner). (C) is an enlargement of white rectangle in (B), showing detail of clotted microfabric that is consists of numerous small aragonite grains. (D) is light microscope image of botryoidal aragonite, showing isopachous layers and multiple stages of mineral growth. (E) is fluorescence image of (D). (F) is SEM image of botryoidal aragonite showing it consists of fibrous aragonite. (G) is an enlargement of white rectangle in (F). (H) is SEM image of a rosette-like morphology. (I) shows tree-like microfilaments attached on the surface of aragonite crystals.

ACKNOWLEDGEMENT

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The Effusion Mechanism of Onikobe Geyser (Japan) from Chemical and Isotopic Study

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INTRODUCTION

Geysers which throw up a jet of thermal water periodically exists near the lakes or rivers where geothermal activity is high. This behavior is similar to phreatic eruption because driving force of both eruptions is steam pressure related to rapid depressurization. However, we can rarely experience the phreatic eruption and it is very dangerous to observe. Therefore, there are some advantages to observe the geyser instead of volcano; the cycle is very short, so it is possible to take a lot of data easily and safely. From this point of view, throughout observation of geyser may provide useful information to estimate the mechanism of phreatic eruption. Many geysers exist in Japan among which Rausu geyser, Shikabe geyser, Onikobe geyser, Tatsumakijigoku geyser are the most famous. We selected Onikobe geyser located in NE Japan (38.80N, 140.67E) to do our study because its cycle is conveniently short and geophysical observation have been done by Nishimura et al.(2006).

In this study, we mainly observed the chemical and isotopic composition of thermal water and an effusion mechanism of this geyser is elucidated.

OBSERVATION

We observed three times, July 27-28, September 21, and November 21-22 in 2006, at Onikobe geyser. Onikobe geyser designates an ensemble of three geysers located at the same spot; Benten, Tamanoyu and Unryu. Our study is mainly focused on Benten which is the most active geyser in this area. During effusion, we collected nine sets (S-I to S-IX) of water samples every 5-10 seconds. Each set made up of 10-12 samples. In addition, we took samples from Tamanoyu, Unryu and underground water (UGW) around the geyser as reference. Water temperature, pH and amount and height of water were measured in situ. Chemical composition was analyzed by IC, ICP and AA and stable isotopic ratios of hydrogen ($\delta^D$) and oxygen ($\delta^{18}O$) were measured by MS.

RESULTS AND DISCUSSION

Average values of chemical composition and stable isotopic ratios are shown in Table.1 together with pH value. From this study, we can say that Benten geyser is characterized as follows, 1) period; 7-13 minutes, 2) duration time; 60-110 seconds, 3) erupting amount; 420-530 liters, 4) spouting height; 12-17 meters, 5) water temperature; 99.0-101°C and 6) pH; 8.3-8.9. Benten geyser is classified as
A weak alkaline spring. Dominant species are Na$^+$ and Cl$^-$. The Mg$^{2+}$ is present as trace. Chemical composition of underground water appears to be very similar to the thermal water’s but in lower concentrations in the exception of Mg$^{2+}$ whose concentration is more than ten times higher.

No variation in chemical composition and other characteristics were noticed during our observations in summer and autumn.

At the beginning of effusion, the water temperature rises very sharply up to 101°C, then gradually decreases during the effusion to 99.0°C. Variations in pH are shown in Fig.1. In one case, S-IX, the pH is 8.6 at the beginning of effusion and increases up to 8.9 within 15 seconds. Then, it tends to decrease and be constant after 40 seconds. The variation of Cl$^-$ concentration shows the same pattern as pH’s while Mg$^{2+}$ has inverse shape (Fig.2). Figure.3 shows the correlation between Cl$^-$ and Mg$^{2+}$. Its negative slope suggests that the geyser is composed of two different kinds of water. One is a high Cl$^-$ but low Mg$^{2+}$ coming from the deeper part and the other one is a low Cl$^-$ but high Mg$^{2+}$ deriving from subsurface water.

The stable isotopic ratio of the thermal water varies from -9.6 to -10% in $\delta^{18}$O and from -60 to -63% in $\delta$D. The values for subsurface water are -9.8% and -60%, respectively. The relationship between $\delta^{18}$O and $\delta$D are plotted in Fig.4 with meteoric water line (Mizota et al. 1994) and average value of magmatic water. Thermal water values plotted right on that line and far from magmatic water value suggests its meteoric origin.

From this study, the mechanism of the effusion of Onikobe geyser can be depicted by following steps.

Step1: The geothermal water from deeper part and the underground water near the surface enter simultaneously to the reservoir and conduit. Then, mixing occurs in the reservoir but not occurs in the conduit.

Step2: The continuous inflow of waters pushes up the water level in the conduit which leads the depressurization.

Step3: Thermal water starts to boil first inside the conduit and throws out the water. Then, drastic boiling expands to the whole reservoir because of the further depressurization. The minimum values in pH and Cl$^-$ and maximum value in Mg$^{2+}$ observed at the beginning of effusion (Fig.1, 2) indicate that the composition of water at the top of the conduit is made up dominantly of underground water which plays the role of a lead to avoid the hot water from deeper part to start boiling as soon as it inflows. The sharp change of these values in the first 15 seconds suggests that the water is constituted mainly with water coming from deeper part. Then, the stable trend of the curves after 40 seconds corresponds to the well mixed water of the two in the reservoir. Finally, waters are supplied to the reservoir again to start next cycle.

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FIGURES AND TABLES

Fig.1: Variation in pH

Fig.2: Variation in Cl⁻ and Mg²⁺

Fig.3: Correlation between Cl⁻ and Mg²⁺
Fig. 4. $\delta D$ vs. $\delta^{18}O$ of samples with meteoric water line and magmatic water value.

Table 1. Chemical composition and Stable isotopic ratio of Water samples

<table>
<thead>
<tr>
<th>Sample</th>
<th>pH</th>
<th>[Cl$^{-}$] mg/l</th>
<th>[SO$_4^{2-}$] mg/l</th>
<th>[Na$^+$] mg/l</th>
<th>[Ca$^{2+}$] mg/l</th>
<th>[K$^+$] mg/l</th>
<th>[Mg$^{2+}$] mg/l</th>
<th>[SiO$_2$] mg/l</th>
<th>$\delta D$‰</th>
<th>$\delta^{18}O$‰</th>
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<tr>
<td>S-I</td>
<td>8.48</td>
<td>246</td>
<td>69.8</td>
<td>180</td>
<td>10.2</td>
<td>15.0</td>
<td>0.034</td>
<td>149</td>
<td>-</td>
<td>-10</td>
</tr>
<tr>
<td>S-II</td>
<td>8.61</td>
<td>245</td>
<td>69.7</td>
<td>183</td>
<td>10.0</td>
<td>15.2</td>
<td>0.034</td>
<td>154</td>
<td>-</td>
<td>-9.8</td>
</tr>
<tr>
<td>S-III</td>
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<td>241</td>
<td>70.8</td>
<td>161</td>
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<td>157</td>
<td>-</td>
<td>-9.7</td>
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<td>246</td>
<td>69.2</td>
<td>153</td>
<td>10.5</td>
<td>15.5</td>
<td>0.049</td>
<td>146</td>
<td>-</td>
<td>-</td>
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<td>S-V</td>
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<td>242</td>
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<td>160</td>
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<td>251</td>
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<td>170</td>
<td>10.9</td>
<td>15.3</td>
<td>0.049</td>
<td>162</td>
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<td>-</td>
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<td>S-IX</td>
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<td>250</td>
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<td>164</td>
<td>10.7</td>
<td>15.9</td>
<td>0.057</td>
<td>153</td>
<td>-60.2</td>
<td>-10</td>
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<td>Tamanoyu</td>
<td>8.73</td>
<td>261</td>
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<td>Unryu</td>
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<td>16.3</td>
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<td>2.70</td>
<td>79.7</td>
<td>-60.0</td>
<td>-9.7</td>
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</table>
Temporal Variations of Gas Compositions of Fumaroles in the Tatun Volcano Group, Northern Taiwan

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ABSTRACT

Hydrothermal activity is commonly found in northern Taiwan. Helium isotopic compositions of fumarolic samples show that more than 60% mantle source was involved in its gas sources. Carbon and nitrogen isotopic results also show significant mantle signature. It infers that a magma reservoir may exist underneath northern Taiwan.

The variations in compositions of fumaroles and bubbling gases of hot springs are believed to be closely related to the volcanic activity. For monitoring purpose, therefore, we systematically analyze the compositions of representative fumarolic gases from Tatun Volcano Group (TVG) by utilizing the Giggenbach-bottle technique. The results show that the dry gas compositions of the gas samples are typical compositions of low temperature fumaroles, which dominated with CO$_2$ (65~85%) and H$_2$S (>10%) and low SO$_2$ (<4%) contents.

The time series results show that the major gas composition and helium isotopic ratios did not show significant variations since 1999. It implies that the degassing system in studied area was quite steady in last few years. However, since August 2004, there is not only a progressive increase of HCl concentrations but an increase of SO$_2$/H$_2$S ratio in fumaroles from Da-You-Keng (DYK), where has the highest helium isotopic ratio been analyzed in this area. The temperature of fumaroles in the TVG is also higher than that in the past, especially in DYK. Both HCl concentration and SO$_2$/H$_2$S ratio fluctuate with temperature. We propose two possible processes to explain observed phenomenon. One is more magmatic gases were released from recent opened fractures; another is magma ascending. These two processes can cause the similar variations of gas compositions. The present surface temperature of fumaroles in DYK is around 116°C and does not show much rising in last few months so that we consider these variations may be related to the local volcanic activity. We need to closely watch the variations of fumaroles and hot springs to check/clarify the possible relationship between the possible local magma activity with other parameters, e.g., seismicity, and flux of fumarolic steam etc.

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Geochemical Earthquake Precursor Studies in NW Himalayas, India

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ABSTRACT

The Himalayas are tectonically active due to the northward movement of Indian plate. The various thrusts and transverse faults show fast rate of tectonic uplift and subsidence. The frequent occurrence of shallow small magnitude and moderate size earthquakes indicate that Himalayas are under unusually high stress and strain. In order to study the geochemical Earthquake precursor in NW Himalayas monitoring stations has been installed in Himachal Pradesh with nodal center at Amritsar. RAD 7 is used for measuring the daily radon concentration in water at Dharamshala, Banikhet and Amritsar. Barasol Probes are installed at Palampur and Sarol (Chamba) for countinous monitoring of soil gas radon, temperature, pressure. Water quality kit has been used to study the daily variation of pH, Conductivity, ORP, Salinity, Temperature and TDS of the ground water at the monitoring stations. The work is in progress. The initial results have shown that the monitoring station is quite sensitive for earthquake precursor studies.
Soil Gas Investigation on the Tapingdi Fault in Northern Taiwan and the Continuous Monitoring Results

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ABSTRACT

More than 100 soil-gas samples were collected and analyzed for gas compositions including He, Rn, CO₂, CH₄, Ar, O₂ and N₂. Results show that helium, radon and nitrogen concentrations in the soil gas reveal anomalies for the specific positions. Trace of these positions coincides with the geological information around the Tapingdi Fault in Kuanshi-Chutung area, NW Taiwan. In this study, the soil gas concentrations data record were used to explore the sensitive sites at the fault zone in order to set up an automatic station for soil gas monitoring. This station is fully automatic and able to transfer the real-time data to laboratory for further analyses synthesis and interpretations. After continuous measurement, variation of radon concentrations show a regular pattern and some anomalous high radon and thoron concentrations can be observed. These anomalies usually appeared a few hours to a few days before the earthquakes, which mainly occurred in northern Taiwan. Hence, our results indicate that Rn concentrations can be used as a tool that reflects changes in regional crustal strain preceding earthquakes.

INTRODUCTION

Many studies in tectonic areas have shown a possible correlation of soil-gas anomalies with tectonic activity (Ciotoli et al., 1998 Toutain et al., 1992; Fu et al., 2005; Walia et al., 2005a). It has been found that active blind faults which are not exposed at the surface can be detected by soil-gas surveys (Fu et al., 2005; Walia et al., 2005a). In noble gases radon and helium play predominant role in fault delineation and earthquake precursory studies (Fu et al., 2005; Walia et al., 2005a; Yang et al., 2005, 2006).

The Dapindi Fault is one of the active faults in NW Taiwan. According to the Central Geological Survey (CGS), the major geological structures are the Tapingdi Fault and the Ruanciao Fault with the NE-SW trends in the area. More than 100 soil gas samples were collected and analyzed within a few hours after sampling using a helium leak detector (ASM100HDS, Alcatel), radon detector (RTM 2100, Sarad) and micro gas chromatography (CP4900, Varian), respectively (Fu et al., 2005). However, up to now, very few studies have used both geochemical and morphotectonic arguments for
RESULTS

In general, helium and nitrogen have constant concentration (5.24 ppm and 78.08 %, respectively) in atmospheric air and background soil gases. The soil gas compositions ranged from 4.426 to 6.138 ppm for He, 57.20 to 96.75 % for N\(_2\) and 0 to 17.23 % for CO\(_2\). Threshold values, which are used for recognizing anomalous concentrations of soil gas data, were calculated using the mean plus two standard deviation of the trimmed data set. Thus, we are able to set the threshold values for He, N\(_2\) and CO\(_2\) at 5.406 ppm, 86.34 % and 9.17 %, respectively. Distribution maps and cross symbols were elaborated to illustrate the variation of soil-gas values and sample sites (Fig. 1).

Spatial variations of soil gases

Distribution of sampling points and soil gas anomalies in study area is shown in Fig. 1. From analysis of helium data (Fig. 1B) it has been found that high helium concentrations (shown with triangle symbols) and its matching with the Tapingdi Fault and the Ruanciao Fault with the NE-SW trends were reported by CGS. From Fig. 1C, the soil-gas (N\(_2\)) anomalous values show almost the same distribution, concerning the helium anomalous values distribution. From Fig. 1D, the soil CO\(_2\) anomalous location indicate the similar with the He map, but some points were not corresponded with soil helium anomalous. However, the distribution of helium and nitrogen anomalous values highlight stresses the presence of the fault patterns of the investigated area. Therefore, the soil gas method is proved to be a useful tool for the exploration of buried faults and/or fractures in study area.

Temporal variations of soil gases

Then, we chose a sensitive site at the fault zone for establishing continues motoring station (shown a star symbol in Fig.1B). Because this site show highest soil helium and nitrogen values. A continues monitoring station has been established at the end of 15\(^{th}\) December, 2005. After several months continuous measurement, the temporal variation of soil gases from 14\(^{th}\) June, 2006 to 5\(^{th}\) January, 2007 (Fig. 2) show a regular pattern and some spike-like anomalous high radon and thoron concentrations can be observed. These anomalous peaks usually occurred few hours/days before the earthquakes, which mainly occurred in northern Taiwan (Table 1 and Fig. 2). Hence, our results indicate that Rn concentrations can be used as a tool that reflects changes in regional crustal strain preceding earthquakes.

REFERENCES


Fig.1: Location map and simplified structural map of the studied area. (A) The area of investigation is marked as rectangle in northern Taiwan and enlarged shown as (B), (C) and (D). Soil-gas distribution maps of the study area for (B)He, (C)N₂ and (D)CO₂. Triangle, circle and square symbols represent the value higher than mean plus two standard deviations. Star symbol represents the location of monitoring station. a: the Tapingdi Fault; b: the Ruanciao Fault.
Table 1: Catalog of related earthquakes occurred from 14th June, 2006 to 5th January, 2007 for monitoring station.

<table>
<thead>
<tr>
<th>No.</th>
<th>Date</th>
<th>Depth (km)</th>
<th>Mag. (M_L)</th>
<th>Int. (M_I)</th>
<th>Distance (km)</th>
<th>Δt (day)</th>
</tr>
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<td>a</td>
<td>2006/6/18 02:21</td>
<td>5.6</td>
<td>3.2</td>
<td>2</td>
<td>29.8</td>
<td>1.5</td>
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<tr>
<td>b</td>
<td>2006/7/7 14:35</td>
<td>14.7</td>
<td>3.6</td>
<td>2</td>
<td>28.7</td>
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<tr>
<td>c</td>
<td>2006/7/22 04:56</td>
<td>5.3</td>
<td>3.5</td>
<td>1</td>
<td>54.9</td>
<td>3.5</td>
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<td>d</td>
<td>2006/8/28 01:11</td>
<td>135.3</td>
<td>6.0</td>
<td>1</td>
<td>193.5</td>
<td>-</td>
</tr>
<tr>
<td>e</td>
<td>2006/9/19 21:00</td>
<td>8.3</td>
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<td>5.5</td>
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<td>f</td>
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<td>88.4</td>
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<td>1</td>
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<td>2</td>
<td>14.8</td>
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<td>2</td>
<td>343.1</td>
<td>-</td>
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</table>

1 The relevant anomalous peak marked in Fig. 2
2 Time difference between peak of the anomaly and the earthquake event

Fig. 2: Temporal variations of soil gas concentrations during the time period 14th June, 2006 to 5th January, 2007.
Evidences Support Nitrogen as Carrier Gas of helium along Hsincheng Fault, NW Taiwan

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ABSTRACT

Helium is widely applied in the studies of fault-finding and seismic activities monitoring. Until now, its migration mechanism in the soil is not fully understood. Because of its low concentration in soil environment, it is impossible for helium to migrate by diffusion but can only by advection. A carrier is needed for helium to move, but as far as we know the gas component which serves as the carrier gas for helium was not discussed in the previous works.

A soil gas survey across an active fault in Northwestern Taiwan provides us the opportunity to find out the most possible carrier gas for helium in this area. Good concentration correlation spatially and temporally between nitrogen and helium could be observed to support the idea that nitrogen is the most possible carrier gas for helium in this study area. Two interpretations were given in order to explain the source of nitrogen. The first interpretation is that nitrogen which serves as the carrier could be recycled from old air. Old air was carried by underground water and recycled back to the near surface. During the migration, most of the oxygen in the old air was consumed so that only nitrogen left which then serve as the carrier gas for helium. The other possible explanation is from the old gas field nearby. Previous works in those gas fields near our study area had observed anomalous high nitrogen concentration from different wells with depth ranged from 24 to 3000 meters. Experimental works also confirmed the possibilities to generate nitrogen in a petroleum system. The true source of nitrogen in this area has to be confirmed by further studies.

From the correlation between different gas components, two soil gas components could be defined in this study. Source A is the gas from deep underground which has anomalous high nitrogen and helium concentration but with very little oxygen and carbon dioxide content. Source B is the mixture of biogenic gas and air which has similar gas component with air with or without carbon dioxide. Oxygen and carbon dioxide in source B follow an inversion relationship which indicates the concentration of those two gas components is strongly related to biogenic activities. Gas from source A migrates fast through well-developed fault system. When the development of a fault system is moderate or bad, the mixture in soil gas from source A is increasing. Signal from source A is a good indicator of seismic activities, but more accurate indication has to be verified by longer monitoring.
Fig. 1: Correlation between various gas components collected in the study area. A is the end member with higher helium and N₂ concentration than atmospheric value (5.24 ppm and 78 %) but with low Ar+O₂ and CO₂ content. B is the end with helium and N₂ concentration close to atmospheric value and the sum of Ar+O₂ and CO₂ keep constant. (a) Concentration correlation between helium and N₂. Good correlations were observed represent a significant relationship between helium and N₂ concentration. (b) Concentration correlation between helium and CO₂. Significant correlations were not observed among them. (c) Mole number correlation between Ar+O₂ and CO₂. The inverse correlation between CO₂ and Ar+O₂ in the samples with helium concentration equals to 5.24 ppm is due to bio-activities. While helium concentration increasing, points in this figure are far away from the regression line. (d) The correlation between helium concentration and the mole sum of Ar, O₂, and CO₂. A and B could be distinctly separated and all their characteristics mentioned in figure 5(a) to 5(c) could be summed up in this figure.
Fig. 2: Model explaining gas mixture and migration mechanism in this study area. From fig. 1 we could classify all samples into three groups according to their gas content. The first group corresponds to the samples with gas from component A. The third group is the situation that gas is from the component B, while the second group is the mixture of component A and B. The development of fault system determines how fast could gas migrate from component A so that affects the degree of mixture between component A and B.
Seasonal Variation of Radon Activity in Atmospheric Air-Nowa Ruda Area (Sudety Mis. SW Poland)

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ABSTRACT

The atmospheric radon activity monitoring has been performed in the post mining area of the various bedrock uranium content ranging from 1ppm to 8 ppm. Obtained results indicate significant seasonal variation and influence of tailings upon the atmospheric radon activity in the period from autumn 2004 to summer 2006. Maximum atmospheric radon activity has been found to be as high as 131 Bq/m$^3$ in the summer 2006.

INTRODUCTION

Nowa Ruda area is an abandoned coal mining district located inside the mountain range of Sudetes. Geological basement of the area is composed of the Upper Carboniferous and Permian sediments bordered from the east by the Old Paleozoic gneisses of the Sowie Mts. Block and gabbro-diabase massif of the Nowa Ruda Slupiec. Increased uranium content (ranging from 2 ppm to 4 ppm) of some Carboniferous coal seams, conglomerates and Permian shales results in high natural radon potential of the area. Important anthropogenic factor is the existence of numerous tailings and agricultural cultivation activity.

Preliminary results of previous investigations (Buratynski et al. 2005) revealed atmospheric radon activity concentration as high as 125 Bq/m$^3$. Because of this the detailed study of geological basement uranium content and repeated seasonal radon activity monitoring has been performed.

METHOD

Measurements of the bedrock uranium content have been performed using Exploranium GR-320 gamma radiation spectrometer with the standard NaI (Tl) GPX-21A detector of 0.35 L volume. According to producers manual impulses supplied by the detector probe were classified using channels 70-204 of the 256 channels of the spectrometer covering the energy window 850-2810 keV. Three bands (Regions of Interests ROI) corresponding to energy windows of radionuclides peaks $^{40}$K, $^{214}$Bi and $^{208}$Tl have been set.

