

## Chemical characteristics of arc magma and seafloor sulfide deposits on back-arc spreading center and off-ridge volcanoes

URABE, Tetsuro<sup>1\*</sup>, KANAMORI, Shuntaro<sup>1</sup>, On-board Scientists of TAIGA Mariana Cruise<sup>2</sup>

<sup>1</sup>University of Tokyo, <sup>2</sup>TAIGA Project

The arc basalt of Mariana Trough is characterized by fluid-dominated chemistry. Stolper and Newman (1994) suggested that the H<sub>2</sub>O-enriched arc magma of the Mariana Trough could be formed as melting mixture between MORB-type mantle source and H<sub>2</sub>O-rich component.

Backarc Spreading Center and the off-ridge volcanoes in Southern Mariana Trough are selected as one of the main targets of TAIGA Project, due mainly to four known active hydrothermal fields; Snail site (120°57.19'N, 143°37.16'E, depth:2861m) and Yamanaka site (120°56.64'N, 143°36.80'E, depth: 2823m) on the spreading-axis, Archean site (120°56.35'N, 143°37.89'E, depth: 2986m), and Pika site (120°55.13'N, 143°38.92'E, depth: 2773m) on the off-axis seamount. Nine BMS (Benthic Multi-coring System) drillings were conducted during the Hakurei-Maru No.2 cruise in June 2010.

Both basalt glasses and associated seafloor massive sulfide ores from these sites are analyzed for their major/minor element contents using ICP-MS. Multi-element plot of basalt glass indicates that both on-axis and off-axis basalts have similar pattern and are categorized as arc basalt and/or arc basaltic andesite. As, Ba, Pb and other elements in sulfide ores show systematic variation across the axis and reflect the influence of subduction zone fluids.

Keywords: Mariana Trough, backarc spreading, hydrothermal deposit, TAIGA project, minor element, incompatible element

## Geomorphological and geological characteristics of hydrothermal system in the southern Mariana Trough

YOSHIKAWA, Shuro<sup>1\*</sup>, Kyoko Okino<sup>1</sup>, Miho Asada<sup>2</sup>, Yoshifumi Nogi<sup>3</sup>, Nobutatsu Mochizuki<sup>4</sup>

<sup>1</sup>AORI, Univ. of Tokyo, <sup>2</sup>JAMSTEC, <sup>3</sup>NIPR, <sup>4</sup>Kumamoto University

To examine the relationship between geomorphological characteristics and hydrothermal activity, and relation of tectonic and volcanic control to hydrothermal system in the southern Mariana Trough, we investigated the five hydrothermal sites using near-bottom swath mapping data collected by SEABAT7125AUV on the AUV Urashima during the cruise YK09-08, and dive observation data acquired by the submersible Shinkai6500 during the cruise YK10-11. The principal findings are as follows. 1) The two on-axis hydrothermal sites (Snail and Yamanaka sites) are possibly locally developed on a 4th order spreading segment, in association with diking events. The three off-axis sites (Archean, Urashima, and Pika sites) appear to represent locations of sustained hydrothermal activity, which has created relatively large-scale hydrothermal features as compared with those observed in the on-axis area. The formation of off-axis hydrothermal sites likely closely related to an off-axis magma upwelling system, as evidenced by the absence of fault systems and the undeformed morphology of the mound and the knoll. 2) The three off-axis hydrothermal sites are mainly composed of breccias assemblages probably originated in hydrothermal activity with black smoker venting. In those areas, numerous ridge lines (height, mainly 1-6 m), conically-shaped mound (height, 50-100; diameter, 250-300m), and bumpy seabed texture are found, in contrast, the on-axis sites are characterized by no ridge lines, and white smoker and shimmering observed on dome-shaped pillow mound (height, 5-30 m; diameter, 250-320 m). Hence, distribution of the ridge lines, mound morphology, and bumpy seabed textures likely to correlate with hydrothermal activity.