Measured activities $^{214}$Bi and $^{208}$Tl were recalculated into uranium and thorium concentrations (in ppm) assuming the existence of equilibrium in uranium and thorium decay series, what is a common practice in this kind of measurements marked by eU and eTh notation instead of U and Th. For each measurement the detector was deployed in the field using geometry as close as possible to 2$\pi$. Sampling time ranged from 15 to 30 minutes depending on local radionuclides content to reach
In the case of atmospheric radon activity measurements passive open type track detectors using Kodak LR115 were exposed at the height of 1.5 m above ground for repeating periods of 3 months. After exposition detectors were etched 90 minutes in 2.5M NaOH. Tracks were counted using optical microscope at the magnification of 100x. Track density was recalculated into radon activity using calibration coefficient in the way described by Srivastava et al. (1995).

RESULTS

Average radon activity in the Nowa-Ruda area is 72 Bq/m$^3$ what is significantly higher than 6.5 the average value for Poland (Jagielak et al 1998). Comparative measurements performed in the Stolowe Mts where quartz sandstones of low uranium content prevail yielded results as low as 3 Bq/m$^3$ indicating that there is no systematic error shifting obtained values towards higher results.

Seasonal variation of radon atmospheric activity, temperature, pressure and humidity for the period from autumn 2004 to summer 2006 has been presented in Fig.1. Seasonal changes of the atmospheric radon activity concentration correlate well with the temperature variation. The highest values have been measured in summer 2006 (131 Bq/m$^3$), the lowest in winter 2006 (15 Bq/m$^3$).

![Fig.1 Seasonal variation of the radon atmospheric activity and main meteorological parameters (values standardized).](image)

Variation of radon atmospheric activity in sites of various geological backgrounds has been shown in Fig.2. On the left side results for interval autumn 2004-summer 2005 have been presented, while values obtained in the time interval autumn 2005- summer 2006 are displayed on the right side. Sometimes results are missing since some detectors have been destroyed. However both diagrams repeat similar trend.

In the upper part of diagrams results of measurements within tailing areas have been presented. These sites are of the highest bedrock uranium content and highest radon activity. Just below them two sites located on the gabbro outcrops with contrasting lower uranium content of the basement and low atmospheric radon activity are presented. Below the gabbro results the sites located on various rocks of the Permian and Carboniferous sequence have been presented. Locally in the case of the black shales uranium content is slightly higher. In the lowest part results for sites located on the outcrops of quartz sandstones of low uranium content have been presented.
Shaded areas within Permian and Carboniferous sequence are located close to the tailings. In this case increase in the atmospheric radon activity can be observed.

Fig. 2. Variation of the radon atmospheric activity in sites of various geological background. Shaded areas/sites on tailing or in their vicinity, triangles, squares, rhombs and circles radon atmospheric activity in autumn, winter, spring and summer respectively, black line uranium bedrock content (all values standardized)
CONCLUSION

In the case of the atmospheric radon activity in the Nowa Ruda area significant seasonal changes have been observed. Distinct influence of tailings upon the atmospheric radon activity has been confirmed for the whole period of monitoring.

REFERENCES


Gas from Neogene Coals in the Northwestern Taiwan Region by Hydropyrolysis

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ABSTRACT

An immature sample concentrated from coaly shale in the Mushan formation of D-2 well were analyzed using closed-system pyrolysis in order to determine its activation energy and products at various artificial maturation stages. These values were used in the GOR software to simulate the generative maturity and origins of natural gases in the northwestern Taiwan region. Carbon isotopic values of these gases fit the modeling result as under 2\textdegree C/My heating rate and 1My cumulated period. Results show that gases derive from kerogene of type III mixed partly with type II. Generative maturities were found to be 1.4 to 1.7\%Ro as products of the gas window.

Outcrop coals from various formations with difference potential in the northwestern Taiwan region were treated with hydropyrolysis to determine its generative potential. Generative volume of gas from these samples were found in this study to be easily calculated using the hydrogen index (\(C_1 = 1.5653(HI)^{0.2194} \cdot C_2^+ = 0.4869(HI)^{0.3126}\)). \(C_1/C_2\) increases with hydrogen index too (\(C_1/C_2 = 8E-0.7(HI)+0.0017(HI)+4.2356\)).

keyword: hydropyrolysis, carbon isotope, natural gas, coal

INTRODUCTION

Hydrous pyrolysis is a laboratory method to simulate hydrocarbon generation during natural thermal maturation of source rocks since 1970. Seifert (1978) applied the products of this method for the oil source correlation. More studies have followed that have helped them understand the hydrocarbon generation of their source rock. (Saxby and Riley, 1984; Winters at. al., 1983; Lewan, 1983; Rullkotter at. al., 1984; Hooring; 1984; Monthioux et al., 1985; Blaszko et al., 1986; Ungerer and Pelet, 1987; Tissot et. al., 1987; Horsfield et al., 1989; Burnham and Braun, 1990; Ungerer, 1990; Shan-Tan and Kaplan, 1990; Behar et al., 1991, 1995; Fowler et al., 1991; Noble et al., 1991; Teerman and Hwang, 1991; Lewan, 1993, 1994; Behar and Hatcher, 1995; Mansuy et al, 1995; Mansuy and Landais, 1995; Tang et al., 1996; Welte et al., 1996).

This study collects coals with different generative potential from the Miocene formations outcropping in the northwestern Taiwan region and treated with Hydropyrolysis to characterize the origin and volume of thermogenic gas generated from it.
REFERENCES


Estimation of the Thickness of the Base of Hydrate Stability Zone in Offshore SW Taiwan Based on Geochemical Data

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**ABSTRACT**

It has been found that Bottom Simulating Reflections (BSRs) widely distribute in offshore southwestern Taiwan which infer the existence of potential gas hydrates underneath the seafloor sediments (Liu *et al.*, 2006). We systematically collected sea waters and cored sediments for dissolved and pore-space gas analysis through eight cruises: ORI-697, ORI-718, ORII-1207, ORII-1230, ORI-732, Marion Dufresne (MD) cruise, ORI-758, ORI-765, ORI-792 and ORI-804 from 2003 to 2006. Some unusually high methane concentrations can be found in offshore southwestern Taiwan (e.g., Chuang *et al.*, 2006; Yang *et al.*, 2006). In addition, through the gradients of sulfate reduction and steady state solutions to diffusion equations, some abnormally high methane fluxes have been determined at some sites (Chuang *et al.*, 2006; Lin *et al.*, 2006). These geochemical data also support that there are abundant gas hydrates in the sediments. It may be the result of dissociation of gas hydrates in a methane-enriched venting source in this study area.

The phase boundary of gas hydrate is the function of temperature and pressure. Although geophysical and geochemical evidences show the occurrences of potential gas hydrates underneath the seafloor sediments, the base of hydrate stability zone (BGHS) is too deep for us to reach until now due to the sampling facilities. Therefore, we cannot confirm the realistic thickness of gas hydrate stability zone yet. The thickness of gas hydrate stability zone is one of the major factors to control the calculation of the abundance of gas hydrates. At the present day, the depths of BGHSs are estimated by BSRs (Chi *et al.*, 2006) or geotherm (Shyu *et al.*, 2006). However the average depth of BGHSs estimated from geothermal gradient data is 54 mbsf shallower than the result from BSR data (Shyu *et al.*, 2006). In this study, we will combine the geochemical data, i.e., chloride concentrations of pore water samples and methane concentrations in the pore space of sediments, and geothermal gradient data to estimate the depth of BGHSs by using gas hydrate phase boundary programs of Sloan (1998). The preliminary result shows the depth of BGHS has shifted upward by 5.5% comparing with those obtained by geothermal data.
Fig. 1: Distribution of methane concentrations (in μL/L) of pore spaces in offshore southern Taiwan.

Fig. 2: Map of methane concentrations (in nL/L) in bottom seawaters distributed in offshore southern Taiwan.
Fig. 3: The gas hydrate stability zone in the marine environment lies between the sediment-water interface and the intersection of the geothermal gradient and three-phase equilibrium curve. The sediment-water interface (1216m below sea surface) and geothermal gradient (4.193°C ± 0.0291°C/m) on this diagram were those for the Site GH10 of ORI-758. The three phase equilibrium curves are calculated from Sloan (1998) (solid lines) and Dickens and Quinby-Hunt (1998) (Dash lines). Blue lines are calculated from the hydrostatic pressure parameters, and red lines are from the lithosatic pressure parameters.

REFERENCES


Gas Biogeochemical Characterizations of Wu-Shan-Ding and Shiao-Kun-Shui Mud Volcanoes in Taiwan

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ABSTRACT

Many mud volcanoes are distributed along the tectonic sutures in southern Taiwan. Among of them the largest and well-preserved active mud volcanoes are situated in Wu-Shan-Ding (WSD) and Shiao-Kun-Shui (SKS). All active mud volcanoes are exhaling mainly methane (CH$_4$>95%)(p<0.05) with respect to other gases like O$_2$, CO$_2$, CO, SO$_2$, H$_2$S, NO, and N$_2$. The composition of gas in the SKS active mud volcanoes was exhibited significantly high with respect to the WSD mud volcano. The ionic concentrations of Na$^+$ and Cl$^-$ were observed very high with respect to other ions like K$^+$, Mg$^{2+}$, Ca$^{2+}$, NO$_3^-$, SO$_4^{2-}$ and F$^-$ However, new erupted active mud volcano in WSD reflected maximum amounts of SO$_4^{2-}$ and F$^-$ ions. The dominated bacteria were found gram negative and spherical shape, in which growth was stimulated in the presence of Na$^+$ and Cl$^-$ ions, favorable high salinity (32ppm), temperature (40°C) and pH (upto 10).

INTRODUCTION

The mud volcanoes may be the most important pathway for degassing of deeply buried sediments, and are one of the remarkable natural sources for atmospheric methane (Dimitrov, 2002; Kopf, 2002; Milkov et al., 2003). Natural gases, mainly methane and carbon dioxide, are continuously emitted from mud volcanoes and constitute an important natural contribution to the atmospheric carbon budget. Estimation of gas from mud volcanoes in the world, hence, becomes an interesting topic for debate of the potential influences on the global climate changes (Judd et al., 2002; Etioppe et al., 2002). Therefore, the quantitative measurements of the discharge of gas through mud volcanoes are very important for such a kind of estimation. There are many reports on the fluids emanating at the surface of the mud volcanoes in Taiwan and suggested that they might be originated from a deep source, which might be from the deeper parts of the accretionary complex (Gieskes et al., 1992). In this study the authors briefly describe the current situation, like gas compositions, chemical compositions and most dominant bacteria of the largest and well-preserved Wu-Shan-Ding and Shiao-Kun-Shui mud volcanoes in Taiwan.

METHODS

Sampling area and Sample Collection:
The mud samples (WSD1 and WSD2) were collected from different eruption points of Wu-Shan-Ding (N: 22° 47’ 53.8” and E: 120° 23’ 50.5”) during March 2007, where WSD2 was a new eruption point. The distance between two-eruption points was 100m. Another sampling point was Shiao-Kun-Shui active mud volcano (SKS1 and SKS2)(N: 22° 52’ 48.3” and E: 120° 22’ 54.4”).
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Young Scientist Poster Session: October 4th (08:30-10:30)-ICGG9A042

(distance between two point=1m). The ground water was collected from Canten (N: 22° 52’ 41.6” and E: 120° 23’ 09.7”), where it is close to Shiao-Kun-Shui. The general parameters like temperature (°C), pH, ionic conductivity, redox, salinity, DO, TDS as well as exhalation gases like \( \text{O}_2, \text{CO}_2, \text{CO}, \text{SO}_2, \text{H}_2\text{S}, \text{NO}, \text{N}_2, \) and \( \text{CH}_4 \) were estimated in \textit{in-situ} conditions. For the chemical analysis in laboratory study, the mixed mud with fluid samples was collected from each location of mud volcano eruption point in sterilize bottles (500ml three bottles) and stored in the laboratory at \( -20^\circ\text{C} \) after flushing with \( \text{N}_2 \) gas.

**Ion extraction from Mud and fluid**

All samples were centrifuged at 9391g for 20 min and filtered through 0.45μm filter paper (Advantec MFS Inc., CA, USA). Supernatant was used for cations (\( \text{Na}^+, \text{K}^+, \text{Mg}^{2+}, \text{Ca}^{2+} \)) and anions (\( \text{Cl}^-, \text{NO}_2^-, \text{SO}_4^{2-}, \text{F}^- \)) analyses with the Ion Chromatograph technique ( Dionex, CA, USA).

**Bacterial extraction and Physiological characteristics of bacteria isolate**

The bacteria were isolated in nutrient agar media (NA), following the method as described by Dubey and Maheshwari (2005). The physiological characteristics of bacterial were determined by different values of pH (2-11), salinity (2-32ppm) and temperature (4-70°C) in Nutrient broth media. The gram tests were performed with the help of optical microscope (Olympus CH2, Tokyo, Japan).

**RESULTS AND DISCUSSION**

**In-situ gas composition and physical parameter**

The gas compositions of representative mud volcanoes and seepages in WSD and SKS are given in the Table 1. The investigated results show that most gases exhaled from typical mud volcanoes and dominant with methane (>95%). This results consistent with those results of Yang et al. (2004). The \( \text{CO}_2 \) were found from all selected mud volcanoes except SKS, in which the \( \text{CO}_2 \) were not detected (ND) successfully. It is interesting to note that the \( \text{NO}_2 \) gases were found at 0.4ppm level only from the WSD volcano. Similarly only \( \text{H}_2\text{S} \) and \( \text{NO} \) gases were found from SKS1 volcano with the level of 11ppm and 5ppm, respectively. The gases like \( \text{O}_2, \text{CO} \) and \( \text{SO}_2 \) were not found in any active mud volcanoes. However, Yang et al (2004) reported that, \( \text{O}_2 \) gases exhaled from SKS and WSD volcanoes are in the range of 0.3-1.09% and 0.28-0.64% in June- July 2002, respectively. The physical parameters like temperature, pH, salinity, conductivity, redox etc were investigated in \textit{in-situ} conditions (Table 2). Data of our present investigation exhibited that the temperature of the WSD volcano was found lesser with respect to the SKS volcano. The pH level was found maximum (pH-8.18) in the new erupted point (WSD2) of the WSD with respect to the other active mud volcanoes. The ionic conductivity of the SKS was found scientifically high (18.6-20.3 mS/cm). The negative redox results were exhibited from all volcanoes i.e. reducing nature, whereas Canten ground water exhibited an oxidizing environment (redox: +143mV). The salinity of the SKS volcano (11-12ppm) was found more than that of the WSD volcano (3.6-3.9ppm).

**Ionic status**

The \( \text{Na}^+ \) and \( \text{Cl}^- \) ion were found in higher concentrations (8835-19998ppm) in all selected active mud volcanoes like WSD and SKS. The \( \text{Na}^+ \) concentration was nearly same between two eruption points of WSD (8835ppm), whereas that was much higher at SKS (19998ppm). However, the \( \text{Cl}^- \) concentration was found to be significantly high (\( p\leq0.05 \)) in the new eruption point (WSD2: 3400ppm) (Fig. 1A). In comparison with the SKS, \( \text{Na}^+ \) and \( \text{Cl}^- \) were found to be in higher concentrations with respect to those of the WSD. However, the \( \text{Na}^+ \) and \( \text{Cl}^- \) concentrations were found significantly lesser (\( p\leq0.05 \)) in the Canten ground water (1%≥) with respect to the concentrations of their nearest SKS.
volcano. The cations like K\(^+\) and Mg\(^{2+}\) were found maximum (>3-4 fold) in SKS with respect to the WSD fluid (Fig. 1B). Interestingly, the result exhibited that the Ca\(^{2+}\) ion concentration was found more than 3 folds (160ppm) from the ground water of Canten with respect to their nearest SKS. Data also exhibited that the concentration of NO\(_2^-\) ion was found to be nearly same for all samples of active mud volcano (Fig. 1C). The SO\(_4^{2-}\) concentration was found more in the new erupted mud volcano (WSD2) with respected to old active volcanoes. In a similar fashion like Ca\(^{2+}\) ion, the SO\(_4^{2-}\) ion concentration was found maximally from the Canten ground water, in contrast to the nearest SKS. Another interesting result was found from new (WSD2) eruption point that exhibited more F\(^-\) concentration (14ppm). However, the F\(^-\) concentration was not found from the ground water of Canten.

Table 1: Gas compositions of representative mud volcanoes. Data represented statistical mean and standard error (n=6)

<table>
<thead>
<tr>
<th>Sample</th>
<th>O(_2) (%)</th>
<th>CO(_2) (%)</th>
<th>CO (ppm)</th>
<th>SO(_2) (ppm)</th>
<th>H(_2)S (ppm)</th>
<th>NO (ppm)</th>
<th>NO(_2) (ppm)</th>
<th>CH(_4) (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>WSD1</td>
<td>0</td>
<td>0.7</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0.4</td>
<td>96.55</td>
</tr>
<tr>
<td>WSD2</td>
<td>0</td>
<td>0.35</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0.4</td>
<td>95.33</td>
</tr>
<tr>
<td>SKS1</td>
<td>0</td>
<td>0.85</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>11</td>
<td>5</td>
<td>ND</td>
</tr>
<tr>
<td>SKS2</td>
<td>0</td>
<td>ND</td>
<td>0</td>
<td>0</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>95.52</td>
</tr>
<tr>
<td>Air</td>
<td>20.3</td>
<td>0.03</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0.3</td>
<td>0</td>
</tr>
</tbody>
</table>

Table 2: In-situ physical parameters of representative mud volcanoes. Data represented statistical mean and standard error (n=6)

<table>
<thead>
<tr>
<th>Sample</th>
<th>Temp (ºC)</th>
<th>pH</th>
<th>Conductivity (mS/cm)</th>
<th>Redox (mV)</th>
<th>Salinity (ppm)</th>
<th>DO (ppm)</th>
<th>TDS (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>WSD1</td>
<td>28.6±0.23</td>
<td>7.7±0.02</td>
<td>6.6±0.02</td>
<td>(-) 256±0.4</td>
<td>3.6±0.02</td>
<td>BDL</td>
<td>ND</td>
</tr>
<tr>
<td>WSD2</td>
<td>27.5±0.18</td>
<td>8.18±0.08</td>
<td>7.14±0.14</td>
<td>(-) 212±0.6</td>
<td>3.9±0.04</td>
<td>BDL</td>
<td>ND</td>
</tr>
<tr>
<td>SKS1</td>
<td>30 ±0.23</td>
<td>7.74±0.12</td>
<td>20.3±0.05</td>
<td>(-) 297±0.5</td>
<td>12.2±0.02</td>
<td>BDL</td>
<td>ND</td>
</tr>
<tr>
<td>SKS2</td>
<td>30.3±0.18</td>
<td>7.45±0.13</td>
<td>18.6±0.05</td>
<td>(-) 260±0.5</td>
<td>11.2±0.04</td>
<td>BDL</td>
<td>ND</td>
</tr>
<tr>
<td>Canten</td>
<td>31.3±0.12</td>
<td>7.01±0.06</td>
<td>0.77±0.05</td>
<td>(+) 143±0.7</td>
<td>0.1±0.002</td>
<td>2.3±0.03</td>
<td>759±1.3</td>
</tr>
</tbody>
</table>

Fig. 1: The bar diagrams represents (mean ± standard error), the ion concentrations of (A) Na\(^+\) and C\(^-\), (B) K\(^+\), Mg\(^{2+}\), Ca\(^{2+}\) and (C) NO\(_2^-\), SO\(_4^{2-}\), F\(^-\), where n=6.
Bacterial observation

The WSD was exhibited $2.6 \times 10^4$ cell/ml bacteria in mud fluid. Gram staining results revealed that most of the bacteria were gram negative and spherical shape. Similarly $3.12 \times 10^4$ cell/ml bacterial counts were found from the SKS. Most of the bacteria were gram negative and spherical shape. The investigation also concentrated on tolerance limit of bacterial isolates at different levels of pH, salinity and temperature. All isolated bacteria can tolerate from 20°C to 40°C (Fig. 2A). The maximum bacterial growth was found in the temperature range of 30-40°C ($147 \times 10^6$ cell/ml) after 36h incubation time. The investigation also reflected that the bacteria of the WSD can tolerate pH between 3-11 ($1.9-1.3 \times 10^7$ cell/ml) (Fig. 2B). The bacterial growth was found in maximum in the pH range from 5-10. More precisely the bacterial growth was found after 36h incubation at pH-8 ($26.6 \times 10^7$ cell/ml). The salinity tolerance level was in the range between 2-32 ppm. However, the maximum bacterial growths were found in the range of 8-16ppm after 30h incubation ($325 \times 10^6$ cell/ml) (Fig. 2C).

CONCLUSIONS

A series of experiments were initiated to study the compositions of gas, physical parameters, ionic concentrations and their bacterial morphology representative mud volcanoes and seepages in the WSD and SKS. Most of the gases emitting from active mud volcanoes are methane dominated. The composition of gas in the SKS was found significantly high with respect to the other selected mud volcanoes. All mud volcanoes exhibited their reducing nature. Na$^+$ and Cl$^-$ were dominated with respect to the other ions like K$^+$, Mg$^+$, Ca$^{2+}$, NO$_2^-$, SO$_2^{2-}$ and F$^-$, whereas new erupted volcano reflected maximum amounts of SO$_2^{2-}$ and F$^-$ ion. Most of the bacteria were gram negative and spherical shape. The bacterial growth is stimulated in the presence of Na$^+$ and Cl$^-$ ion, favorable high salinity, temperature and pH. This implies that the WSD and SKS active mud volcanoes are related to the deep-sea depositional environment

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Evaluating the Potential of Anaerobic Methane Oxidation in Terrestrial Mud Volcanoes of Southern Taiwan

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ABSTRACT

Anaerobic oxidation of methane (AOM), mediated by anaerobic methane oxidizing euryarchaeae, is a well-known phenomenon constantly observed in worldwide methane-rich marine environments. Such a process is often syntrophically coupled with sulfate reduction and has been found later as a new type of symbiosis with denitrification in freshwater environment. Terrestrial mud volcanoes in southwestern Taiwan originating from marine environments are characterized by abundant methane and less sulfate and chloride when compared with modern seawater, thereby serving as the ideal materials to explore whether ANME members could proliferate under less favorable conditions, and whether the syntrophic relationship with sulfate reduction remains the same.

Four push cores were collected from a mud volcano in Chunglun because sulfate of pond water is at abundances of one fifth of that of seawater and methane is the second major gas component. Cores with a length less than 20 cm were sectioned at a 3-cm interval and collected in designate vials for analyses of aqueous and gas geochemistry and microbial experiment. Analysis of pore water and dissolved gases yielded variable patterns of aqueous and gas chemistry. Decreasing sulfate concentrations from 5 mM to nearly none with increasing methane concentrations from less than a hundred μM to several hundred μM as the increase of depth were observed at soft, wet sites, whereas almost constant sulfate and slightly increasing methane concentrations were recovered from a bubbling site. Methane abundances obtained from microcosm experiments did not decrease through time. Although the coupling between the depletion of sulfate and the profuseness of methane is consistent with those commonly observed in typical marine, methane rich environments, microcosm experiments did not permit direct indication to the existence of AOM in Chunglun mud volcano. Other processes including advection, evaporation and diffusion also play a role to regulate the final geochemical pattern.
Inventory of metabolic energy deduced from aqueous and gas geochemistry of hot springs in northern Taiwan

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ABSTRACT

Volcanic hot spring is a natural habitat to diverse thermophilic, acidophilic microorganisms. These microorganisms harvest metabolic energy from disequilibrium imposed by various combinations of aqueous and/or gas compounds derived from deeply-sourced water-rock interaction and subsequent exposure to oxic surface environments. Assessment of potential metabolisms, however, is often hindered by the limited sample size, the biases introduced during cultivation and molecular analysis, and the contamination associated with sampling. Thermodynamic modeling of free energy yields provides advantages over other methodologies to verify a broad spectrum of possible metabolic pathways in volcanic hot springs. Here, we adopted aqueous and gas geochemistry associated with hot springs in northern Taiwan to evaluate how availability and abundance of energetic substrates govern the potential for expression of metabolisms under extremely acidic conditions.

Nine hot springs possessing various chemical characteristics were chosen for sampling of aqueous and gas geochemistry. Samples for aqueous geochemistry were collected with 0.2-μm filtration and appropriate preservatives. Samples for dissolved gases were collected with a peristaltic pump that continuously drives fluids through impermeable tubing to vacuumed serum bottles in order to omit possible atmospheric contamination. Gas compositions released in the headspace were measured by gas chromatography and then converted to their dissolved gas concentrations with Henry’s law constants.

Values of overall Gibbs free energies of several tens metabolic reactions were calculated with abundances of aqueous and gaseous species at the in-situ temperatures. These reactions included a number of electron donors such as H₂, NH₄⁺, Fe²⁺, H₂S, S, CH₄ and carboxylic acid, and electron acceptors such as O₂, NO₃⁻, Fe³⁺ (iron oxides), SO₄²⁻, S and CO₂. In general, oxidation reactions with O₂ as the electron acceptor could yield more energy than the others. Extremely low pH values and low dissolved organic carbon at some sites seem inhibit some organotrophic, anaerobic metabolisms (such as sulfate reduction and methanogenesis) commonly observed in other ambient environments.
Helium and Argon Isotopes Measured in Spinel peridotite Xenoliths from Mt. Quincan, North Queensland, Northeast Australia

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ABSTRACT

Helium and argon elemental and isotopic composition have been determined by stepwise crushing and stepwise heating in spinel-peridotite xenoliths from Mt. Quincan (Fig. 1), North Queensland (Northeast Australia). The helium isotopic ratios determined by stepheating and crushing do not show significant differences suggesting the helium being trapped in the fluid inclusions. The $^{3}\text{He}^{4}\text{He}$ ratios trapped in fluid inclusions cover a narrow range (7.7-9.7Ra) which agree well with values reported in MORB (8±1Ra; Hilton et al., 1993). The observed $^{40}\text{Ar}^{36}\text{Ar}$ (315-4165) ratios and $^{3}\text{He}^{36}\text{Ar}$ (0.0012-0.07) show large variation with lower values than that assumed for MORB source ($^{40}\text{Ar}^{36}\text{Ar}$=44000, $^{3}\text{He}^{36}\text{Ar}$=0.7; Moreira et al., 1998). The correlation between $^{40}\text{Ar}^{36}\text{Ar}$ and $^{3}\text{He}^{36}\text{Ar}$ (the latter corrected for some recent elemental fractionation) ratios can be explained by a mixing between air-like and MORB-like components (Fig. 2). Thus, both helium and argon isotopic compositions suggest a MORB-like source, as a primary source of fluid in samples. Apparently, this component should have been added by some percolating metasomatic fluids derived from the asthenospheric mantle reservoir. Probably this entrapment is associated with relatively recent magmatic activity as the absence of subduction-related noble gas signature (e.g., no correlation between $^{3}\text{He}$ and $^{36}\text{Ar}$) precludes the preservation of fluids in the xenoliths added during the Paleozoic subduction at eastern margin of Australia. Note that Sr, Nd isotopic characteristics of Mt. Quincan xenoliths also suggest that there is no indication of the subduction-related metasomatism, instead, these samples showed the depleted isotope signatures (Handler et al., 2005). Present noble gas results reinforce the view that the geochemical feature of this part of the mantle is dominated by the influence from underlying asthenospheric mantle source. We also note that there is no mantle-plume noble gas signature found in the Mt. Quincan xenoliths, although it is suspected to be close to the hotspot track across the eastern Australia. Finally, further implication of this result can be that the subcontinental lithosphere mantle is not homogeneous on global scale that was suggested by some models (e.g: Gautheron et al., 2005).
Fig. 1: Basalt distribution in Eastern Australia and the locality (Mt. Quincan, northeastern Australia) of the studied xenoliths (Map modified after Zhang et al., 2001). The lava-field volcanic provinces (black squares) are abundant in mantle xenoliths. The central-volcano provinces (black circles) represent the magmatism which is related to the hotspot activity beneath Eastern Australia. The dashed lines are the state boundaries.

Fig. 2: The $^{3}$He/$^{36}$Ar and $^{40}$Ar/$^{36}$Ar ratios observed in xenoliths from Mt. Quincan are plotted on the mixing line between air and MORB component determined Moreira et al. (1998). The $^{3}$He/$^{36}$Ar ratios were corrected for the elemental fractionation by using the values calculated from measured $^{3}$He/$^{40}$Ar$_{ma}$ and unfractionated mantle $^{4}$He/$^{40}$Ar$_{ma}$ of 1.6.
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$^{40}$Ar / $^{39}$Ar dating of the Jiali and Gaoligong Shear Zones and its tectonic implications to the crustal deformation around the Eastern Himalaya Syntaxis

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ABSTRACT

Comprehensive $^{40}$Ar/$^{39}$Ar geochronological investigation of the Jiali, Gaoligong shear zones and their adjacent faults provide constraints on the Cenozoic tectonic evolution around the Eastern Himalayan syntaxis (EHS). Our recent dating results display that the main phase of deformation along the Jiali and Gaoligong shear zones occurred between 26 to 9 Ma, and 18 to 13 Ma. By comparing deformation record between the Jiali, Gaoligong and other major shear zones in Southeast Asia, we recognized coincidental Cenozoic dates of the Jiali, and Ailaoshan–Red River (ASRR) shear zones. Coeval records imply that shearing occurred during Late Oligocene when the Jiali and sinistral ASRR shear zone formed the northern boundary fault of the southeastward-extruded Indochina. After the cessation of sinistral shearing along the ASRR zone, the Jiali fault changed its shear sense to dextral in the Middle Miocene (~18 Ma), and associated with the dextral sheared Gaoligong fault. The Jiali and Gaoligong shear zones may form the southern boundary of the clockwise rotated fragment around EHS as revealed by GPS studies, since the Middle Miocene. The temporally correlation between dextral shearing along the Jiali and Gaoligong shear zones and normal faulting in southern Tibet further suggests that the oblique convergence of India and Eurasia may account for the change of deformation pattern from eastward extrusion of Indochina to block rotation around EHS.
3-D Plane-fitting Program in \(^{40}\text{Ar}/^{39}\text{Ar}\) dating

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ABSTRACT

In an ideal K-Ar isotopic systematics, the measured concentrations of three argon isotopes \(^{36}\text{Ar},^{39}\text{Ar},^{40}\text{Ar}\) would satisfy a plane equation: \(^{40}\text{Ar} = \alpha^{36}\text{Ar} + \beta^{39}\text{Ar}\). In other words, the sample data should lie close to a plane in three-dimensional, XYZ space. If analytical errors are responsible for the scatter of data points on the \(^{36}\text{Ar}-^{39}\text{Ar}-^{40}\text{Ar}\) isotope correlation plot, the regression plane can be fitted using two steps. First, we employ matrix algebra to lay out the method of maximum likelihood for fitting a plane equation between any number of variables in the equation, all subject to analytical errors with known variances and covariances, although these may vary among the data points. In addition, the well-known Newton-Raphson method can subsequently be adopted in optimization. Secondly, in order to examine the maximum likelihood method of regression and to determine the standard errors of the parameters of a best-fit plane, the efficient-accurate methods can access standard errors, goodness-of-fit parameter, and MSWD (mean square weighted deviate) value. If the data are well fitted to the regression plane, the estimates of regression parameters \(\alpha\) and \(\beta\), will lead to estimates of the trapped argon composition and the radiometric age for sample.

To publish the above efficient algorithms and easy-to-use method, the present project designs a user-friendly Matlab-based graphical program, namely ArArPLOT, to perform the methods in age calculation and their corresponding diagrams (isotope abundance diagrams, isotope correlations diagrams) for \(^{40}\text{Ar}/^{39}\text{Ar}\) geochronological studies. The program is portable between computer operating systems supported by Matlab. The major benefit of this program is capable of clarifying whether the data points from a single sample representing different isotopic systematics, using plane fitting methods in XYZ space, as mentioned above.

In contrast to 2-D isotope correlation diagrams which utilize projection technique, this 3-D plane fitting program exhibits the following advantages: (1) it allows to clearly display the spatial relation of data points, and to improve the precision of error calculations; (2) it can be used as means in clarifying different isotopic systematics in sample; (3) the interpretation of isotope abundance diagrams becomes much easier because of better visualization of data distribution in 3-D space. In summary, the current project successfully designs a user-friendly program which is powerful in data analysis in \(^{40}\text{Ar}/^{39}\text{Ar}\) geochronology and is potentially useful to data analyses of other isotopes in compositional space.
Presence of Insoluble Organic Matter in Chondrule Precursors

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ABSTRACT

Nitrogen and noble gases were analyzed in 68 individual chondrules from 6 ordinary (O), 2 enstatite (E) and 2 carbonaceous (C) chondrites by using laser microprobe technique. It is observed that N composition of chondrules in OC and CC are different from their host chondrite, while for EC, they are similar. A large spread in N composition of chondrules from OC and CC is observed. These imply that the precursors of chondrules from OC and CC are different and preserve their heterogeneity whereas the precursors of EC chondrules are homogeneous and similar to E chondrites. Chondrules from E chondrites seem to be formed in the same location as their parent chondrite. Nitrogen results suggest the presence of at least three N components (HL, Q and IOM) for OC and CC chondrule precursors. Presence of IOM in chondrules provides important clues on chondrule formation process(es).

INTRODUCTION

Spherical objects of ~1mm size called chondrules are major constituent (up to 80 vol %) of most chondrites (Fig. 1). Chondrules are one of first solids to form in our solar system. Large fraction of aggregated earlier solids must have been utilized for chondrule formation. To understand their formation, it is important to know the nature of these chondrule precursors. Isotopic signatures of trapped nitrogen and noble gases can provide information about the precursors of chondrules and process(es) of chondrule formation. Study of nitrogen is virtually unexplored in chondrules. N composition (\(^{15}\)N) of chondrules is also expected to differ with their hosts, similar to oxygen isotopic composition (Clayton, 1993).

A number of studies have been carried out for noble gases in chondrules so far (Okazaki et al., 2001, Vogel et al., 2004, Polnau et al., 1999, Polnau et al., 2001) but N studies are very sparse (Fredriksson et al., 1983, Mahajan and Murty, 2003). The present work is the first systematic approach for the simultaneous nitrogen and noble gas studies in chondrules.
Table 1. Summary of N data from chondrules of OC (6), CC (2) and EC (2)

<table>
<thead>
<tr>
<th></th>
<th>Bulk</th>
<th>chondrules</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>N (ppm)</td>
<td>$\delta^{15}N_t$ (‰)</td>
</tr>
<tr>
<td>OC</td>
<td>2 - 40</td>
<td>-16 to 2</td>
</tr>
<tr>
<td>CC</td>
<td>CV 12 – 19</td>
<td>-36 to -47</td>
</tr>
<tr>
<td></td>
<td>CM 1000</td>
<td>48</td>
</tr>
<tr>
<td>EC</td>
<td>140 - 200</td>
<td>-22 to -31</td>
</tr>
</tbody>
</table>

The following meteorites have been analyzed: OC (Dhajala, Bjurböle, Udaipur, Chainpur, Tieschitz, and Saratov), CV (Allende), CM (Murray) and EC (Parsa, Qingzhen).

**EXPERIMENTAL PROCEDURES**

Chondrites with lower petrographic grades were selected for this study because the effect of secondary processes on these chondrites is expected to be minimum. These meteorites are listed in Table 1 (footnote). Chondrules are separated from bulk meteorites, either by gentle crushing to dislodge chondrules or by repeated freeze thaw process to disaggregate the meteorite, liberating the chondrules. Chondrules are hand picked under optical microscope; any adhering matrix material is gently removed by dental tools and by cleaning in alcohol and acetone mixture, under ultrasonication. Each chondrule is documented as well as accurately weighed by a microbalance. For chondrules with mass $\geq 1$ mg splits were used for chemical, mineralogical and textural characterization by EPMA. Nitrogen and noble gases in individual chondrules have been analyzed by using a specially designed laser...
RESULTS AND DISCUSSION

Measured values of nitrogen and noble gases mainly consist of trapped and cosmogenic and/or radiogenic components and by employing well established standard procedures these components have been decoupled (Mathew and Murty, 1993).

Trapped nitrogen: Large variation of $^{15}$N in chondrules of O and C chondrites is observed compared to their host chondrites whereas chondrules from E chondrites show $^{15}$N similar to their host chondrites (Table 1). The reasons for the large variation of $^{15}$N in chondrules of ordinary and carbonaceous chondrites could be either primary or secondary. It is possible that primarily precursors of chondrules were having heterogeneous nitrogen components. On the other hand, as chondrule formation is a high temperature event, extensive loss and rearrangement of volatiles like nitrogen and noble gases are expected. Additionally, interaction with surrounding environment is another possibility if chondrule formation was an open system event. Effects of secondary alteration on the parent body can further complicate the final N composition of chondrules. However, extent of such processes is expected to be minimum in case of chondrules from low petrographic grade chondrites. In contrast to this, similarity in $^{15}$N values for chondrules and their bulk chondrite is observed for E chondrites suggesting similar environment for chondrule formation and/or similar precursors for both. This inference implies different formation mechanism for chondrules from E chondrites. Different $^{15}$N in splits of a given chondrule from O and C chondrites are observed. The presence of heterogeneous phases within chondrules even after experiencing high temperature chondrule forming event is evident.

Generally, in nebular environment, nitrogen behaves similar to trapped Ar. However, like trapped noble gases, $^{15}$N of OC and CC chondrules cannot be explained by mixing the two components Q and HL. As listed in Table 1, OC and CC chondrules seem to have a third component with $\delta^{15}$N $> 100 \%$ and very low $^{36}$Ar/$^{14}$N. Insoluble organic matter (IOM) is the most appropriate candidate that fits this requirement. Hence, the observed range of $\delta^{15}$N in chondrules from ordinary and carbonaceous chondrites can be explained by three components: Q, HL and IOM (Fig. 2).

$^{15}$N of chondrules from E chondrites is found similar to their parent chondrites unlike the case of O and C chondrites (Table 1) as well as splits of EC chondrules show similar $\delta^{15}$N. These observations suggest: (a) EC chondrules as well as E chondrites are different from O and C chondrites, (b) EC chondrules and their parent bodies possibly formed from similar material and same environment.

Based on similar $\delta^{15}$N of EC chondrules, we propose that the formation of EC chondrules occurred from aubritic parent bodies. Processes like impact or volcanic activity on parent planetesimals seem more viable for the formation of EC chondrules. Similar inferences can also be drawn from other independent studies (Sears, 1980; Kallemeyn and Wasson, 1986; Shukolyukov and Lugmair, 2004; Whitby et al., 2002; Schneider et al., 2002). This kind of chondrule formation is different from the one involved for the formation of chondrules from O and C chondrites possibly due to different location of their formation.
Fig. 2 Elemental ratio $^{36}\text{Ar}/^{14}\text{N}$ vs. $\delta^{15}\text{N}_t$ of chondrules and their respective bulk for all chondrites The three components HL, Q and IOM can explain data of chondrules from OC and CC. Chondrules and bulk samples of EC overlap and show narrow cluster.

**Implications to chondrule formation process(es)**

Presence of HL, Q and IOM components are required in OC and CC chondrules to explain the large variation trapped N composition.

Following scenario can be proposed during chondrule formation: Chondrule precursors were heterogeneous and having different phases like silicate, metal and organic matter. These precursors (or some of them) received solar radiation before the event of chondrule formation. During the chondrule formation event, initially organic matter might have decomposed and dissolved in metal phases present in chondrule precursors. After this initial relatively low temperature setting, the fractionation between silicate and metal takes place subsequently. The further rearrangement of trapped nitrogen and noble gas compositions takes place during this fractionation. It is likely that these rearrangements (between organic matter, metal and silicate phases) erased earlier records of possible solar radiation in chondrule precursors partly or completely. However, during chondrule formation event different phases could not have achieved the equilibration fully, resulting in heterogeneous distribution. The final composition of trapped noble gases can be explained by the rearrangement of different phases (mainly metal and silicate) whereas for nitrogen results, presence of organic matter is also required.
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Multi-parametrical Monitoring of Deep Seated Fluids for the Characterization of Medium-short Term Transients in the Crustal Strain Field

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ABSTRACT

In the recent years increasing attention has been devoted to the analysis of medium-short term transients in the crustal strain field in connection with ongoing seismogenic processes. In this context, monitoring of deep seated fluids can be of great concern since confined reservoirs are can be considered as sensitive strainmeters. In this perspective, extensive monitoring of piezometries, temperature and gaseous emissions at deep wells has been carried out in Georgia and in North Italy. Both periodic and automatic measurements have been collected for several years at regional scale. The data collected by both periodic and automatic measurements have been statistically processed to remove more obvious effects of local meteoroclimatic conditions, Earth tides and anthropic activity. Medium-term fluctuations (several months to years) in the residual time series have been interpreted as the affect of crustal strain field perturbations propagating inside a rheologically stratified lithosphere.

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Correlation between Radon Anomaly with Meteorological Parameters and Earthquake

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ABSTRACT

Sub-soil radon is monitored with SSNTD in 39 locations, which fall on three prominent lineaments in Guwahati from Dec.'05 to Mar.'06 and from May'06 to Aug.'06. From these 39 locations, a suitable site is selected on the basis of sensitivity of radon concentration variation with respect to time, no rock structure in the background and low water level in the summer season also. At that site we are continuously monitoring radon concentration along with ambient temperature, atmospheric pressure and relative humidity by AlphaGUARD from 18th Jan.'07. Till now it is observed that radon concentration varies with relative humidity and atmospheric pressure. The effect of atmospheric pressure and relative humidity on radon concentration is summarized and we try to correlate these parameters with recorded earthquake (data being collected from USGS). Experiment is still going on and the results will be reported later on.
Continuous Radon Monitoring in the Hot Spring of Sirch as an Earthquake Precursor

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ABSTRACT

The first continues radon monitoring site in the water of the hot springs at Iran has been installed in the Sirch hot spring. This spring is located on the geological active fault of Gowke (Golbaf) at SE of Iran. Radon concentration in water of this spring has been measured using AlphaGUARD (model PQ2000PRO) in 10 minutes periods. The environmental parameters such as air temperature, pressure, humidity and groundwater temperature also have been measured in 10 minutes periods. Artificial intelligent systems have been used to analysis of the measured data for earthquake prediction.
Submarine Gas Flow Monitoring at Panarea Volcano, Italy

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ABSTRACT

Long-term records of submarine gas exhalations are rarely presented in literature. Long-term recording of submarine gas exhalations at shallow depths are difficult due to harsh conditions, highly corrosive water, impact of waves, tidal currents, fisher nets, anchors, and vandalism attacks. Low power consumption is a must since any external power supply would increase the risk of fail functioning. A robust device based on indirect gas flow monitoring by means of acoustic noise recording emitted during the gas emission was developed. This kind of acoustic “bubble counting” utilises acoustic oscillations generated during the bubble forming at the vent’s nozzle and the bubble stream knocking at the device. A self designed circuit consist of a microphone, preamplifier, counter, and data logger. The main advantages of this device are high acoustic (gas flow) sensitivity combined with low power consumption. A temperature probe inside of the sensor box gives further information about the fluid temperature variation. The recorded values are relative information about the gas flow variation, which is sensitive enough for the most geophysical purposes. The unit of gas flow is in that case an especially kind of frequency. A conversion into litre/min is not possible without individual calibration because the results depend on the physical conditions on each site (water depth, size of the vent, etc). The geophysical interpretation utilises the temporal variations of the recorded signal and in comparison with neighbouring stations. The time interval of each record is free selectable. For a monitoring period of three months, we prefer a 10 min logging interval. First laboratory tests showed logarithmic dependences between gas flow rate and acoustic noise records. That means the installation on vents should be preferred on low to medium strong gas emission sites to record in the optimum range of the instrument’s sensitivity. A first application at Panarea provides an important insight into different gas flow variations. Besides well-known influences by earth tides, also unpredicted fluctuations are shown by long term records. The correlation with recent tectonic and volcanic processes will be discussed.
Plant Based Detection of Dry Mofettes – an Example from the Volcanic Laacher See District, Germany

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ABSTRACT

Magmatic CO$_2$ exhalations as mofettes are common features in volcanic areas. However, they are difficult to detect if they are located outside open water. As natural CO$_2$ released from mofettes is not only of economic interest or exerts deleterious effects on the local fauna (and humans), but also contributes to the greenhouse effect, identification of dry mofettes and their volume flux are of vital importance.