## Electromagnetic constraints on a melting region beneath the central Mariana back-arc spreading ridge

MATSUNO, Tetsuo<sup>1\*</sup>, EVANS, Rob. L.<sup>2</sup>, SEAMA, Nobukazu<sup>1</sup>

<sup>1</sup>Kobe University, <sup>2</sup>Woods Hole Oceanographic Institution, <sup>3</sup>JAMSTEC

An electrical resistivity profile across the central Mariana subduction system shows high resistivities in the region of upper mantle beneath the back-arc spreading ridge where melt is supposed to exist. The question arises as to why the 2D magnetotelluric (MT) experiment failed to image the melt at the place where seismic attenuation structures showed a signature of the melt but seismic velocity structures did not strongly show it. We have run forward models that test possible melt geometries that are consistent with other observations from the region, and that we use to place upper bounds on the possible extent of melt beneath the spreading center. The tests are carried out by examining the differences in MT response between a starting 2D model which is essentially the result of inversion of data from the region and models with 3D melt bodies superimposed on this background starting model. If differences in the predicted MT responses are above a threshold level determined by the uncertainties in the field data, then we argue that such a feature should be resolvable and therefore is not compatible with our data. Features which do not greatly perturb the MT responses, within the error, could be considered acceptable. The tests with the across-strike real data profile and an along-strike hypothetical data profile show that perturbations in the off-diagonal elements of the MT response behave similarly in both profiles, and that weak signals from melt bodies in diagonal elements of the MT response may not be detected within the observational error. Taking into accounting melting regions suggested by other geophysical studies, as well as the likely effects of melt focusing, the most likely melt region has a pyramid shape and a resistivity of 100 Ohm-m, whose value is close to a dry olivine on mantle adiabat and could indicate the interconnected silicate melt of ~1%-0.1%. In contrast to the superfast spreading southern East Pacific Rise, the 3D melt region with a modest detectable melt supply suggests that buoyant mantle upwelling is the dominant process beneath the slow-spreading central Mariana back-arc spreading ridge.

## Appearance of iron-dependent chemosynthetic ecosystem at the Southern Mariana Trough

KATO, Shingo<sup>1\*</sup>, NAKAMURA, Kentaro<sup>2</sup>, TOKI, Tomohiro<sup>3</sup>, ISHIBASHI, Jun-ichiro<sup>4</sup>, TSUNOGAI, Urumu<sup>5</sup>, HIROTA, Akinari<sup>6</sup>, Moriya Ohkuma<sup>1</sup>, SUZUKI, Katsuhiko<sup>7</sup>, YAMAGISHI, Akihiko<sup>8</sup>

<sup>1</sup>JCM, RIKEN-BRC, <sup>2</sup>PEL, JAMSTEC, <sup>3</sup>Faculty of Science, University of the Ryukyus, <sup>4</sup>Department of Earth and Planetary Sciences, Faculty of Science, Kyushu University, <sup>5</sup>Faculty of Science, Hokkaido University, <sup>6</sup>Volcanic activity Research Group, Institute of Geology and Geoinformation, AIST, <sup>7</sup>IFREE, JAMSTEC, <sup>8</sup>Department of Molecular Biology, Tokyo University of Pharmacy and Life Science

Microbial community structures in deep-sea hydrothermal vent fields may be constrained by available energy yields provided by inorganic redox reactions. Variability of fluid geochemistry of deep-sea hydrothermal vents in three geographically different areas of the Southern Mariana Trough (SMT) have been reported, and an unparalleled microbiological dataset of various samples (i.e., sulfide structures of active vents, iron-rich mats, borehole fluids and ambient seawater) collected in these areas are available for comparative analyses. Here, we summarize the microbiological and geochemical characteristics in the SMT and assess the relationship between the microbial community structures and the fluid geochemistry in the SMT by thermodynamic modeling. In particular, aerobic sulfide-oxidation has the potential to yield large amounts of bioavailable energy in the vent fluids, which is consistent with the detection of species related to sulfide-oxidizing bacteria (such as *Thiomicrospira* in the Gammaproteobacteria and *Sulfurimonas* in the Epsilonproteobacteria). Notably, the bioavailable energy yield from aerobic iron-oxidation reactions in the fluids collected from man-made boreholes and several natural vents were comparable to or higher than those from sulfide-oxidation. This is also consistent with the detection of species related to iron-oxidizing bacteria (*Mariprofundus* in the Zetaproteobacteria) in such samples. The combination of microbiological, geochemical and thermodynamic analyses in the SMT will provide novel insights into the presence and significance of iron-based microbial ecosystems in deep-sea hydrothermal fields.