Several techniques have been used to detect mofettes in volcanic fields, however, use of vegetation is especially promising. The East Eifel Volcanic Field is one of the known European areas of mantle CO$_2$ exhalations. Several natural carbon dioxide springs outside of the Laacher See proper were recognized within the surrounding oak and beech forest by their azonal vegetation, consisting mainly of helophytes. These plants are equipped with mechanisms that allow facilitated oxygen transport from above-ground plant organs to below-ground roots and rhizomes, thus ensuring normal respiration within the rhizosphere. The mofette stand is species-poor. Two grasses are dominating within the highly degassing centre. Growth of *Carex acutiformis* occurred only at sites of high to extremely high (60-95%) CO$_2$ concentrations within the upper soil layer (20-30 cm). The monospecific *Carex* stand was abruptly out competed by *Deschampsia caespitosa* when upper soil CO$_2$ dropped below 30%. Lower soil CO$_2$ concentrations were associated with growth of *Vinca minor* and/or *Symphoricarpos albus*. However, measurements in a depth of 80 cm indicated that the area of CO$_2$ saturation extended even further outward. Soil profiles differed from the surrounding forest soils in that the cover of organic matter increased from a few mm to thicknesses of 40 cm and consisted only of non to partially decomposed litter (raw humus to coarse moder). As many mofettes within central Europe show similar features with a prevailing azonal, helophytic vegetation, dry carbon dioxide springs can be detected via vegetational changes.
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Experimental Investigation of Mechanism of Hydrogen Generation in Hydrothermal Serpentinitization of Ultramafic Rocks

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ABSTRACT

Since the discovery in the late 1970s, deep-sea hydrothermal systems have been considered as the most likely candidates for the origin and early evolution of life on Earth. Phylogenetic, biochemical and geochemical consideration all possibly point to the early evolution of hydrogenotrophic chemolithoautotrophy such as methanogenesis and sulfur-reduction, thus pinpointing the availability of hydrogen as one of the key elements required for the early evolution of earthly life. For clear understanding of the significance of hydrogen on the earliest eco-system, we estimated hydrogen production (0.033 mol H₂ / mol peridotite) in serpentinitization of ultramafic rocks collected at the Kairei hydrothermal field near the Rodriguez Triple Junction (RTJ) in the Indian Ocean. In addition,
we conducted hydrothermal experiment of Horoman harzburgite in pure water at 350 °C and 50 MPa for four weeks. We will present preliminary results of this experiment.

INTRODUCTION

Deep-sea hydrothermal systems have been considered to contribute to the origin and early evolution of life on Earth. However, while subsequent investigations have revealed a great diversity of modern deep-sea hydrothermal ecosystems, they have done little to shed light on the issues of the origin and early evolution of life, metabolism, cells, or communities. Phylogenetic, biochemical and geochemical observation are likely to connect to the early evolution of hydrogenotrophic chemolithoautotrophy such as methanogenesis and sulfur-reduction. Thus, the early evolution of earthly life requires hydrogen as one of the key elements. Hydrogen-driven, photosynthesis-independent communities are very rare on the contemporary Earth, however, being unambiguously found only in subsurface environments of H₂-dominated hydrothermal systems. Such systems have been termed hyperthermophilic subsurface lithoautotrophic microbial ecosystems (HyperSLiMEs) (Takai et al., 2004; Nealson et al., 2005). The supply of abundant hydrogen and available inorganic carbon sources to power such communities is the most likely coupled to hydrothermal serpentinization of ultramafic rocks and input of magmatic volatiles, both of which are related to specific geological settings. We proposed, on the basis of findings in the modern Earth and implications for the deep-sea hydrothermal systems in the Archean Earth, that “Ultramafics-Hydrothermalism-Hydrogenesis-HyperSLiME”, a linkage we refer to as Ultra H³ provided a suitable habitat for the early microbial ecosystem on the early Archean Earth (Takai et al., 2006).

Significant hydrogen production in hydrothermal reaction with ultramafic rocks has been reproduced based on laboratory experiments (Berndt et al., 1996; McCollom and Seewald, 2001; Voglesonger et al., 2001; Normand et al., 2002; Allen and Seyfried, 2003). Here we estimated hydrogen production in serpentinization of ultramafic rocks collected at the Kairei hydrothermal field near the Rodriguez Triple Junction based on characterization and chemical compositions of serpentines for better understanding of the significance of hydrogen on the earliest eco-system. Since Archean Earth surface environment is quite different from modern one, we conducted the hydrothermal experiment of Horoman harzburgite in pure water at 350 °C and 50 MPa for four weeks. We will present preliminary results of this experiment.

EXPERIMENTAL

An experiment in water-rock interaction (temperatures and pressures up to 350°C and 500bar) was conducted using newly designed hydrothermal apparatus with fluid-flow systems (Fig. 1). For better understanding of the reaction processes, we have also established systems of direct analysis of H₂, CH₄ and CO₂ gases in hydrothermal solutions through tandem-gas chromatography. The system gave a linear calibration curve of these gasses and we can measure even trace amounts of gasses in fluid samples with a few μ mol/L. Trace element analyses of ultramafic and mafic rocks are done through ICP-MS equipped with a collision cell.
ESTIMATION OF HYDROGEN GENERATION BASED ON NATURAL SAMPLE

Comparison of the experimental results with natural samples is important to constrain the natural conditions of serpentinization of ultramafic rocks. We petrographically characterized the natural serpentinized peridotite collected from the Kairei hydrothermal field (25°19'23"S, 70°2'20"E) near the RTJ and the experimental products reacted at 350 °C and 50 MPa for four weeks. The Kairei natural sample is characterized by mesh texture (Fig. 2). Three kinds of serpentine are commonly found in natural samples; chrysotile, lizardite and antigorite. Chrysotile and lizardite of RTJ and well crystallized lizardite (secondary re-crystallization?) were found by Raman spectroscopy in mesh core and rim, respectively (Fig. 2).

Fig. 3. The most likely reaction in the serpentinization of RTJ peridotite.
The formula (1) and (2) in Fig. 3 express the reaction in natural serpentinization. Based on the chemical compositions of serpentines analyzed by EPMA, we determined the values of x, y and z in the formula (2). As a result, we estimated the possible maximum hydrogen production in the serpentinization of the RTJ peridotite as 0.033 mol H₂ / mol peridotite.

**EXPERIMENTAL PRODUCT – PRELIMINARY OBSERVATION**

Chrysothile and brucite were found along the rims of the minerals in experimental products after reaction with pure water at 350 °C and 50 MPa for four weeks (Fig. 4). The actual reaction is possibly expressed as follows:

\[
\text{Olivine} + \text{H}_2\text{O} = \text{Brucite} + \text{Chrysothile (Fe}^{3+}\text{)} + \text{H}_2？
\]

We have not estimated the hydrogen production. We are planning to geochemically analyze the experimental product and to compare it with the natural samples in order to put better constraints on the hydrogen generation mechanism in the deep ocean, which will lead to better understanding of the environment of the early evolution of earthly life.

Fig. 4. BSE image and Raman spectra of experimental product.
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Noble Gases in Stalagmite Inclusion Fluids: Preliminary Results

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ABSTRACT

In order to find out the possibility for utilizing speleothem inclusion fluid as paleoenvirionmental proxy, we attempted to analyze noble gas elemental and isotope abundances in water-rich inclusions particularly abundant in the stalagmite sampled at Villars Cave in France. Determination of elemental and isotope composition of these stalagmites appeared to be difficult as the extraction by crushing resulted in significantly high pressure of H$_2$O that overwhelmed the amount of noble gases released from the inclusions. However, we managed to obtain elemental and isotope composition of noble gases from some of our H$_2$O-rich stalagmites. These results indicate that noble gases in these samples are not isotopically fractionated each other, while they showed preferential enrichments in heavier noble gases. This is consistent with atmospheric noble gases being dissolved into water, but there is also an indication that an unfractionated atmospheric component also exits in the samples. Potentially, the observed fractionated air can be utilized to estimate the ambient noble gas temperatures, if we can achieve analysis with sufficiently smaller uncertainties, for example, by developing a purification system with better removal of H$_2$O-rich vapor enabling larger sample (i.e., more noble gases) to be subjected for the mass spectroscopic analysis.

INTRODUCTION

Elemental and isotopic composition of noble gases in trapped fluids during speleothems formation might provide some insights to resolve the following palaeoenvirionmental open questions:

(1) If speleothems had trapped air-derived helium upon their formation in the past, the analysis of 3He/4He ratios in such samples could give us some clues of the variation of the isotopic composition of helium in the atmosphere (over last few hundreds or thousands years). This should have changed in the last century, by emissions of important amount of hydrocarbons and related gases (Sano et al., 1989). Genty and Massault (1999) have reported some variations in the $\delta^{13}$C values of calcite in some recent speleothem. This variation could be related to the emission of C by human activity. If this interpretation is correct, the combined analysis of $\delta^{13}$C and $^3$He/$^4$He in speleothems should allow tracing human-induced variation in the atmosphere chemistry in the last few centuries.
(2) The atmosphere-derived noble gas amounts in the inclusion water should be proportional to the ambient temperature of deposition (as observed in the aquifers). Thus, their analysis could give clues on the paleotemperature during the precipitation of calcite, making them a reliable paleoclimatic record.

(3) Physical processes could also fractionate the noble gas amount and isotopic composition. An example is Rayleigh distillation during water evaporation. Thus, noble gases, if coupled with other isotopic records, could be useful to distinguish the isotopic variations due to physically driven fractionation over real paleoclimatic signals.

Here we report our preliminary results of our attempts to analyze noble gas elemental and isotope compositions from some stalagmite samples which had been documented to be enriched in fluid inclusions (Genty et al., 2002).

SAMPLE AND ANALYSIS

Noble gases are extracted from ca. 1-2 grams of samples by vacuum crushing gas extraction. This is to selectively obtain signatures of fluid inclusions of the samples. Amount of total gas released from the samples were monitored by on-line Schultz gauge, and samples are crushed until we observe significant increase in the pressure (indication of breaking the water-rich inclusions). Pressures being higher than 0.01 torr were observed during some of the experimental runs. When we found H$_2$O pressure is too high to be purified to the level acceptable for noble gas mass spectrometry, we abandoned the sample and proceeded to the bake-out procedure for next trial. Typically, we managed to obtain one data out of four to five attempts (i.e., in most of cases, we had too much water released from the samples). So far we managed to analyze four speleothem samples (VIL-GN1, VIL-GN2, VIL-24 & VIL27). Except for VIL-GN2 (that is dark compact calcite), these samples are white porous calcites. They are all from the Villars Cave, which is located in the north of the French department of Dorgone, 50 km South of the town of Limoges. The cave developed inside an oolitic carbonate formation of the Middle Jurassic, but its formation is likely during Tertiary or the start of Quaternary, as most of the karsts caves in Dorgogne. Villars Cave contains speleothems dating back at 80,000 years that recorded rapid climatic events of the last glacial period, particularly the "Dansgaard-Oeschger" and the "Younger Dryas". These samples are particularly rich in water-filled inclusions and subjected for some stable isotope study (Genty et al., 2002). Because previous attempt to obtain paleotemperature record from speleothems had been unsuccessful because of small amount of water and associated noble gases (e.g., Ayliffe et al., 1994), our samples might be more suitable for testing the possible use of speleothems for noble gas study.

RESULTS AND DISCUSSION

ISOTOPTIC COMPOSITIONS: Isotopic composition of helium has not been determined from all samples because of their release of $^3$He being well below the detection limits. Figure 1 plot neon, argon, krypton and xenon isotopic ratios, respectively. All ratios show general agreement with isotopic composition of the modern air. Some argon results show possible indication for the mass dependent isotope fractionation, but with the relatively large analytical uncertainties, it is premature to be conclusive. Thus, these results indicate that the noble gases contained in the samples (and those released by vacuum crushing extraction technique) are of atmospheric origin.
ELEMENTAL ABUNDANCES:
Relative noble gas abundances, being expressed as F-values, are reported in Fig. 2. Noble gas elemental abundances in air-equilibrated water at 0 to 30°C have also been reported for comparison. These latter values should give an indication of the expected relative abundances of noble gases in inclusion fluids of the samples. Unlike the case for their isotopic compositions, noble gas elemental abundance ratios deviates from the atmospheric composition. It is interesting to note that some samples yielded F-values (F(Ne), F(Kr) and F(Xe)) that is consistent with a two component mixing between unfractionated air and atmospheric gases dissolved in water at possible ambient temperature. This suggest the samples and their noble gases trapped in fluid inclusions could be useful to obtain information regarding the temperature of calcite precipitation. However, because some samples yielded elemental ratios unexplainable with a binary mixing model, the meaningful estimates of speleothem formation temperature using a simple two component noble gas mixing model appears not plausible.

Fig. 1: Isotope compositions of Ne, Ar, Kr and Xe in the present samples plotted with respective two sigma uncertainty. Solid lines in Ne and Ar diagrams are mass dependent isotope fractionation lines.
Fig. 2: Elemental abundances of the present samples, expressed as F-values (see definition in Fig. B2). F-values expected for air-saturated water at given temperatures are also shown. Solid lines are examples of mixing trends with noble gases dissolved in the water and unfractionated air.

Finally, because the analysis inevitably introduced significant amount of H$_2$O to the gas handling and purification system that is kept under ultrahigh vacuum condition for our routine isotope analysis, production of one data set from the speleothem was usually followed by cycles of painstaking bake-out and by an instable ion source condition due to incomplete removal of H$_2$O even after a series of gettering. Thus, we need to establish a better methodology to determine more precisely the relative elemental abundance of noble gases in these samples before utilizing them as reliable paleotemperature proxy.

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Experimental study for noble gas release and exchange under high-speed frictional melting

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ABSTRACT

Noble gas isotopes are not concerning a chemical bond under the typical condition in rock as a particular mineral or of minerals. Thus, noble gas isotope ratio in particular minerals seems to be easily modified by their ambient reservoirs when minerals have been caught higher temperature than their closure temperature, in general. Therefore, quantitative analysis of thermal history of a rock or a geologic event including fault movement could be performed using radiometric dating method derived from different minerals. However, because it is not easy to evaluate either their ambient temperature exceeds the closure temperature of minerals phenomenally, there is a problem to apply radiometric dating for the purpose in the case of faulted rocks.

Here we report a preliminary experiment that effectuates high temperature frictional melting experiments with using a high-velocity friction apparatus in Kyoto University in order to test whether noble gas isotope is reset their ratio by frictional heating of fault or not. In the experiment, the temperature on the modeled fault plane is well above the closure temperature of K-Ar system. Due to rapid equilibrium of volatiles during frictional melting of rocks, we expect that the noble gas isotopes should be reset by this experiment. We determined noble gas isotopes of gabbro sample processed by the apparatus and checked the age-initialize resulted from frictional high temperature degassing. Initializing the noble gas is only observed in glass completely melted. In a field observation, such glassy materials, indicating rocks completely melted, are faced on fault planes. In addition, the outgas sample, collected into small aluminum tube after the friction experiment under condition of the nitrogen atmosphere, contains carbon dioxide, water vapor, and helium released from the rock samples.

INTRODUCTION

Radiometric age is defined as a cooling age or a closure age of a particular mineral or of minerals. Such ages should be rejuvenesced when minerals have been caught higher temperature than their closure temperature, in general. Therefore, thermal history of a geologic body or geologic events accompanying with frictional heating (e.g. fault movement) could be interpreted quantitatively in comparison with radiometric ages among various minerals and methods. For example, either an ESR age, a FT age or an U-He age of a thermal sensitive mineral is expected as a good geological tool for
detecting thermal events. However, because it is not easy to evaluate whether their ambient temperature exceeds the closure temperature of minerals phenomenally, there is a problem to apply radiometric dating for the purpose in the case of faulted rocks.

Because the closure temperature of K-Ar system is rather high, a kind of melted-rocks under much high temperature, such as pseudotachylytes, are widely applied to determining fault activity with K-Ar dating method. To obtain reliable ages of fault activities, it is a key issue whether the ages were initialized by re-equilibrating their noble gas isotopes with atmospheric ratio. In the case that such a rejuvenescence can explicate one of a geochemical phenomena besides the filed observation, analyses of apparent K-Ar ages could be applied for fault rocks for thermal history analysis.

FRICIONAL MELTING EXPERIMENT

High temperature frictional melting apparatus was applied to the gabbro-fragment in order to test whether age is reset by frictional heating of fault or not. A pair of gabbro chunks cut into hollowed cylinder was slid at a slip velocity of 1.3 m/s and a normal stress of 1.4 MPa with a high-velocity friction apparatus in Kyoto Univ.

Under this condition, local frictional melting started into 5 sec. and temperature around a modeled fault plane reached around 1100 °C in ca. 20 sec. It is indicate that frictional plane is well above the closure temperature of K-Ar system. We also attempted to detect the degassing of carbon dioxide, argon and helium from the rock samples during frictional melting.

ANALYSIS AND RESULT FOR NOBLE GAS

Bulk rock measurement of noble gas isotopes were analyzed with GVI-5400 noble mass spectrometer in JAMSTEC Yokosuka-HQ. In situ measurement for noble gas isotopes were done with fiber laser fusion system of GVI-5400 in KOCHI JAMSTEC. The peak comparison method applied to calculation of all K-Ar ages (e.g. Takaoka 1989, Matsumoto et al., 1995). Potassium contents were referred from Shimamoto (1992). Outgases released from frictionally melted rock under the nitrogen atmosphere were analyzed, which contains carbon dioxide, water vapor, helium and argon from the rock samples.

(1) In situ measurement for noble gas isotope (Fig.1a)

The extracted noble gases residing in the specimen increase from the frictional surface to the 1.2 mm position. It is almost constant 1.2 mm and further from frictional face to the end of fracture zone. This change of noble gas abundance is similar to the observation in the natural metamorphic area, However, the size of metamorphic area is slightly small compared those in field observation.

It suggest interfuse of extraneous component from un-melted fragments around. Such fragments possibly include extraneous noble gas component, in case that original rock included contains the non-atmospheric component. Radiogenic noble gas contents are a constant degassing such as \(^{40}\text{Ar}\) and \(^{4}\text{He}\). \(^{4}\text{He}\) is degassed from the glass and the glassy material.

Noble gas isotope analysis was applied to thin section sample after frictional melting. Between 3.0 to 0.2 mm range of the processed specimen shows older K-Ar ages than those of the outer zone. It is not only effect of fractionation but excess components transferred from heated area or mixing components of broken fragment in contact. A similar age increase, near the contact heating rock body, was also observed in natural metamorphic zone (c.f. Iwata et al., 2000). Ar isotope is not either explained solely by an equilibrium balance for atmospheric ratio, nor by melted rock effected for disequilibrated
melting even in the frictionally melted zone includes excess potassium. If this part is analyzed by Ar-Ar dating method, their age should not indicate the plateau age due to the age spectrum should be disturbed.

(2) Volatiles released under friction (Fig. 1b)

The volatiles, released from the specimen under the friction of nitrogen atmosphere, were collected into small aluminum tube after the experiment after the friction experiment among/in nitrogen atmosphere. It contains carbon dioxide, water vapor, helium and argon release from the rock specimen. The gas components, which are C, N$_2$, $^{40}$Ar, CO$_2$, H$_2$, $^4$He, $^{36}$Ar, $^{38}$Ar, are increasing under the experiment, and noble gases degassed by frictional melting of rock are slightly higher concentration after experiment. H$_2$ gas shows higher concentration than H$_2$O gas, which is possibly caused by high temperature decomposition for in situ and/or atmospheric H$_2$O. It is consists on Wakita et al. (1980) that the natural faulting could seems to effect the quantity H$_2$ increase by water.

Fig. 1

a. Noble gas isotope content plotted by the distance from frictional face. The spot fusion sample is melting by fiber laser, 2W, 20X-magnification and 5 seconds-long heating. Laser spot diameter is ca. 0.1 mm. In thin section, the metamorphic area is as wide as 2 mm, and displacement area is as large as 3-5mm. Point of spot analysis are 7, which are 0, 0.2, 0.4, 0.8, 1.2, 2.0 and 3.0 mm distance from frictional face.

b. N$_2$ normalized relative abundance pattern of the released volatiles by frictional experiment. H$_2$ gas is higher than H$_2$O gas, is caused by high temperature decomposition for in situ and/or atmospheric H$_2$O.

Due to kinetic disequilibria of volatiles enhanced by frictional melting of rocks, we expect that the noble gas isotopes should be disturbed by this experiment. We determined K-Ar age of processed gabbro specimen, and evaluated whether K-Ar age was initialized by frictional high temperature degassing. The age-reset is only observed in glass completely melted. Such glassy materials, indicating complete melting of rocks, are frequently found on the fault plane (pseudotachylytes). Thus, the age of such glassy materials are regarded to be initialized during fast fault movement and high temperature by re-equilibration of Ar isotopes to atmospheric ratio at the faulting event. An apparent incomplete initialize was observed in the part including some un-melted gabbro fragments. In the part,
mechanically fractured pieces are mixed in the glass matrices in the frictional face or zone. That is why the Ar isotope ratio might not be re-equilibrated in the experiments. Similarly, U-He age is also initialized as for re-equilibration of He isotopes even in low speed and low temperature, or just fractured rocks. This indicates that U-He age is much sensitive because He should be degassed earlier than Ar.

CONCLUSIONS

We determined K-Ar age of gabbro sample processed by the high-velocity friction equipment and checked the age-initialize resulted from frictional high temperature degassing.

As the result of the kinetic disequilibria of volatiles enhanced by frictional melting, which are effecting for friction and fractures, the noble gas contents were changed along the distance from the frictional plane. Also noble gas abundance does not equilibrate for atmospheric ones near position for the frictional zone.

The age-reset is only observed in glass completely melted. An apparent incomplete initialize was observed in the part including some un-melted gabbro fragments generated in the experiment. That is why the noble gas isotope ratio might re-equilibrate in the experiments. U-He age is also initialized as for re-equilibration of He isotopes, which is more sensitive and degassed earlier than Ar isotopes.

The outgas sample, collected into small aluminum tube after the friction experiment in nitrogen atmosphere, contains carbon dioxide, water vapor, and helium from the rock samples. The gas components, which are C, N₂, ⁴⁰Ar, CO₂, H₂, ⁴He, ³⁶Ar, ³⁸Ar, are increasing under the experiment, and noble gases degassed by frictional melting of rock are slightly higher concentration after experiment. H₂ gas is much contained than H₂O gas in outgas, which is caused by high temperature decomposition for in situ and/or atmospheric H₂O.

REFERENCES


Geoelectrical Investigation of Magmatic Degassing Zones in the Eger-rift (central Europe): A Case Study of the Hartousov Mofette Field

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INTRODUCTION

The western Eger rift, NW-Bohemia/Czech Republic, with its large number of mineral springs and mofette fields, is also characterised by two quaternary volcanoes, anomalies of mantle derived He and the periodic occurrence of earthquake swarms. Geochemical study (Bräuer et al., 2005) indicate, that the recent active magmatic processes in the earth's crust may have an influence on the degassing behaviour and the generation of swarm earthquakes.

To understand the transport processes of CO₂ from the active magma reservoir in the subcrustal mantle to the earth's crust we suggest extending the scope of multi-parameter monitoring. Questions are focused on the quantification of external influences (meteorological/ hydrological), which affect the degassing at the earth's surface, and seasonal trends are important in this context.

We selected a gas emission site, Mofette field Hartousov for investigations with geoelectrical methods. That mofette field is located in the N-S trending Počatky-Plesna fault zone which is partly seismoactive (mostly at depths between 6.5 and 10.5 km).

A combination of 3-D electrical resistivity tomography (ERT) and measurements of the natural electrical field (self-potential SP) provides first insights into the near surface structure down to 15m and patterns of fluid movements.

INVESTIGATION METHODS

Electrical resistivity varies significantly as a function of rock porosity, water/gas saturation, pore fluid conductivities, clay content, and temperature. Therefore geoelectrical measurements are very useful to describe pore space related processes.
The method of electrical resistivity tomography (ERT) is based on the measurement of abundant transmitter-receiver configurations, each yielding a weighted spatial average of resistivity in the subsurface. The spatial model of resistivity distribution is extracted by use of inversion programs. The measurements were conducted along a set of profiles (each 50 to 75m) across the mofette (diameter 2m) with an electrode spacing of 1m. Accounting lateral variations of resistivity (3-D geometry of the mofette), 2-D field array and 3-D inversion were used to define complex structural heterogeneities. Self potential (SP) measurements were obtained with a spacing of 2m along the profiles. The reference electrode (Cu/CuSO₄) was placed at the starting point of the central profile P1 and the difference of electrical potential between this electrode and a moving electrode (Cu/CuSO₄) was measured with a high impedance voltmeter.

Several mechanisms, electrokinetic, electrochemical, and thermoelectric, have been proposed to generate natural electrical voltages. Primarily, SP anomalies have been attributed to the electrokinetic effect that involves the separation of charges at mineral-fluid-interfaces, which may be caused by the flow of water and gas in a porous material. As a consequence, fluid flow pathways characterised by high permeability should have a typical electrical pattern at the surface depending on the relation of gas upflow or infiltration of rain water.

CO₂ flux and CO₂ concentration measurements and sediment study complete the field investigations carried out in August 2006, March and May 2007 to study the seasonal and hydrological influences at this location.

FIRST RESULTS

Results of ERT data (Figure 1 comprises the 2-D results for a selected profile P1) show the shallow structure of the surrounding of the mofette through the resistivity distribution. Near surface down to approx. 2m we find values of resistivities up to 250 m in small anomalies. The part below the mofette field can be clearly distinguished by lower values of the resistivity, whereas the areas in the same depth (2-7m) show resistivities up to 500 m. Lower resistivities (20-200 m) are characteristical for depths below 7m.

Measurements of SP (April 2007) display the area where the gas ascends as a significant negative anomaly (-20mV). The descent of rain water on permeable pathways could be the explanation for that.
Statement
The combination of 3-D geoelectrical measurements, self potential mapping, CO₂ data and sediment study enables us to derive information on the structure of the degassing area and its depth extension. Circulation of fluids is controlled by geometry and changes of these structural conditions. The quantification of seasonal effects is possible with repeated measurements of the resistivity distribution. The area where we observed ascending fluids and the seepage of surface water as linked processes shows significant anomalies in resistivity and the natural electrical field distribution.

REFERENCE
Geochemical Surveillance of Reactive Gas from Pozzuoli Solfatara (Naples, Italy): Chronological Evolution and Local Ground Displacement

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ABSTRACT

Since 2000, the team of Geoscience and Earth Resources that is working on the area of Phlegrean Fields started again with systematic sampling on fluids emission from Pozzuoli Solfatara, specifically into fumaroles named Bocca Grande, following a similar work on the same parameters of our team from 1982 to 1985 and carry on by Cioni et al. from 1982 to 1997.

The examination of results of chemical analyses of most reactive gases like H$_2$, CH$_4$, H$_2$S from 2000 till now shows very particular trend that is well emphasise on triangular diagram, fig. 1c.

The main aspect of this trend consists on the fact that time evolution of chemical composition of named gases in Pozzuoli Solfatara during 2001-2005 is refocusing towards measured values during the period from 1983/85, characterized from accentuate of the phenomena of negative bradisism.

In fact in that period there were an evolution of chemical composition of gases in argument very similar to what nowadays observed (fig 1c).

In coincidence of maximum displacement of bradisism happened at the end of 1984, were measured similar values to actually measured.

Also the period from 1989-1997 (fig.1d) shows simila evolution of chemical gas composition.

Compared observation of triangular diagrams H$_2$, CH$_4$, H$_2$S (fig. 1c, d, e) with the graphic about altitude variation till 2003 (fig. 1b), shows a correspondence between the evolution of relative gas concentrations and the trend of bradisism.

In particular, on the base of datas available, we can observe a trend characterized from a relative increase of H$_2$S, a decrease of H$_2$ and prevalently CH$_4$ during the phase of negative bradisism.

What upper evidencied should be verified through a careful comparison with new measurement of movement of the ground.

Another confirmation about correspondence between temporal evolution of gas chemical composition and a new emphasize of bradisism, should attest the contribution on anticipation aspects of major environmental impact of the phenomena also from the geochemical monitoring of these parameters.

REFERENCES


Radon Emanation from Coal Ashes

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ABSTRACT

The radon emanation coefficient has been measured for the samples of coal ashes by the “can technique”. In this technique the ratio of the radon activity in the air inside the can and the total radium content of the sample is regarded to be the approximation of the emanation coefficient. In fact it is the measure of the exhalation from the sample. Analysis of the relation between so defined emanation coefficients and the sample thicknesses resulted in the exponential function which enables calculation of the proper emanation coefficient describing emanation of radon from mineral grains into internal pores of the sample.

INTRODUCTION

Radon emanation coefficient describes the fraction of Rn atoms which are able to leave the mineral skeleton of the sample and enter air in the open pores. In the case of the can technique (see Azam et al. 1995) radon activity in the air inside the can is measured and divided by the total radium content of the sample. It is in fact the measure of the exhalation rate which depends also on the sample thickness since radon atoms must leave not only minerals but the whole sample. In this study fine grained ash, remains of Carboniferous coal burning of $^{226}\text{Ra}$ content 55 Bq/kg were used to study the influence of the sample thickness upon the radon activity in the air inside the can.

METHOD

Measurements of radium content have been performed using Exploranium GR-320 gamma radiation spectrometer with the standard NaI (Tl) GPX-21A detector of 0.35 L volume. Measured activities of $^{214}\text{Bi}$ were recalculated into $^{226}\text{R}$ concentration (in Bq/kg) assuming the existence of equilibrium in the uranium decay series.

Radon exhalation has been measured using can technique described by Azam et al (1995) modified by Solecki (1999). Three homogenized samples of ashes of 55 Bq/kg $^{226}\text{Ra}$ activity were placed in iron cans 0.2 m high of 5 dm$^3$ volume. Three various sample volumes has been taken into account to form layers of various thickness (0.05, 0.10 and 0.15 m on the bottom of cans). Passive open type track detectors Kodak LR115 were fixed at the top of cans and cans sealed. After 21 days iron cover held by the magnet was removed and detector exposed for 21 days. After exposition detectors were etched 90 minutes in 2.5 M NaOH. Tracks were counted using optical microscope at the magnification of 100x. Track density was recalculated into radon activity. Total radon activity in the air inside the can was divided by the total radium activity of the sample resulting in the ratio which can be regarded as the approximation of the emanation coefficient.
Mineral composition of the ash has been studied by XRD method. Volumetric density, specific density and porosity of samples were measured by water flooding method.

RESULTS

Following crystalline phases have been identified in the ash by means of XRD method: quartz, mullite, calcite and gypsum. Basic physical parameters of ash are listed in the Table 1.

<table>
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<th>Specificity</th>
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<tr>
<td>Porosity (%)</td>
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</tr>
<tr>
<td>$^{226}$Ra (Bq/kg)</td>
<td>55</td>
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Emanation coefficients calculated for three samples of various thicknesses are shown in the Table 2.

<table>
<thead>
<tr>
<th>Sample number</th>
<th>1</th>
<th>2</th>
<th>3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thickness (m)</td>
<td>0.05</td>
<td>0.1</td>
<td>0.15</td>
</tr>
<tr>
<td>Total Radium content (Bq)</td>
<td>2</td>
<td>2.6</td>
<td>2.9</td>
</tr>
<tr>
<td>Total Rn activity in air inside can (Bq)</td>
<td>51.5</td>
<td>97.2</td>
<td>157.6</td>
</tr>
<tr>
<td>Emanation coefficient</td>
<td>3.9</td>
<td>2.7</td>
<td>1.8</td>
</tr>
</tbody>
</table>

Relation between sample thickness and emanation coefficient is shown in the Fig.2. Increasing thickness of the sample results in decreasing emanation coefficient.
Fig. 2: Relation between emanation coefficient and the sample thickness

CONCLUSIONS

Emanation coefficient calculated as the ratio of the total exhaled radon inside the can to the total radium content of the sample is in fact the measure of the exhalation and should be regarded only as the first approximation of the emanation coefficient defined as a fraction of radon atoms which are able to penetrate from mineral skeleton into the open pores of the sample. Obtained exponential function shown in Fig. 1 for the sample thickness equal zero reaches the value 5.97. This value can be regarded as the true emanation coefficient. Obtained results indicate that at least three measurements of exhalation for various sample thickness are necessary to obtain the equation which enables correct calculation of the emanation coefficient.

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Radon in some Jurassic caves in Southern Poland

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ABSTRACT

Radon ($^{222}$Rn) is naturally occurring noble gas, the member of uranium series. The main source of radon is bedrock, sometimes building materials, drinking water and gas. The potential risk that stems from radon and its progeny in underground mines and dwellings is well documented. In caves in different countries radon concentrations have been identified as elevated (Ball et al., 1991). In Poland radon measurements have been performed in the region of Sudety Mountains where the elevated background of natural radiation occurs (Przylibski, 1999).

In the paper results of measurements of radon concentrations in 11 caves of Wyżyna Krakowsko-Częstochowska are presented.

RESULTS OF MEASUREMENTS

Radon concentrations in investigated caves are not high by world standards (Friend, 1996, Gilmoore et al., 2005). Performed investigations showed, that the average concentrations of radon in Jurassic caves are within the range between few tens to several thousands Bq/m$^3$ (fig.1). It’s well know, that radon level in the cave depends on many factors, among them type of the rocks, presence of faults, fissures and cracks, enabling easier migration of gases.

![Fig. 1. Radon concentrations, grab samplings and long-term measurements.](image)

The assessment of effective dose for tourists and guides has been made, accordingly to the procedure, proposed by Denman and Perkinson (Denman, Perkinson, 1999). The annual doses calculated to
long-term users of caves and tourists guides are in some caves higher than 15 mSv. It means that doses to cave users might be higher than to miners of Polish underground coal mines (Raport, 2004). In case of tourists, sporadically visiting caves – for example students during school excursions, participants of speleological courses – committed doses are negligible.

In my opinion, very important would be information for speleologists, that due to caving for many hours per year, they might be exposed to enhanced doses caused by inhalation of radon progeny. Such knowledge is not common in Poland right now. For precise calculations of doses from radon and its progeny to tourist’s guides the data from personal dosemeters are necessary. Personal dosimetry would give possibility to assess more precisely doses for speleologists and basis for more clear planning of the time, spending underground, to optimize radiation risk.

<table>
<thead>
<tr>
<th>Classification of cavers by number of trips</th>
<th>Annual time underground (h)</th>
<th>Estimated dose from radon (calculated on basis of long term measurements) mSv/y</th>
</tr>
</thead>
<tbody>
<tr>
<td>Casual</td>
<td>24</td>
<td>0.002 - 0.46</td>
</tr>
<tr>
<td>Sporting</td>
<td>120</td>
<td>0.010 - 2.3</td>
</tr>
<tr>
<td>Occupational (group I)</td>
<td>600</td>
<td>0.02 - 11.5</td>
</tr>
<tr>
<td>Occupational (group II)</td>
<td>800</td>
<td>0.06 - 15.3</td>
</tr>
</tbody>
</table>

CONCLUSIONS

As a result of performed investigations it has been found that in Jurassic caves in Southern Poland radon level varies in a wide range. Therefore the personal dosimetry for guides, working in those caves, should be applied for more precise assessment of individual doses due to inhalation of radon progeny. Next step of the investigations will be measurements of radon level in houses located on the surface above caves.

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Assessment of the Average Effective Dose from the Analysis of $^{226}$Ra, $^{232}$Th and $^{40}$K in soil samples from Punjab, India

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ABSTRACT

The activity concentrations of the natural radionuclides namely $^{238}$Ra, $^{232}$Th and $^{40}$K is measured for soil samples collected from some locations of Malwa region of Punjab. HPGe detector, based on high-resolution gamma spectrometry system is used for the measurement of activity concentration. Radium equivalent activities are calculated for the analyzed samples to assess the radiation hazards arising due to the use of these soil samples in the construction of dwellings. The absorbed dose rate is also calculated from activity concentration of $^{226}$Ra, $^{232}$Th and $^{40}$K. The external hazard index ($H_{ex}$) for the soil samples of the study area are lower than unity, therefore, according to the Radiation Protection 112 (European Commission, 1999) report, soil from these regions is safe and can be used as a construction material without posing any significant radiological threat to population.

Topics: (6) Air pollution and environmental monitoring
Radon and Helium in Thermal and Natural Water Springs of Upper Bhagirathi, Mandakini and Yamuna Valley, Garhwal Himalaya

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ABSTRACT

Springs are manifestations of groundwater resources in the Himalayan region. Radon and helium measurements have been carried out in the thermal and natural (cold-water) springs of the Yamuna, Bhagirathi and Mandakini valley of the Garhwal Himalaya. The radon and helium concentrations in thermal springs varies from 3.2 Bq/L to 86 Bq/L and 23 to 3077 ppm, respectively. In natural (cold-water) springs radon varies from 3.4 Bq/L to 105.4 Bq/L and helium is present below the atmospheric level (< 5.2 ppm). Radon and helium shows no correlation with temperature, conductivity and TDS of water.

The thermal springs are generally present along valley in granite and augen gneiss or in quartzite rocks in close proximity of fault and thrust. Helium enrichment in certain thermal springs is possibly related with redistribution of heat and or longer residence time of deep fluids in the upper crust. The helium and temperature anomaly in three valleys is related to different permeability of the rock mass due to lower degree of fracturing and or a different depth of the faults. The radon and helium concentration in natural springs is related with the permeability of rock mass, residence time of water and localized uranium enrichment in upper rock/soil mass and in shear zones.
Soil Gas Survey in Mandi – Sundernagar Area, NW Himalaya, India: Prospecting in Fault Delineation Studies

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ABSTRACT

In an effort to signify the role of radon and helium as a productive tool to delineate some active faults and lineaments, measurements were made in the soil-gas in and around the Mandi-Sundernagar area of Himachal Pradesh. The Himachal Himalayas are broadly divided into two major tectonic zones viz the Lesser Himalayan tectogen in the south and Tethyan Himalayan tectogen in the north. The lesser Himalayan tectogen lies mainly on the southern part of Himachal Pradesh state and is bounded between Main Central Thrust (MCT) and Main Boundary Thrust (MBT). The MCT and MBT are associated with evolution of Himalayan orogeny. Besides the longitudinal lineaments several transverse lineaments occur as faults and fractures trending normally or obliquely to Himalayan trend.

As a step in identification of active faulting and structural investigation, we will discuss the specific geophysical studies applied in Mandi-Sundernagar area of Himachal Himalayas with aim of further identifying active faults and also complementing and specifying remotely sensed structures and zones. Around fifty soil gas samples were collected along and transverse to the major thrusts in the study area.
Continuous Monitoring at Three Volcanoes

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Geophysical Krakatau Team

ABSTRACT

Since a few years we have experience to install and maintain technical systems for continuous measurements of fumarole gases like CO$_2$, H$_2$S, SO$_2$ and physical parameters such as fumarole temperatures and pressures of fluids escaping from fractures at volcanic active craters (Faber et al., 2003, Teschner et al., 2005). The lengths of operating periods are strongly influenced by the activity of the volcano and by conditions of technical system components. Systems are usually placed very close to or inside a fumarole, so increasing volcanic activity may cease data acquisition efforts due to ash fallout covering solar panels and/or rocks which are ejected from the volcano, inhibiting power supply or destroy the technical monitoring equipment.

At Galeras (Colombia), Nisyros (Greece) and Krakatau (Indonesia) volcanoes gas-geochemical monitoring systems have been installed for data collection with subsequent radio transmission to an observatory with the aim to monitor and research the volcano systems in near real-time. Installed monitoring equipments are similar on all the three volcanoes. Electronic parts of the systems are powered by solar panels with battery back-up. Fumarole gases, temperatures and pressures are measured by appropriate sensors. Digitized data are transmitted and available for analyses in the observatories. Data sampling rate is typically set in the range from 5 to 15 seconds but may be adjusted if necessary. Meanwhile time series collected over weeks or months are available for the three volcanoes and some of them will be presented and discussed.

In July 2004 it was registered a change from a quiet to an active state at Galeras volcano (based on geophysical observations) and it is active up to now. This volcano behaviour gives us the opportunity to compare baseline data at low volcanic activity with those of a period with increased seismicity followed by high steam, ash and rock exhalations. In the installed monitoring system at Galeras volcano, these changes have been tracked for some parameters like gas concentrations, temperatures in and in the surroundings of fumaroles, pressure in a fumarole and in the frequency content of daily/semidiurnal variations in gas concentrations. Some of these variations have been observed prior to seismically manifested increases in the activity state of the volcano. They are considered as early
warning signals which have been observed within weeks to hours prior to the volcanic unrest, giving us an additional tool to study the volcanic dynamics. Examples of these signals from Galeras volcano will be presented. They are compared with data sets collected from the systems installed at Nisyros and Krakatau volcanoes.

Although we have successfully operated continuous monitoring systems on different volcanoes for periods of more than only a few days or weeks, we will have to work in further improvement of their technical reliability. Also, data gathered for long time intervals basically help to detect or identify more signals (events) which may contribute to understand volcano dynamics. Meteorological impact on gas-geochemical and physical signals, demonstrated here for data series collected at Nisyros volcano, has to be monitored and interpreted carefully and stresses the necessity for a continuous monitoring of volcanic exhalations with high time resolution.

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Arsenic eaters, arsenic drinkers and arsenic breathers – are we prepared for the next big volcanic eruption?

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ABSTRACT

During the last ca. 200 years science made progress to recognize and partially tackle environmental hazards. Very little planning exists for future volcanic hazards as we would like to exemplify for arsenic. Until the 19th century arsenic eating had been practiced by people in Austria. $\text{As}_2\text{O}_3$ forms as a sublimate in chimneys of smelters. The old local name for $\text{As}_2\text{O}_3$ is Hitrach (germ. Hüttenrauch = smoke from smelters). As-bearing Ag ores had been processed in Carinthia, native As is known there as well. According to legends traveling merchants (germ. Venedigermandeln = men from Venice?) traded Hitrach all over the Alpine area. It is reported that known human subjects eating arsenic became addicted but also enjoyed a long life up to 70 and more years. It had been also used to “cure” sick horses, one became “fat and brave” (Schäfer, 1860). A mineralogy book (Weidmann, 1963), recommended by the ministry of education, Austria, refers to the garlic-like smell of As vapors as an indicator of mineral chemistry. It is unknown if “butter of arsenic” ($\text{AsCl}_3$) refers to a tradition of consumption of arsenic. Nowadays the toxicity of As is well documented and USEPA and WHO published guidelines of permitted As contents in i.e. drinking water. Khan et al. (2000) introduced a purification system for As contaminated water as an important relief for the population of Bangladesh. This easy-to-assemble 3-kalshi (pitcher) system is [not tested yet if it would provide also] [is going to be tested if it would work for] purification of volcanically polluted water after explosive or long lasting effusive eruptions (http://www.geolsoc.org.uk/template.cfm?name=Super1) [utilizing diluted fumarole condensate]. Laki 1783-5 released as a minimum 1 t of Pb and Cd (Hong et al. 1996). Fumarole condensates are not representative fluids for all types of volcanic activity but are probably the most toxic variety of volcanic fluids. Most of the time they are the product of degassing magma and leaching of various rocks by hydrothermal water-rock-interaction. Their contents of As, Cd, Hg, Pb and Tl are (+/-) well documented. The fumaroles of White island, NZ release ca. 16 kg of As per day (Durand et al., 2004). The condensate of the fumaroles of La Fossa v., Vulcano island, Italy are known to contain the highest amount of As (1.2 – 30 ug/g) worldwide (Signorelli, 1997). The speciations of volcanic As gases are not determined yet. At volcanoes $\text{As}_4$ is likely; $\text{AsH}_3$ (decomp. at 300°C), $\text{AsCl}_3$, $\text{As,S}_2$ etc. are possible according to primary fluid chemistry and temperature (Mambo et al., 1991) and As ions forming i.e. kirkite ($\text{Pb}_{10}(\text{Bi, As})_6(\text{S, Se})_{19}$ – Borodaev et al. 1998). Neither exist concentration measurements in the air and evaluation of risks according to exposure time of humans. At the base of La Fossa v. no As could be detected in passive vapor collection experiments (Obenholzner et al. 2007). Some toxic metals can also be absorbed from the air by the skin. A webGIS
of Vulcano island is available at http://ereiter.free.fr/Vulcano. Gas mask producers do not test their products in volcanic environments and therefore no information exists when filters have to be changed. In case of global volcanic crisis air filter systems are not tested as well. We could demonstrate that even after ca. 0.5 years past a fumarole vent clogging experiment (La Fossa v.), pre-filtered ambient air at room temperature could mobilize arsenic from the exposed glass wool (ca. 4000 cm³). Arsenic (nanoparticles or AsH3?) passed a 0.02 µm track-etch membrane filter at ca. 1L/min and got adsorbed in H2O-filled bubblers. Detected amounts of As after 3 days are very low (ca. 1 ppb by ICPMS). FESEM/EDS could not detect As-bearing particles on the glass wool exposed to the fumarole. Leaching experiments at 100°C of the glass wool document 6 - 4000 ppb of As. On quartz grains Pb- and Tl-halogenides/sulfides nucleated. A preliminary conclusion of these data is that air filters commonly made from glass fibers can release toxic species even after a long time past a limited exposure to volcanically polluted air. It has to be emphasized that our experiment had been performed in a fumarole vent at ca. 300°C for 4 hours. It is possible that many air conditioning systems designed for normal atmospheric conditions but operated in volcanic or hydrothermal areas cannot guarantee healthy in-door air quality. Peat as an emergency filter material had been tested for reduced S species but not for toxic trace metals. Many publications exist about ombrotrophic peat bogs and their uptake of Pb and Hg from polluted atmospheres. Investigations concerning positive and negative health effects of As remain controversial (http://phys4.harvard.edu/~wilson/arsenic/arsenic_project_introduction.html); Navas-Acien, A. et al., 2006).
Nucleated As-S (light grey) and S (?) (dark grey) on ceramic filter from Bocca Nuova vent (Solfatara crater, Italy). The sample had been collected at ca. 65°C and a pH of ca. 6-7. The authors acknowledge the ESEM study (back scattered electron image) and EDX analysis by M. Hiltl (ZEISS NTS GmbH, Germany).