Keywords: Chemosynthetic ecosystem, Deep-sea hydrothermal vent field, Iron-oxidizing chemolithoautotrophic bacteria, Thermodynamic modeling, Crustal fluid

## History of hydrothermal activity in the Mariana Trough estimated by population structure of vent-endemic snails

KOJIMA, Shigeaki<sup>1\*</sup>, Hiroka Hidaka<sup>1</sup>, Yasunori Kano<sup>2</sup>, Hiromi Watanabe<sup>3</sup>

<sup>1</sup>Graduate School of frontier Science, The University of Tokyo, <sup>2</sup>Atomosphere and Ocean Research Institute, The University of Tokyo, <sup>3</sup>Japan Agency for Marine-Earth Science and Technology

A hairy snail *Alviniconcha hessleri* is endemic to hydrothermal vent fields in the Mariana Trough and the dominant species of chemosynthesis-based communities in this sea area. We analyzed the genetic population structure of this species using specimens collected at five vent sites in the Mariana Trough, namely, the Alice Springs Field in the central Mariana Trough, the Forecast Vent Field in the southern Mariana Trough, and the Snail, Archaean, and Urashima sites in the southernmost part of the trough. A local population of the Forecast Vent Field showed the highest genetic diversity among five local populations. Individuals of *A. hessleri* were divided into two genetically deviated groups. The first group contained more individuals and showed higher genetic diversity than the second group. Although individuals of both groups were collected at all five vent sites, frequency of the second group were very low in the Alice Springs Field. Both groups were shown to have experienced rapid expansion of population size and estimated ages of the expansion is older for the first group than the second one. Within the trough, the southward gene flow (larval dispersal) was estimated to be much larger than the northward one. Based on these results, we reconstruct the population history of this species, namely, the reduction of population size and the isolation between the local populations of the central and southern regions, genetic deviation between them, the expansion of the central population, and the expansion of the southern population. In this presentation, we discuss about the correspondence between the ages of these events estimated on the basis of the molecular phylogenetic analysis of provannids, which contains *A. hessleri*, and the history of hydrothermal activities estimated by geochemical studies.

Keywords: Marina Trough, *Alviniconcha hessleri*, population structure, history of hydrothermal activity

## Population genetic structure of deep-sea vent chemolithoautotrophs

MINO, Sayaka<sup>1\*</sup>, Satoshi Nakagawa<sup>1</sup>, Junichi Miyazaki<sup>2</sup>, Makita Hiroko<sup>2</sup>, Tomoo Watsuji<sup>2</sup>, Takuro Nunoura<sup>2</sup>, Masahiro Yamamoto<sup>2</sup>, Ken Takai<sup>2</sup>, Tomoo Sawabe<sup>1</sup>

<sup>1</sup>Hokkaido Univ., <sup>2</sup>JAMSTEC

Deep-sea hydrothermal fields are areas on the seafloor of high biological productivity fueled primarily by microbial chemosynthesis. Chemolithoautotrophic *Epsilonproteobacteria* with an ability to utilize inorganic substrates such as H<sub>2</sub>S and H<sub>2</sub> are dominant in deep-sea hydrothermal vents around the world. Beside the non-pathogenic deep-sea chemolithoautotrophs, the class *Epsilonproteobacteria* contains important human pathogens, i.e. *Helicobacter pylori* and *Campylobacter jejuni*. These pathogenic *Epsilonproteobacteria* have extremely high frequencies of genetic mutation and horizontal gene transfer. Little is known, however, about deep-sea epsilonproteobacterial population genetic structure. In our previous study, we clarified that *Epsilonproteobacteria* Group B population were geographically separated, and that they had high mutation rates. However, there are still many questions to resolve, e.g. whether these trends are common to all epsilonproteobacterial subgroups and non-epsilonproteobacterial chemolithoautotrophs. In this study, we performed multi-locus sequence analysis (MLSA) on deep-sea vent chemolithoautotrophs of *Epsilonproteobacteria* Group A, B, F and the genus *Persephonella* to clarify their population genetic structures.

Chemolithoautotrophic strains used in this study were isolated from chimney structures, vent fluids, and hydrothermal sediments. The hydrothermal samples were collected from geographically separated hydrothermal areas of the South Mariana Trough, Okinawa Trough and Central Indian ridge. We carried out various population genetic analyses including the construction of phylogenetic trees, estimation of mutation and recombination rates based on sequences of various housekeeping genes.

The MLSA revealed that the deep-sea chemolithoautotrophs commonly had extensive genetic diversity and their population genetic structure were influenced by geographic location. In addition, we found that their genetic diversity were controlled by mutation rather than recombination.

In our presentation, we will discuss the biogeography and evolution of deep-sea chemolithoautotrophs.

## Diversity of seafloor massive sulfide ores in the Okinawa Trough

ISHIBASHI, Jun-ichiro<sup>1\*</sup>, OOKI, Mitsuhiro<sup>1</sup>, SHIMADA, Kazuhiko<sup>1</sup>, NOZAKI, Tatsuo<sup>2</sup>, YOSHIZUMI, Ryoto<sup>3</sup>, URABE, Tetsuro<sup>3</sup>, SATO, Hiroshi<sup>4</sup>

<sup>1</sup>Faculty of Science, Kyushu University, <sup>2</sup>JAMSTEC, IFREE, <sup>3</sup>School of Science, University of Tokyo, <sup>4</sup>Senshu University

The Okinawa Trough is one of exploration target areas for seafloor mineral resources around Japan, where eight active hydrothermal fields have been discovered. Since the Okinawa Trough is located in the continental margin, these hydrothermal systems develop within sediment layer. Subseafloor hydrothermal fluid flow within sediment layer may enhance accumulation of hydrothermal precipitates and preservation of hydrothermal ores, therefore large size sulfide ore deposits are expected to be discovered in the Okinawa Trough.

In 2011, two dive expeditions were conducted under framework of Taiga project, focusing on studies of seafloor hydrothermal ore deposits in the Okinawa Trough. NT11-15 expedition conducted in August investigated Jade and Hakurei sites in the Izena Cauldron, and active sites in the Iheya North Knoll. NT11-20 expedition conducted from September to October visited Minami-Ensei Knoll, Yoron Knoll, Izena Cauldron, Irabu Knoll and Hatoma Knoll. In this presentation, we will discuss diversity and commonality of mineralogy and geochemistry among hydrothermal ores collected from these active hydrothermal fields.

In some active hydrothermal fields in the Okinawa Trough, occurrence of sulfide and sulfate deposits is separately observed. Only sulfate precipitates were observed in chimney structures above the seafloor, while sulfide deposits were observed in mound structures buried in the seafloor. This signature could be attributed to phase separation of hydrothermal fluid just beneath the seafloor. Phase separation generates two different types of (vapor-rich and brine-rich) hydrothermal fluid, which could be related with sulfate and sulfide mineralization.

Hydrothermal ore deposits in the Okinawa Trough are characterized as enrichment in Zn and Pb, which corresponds to dominant occurrence of sphalerite, wurtzite and galena. Among trace elements, enrichment in Ag is notable. Ag is mainly included in tetrahedrite being associated with replacement of As by Sb. These chemical signatures could be attributed to formation of hydrothermal ores at rather low temperature.

Keywords: hydrothermal activity, volcanic massive sulfide, seafloor hydrothermal ore, back-arc basin

## Microbial community and activity beneath the hydrothermal vent at the Iheya North field of the Mid-Okinawa Trough

YANAGAWA, Katsunori<sup>1\*</sup>, Takuro Nunoura<sup>2</sup>, KAWAGUCCI, Shinsuke<sup>2</sup>, Miho Hirai<sup>2</sup>, SUNAMURA, Michinari<sup>1</sup>, TAKAI, Ken<sup>2</sup>

<sup>1</sup>Department of Earth and Planetary Science, University of Tokyo, <sup>2</sup>JAMSTEC, SUGAR

Deep-sea hydrothermal fluid harbors peculiar microbial community apparently different from that in the ambient seawater. These distinctive microbes are regarded as messengers transported along hydrothermal vein from subvent biosphere. We have explored scientific drilling at the hydrothermal vent on the Iheya North field of the Mid-Okinawa Trough in Sept. 2010 (IODP Expedition 331) and collected core sample of subseafloor biosphere beneath the hydrothermal field.

IODP Site C0014 was located 450 m east off the main hydrothermal vent. Temperature exceeded the limit of life at the depth of approximately 40 m below the seafloor. Both microscopic and molecular-based analysis successfully detected microbial populations in the shallower zone at 20 mbsf. Microbial community definitely shifted according to physicochemical conditions of their habitat. Additionally, microbial activities of methanogenesis, anaerobic methane oxidation, and acetogenesis were consistent with the geochemical interpretations. These results represented the direct evidence of active subvent biosphere on the edge of uninhabitable zone beneath the hydrothermal vent.