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Obenholzner et al. (2007), IUGG – Perugia.
GIS: A New Tool for Volcanic Gases’ Survey – A Case Study at Vulcano Island, Southern Italy

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ABSTRACT

Southern Italy is characterized by several active volcanic regions like Mt. Vesuvio, Campi Flegrei, Etna and the Aeolian Islands. Some of them are surrounded by some of the most densely populated areas in Europe like Napoli and Catania or are major targets for modern tourism, like Vulcano Island. Therefore in view of hazard mitigation it is very important to understand the structural and geological settings of these areas.

Temperature of the fumaroles is one parameter (with chemical composition of the gases) which could indicate a future eruption. In this purpose, the variations of the temperature have to be particularly studied. That is why we created:

i) a web site collecting the temperatures’ measurements of the fumaroles’ vents of La Fossa crater, Vulcano and

ii) an add-on for Google Earth showing the location of the fumaroles’ vents. The purpose of the project is to create an internet resource which saves time to all researchers as it will publish available and future temperature measurements of fumaroles from La Fossa crater, Vulcano Island.

The base of the system consists of interactive digital maps and photos of the interested area. Each map is a layer of the system. Each layer represents data for a date of temperature measurements. The user can select in a menu one or more layers to be seen in the software. The background of all layers is the geological map of Vulcano Island or an aerial photo of La Fossa crater. Clicking on the location of a fumaroles’ vent, a new web page appears, summarizing the temperature’s evolution versus time appears, the gases’ composition and photos of the fumaroles’ vent (when they are available).

During the same project, we develop an add-on for Google Earth allowing a nicer interface to locate the fumaroles’ vents. Http links between the add-on and the web site exist to view the temperature’s evolution of each fumarole.

This program can be adapted for all volcanoes and a lot of kind of data (isotopic compositions, deformation, epicenters’ location, data from reduction capacity sensor or economic, population data around the volcano). It will run on and off-line. So you can have it on CD-Rom with your own data to study them.

An internet GIS can also be a source of information for the educated tourists and a base to train local guides.
VolcanoGasML: A New Format for Geochemical Volcanic Gases Data

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ABSTRACT

Chemical analyses of volcanic gases consist of: location of sampling, date of sampling, identification of the sampling, physical and/or chemical data. Nowadays, these data are generally represented in different formats. All of them are inflexible and machine dependent.

In recent years, the World Wide Web Consortium (W3C) has developed numerous standards and recommendations for data representation and handling. They reflect the increasingly recognized needs for easy and flexible data exchange. Basically, XML is the center point of these technologies. XML is a markup language and probably the most flexible data representation.

XML becomes the most important method of transferring data between computers. VolcanoGasML is a new format, based on XML, for the chemical analyses of volcanic gases. Its definition is divided into several layers: the first one describes the general information concerning the sample, the second, which is organized in several sub-layers, contains the chemical data.

The VolcanoGasML definition, described in the XSD schema language, is divided into several layers:

Layer 1 describes the general information concerning the sample. Two of these data are required: the volcano name and the identification number. The rest is optional.
Layer 2 describes the chemical data. It is organized in several sub-layers (T and pH, major species, trace species, isotopic analyses, ratios).

The advantages of VolcanoGasML are:

Missing data in catalogs of historic geochemistry causes problems when using fixed-column formats. In VolcanoGasML, any information except the volcano’s name and the sample’s identification is optional and can be extended by error information of any length and precision.
Any XML definition can be extended in two ways, either by including additional user specific fields (tags) or by including itself into another XML definition. VolcanoGasML files can be included in any given XML file or can reference pictures which could be easily inserted in a target format.
Chemical Changes in Rainwater in a Time of Extremely Rapid Urban Development of Guangzhou, China

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ABSTRACT

A total of 90 rainwater samples collected from October 2003 to September 2004 were measured for pH value and ionic composition. The results show that pH varied from 3.29 to 7.75 with an annual volume-weighted mean of 4.38 that fell in the acidic rain range. Of the 90 rain events, the frequency of acid rain (pH<5.0) was 67%, whereas 18% recorded as neutral rain (5.0≤pH≤5.6) and 15% as alkaline rain (pH>5.6), respectively. The analyses for ionic composition indicate that the concentrations of the target ions varied over a broad range with SO$_4^{2-}$, Ca$^{2+}$, NH$_4^+$ and NO$_3^-$ as the dominant ions. The equivalent concentrations were generally in the order SO$_4^{2-}$ > Ca$^{2+}$ > NH$_4^+$ > NO$_3^-$ > Na$^+$ > Cl$^-$ > Mg$^{2+}$ > HCOO$^-$ > K$^+$ > C$_2$O$_4^{2-}$ > CH$_3$COO$. The ratio of SO$_4^{2-}$/NO$_3^-$ in the rainwater ranged from 0.63 to 27.5 with an average of 3.04, the lowest since 1985. The general increase in the concentration of NO$_3^-$ and the occasional occurrences of NO$_3^-$ dominant over SO$_4^{2-}$ as the predominant ion in the rainwater suggests that NO$_3^-$ has played a competent role in determining the rainwater acidity. On the other hand, Ca$^{2+}$ as one of the dominant ionic components was found to be the major neutralizer and it has played a significant role in neutralizing the acidity of precipitation.
Differences in Noble Gas Signatures in Two Active Geothermal Systems in the Philippines

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ABSTRACT

Noble gas isotope and bulk chemical analyses were performed on dry gas samples collected from production wells in the Bacon-Manito (Bacman) and Palinpinon geothermal fields in the Philippines. Of the noble gases measured in the Bacon–Manito geothermal field, the most significant findings were derived from R/Ra ratios of the well fluid samples, where a rather wide range of R/Ra ratios were recorded. The highest ratio is close to 7, characteristic of a mantle He source, in the vicinity of the upflow sector of the hydrothermal system. The lowest ratio, on the other hand, is slightly higher than 2, observed in the westerly and southerly wells. The peripheral fluid of the geothermal system appears to be enriched in $^4\text{He}$, thus the low ratios, most probably sourced from U and Th decay in old igneous rocks. These two end-member fluids mix, producing the range of R/Ra ratios observed in the other wells included in this study. Helium isotope ratios of Palinpinon well fluids, on the other hand, fall within a very narrow, almost constant, R/Ra range of 6.5-8.

In Palinpinon, single step and/or multi-step boiling are the main processes reflected by noble gas data, while simple single-step and multi-step boiling models do not fit the Bacman noble gas data, further signifying that mixing is the main and probably the only process controlling noble gas elemental and isotopic compositions in this geothermal system.
Tritium as Vapour-Phase Tracer in Leyte Geothermal Eothermal Production Field: Initial Results

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**ABSTRACT**

Liquid tracers form an integral part of PNOC-EDC’s resource management strategies in terms of mitigating deleterious effects of reinjection fluids. Tracers, such as naphthalene disulfonate (NDS), Iodine-125, Iodine-131, have been previously utilized mainly to validate flow paths and quantify fluids returns to the production sectors. Several proven mitigating measures have been put in place to counteract effects of injection fluids in the Tongonan resource. These include optimizing the injection capacities of the injection wells, production and injection well utilization strategy, modification of new injection well designs, and preferential injection into the liquid zone and inter-sector steam sharing arrangements.

However, with some production fields becoming more steam dominated, these liquid tracers become ineffective. In vapor-dominated or dry geothermal fields worldwide, such as in Indonesia, USA and South America, alcohols, tritium and hydrofluorocarbons (HFC) have been experimented on as vapor tracers. Some of these countries have reported successful application of these tracers in vapor-dominated systems.

PNOC-EDC in collaboration with the International Atomic Energy Agency conducted tests in Leyte Geothermal Production Field on the usability and applicability of tritium as vapour tracers in the now vapor-dominated reservoir in Tongonan. Tritium tracer was injected in well 1R8D, a reinjection well for the Tongonan sector, and breakthrough was observed in the monitored wells, such as well 2R3D, 101, 109D, 105D, 214. Tritium appeared earlier in the watery well 2R3D than in the vapor-dominated wells.

**INTRODUCTION**

The use of liquid tracers for water-dominated geothermal reservoirs is now a standard resource management tool in Philippine National Oil Company Energy Development Corporation (PNOC EDC) producing fields (i.e. Leyte, Bacon-Manito, Mindanao and Southern Negros Geothermal Production Fields), used mainly to detect reinjection flow paths and quantify the fluids that return to the production sectors. The preferred tracer being used is naphthalene disulfonate (NDS), although other tracer such as sodium fluorescein (NaF), Iodine-125, Iodine-131 have been previously utilized.

However, with some of PNOC-EDC’s producing fields already becoming more steam-dominated due to sustained exploitation, the effectiveness of liquid tracers is significantly reduced. Thus, the need to
search for and test tracers appropriate for steam-dominated types of reservoirs was envisioned. The most common tracers used in vapor-dominated geothermal reservoirs are tritium, alcohols, hydrofluorocarbons (HFC) and sodium hexafluoride (SF$_6$). These have been applied in several geothermal fields worldwide, such as Kamojang (Indonesia), Geysers (USA) and in some South American geothermal fields.

PNOC EDC, along with other countries like Indonesia, Vietnam, China, Pakistan are collaborating with the International Atomic Energy Agency (IAEA) on a research program on the “Application of Tritium and Hydrofluorocarbon as Vapor Tracers for Geothermal Reservoir Management” (RC/13130). This collaborative and coordinated research activity on gas tracing can aid PNOC EDC in the field testing of selected vapour tracers, with the end objective of vapour tracers becoming a critical tool in steamfield reservoir management. The research program aims to develop PNOC-EDC’s capabilities in gas tracing using tritium and hydrofluorocarbons (HFC).

Tritium injection comprises the first phase of the program, while the next stage involves hydrofluorocarbon application. The results of these two tracers shall be evaluated and compared for future application to other geothermal areas with developing or expanding steam zones. This paper presents the results for tritium injected in Leyte Geothermal Production Field, specifically in its Tongonan sector where the effects of mass extraction are highly manifested by pressure drawdown; injection fluid returns; and cold water inflows (Fig. 1). The original water-dominated reservoir has now been transformed into a highly two-phase or steam-dominated reservoir. This reservoir phase change brings with it unique problems in resource management. Maintaining pressure support, for instance, becomes crucial due to peripheral coldwater incursion. Rapid injection returns to the production zone likewise has detrimental effect on the reservoir, including the two-phase horizon (Dacillo, 2003). Gas tracing is expected to identify fluid flow paths between the cooler/injectate water and production sector fluids. This is important in implementing measures to mitigate if not prevent quenching of the steam horizon, which will reduce the steam supply to the Tongonan Power Plant.

![Fig. 1: Location Map of Leyte Geothermal Production Field (LGPF) showing welltracks. Underlined wells are those being monitored for tritium breakthrough. Well IR8D is the tritium injector well.](image)
Methodology

In any tracer test program, the quality of data collected and its subsequent evaluation will largely depend on the design of the program (i.e., selection of the proper injector and monitor wells). Well 1R8D was chosen as the injector well, basically because it is being used for brine injection. Tritium breakthrough is being monitored in ten production wells, namely, 101, 103, 105D, 109D, 202, 209A, 212, 214, 2R2, 2R3D. These wells are discharging almost pure steam (H $\sim$ 2600 – 2700 kJ/kg). The chemical signatures (i.e. gas indicators) of these wells have been observed to respond to the usage of well 1R8D as brine injector.

Aside from monitoring purely steam wells, wells with considerable water fraction were also chosen as additional monitor wells to determine fractionation of tritium in water and vapor phases. As a basis for selecting samples from watery wells, 80 kgs of 1.5-naphthalene disulfonate (NDS) was injected last June 14, 2006 in 1R8D. The wells that showed NDS breakthroughs are also monitored for tritium. Figure 2 shows the result of the NDS tracer test. Among the wells in Tongonan nearest to 1R8D, two wells that showed NDS breakthrough after about 19 days were wells 2R3D and 2R4D. Well 214 manifested NDS breakthrough 40 days after injection.

It is expected that similar to NDS breakthrough, tritium will also appear in 2R3D. It is postulated, further, that tritium could appear in the vapor wells much earlier given velocity differences between vapour and liquid.

As a safety consideration, the activity of the radiotracer was ensured to be below the maximum permissible concentration and above the detection limit of the scintillation counter to be used. A total of 10 curie (Ci) of tritiated water, in two 25 cc glass vials of 5 Ci each, were injected into well 1R8D on July 12, 2006. Sampling of the monitor wells commenced two days after the injection. However, two weeks prior to the injection, the monitor wells were sampled for baseline tritium content. A thrice-weekly sampling program for all the wells is currently being implemented.

Fig. 2: Plot showing the breakthrough of wells from NDS tracer injected at well 1R8D.
For wells discharging purely steam, condensate samples were collected using a stainless steel cooling coil (condenser equipment) connected to sampling ports along the two-phase lines. Wells with water component are sampled for steam condensate and its separated water using a weber separator.

RESULTS AND DISCUSSION

Figure 3 shows the plots of initial results for the five wells monitored for tritium breakthrough. The plot shows dominant and short breakthrough time in well 2R3D. The peak was attained in about 40 days and the subsequent data points showed a declining trend. The other monitor wells, 105D, 101, 109D, 214, have positive tritium unit values of between 0.5 – 8 TU. These values are within the environmental or the normal tritium values in this region, and thus cannot be interpreted as clear tritium breakthroughs in these wells. Moreover, TU values of <10 is also still considered as background values (Choudry, pers. comm., 2007). However, it can be noted based on the available data that well 214 is exhibiting an increasing trend.

Fig. 3: Plot of tritium breakthrough among the wells

Structural correlation of the fault intercepts by the wells indicated that the main path of the tritium from 1R8D to wells 2R3D (and apparently 214) is the Sambaloran Fault. Figure 4 shows the schematic of the tritium-bearing injectate fluid flowpath.

Fig. 4: Map showing the interpreted path of the tritiated fluids from 1R8D
The absence, at this point, of tritium in wells 105D, 101, 109D could indicate two things. One, that there is not enough tritium injected at well 1R8D to effect a breakthrough in these northern Tongonan wells. Or two, the tritium-bearing injectate is more diffused in this part of the reservoir, thus breakthrough could occur at a much later time. These can be validated upon the availability of more data points from future analyses.

Quantification of the tritium observed in 2R3D, using modeling softwares like TRINV (Axelsson) and Anduril (Maggio), will be done upon the availability of data points in the breakthrough curve. Currently, sampling/monitoring is still being implemented for all the production monitor wells. The other monitor wells identified as less priority wells (103, 2R2, 202, 209A, 212) will also be analyzed for tritium, albeit on selective basis, to determine probable breakthroughs in these wells.

CONCLUSION AND RECOMMENDATION

The initial results of tritium counting have confirmed breakthrough in at least one monitor well, 2R3D and a suspected breakthrough in well 214. For a complete evaluation on cooling predictions and quantification of the amount of tracer recovered from each well, complete breakthrough curves need to be obtained from these wells. Thus, it is critical that continuous monitoring of the wells be implemented until such time that enough information have been collected to allow for a complete evaluation of the study.

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Hydrocarbon Migration and Gas Survey Efficiency in Different Tectonic Settings

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ABSTRACT

Surface (near-surface) direct geochemical methods for oil and gas exploration were widely applied in different regions of the world but the efficiency of these methods varies considerably in different geotectonic settings. Analysis of the intensity of gas flux and effectiveness of gas survey at different tectonic settings has shown that gas survey is most effective in mobile folded areas (table 1). Intensive structuring, faulting, seismicity in these mobile areas favor intensive subvertical migration of hydrocarbons (HC) towards earth surface and formation in near-surface deposits and even in near-ground atmosphere its high concentration in comparison with more stable cratonic areas. Comparison of gas flux and HC gas concentration in near-surface deposits (table 2), marine bottom sediments (table 3) and near-ground atmosphere (table 4) within the Mediterranean-Alpine mobile tectonic belt and Eastern European craton confirms this conclusion. Higher efficiency of the gas survey in the cratonic basins is attained by means of deepening survey depth (150-500m) (table 5).

Table 1: Gas survey efficiency in the different geotectonic settings

<table>
<thead>
<tr>
<th>Geotectonic zones</th>
<th>Positive forecast, %</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>CRATONS:</strong></td>
<td></td>
</tr>
<tr>
<td>Eastern European</td>
<td>44</td>
</tr>
<tr>
<td>Misian (Romania)</td>
<td>70</td>
</tr>
<tr>
<td><strong>Average</strong></td>
<td>57</td>
</tr>
<tr>
<td><strong>ALPINE INTERMOUNTAIN DEPRESSIONS:</strong></td>
<td></td>
</tr>
<tr>
<td>Pannonian (Eastern Europe)</td>
<td>100</td>
</tr>
<tr>
<td>South Caspian (Azerbaijan part)</td>
<td>87</td>
</tr>
<tr>
<td>Middle-Lower Kura (Azerbaijan)</td>
<td>75</td>
</tr>
<tr>
<td>Rhion (Georgia)</td>
<td>76</td>
</tr>
<tr>
<td><strong>Average</strong></td>
<td>84</td>
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</tbody>
</table>

Table 2: Gas flux intensity in different geostructural zones

<table>
<thead>
<tr>
<th>Geotectonic zone</th>
<th>CO₂</th>
<th>CH₄</th>
<th>N₂</th>
<th>H₂</th>
<th>He</th>
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</thead>
<tbody>
<tr>
<td>Ukrain and Baltic shield (craton)</td>
<td>6.5</td>
<td>8.0</td>
<td>3.0</td>
<td>6.5</td>
<td>0.3</td>
</tr>
<tr>
<td>Alpine folded zone</td>
<td>150-200</td>
<td>200-250</td>
<td>30-35</td>
<td>7.5</td>
<td>0.03</td>
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</table>
Table 3: Gas content (average) in the bottom sediments of seas in the different geostructural zones

<table>
<thead>
<tr>
<th>Seas/Geotectonic zones</th>
<th>Number of samples</th>
<th>He, $10^{-5}$ cm$^3$/kg</th>
<th>CH$_4$, cm$^3$/kg</th>
</tr>
</thead>
<tbody>
<tr>
<td>The Barents-Norwegian Seas (Craton)</td>
<td>340</td>
<td>350</td>
<td>1700</td>
</tr>
<tr>
<td>The Black Sea (Alpine tectonic belt)</td>
<td>310</td>
<td>560</td>
<td>70000</td>
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</tbody>
</table>

Table 4: Methane content (ppm) in near-ground atmosphere over different geostructural zones

<table>
<thead>
<tr>
<th>Geotectonic zones</th>
<th>Areas</th>
<th>Turkmenistan</th>
<th>Caspian sea</th>
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</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>2.6 (74)*</td>
<td>2.27 (7)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>3.75 (29)</td>
<td>3.44 (3)</td>
</tr>
</tbody>
</table>

*CH$_4$ average content (number of samples)

Table 5: Effectiveness of the gas survey on platforms (Eastern European and Siberian) at the different depth levels

<table>
<thead>
<tr>
<th>Country/Region</th>
<th>Number of studied fields</th>
<th>Number of fields confirmed by HC anomalies</th>
<th>Effectiveness, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Russia (Volgograd)</td>
<td>21</td>
<td>Well depth 2-3 m</td>
<td>43</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Well depth 20-30 m</td>
<td>71</td>
</tr>
<tr>
<td>Kazakhstan</td>
<td>14</td>
<td></td>
<td>50</td>
</tr>
<tr>
<td>Russia (Volgograd)</td>
<td>4</td>
<td></td>
<td>67</td>
</tr>
<tr>
<td>Russia (Eastern Siberia)</td>
<td>3</td>
<td></td>
<td>67</td>
</tr>
<tr>
<td><strong>Total/Average</strong></td>
<td><strong>21</strong></td>
<td><strong>14</strong></td>
<td><strong>66</strong></td>
</tr>
<tr>
<td>Russia (Saratov)</td>
<td>25</td>
<td>Well depth 100-150 m</td>
<td>88</td>
</tr>
<tr>
<td>Russia (Krasnodar)</td>
<td>6</td>
<td></td>
<td>83</td>
</tr>
<tr>
<td>Russia (Groznyi)</td>
<td>3</td>
<td></td>
<td>67</td>
</tr>
<tr>
<td>Ukrain</td>
<td>4</td>
<td></td>
<td>75</td>
</tr>
<tr>
<td><strong>Total/Average</strong></td>
<td><strong>38</strong></td>
<td><strong>32</strong></td>
<td><strong>84</strong></td>
</tr>
</tbody>
</table>
Dynamics of CH$_4$ and N$_2$O Emission Flux from Bhitarkanika Mangrove Sediments of Eastern Orissa, India

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ABSTRACT

Coastal areas have been recognized as major marine contributor to the atmospheric flux of CH$_4$ and especially N$_2$O. Mangrove forests receive high inputs of organic C from the forest detritus and large-scale loading of terrestrial N from the anthropogenic activities in the intensely habituated hinterland. Experimental in situ determination of emission fluxes exhibited large-scale spatial and temporal variations. Emission fluxes yielded rates between 0.09 to 3.23 mg CH$_4$.m$^{-2}$.h$^{-1}$ and 0.19 to 253.78 ng N$_2$O.m$^{-2}$.h$^{-1}$. CH$_4$ and N$_2$O emission fluxes varied greatly depending upon the season and was lowest during the pre-monsoon and followed the order of monsoon > post-monsoon > pre-monsoon. CH$_4$ and N$_2$O yields varied depending upon both the magnitude and chemical nature of the sediment C and N sources and microbial activity that was in turn affected by the salinity. Results indicate that mangroves constitute a significant and hitherto unrecognized source of greenhouse gases to the global GHG budget.
Diffuse CO$_2$ emission and volcanic activity

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**ABSTRACT**

Recent observations of diffuse CO$_2$ emission from volcanic systems through continuous and discrete monitoring clearly suggest the close relationship between volcanic activity and this geochemical parameter. Therefore, monitoring diffuse CO$_2$ emission is becoming an important geochemical tool for seismic-volcanic surveillance programs at active volcanoes.

**INTRODUCTION**

Over the last 20 years, studies of diffuse CO$_2$ degassing carried out at volcanic areas have shown that volcanoes release large amounts of CO$_2$ to the atmosphere even during periods of non-eruptive activity (Baubron et al., 1990; Allard et al., 1991; Farrar et al., 1995; Pérez et al., 1996; Chiodini et al., 1998; Sorey et al., 1998; Giammanco et al., 1998; Rogie et al., 2001; Hernández et al., 2001a, 2001b; Salazar et al., 2001; Notsu et al., 2005). Since CO$_2$ is the major gas species after water mostly generated by subsurface magma degassing bodies (Gerlach and Graeber, 1985), as CO$_2$ travels upward by advective-diffusive transport mechanisms and manifest itself at ground surface, changes over time in its flux pattern can provide information about subsurface magma movement. Monitoring diffuse CO$_2$ emission is becoming an important geochemical tool for seismic-volcanic surveillance programs at active volcanoes (Hernández et al., 2001a, Rogie et al., 2001; Salazar et al., 2002; Carapezza et al., 2004; Granieri et al., 2006; Pérez et al., 2006). Diffuse degassing surveys covering a specific area of the volcanic edifice have been the most common monitoring tool to evaluate the spatial distribution of diffuse CO$_2$ degassing, its relationship with the main structural features of the volcano and to estimate the total CO$_2$ output to the atmosphere (Chiodini et al., 1998, 2001; Frondini et al., 2004; Notsu et al., 2004; Granieri et al., 2006; Pérez et al., 2006). However, in the last 7 years, continuous monitoring of CO$_2$ efflux have provided an important information for volcanic surveillance and seismotectonic monitoring (Rogie et al., 2001; Salazar et al., 2002; Carapezza et al., 2004; Pérez et al., 2003, 2004, 2006).

**DIFFUSE CO2 DEGASSING AND VOLCANIC ACTIVITY INDEX**

An additional approach to evaluate the relationship between diffuse CO$_2$ emission and volcanic activity is to compare diffuse CO$_2$ degassing rates from volcanoes with different eruptive history. The total output of diffuse CO$_2$ emission from the volcano cannot be used as geochemical parameter for
this evaluation since this value is strongly dependent of the covered area of the survey. Statistical-graphical analysis of diffuse CO$_2$ degassing surveys following Sinclair’s method (1973) is a simple and useful tool to detect overlapping geochemical populations: background and peak populations. Peak values of diffuse CO$_2$ degassing are mainly due to deep perturbations of the magmatic-hydrothermal system on the surface environment. Therefore, mean values of CO$_2$ ground efflux peak population could be a useful geochemical parameter to compare diffuse CO$_2$ degassing rate among different volcanic systems under similar volcano-tectonic and climatological conditions. The binary plot of the mean values of CO$_2$ ground efflux peak population, as a multiple of the background mean values of CO$_2$ ground efflux, versus the number of historical eruptions per year - Volcanic Activity Index - related to several volcanic systems with similar volcano-tectonic and climatological conditions shows a strong relationship ($r^2 = 0.99$) indicating clearly the close relationship between diffuse CO$_2$ and volcanic activity (Fig. 1).

Fig. 1: Relationship between diffuse CO$_2$ emission and Volcanic Activity Index in the oceanic volcanic islands of the Canaries, Cape Verde and Galápagos.

FORECASTING VOLCANIC EVENTS AND DIFFUSE CO$_2$ EMISSION

The detection of precursors is crucial for volcanic forecasting research. Material Failure Forecast Method (FFM) proposed by Voight, 1988, after his experience with the eruption of St. Helens volcano, is applied to forecast the time for the earthquake and volcanic eruption occurrences using diffuse CO$_2$ emission as observable. Empirical model of material failure is described using the equation:

$$\left( \frac{d^2\Omega}{dt^2} \right) = A \left( \frac{d\Omega}{dt} \right)^n$$  (1)

where $\Omega$ is the observable (deformation, seismic energy, gas emission, etc.), and A and n are two different constants. An experiment series, assumed to be solution of such equation, can be used to extrapolate the descending sections of the inverse of the observable in order to get a forecast time of a geological event. In the case of CO$_2$ efflux, the term of the equation 1 is the change with time of the diffuse degassing rate. The FFM graphical technique is based on an inverse representation of the characteristic parameter rate ($1/\Phi_{CO2}$) versus time. A volcanic eruption or seismic event time is found by simple extrapolation of the data set or linear fit towards the time axis. At this time the parameter
would reach an infinite value. The application of this approach on the observed changes of soil CO\textsubscript{2} efflux measured at the summit of Teide volcano (Tenerife, Spain) prior a near by seismic event of magnitude 2.7 provided an excellent result. (Figs. 2a and 2b). The differences between the real time and the forecast time for the earthquake were less than 1 hour (Fig. 3).

Fig. 2: Temporal variations of diffuse CO\textsubscript{2} emission at Teide volcano (b) related to a seismic event at, Tenerife, Canary Islands (a).

Fig. 3: MFF method applied for the precursory geochemical signature of the seismic even
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Gas Discharges from the Nyiragongo Volcano (D.R. Congo) and Surrounding Areas: Implications for Environmental Impact and CO₂-Related Risks from Dry Vents

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ABSTRACT

Nyiragongo volcano resumed its activity in January 2002 with several productive vents from where about $20 \times 10^6$ m$^3$ of highly fluid lava were discharged. Lava flows were emitted from a NS oriented fracture system that cut the southern flank. In May 2002 a small lava lake appeared on the crater summit that is still growing and releasing a gas phase mainly composed by SO$_2$ (up to 60 kton/day), CO$_2$, HCl and HF. The prevailing EW blowing winds displace the acidic gas-rich volcanic plume up to few hundreds of km, affecting forests, crops and the quality of water resources for the local populations. Besides, the northern shore of the Lake Kivu, at about 20-30 km from the volcanic summit, is characterized by the presence of CO$_2$-rich dry vents whose behavior is intimately related to the volcanic degassing activity of Nyiragongo. Low-cost remediation systems to mitigate the environmental impact and the CO$_2$ hazards deriving from these volcanic phenomena are evaluated.

INTRODUCTION

Volcanic degassing activity (Oppenheimer et al., 2003) is a threatening phenomenon that can affect a certain area from months to years. The resulting impact on the environment may be devastating (e.g. Thorarinsson, 1979; Cronin & Sharp, 2002) and able to alter the daily life of the affected populations. Acidic rains, crop destruction, cattle deaths, effects on the surficial and ground water systems are examples of the pressure that the degassing activity may act. Furthermore, distal areas of active and quiescent volcanic systems are often characterized by long-term degassing activity, mainly consisting of CO$_2$-rich gas exhalations due to the removal of the most acidic gases through scrubbing processes (Symond et al., 2001). The Nyiragongo volcanic edifice (3,470 m high, with a 1.3 km wide crater), after experiencing the January 2002 eruptive event that has discharged through a NS-oriented fracture system in the southern flank of the volcano about $20 \times 10^6$ m$^3$ of highly fluid lava flows, two of which cut the city of Goma (ca. 500,000 inhabitants), 15 km away from the crater summit (Tedesco et al.,
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2007b), resumed its activity in the main crater. Here, a lava lake has emplaced since May 2002 and it is presently giving rise to a acidic gas-rich volcanic plume that has occasionally been detected as far as 300 km to the West, being mainly displaced by the EW-oriented blowing winds. Moreover, more gentle, though important, degassing activity is present in the northern shoreline of Lake Kivu (Fig. 1).

A large number (almost one hundred sites have been surveyed) of CO\textsubscript{2}-rich dry vents is present and they are located in topographic depressions inside the lava fields that were formed by either Nyiragongo or Nyamulagira (a very active volcano of the former-Zaire located in a remote area at about 12 km NW from Nyiragongo) volcanic activity or inside the monogenetic volcanoes that distribute mainly along NE-SW and NS fault systems. These vents (named locally as mazuku, “evil’s wind”) are lethal traps when the atmospheric conditions allow the accumulation of CO\textsubscript{2}, this gas being heavier than air, and, consequently, they represent a serious hazard for the populations leaving nearby, particularly for elderly people and kids. It is indeed frequent to find dead lizards and other reptiles, birds and monkeys. In this paper, we have carried out a geochemical survey on the meteoric waters and on fine scoria, ash material and Pelee’s hairs emitted from the summit crater downwind that interact with the volcanic plume. Geochemical investigations on both the crater gases and the dry vents have been done to verify the relationships between these typologies of gas discharges. The main aim is that to suggest low-cost measures and recommendations to mitigate these gas-related risks.

![Diagram of Nyiragongo and Nyamulagira volcanoes with a view of the inner crater from the 2nd platform and the CO\textsubscript{2} degassing area in the northern shoreline of Lake Kivu.](image)

**Figure 1** – Location of Nyiragongo and Nyamulagira volcanoes with a view of the inner crater from the 2\textsuperscript{nd} platform and the CO\textsubscript{2} degassing area in the northern shoreline of Lake Kivu.

**MATERIAL AND METHODS**

Meteoric waters have been collected in different locations, i.e. from both the crater summit and the degassing area located between Goma and Sake villages (Fig. 1), through plastic bottles and/or scorimeters from which scoria, ashes and Pelee’s hair were sampled. The crater fumaroles are located in the fissures resulting from the cracking of the 2\textsuperscript{nd} platform (up to 400 °C) that was formed by the cooling of the 1995 lava lake (Tedesco, 2002/2003) and between the 1\textsuperscript{st} (formed by the cooling of the 1977 lava lake, Durieux, 2002/2003) and the 2\textsuperscript{nd} platform (80-85 °C). Crater gases have been collected by using a titanium tube connected to a dewar glass line at which pre-evacuated 50 mL gas vials filled with 4 M NaOH solution and a 0.15 M Cd(OH)\textsubscript{2} suspension were attached. Condensates were sampled by cooling down (at about 63 °C) with water 2 glass tubes connected to the titanium tube. Gases from the dry-vents have been sampled with the same type of gas vials connected to either a plastic tube or up-side-down positioned funnel. The pyroclastic material was gently crushed in an agate mortar and 1
g was let to react with 50 mL of MilliQ water for 12 hours during which periodical swirling was carried. The suspension was then centrifuged and the supernatant was analysed for the determination of Cl, F and SO$_4$ contents by ion chromatography. After drying and then weighing the pyroclastic material, 50 mL of MilliQ water were once again added and let to react for 1 week, after which the analysis of main anions was performed. The same procedure was repeated after 14 days of leaching.

RESULTS AND DISCUSSION

Crater and mazuku gases

Temperatures up to 400 °C have been measured in the fumarolic field eastwards of the presently active lava lake. The gas composition of the crater gases is relatively poor in H$_2$O (up to 48,000 μmol/mol), whereas CO$_2$ contents reaches 70,000 μmol/mol. SO$_2$, H$_2$S, HCl and HF are up to 900, 614, 5,600 and 20,000 μmol/mol, respectively, with HCl/SO$_2$ and HF/SO$_2$ ratios up to 5 and 17. Hydrogen, CH$_4$ and CO have abundances of 3,500, 780 and 2,258 μmol/mol, respectively. The δ$^{13}$C-CO$_2$ values are relatively constant, being comprised between −4 and −3.5‰ (V-PDB), whereas those of $^{3}$He/$^{4}$He range from 6.4 to 8.2 (as R/Ra) (Tedesco et al., 2007a). The mazuku gases are dominated by CO$_2$ (up to 70 % by vol.) with variable contents of atmospheric compounds, whose presence is likely due to ingressation of air, allowed by secondary permeability, in the old to recent lava fields that host the gas vents. The δ$^{13}$C-CO$_2$ values are slightly more negative than those measured at the crater summit, being included between −12 and −4.8‰ (V-PDB) (Vaselli et al., 2002/2003), whereas the R/Ra ratios are as high as 7.5 (Tedesco et al., 2007a).

Meteoric waters and scoria, ash and Pelee’s hair leachates

Concentrations of SO$_4$, F and Cl were determined in rain waters and ashes that, carrying dissolved volcanic gases and aerosol-derived compounds, respectively, can be considered the liquid and solid carriers of the volcanic plume chemical components released into the atmosphere. These analyses have been performed in samples collected in a span of time of about three years (2003-2006), from the surrounding areas of Nyiragongo volcano, mainly along the prevailing winds that displace the volcanic plume to the West. Rainfalls with low pH (<2) and high concentrations of Cl, SO$_4$ and F (up to 1,000, 500 and 300 mg/L), deriving from the dissolution of plume-related volcanic gases, were collected close to the crater rim. More than the 50% of the rain water samples have F contents (up to 30 mg/L) higher than the maximum level suggested by WHO, i.e. 1.5 mg/L. Scorias and Pelee’s hairs, after 12 hours-leaching, release F, Cl and SO$_4$ whose concentrations are up to 1,500 mg/kg. The prolonged leaching procedure suggests that while Cl and S-compounds are promptly dissolved, F-salts show a different behaviour. One third of F-salts (e.g. NaF and CaSiF$_6$) readily dissolve (12 hours leaching), whereas others (e.g. CaF$_2$, AlF$_3$, Ca$_5$(PO$_4$)F) persist longer (two weeks leaching).

CONCLUSIONS

Villages around the western flank of Nyiragongo are inhabited by at least 50,000 people who have no direct access to drinkable water. As a consequence, they are forced to use rainwater. The effects of the acidic gases released from the volcanic plume are evident on the crops and plants located downwind. As meteoric waters are driven through gutter pipes to water tanks and then distributed to the population, in situ measurements of, at least, pH and F contents should be performed before any use. The GVO (Goma Volcanological Observatory) is sporadically trying to carry out chemical analysis on both meteoric and surficial waters. In case of poor water quality, filters composed by Ca-bearing material, e.g. tomatoes, bones, should be used for the removal of F via the precipitation of CaF$_2$. It
should also be taken into serious account the possibility to provide medical controls on the population and, particularly, on the kids since they may develop symptoms of dental and/or crippling fluorosis, the latter being a lethal disease.

The mazuku gases represent a daily hazard and most of the people are not aware of the fact that the atmospheric conditions play a fundamental role in favouring the CO$_2$ accumulation, particularly in windless, high pressure and cloudy days. Some of the most important mazuku areas are indicated by warning signs in two languages (French and Swahili) but the presence of at least 100 spots from where CO$_2$ is released makes difficult to cover the whole degassing area, corresponding to the northern shoreline of Lake Kivu. Direct contacts with the local people via GVO personnel may help in this respect particularly considering that most of the deaths regards kids who ignore the risks associated to the CO$_2$ discharge.

By a scientific point of view, mazukus represent the preferential paths from which distal volcanic CO$_2$-rich degassing occurs. The study of these gas emissions may be extremely useful to both understand the degassing mechanisms and the plumbing system of Nyiragongo volcano and assess in terms of budget the amount of CO$_2$ discharged from an area that is emitting SO$_2$ quantity comparable to those of Etna volcano (Carn, 2002/2003).

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Continuous Measurement of Geo-chemical Parameters in Aggressive Environment

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ABSTRACT

To measure precise longtime data from geochemical parameters for studies of deep fluid streams in volcanic areas, hydro geological studies and reservoir management in geothermal fields robust and high reliable measuring systems are necessary.

A progress in this field is presented in this paper with the development of a new versatile measuring system called MEDAS (MEDAS – Modular Environmental Data Acquisition System) based on experiences and recent results from different research groups. MEDAS is an innovative multi-parameter station, which can continuously record as a function of time up to more than 100 geochemical and physical parameters suitable for many applications. A microcomputer system inside the MEDAS handles data exchange, data management and control and it is connected to a modular sensor system. The number of sensors and modules can be selected according to the needs at the measuring sites.

The main problem was the shielding of the system against the aggressive environment and to develop sensors, which survive in extreme acidic gases like in geothermal fields or in fumaroles. In the presentation the system will be described the technical solutions for this big problem. With this system it was possible to measure Radon and Thoron gas concentrations over longtime in from deep reservoirs directly with high time resolution.

A MEDAS has been installed in four production wells in the Mahanagdong production sector of the Leyte Geothermal Production Field located in the island of Leyte, central Philippines. This field is chosen because: 1) it is the largest geothermal field in the Philippines with five separate power plants with total installed capacity of about 700 MW, and 2) the area is bisected by the Philippine Fault, a major left-lateral transcurrent fault similar to the San Andreas fault.

Results of long time measurement on Radon, Thoron and CO$_2$ concentrations; gas flow, temperature and humidity; water temperature and pH; the Redox potential and conductivity will be presented. These parameters will be correlated with the historical and current data from the PNOC EDC established monitoring set-up for seismicity, micro-gravity and precise levelling surveys, wellhead pressure trends and well bore chemistry changes from monthly production sampling.
Efficient and sustainable production of geothermal energy requires constant monitoring of changes occurring in the reservoir. These changes, which may result from mass extraction for production, waste fluid injection for disposal and pressure support, and from natural geologic processes, are usually manifested in the chemistry and physical characteristics of the wells. Experience has also shown that these changes are related to the structure of the reservoir—the faults that transect the field as well as smaller fractures contained in the reservoir rocks. Identification and evaluation of chemical changes, and their correlation with the structural features, require among others the constant analysis of hot brine and gases discharged by the wells.

Changes in water and gas chemistry, for example, can indicate: 1) lowering in the water level of the reservoir, 2) invasion of cold and degassed re-injection fluids, 3) entry of shallow acidic steam condensates and deep corrosive volcanic-related fluids, 4) precursor of an earthquake, etc. Any of these changes can significantly alter the short- and long-term viability of the geothermal operation. Hence, it is critical that up-to-date collection and analysis of water and gases be undertaken. However, since almost all of the production wells are connected to the power plant, it is rarely possible to disconnect the wells in order to collect samples for analysis because such disconnection will result in shortfall in power generation. In addition, the process is time-consuming and significant lapse is achieved from sample collection to the availability of the information. There is therefore a pressing need for a continuous and on-line system of measuring chemical parameters in the field.

DATA AND RESULTS

In Mahanagdong, the CO$_2$ and Rn gas levels of the monitored wells were likewise measured and correlated with the recorded local seismic events. Based on the CO$_2$ and Rn trends shown in Fig. 1, wells MG18D, MG19 and MG23D have relatively stable CO$_2$ and Rn gas levels. The fluctuations observed in the data may be correlated to the local seismic events within the project site of PNOC-EDC. No major events were observed within the period September to November 2005. Thus correlation of Rn and CO$_2$ gas trends during micro seismicity event could be established.

Figure 2 shows the Cl trends of geothermal fluids from wells MG18D, MG19 and MG23D as measured on-line using the MEDAS. The Cl data obtained may still be used to check the reservoir processes which may have affected these wells. Though, care should be taken in interpreting these data, and correlation with other parameters should be conducted. Below are some of the observations deduced from the Cl plots (Fig. 2)

1. The decreasing trend in Cl of well MG18D between September to October may reflect the unstable condition of the well after its bullhead acid zing, which also coincided with the lowering of the fluid pH during this period. Although this is not reflected in its CO$_2$ trends.

2. The general increase in Cl level of well MG23D in November as well as the slight decline in CO$_2$ level may indicate recovery from effects of cooler, degassed and low saline fluids mixing. The inflow of this type of water was the dominant reservoir process observed for this well. The increased Cl after the higher seismic activity in beginning of November can be caused by a higher deep fluid inflow in the reservoir.
Fig. 1: Correlation of Radon and CO$_2$ gas trends with the recorded local seismic events.
Fig. 2: Fluid salinity trends (in terms of chloride) as measured on-line using MEDAS.

Fig. 3: Longtime measurement of the radon concentration in MG23 D

Figure 3 demonstrate that after 2 years the radon sensors are still working without influence of the aggressive gases in the geothermal field. The missing valued are caused by the missing of cooling water for the mini separators. In this time the steam flow was stopped and only the radon in the measuring chamber was decayed. Stable working periods without interruption was in May 2006 and in November 2006.
SUMMARY

The MEDAS system was able to demonstrate its capability to collect and record data continuously from the monitored production wells. Moreover, no major events were observed within the period September to November 2005 thus correlation of Rn and CO₂ gas trends during small micro-seismicity event could be established.

As for the second objective of monitoring on-line the chemistry and physical characteristics of producing wells to evaluate reservoir changes, initial data indicated good correlation with the pH, Cl, CO₂ and redox potential. The pH level measured on-line through MEDAS generally gave values closer to the actual fluid pH of the three monitored wells. Fluctuations though in the readings (pH<4.0) given by the MEDAS indicate the need for periodic recalibration of the pH electrodes to pH standard solutions.

The special radon detector technology gave the chance to get long-time measurement in aggressive environment longer than 2 years without replacement of the detectors.

REFERENCE

Methods and Apparatus for Feeding Samples of Gas at Controlled Pressure into Gas Chromatographs (International Patent US 11/718,896 and IT/12.11.04 ITA PI20040083) and its Application in Geochemical Surveillance

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ABSTRACT

This new apparatus (International patent Caprai-CNR pending no. PCT/IB2005/001568) for use in the analysis of gas mixtures can be fitted on one or more gas chromatographers working in parallel or at different times, and used to adjust the internal pressure of the gas to the value most convenient for introducing the sample into the analyzer. It can also be used for only one or two points of calibration of a pure gas standard (no preparation of a particular external standard is necessary). No detector overloading of any kind will occur.

MAIN USES

It can be applied to any kind of gas analysis, but is particularly suited to environmental and geochemical investigations.
1. Where a number of runs are required, there is no need to take different samples of gas from the flask.
2. We have a continual knowledge of the internal pressure of the flasks.
3. We achieve similar conditions for standards and samples.
4. We simplify the standardization procedure.
5. We can increase pressure so as to introduce more absolute small quantities of a given component.

Advantages

The advantages of this system include:
1. Analytical error is minimized because pressure is completely under control.
2. One quantity of sample only can be analyzed several times in different gas chromatographers.
3. The pressure inside the flasks is legible.
4. Both sample and standard can be introduced at the same pressure.
5. Excellent standardization can be achieved with two calibration points.
6. Errors in preparation of standards can be avoided.
7. The pressure of low-pressure samples can be increased.
Natural Radioactive Isotopes in Glacier Studies

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ABSTRACT

Radon 222 (222Rn) is a naturally radioactive noble gas occurring in the decay series of Uranium 238 (238U). After creation, if it is located close to grain boundaries, it has the possibility to join the gaseous or liquid surroundings in contact with the hosting rocks and soils. Soluble in water, radon can be carried over longer distances during its mean life time of 5.5 days. Radon can be used in nature as a suitable tracer for studying short-lived phenomena.

In hydrology, a classic isotope hydrograph separation leads to a quantitatively portioning of water runoff into a stream or a river among contributions from different waters: superficial runoff, interflow water and groundwater (Kraemer et al., 1998). Environmental isotopic tracers, such as 222Rn and 18O were used to separate the runoff into the different components during rain events (Kies et al., 2005). Unlike chemical tracers, isotopic tracers are relatively conservative in reactions with catchments’ material; they are chemically and physically inert. Isotope hydrograph separation is based on the assumption that the isotopic compositions (e.g. 222Rn) of the involved runoff compartments are distinctly different and that the isotopic signal within each compartment stays constant in space and time.

The present paper relates the possibility to use radon, in a similar way as described before, for hydrograph separation in glaciers.

Information how water flows at the glacier bed is important for the understanding of two major problems in glacier dynamics: the detailed mechanisms of glacier sliding and the associated deformation of sub glacial sediments as well as the causes and mechanics of glacier surges. The surface meltwater is the prevalent contribution to the water output in temperate glaciers. In summer water flows on the ice surface in a network of channels; much of the water enters the glacier through cracks and vertical passages. Water emerges at the terminus in more or less large channels. Understanding the flow system in and under the glacier is a major problem. In winter the high pressure resulting from the downward gradient of ice flow leads to the closing of channels when surface melting stops.

Glacier meltwater has negligible radon concentrations, as there exist nearly no sources of radon in/on the ice; without contact to rocks water will keep negligible levels. Depending on the duration of contact with rocks and till at the glacier bed, melt water will be charged with radon that can be
measured at the resurgence, if the time delay between radon charge and resurgence is not above about 4 decay periods of radon, i.e. 15 days.

Meltwater at the resurgence is a mixture from different contributions: direct melt water and rapid flowing water has very low radon concentrations whereas melt water in contact with the bed rocks and sediments is charged with radon. Variations of radon concentrations over time, together with continuous information on conductivity, temperature, pH, dissolved gases as CO$_2$ and oxygen, can lead to a sort of glacier hydrograph separation. The obtained information is useful in the overall study of the behavior of the glacier and has to be discussed in combination with the results from meteorological parameters and ice movement.

A major problem of radon is the easy degassing of radon when water is flowing in not confined aquifers. Therefore the ideal investigation locations are glaciers with artesian meltwater outflow. In Hornsund (Spitsbergen) measurements from meltwater were performed starting September 2006 at two different glaciers: Werenskioldbreen and Ariebreen, close to the Polish Polar Station. In September 2006, at the end of the melting period, meltwater was sampled at open outflow tunnels at Ariebreen. Especially due to turbulent water flow, radon had degassed. Mean radon concentrations were 0.070 +/- 0.020 Bq/l. The effective electrical conductivity of 53.3 $\mu$S/cm documented meltwater that had been in contact with the basement but, as expected.

Fig.1: Location of the sampling points at Werenskioldbreen together with the measurements done on September 20th 2006.

The main outflows of Werenskioldbreen, a model glacier of land based target glaciers of the IPY project GLACIOodyn, are artesian. Different water channels were sampled in mid-September 2006, at the end of the melting period (fig. 1). Most of them showed to be actually surface water, or water not
in contact with bedrock. Radon concentrations varied between 0.15 to 0.29 Bq/l, the low electrical conductivity of 5 μS/cm indicated superficial water. The measurements performed at the largest artesian outflow at the central part of the glacier front gave radon concentrations of 18 to 22 Bq/l, the electrical conductivities ranged from 76.6 to 77.2 μS/cm. The conductivity measurements were similar to those reported from previous campaigns at the same time period (Pälli et al., 2002). The geochemical fingerprint of the water at the terminus of Werenskioldbreen was:

\[
\begin{align*}
&^{238}\text{U}: \quad 8.9 \pm 0.4 \ \text{mBq/l}; \quad ^{234}\text{U}: \quad 9.9 \pm 0.4 \ \text{mBq/l}; \quad ^{235}\text{U}: \quad 0.30 \pm 0.02 \ \text{mBq/l} \\
&^{232}\text{Th}: \quad 0.6 \pm 0.1 \ \text{mBq/l}; \quad ^{230}\text{Th}: \quad 0.7 \pm 0.1 \ \text{mBq/l}; \quad ^{228}\text{Th}: \quad 1.7 \pm 0.1 \ \text{mBq/l} \\
&^{226}\text{Ra}: \quad 7.6 \pm 0.7 \ \text{mBq/l}; \quad ^{210}\text{Pb}: \quad 5.5 \pm 0.7 \ \text{mBq/l}; \quad ^{210}\text{Po}: \quad 7.3 \pm 1.8 \ \text{mBq/l.}
\end{align*}
\]

Encouraged by the unexpected high radon concentrations we decided a study of radon concentration over longer time periods together with at least one other parameter measured continuously. We used temperature, electrical conductivity, pH and dissolved oxygen.

The main aim of a stay of 3 weeks at Hornsund in April 2007 was to confirm the measurements of September and that radon concentrations are high enough to allow its use as tracer.

At 7 days, expeditions were conducted to the terminus of Werenskioldbreen with samplings there where flowing water could be detected.

Together with radon, were measured in situ electrical conductivity, precise water temperature (1 m°C resolution) and partly pH and dissolved oxygen; radon and pH measurements were done in the laboratory at the base. 12 chosen water samples were taken to the Radiation Physics Laboratory at the University of Luxembourg for the complete investigation of natural radionuclides. Radon measurements were performed on a portable liquid scintillation device from Hidex (Triathler) with α-β separation, limit of detection 10 mBq/l. Temperature and conductivity were performed by a combined electric resistivity - temperature (res 1 m°C) logger from RBR (Canada). A multi logger TROLL measured temperature, el. conductivity, pH, ORP, dissolved oxygen.

Over 70 samples were analyzed at the chemical laboratory at the base.

The radon measurements confirmed the findings from September 2006 that radon is present in subglacier water in very high amounts (same order of magnitude as in the Jurassic sandstone aquifer in Luxembourg, our study object in Luxembourg!).

At Werenskioldbreen we measured radon concentrations varying in the range of 2 orders of magnitude for different locations, between very low concentrations, lower than 0.5 Bq/l, up to 28 Bq/l. We concentrated on 3 different areas where running water could be accessed, either water was flowing out of cracks on ice domes, or running water, often under pressure, was accessible after breaking the ice cover. Some water outputs could be sampled over days before the outflow was frozen. During the sampling period the temperature varied between -20 °C to -5 °C, for one day the temperature went up to +5 °C. Inside an area radon variations were rather small, but big variations were observed between the different zones. The same was observed with conductivity with values between 100 and 500 μS/cm. At one outflow conductivity as high as 2000 μS/cm was measured together with the highest radon concentration of 28 Bq/l. Less important variations were observed for the other parameters.
The most analyzed outflows were in the Kvisla River area north of the central moraine. A small intermediate moraine subdivides this area in two zones: the northern one (B) close to the lateral moraine with extremely low radon concentrations (with two exceptions) but electrical conductivities of 200 $\mu$S/cm, proving contact with the bedrock. The zone closer to the central moraine (A) showed the highest radon concentrations around 20 Bq/l.

It was not possible to take a sample at the location of the outflow location sampled in September south of the central moraine. The presence of outflow domes were noticed but it was impossible to access flowing water.

After inspection of the most southern glacier front we were able to detect open outflows here (C). The measured radon concentrations were rather constant 10 Bq/l; roughly half compared to those in zone A. An interesting fact was that, with 100 $\mu$S/cm, electrical conductivity was also slightly two times less than in A. Except the locations closed to the Northern lateral moraine, a trend of increased radon concentration coupled with increased conductivity could be noticed.

First results from measurements done after April 2007, show at most of the measured locations very low radon concentrations around 0.1 Bq/l. Decreasing concentrations were observed with the ongoing melting period. In 2 outflows radon concentrations were still 3 Bq/l in July, at the maximum of thaw. A continuous device was unfortunately put out of service due to fountain like outflows.

To conclude, we are confident that radon is a promising new parameter to investigate dynamics of glaciers. Measured continuously over the melting period, its variations can give a hint to the built-up of different contributions.

We would like to express our gratitude to the Polish Polar Research Station Hornsund, Svalbard.

REFERENCES


Methane Seepage Hazard for Urban Development Areas – a Case Study

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ABSTRACT

The paper describes a case of methane emission in an urban development area in Romania, generating important risks to the local population and buildings. Until now, more than 100 houses were built in the concerned area. Twenty five wells were drilled in order to assess the extension of the emission area, and to identify the source of gas. Most likely, methane is coming from an unknown deep reservoir, through faults. The gas emission represents a serious hazard for the local population, due to its explosive and asphyxiating potential.

INTRODUCTION

A significant amount of data showing the large extent of offshore and onshore methane seepage worldwide was gathered, especially in the last decade. In some conditions, methane flux from geologic reservoirs or generated in shallow environments by biogenic processes can represent important hazards for the local communities. However, few cases were presented in the scientific literature until now. Etiope et al. (2005) describe methane and hydrogen sulphide emissions in NW Peloponnesus (Western Greece). The gas seeps in the harbour area of Katakolo put into danger the facilities and buildings. The relatively high content of hydrogen sulphide may induce health risks as well. Another methane emission affecting a local elementary school in Chatsworth, California, was reflected by mass-media since the 1980’s. It seems that gas was generated by the decay of organic matter buried in the alluvium some 30,000 years ago. An interesting case occurring in Romania, similar to the previous in some features, is described below. As agreed with the local authorities, the exact location will be named after the investigations will be finished, and final conclusions will be drawn.

GEOLOGICAL SETTING

The study area is located on a Precambrian platform covered by Mesozoic and Neozoic sediments. The metamorphic basement supports a pile of Triassic, Upper Cretaceous, and Miocene deposits. The Upper Miocene level, more than 2,000 m thick, contains oil and gas reservoirs. Its lower part, more permeable, is dominated by marls intercalated with sands and sandstones, while the upper part
contains fine-grained, impermeable sediments. This entire suite is covered by Quaternary alluvial deposits. The Miocene sedimentary formations are almost horizontal, slightly bending to the south-east. The seismic activity in the area is important, with intensity grade up to VIII on the MSK scale, and a recurrence time of a few decades. The closest hydrocarbon reservoir is located a few km eastward from the concerned area. The structure contains some gas-bearing horizons, located more than 1,500 m deep.

RESULTS AND DISCUSSION

The study is focused on the natural gas emissions identified in the suburban area of a 200,000 inhabitants town. A dwelling area composed of two-floor houses started to develop, and more than 100 houses of the total of 250 are built, and some of the owners already moved in. In that moment, a methane leak in the cellar of a house was accidentally discovered. The works were stopped and an investigation program for identifying the gas source and extension of the concerned area was proposed.

Until now, 24 shallow wells were drilled, with an average depth of 15 m. Additionally, a 96 m deep well was drilled, in order to clarify a deeper geological structure of the area. The lithological composition was found to be relatively similar in the investigated wells, with alternating permeable and impermeable deposits. An important flux of methane, in the order of 2 to 4 m$^3$ h$^{-1}$, was identified in some of the wells, the gas burning freely at the end of the well casing. In other wells, the gas is bubbling in groundwater, that is rising to about 4.5 m depth. Some wells do not show any gas emission.

Very likely, gas is migrating through faults from a deep reservoir, possibly located at a certain distance from the concerned area. The chemical composition of the gas is an argument for its deep origin. A surface geochemical survey, aimed at assessing extension and intensity of the methane emission anomaly, including methane isotopic analyses, is in progress.

Methane accumulation, especially in confined spaces, is able to induce a potential explosion and asphyxiation risk. Long term exposure to methane may represent a health hazard for people that are asthmatic, allergic, or chemically sensitive. The high content of methane in the ambient air may affect the human brain. As a consequence, the situation can be defined as a severe one. More detailed research is needed in order to design technical solutions able to increase the safety of the site.

REFERENCE

Environmental Radioactivity Monitoring around the Tusham Ring Complex, Haryana: A Case Study

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ABSTRACT

In present study, long-term measurements by using the Solid State Nuclear Track Detectors (LR-115 Type II), have been carried out to investigate the distribution of environmental radioactivity concentrations in the dwellings around Tusham ring complex, which is famous for acid volcanic & the associated high heat producing granitic rock formations. The indoor radon concentrations and the inhalation dose, have been measured in the wide range of dwellings around this ring complex area using both the peliculable & non-peliculable type of the SSNTDs. The indoor radon concentration levels in these dwellings have been found to be varying from 120.5± 95 to 915.2 ± 233 Bqm-3. The indoor radon levels have not only been found to be varying with the mode of construction of houses & building materials utilized, but also especially on their location with respect to the nearby high heat producing granite rocks. The indoor radon concentration levels at some places, especially those on or close to granite rock formations have been found to be considerably higher and even exceeding the international recommended limits of the ICRP. The annual effective dose equivalent in the study area has been found to be varying from 2.13 to 15.6mSv/y. Another objective of the study was to investigate a possible correlation between indoor radon and gamma activity in this region of high heat producing rock formations and a good correlation between indoor radon & gamma activities has been found in case of dwellings situated around the exposed high heat producing (HPP) granitic rock formations.
Method of Simultaneous Measurements of Radon and Radon Progeny in Air

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ABSTRACT

Investigation of radon and radon progeny levels outdoors is a difficult task due to low concentrations of these radionuclides. A liquid scintillation counting is a measuring technique, broadly applied in environmental monitoring of different radionuclides. One of the possible applications of liquid scintillation counting is measurement of radon progeny. There are certain advantages of this method, especially high counting efficiency for alpha and beta particles emitted by $^{218}$Po, $^{214}$Pb, $^{214}$Bi and $^{214}$Po.

This advantage has been pointed out several years ago, when such methods were applied to calibration of portable monitors for radon progeny, especially due to the fact that in the case of radon progeny no standard atmosphere exists. Radon progeny might be collected on a filter, which after immersion in the liquid scintillator became transparent and could be counted without significant quenching. Therefore such a method can be stated as an absolute one and used very widely for radon progeny monitoring. The main drawback for a long time was the lack of the portable LS counters, however in the last several years such counters have become available.

Furthermore, radon concentration in air can be measured by application of charcoal canisters to collect radon and further extraction of radon into a liquid scintillator. A very quick measurement (5 minutes grab sampling) for outdoor radon is possible, when the charcoal layer is very thin. A combination of both methods enables quick and reliable measurements of radon and radon progeny concentration in outdoor air as well as in dwellings.

Simultaneous measurement of radon and progeny by LSC methods

It’s possible to measure radon concentration with the use of charcoal canisters and LSC and it’s possible to measure radon progeny concentration by means of air filtration and filter measurement in LSC.

One of the approaches to this problem was to apply charcoal in the scintillation vials for radon monitoring (but the exposure time was at least 6 hours) and simultaneously to make grab sampling of radon progeny and measurement in portable LS spectrometer – Triathler [Chalupnik and Kies, 2003]. Such technique can be used for measurement in dwellings, or other places with relatively stable radon concentration. But for measurements in outdoor air the response time of charcoal canisters in vials is too slow. Therefore a new technique of charcoal exposure is purposed – in this case single layer, open face charcoal detector can be used. Despite the fact, that such detector is very sensitive to air humidity, the response time of such detector is very quick, only several minutes (5-8 minutes). It enables simultaneous sampling of air for radon and radon progeny monitoring.
The method of simultaneous measurement of radon and radon progeny in air by means of LSC techniques can be described as follows:

- This method requires two LS spectrometers – low level counter for radon measurements and a portable LS spectrometer for radon progeny monitoring.
- For the sampling of air for radon progeny a pump with high flow-rate is necessary (at least 100 l/min.) and filters, which become transparent in toluene based liquid scintillator (membrane or fibreglass filters).
- The sampling of radon progeny is done during 10 minutes and after that filter with collected aerosols is merge into vial with liquid scintillator and measured, accordingly to Thomas method in the portable LS spectrometer - Triathler.
- For radon monitoring charcoal detector is required, which is exposed during the same period as air sampling for radon progeny as a single layer, open face bed.
- The exposure time should be between 5-8 minutes and after the exposure the charcoal must be quickly transferred into the vial, which must be capped immediately.
- Extraction of radon from charcoal and measurement of the obtained sample can be done in the laboratory. Measurement should be done by means of low level LS spectrometer to ensure low detection limit for radon. If the LS spectrometer is equipped in alpha/beta separation feature, the LLD level for radon concentration is lower.

SUMMARY

We tested a possibility of application of a portable LS counter (Triathler, Hidex Oy, Finland) for measurement of radon progeny concentration in air. Tests were performed in Centre Universitaire, Luxembourg. Results of preliminary measurements were satisfactory.

The application of high volume pump enables application of the method for outdoor measurements. The sampling time must be short enough to allow an accurate calculation of potential alpha energy concentration – usually 10 minutes, followed by the transfer of the filter into liquid scintillator and measurement done, accordingly to Thomas method. Thus the detection limit can be very low, in case of potential alpha energy concentration at level $\approx 0.001 \mu$J/m$^3$. We would like to point out, that the method can be stated as the absolute one, and problems with the calibration can be avoided.

Application of charcoal detectors enables measurement of low concentration of radon in air, when single layer, open face detectors are used. The exposure time of such detectors shouldn’t exceed 10 minutes. The extraction and measurement is done in laboratory conditions. When low level LS spectrometer is used, like Quantulus, than the lower limit of detection for this method can reach 0.5 Bq/m$^3$. Sampling of air for radon and radon progeny can done simultaneously and detection limits for both methods as sufficient to allow measurements of latter values even in outdoor air with very good precision and accuracy.

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Geological Evidence of Natural Radioactivity in Southern Tamil Nadu, India - Impact on the Human, Animal Health and Natural Environment

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ABSTRACT

Detection and quantification of radioactivity has become significant in recent years with the recognition of the importance and urgency of environmental problems around the world. With the increased public concern over radiation safety, the studies on natural background radiation areas provide a good scope for evaluating biological effects caused by low-level radiation exposures on a long-term basis. The radioactivity even in minor quantities will build up in human body and subsequently, lead to unknown and unpredictable health complications in particular those related to sustainable development, agricultural production, habitat, ecosystem and forest. This paper presents a study report of Radioactivity surveys conducted in Kanyakumari district of southern Tamil Nadu using portable gamma radiation survey meters to map the distribution of natural radioactivity. Detailed radiation exposure rates at closely spaced intervals have been obtained along the beach sectors from Thengapattanam to Kanyakumari and the surrounding hinterlands. High intrinsic radioagenic source, with radiation exposure rate ranging from 500 to 2600 $\mu$R/h, have been identified in the weathered hillocks around Inayam and Midalam localities. In addition, a very high radiation exposure rate ranging from 1000 to 6000 $\mu$R/h were found within the rock population of syenite body and in the boulders around Puttetti. Further, the radiation exposure rate along the connected beaches around Midalam, Kurumpanai and Manavalakurichi is observed to be lower than that of hinterlands ranging from 200 to 1600 $\mu$R/h. These observed radiation levels are presumably the highest concentration in southern India. Study, indicates a very high intrinsic radiogenic source in the hinterlands around Puttetti, Inayam and Alanchi in western part of Kanyakumari district. The presence of radioactivity in this region can affect the biological condition of the inhabitants. People living in a region of high natural background radiation are expected to receive significant radiation, which may get accumulated in the human body. Inhalation of Thoron and Radon gases emerging out of these minerals may cause concern for health disorders. Dense population is exposed to the natural radiation from the beach placers since ages. People living in the region are expected to receive significant radiation, which may get accumulated in the human body. Public concerns of radiation exposure of safety in high background areas are of great social relevance. Significant radiation doses will certainly enter the human body as most of the people have the habit of sitting and sleeping on the floor.
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