Site C0017 located 1.6 km east off the hydrothermal vent is a potential seawater recharge zone of the hydrothermal system, where seawater penetrates into the oceanic crust. The lithostratigraphy consists of characteristic coarse angular pumiceous gravel, lying above and below hemipelagic mud, suggesting that this layer is probable main pathway of entrained seawater. As is the case with deep sedimentary environment, uncultivated archaeal groups were dominantly detected in the hemipelagic sediment above and below pumice layer. In contrast, ammonia oxidizing archaea of order Nitrosopumilales were outstandingly dominant at pumice layer of around 20 mbsf, possible because of oxidative seawater transport. Though hydrothermal components were not observed from the entire core of Site C0017, deeper layer at around 150 mbsf showed high temperature up to 90°C. There, microbial community structure was similar to that from limit of habitable zone of Site C0014. Our data suggests that high temperature gradient due to hydrothermal activity might be one of the control factors of gradual change of microbial community structure in the subvent biosphere.

Keywords: hydrothermal vent, subvent biosphere, methanogenesis, anaerobic oxidation of methane



## Decrease of arsenate adsorption onto bacteriogenic iron oxides (BIOS) by the presence of organic material

KIKUCHI, Sakiko<sup>1\*</sup>, TAKAHASHI Yoshio<sup>1</sup>

<sup>1</sup>Graduate school of science, Hiroshima University

The adsorption behavior of trace elements onto iron (Fe) oxides has been well demonstrated for their importance in water chemistry. Especially, bacterial-induced Fe oxides (Bacteriogenic iron oxides: BIOS) are of common interest because of their ubiquity and characteristics of adsorption of various ions. Indeed, it is previously reported that the adsorption of heavy metal ions onto BIOS exhibited adsorption trend different from synthetic iron oxides [1]. In this study, arsenate adsorption behavior onto (A) synthetic ferrihydrite, (B) natural BIOS collected from Okinawa hydrothermal vent, and (C) synthetic BIOS obtained by incubation of iron-oxidizing bacterium (*Mariprofundus ferroxydans*) were compared. BIOS synthesis was performed using a set of diffusion cells by which we can obtain pure BIOS free from other inorganic and organic materials which are abundant in natural BIOS (e.g., silica, clay minerals, and other ions adsorbed on BIOS). Adsorption experiments were performed under sea water condition (I: 0.70 M; initial arsenate concentration: 70 mg/L; adsorbent: approx. 0.5 mg) as a function of pH 4-10. Iron mineral species of iron oxides were specified by Fe K-edge X-ray absorption fine structure (XAFS) [2] and adsorption structure of arsenate was examined by As K-edge XAFS analysis.

Iron K-edge XAFS analysis revealed that both natural and synthetic BIOS consisted mainly of ferrihydrite with 45-55 % of highly amorphous Fe hydroxides that is characterized by the primitive Fe hydrolysis stages. The crystal size was nano-scale which was smaller than the synthetic ferrihydrite. Thus, it was expected that BIOS should have more arsenate adsorption capacity than synthetic ferrihydrite. However, the amount of arsenate adsorbed onto each iron oxides decreased in the order of synthetic ferrihydrite > natural BIOS = synthetic BIOS with a same adsorption trend as a function of pH. XAFS and micro-XRF analysis indicated that arsenate was mainly adsorbed onto Fe phase within natural and synthetic BIOS forming inner-sphere complexation to the Fe oxides. These results were consistent with previous results on As adsorbed onto synthetic ferrihydrite. Contrary to their reduced crystal particle size, specific surface areas of synthetic BIOS was decreased by 25% from synthetic ferrihydrite, which is possibly caused by the coprecipitation of Fe oxides with organic materials [3]. Thus, it is suggested that strong aggregation of Fe particles by the presence of organic materials reduces (i) the surface area and/or (ii) the active adsorption site within BIOS, which may ultimately result in the decrease of the arsenate adsorption onto BIOS. These results also suggest that direct and indirect effects of organic materials should be taken into account to evaluate the anion adsorption onto BIOS.

[1] Katsoyiannis et al. (2006) *Water Research* 40, 3646.

[2] S. Kikuchi et al. (2011) *Chem. Lett.* 40, 680-681.

[3] Mikkuta et al. (2008) *Geochim. Cosmochim. Acta.* 72, 1111.

Keywords: iron oxides, arsenate, ferrihydrite, iron-oxidizing bacteria, XAFS, adsorption

## Solid-water distributions of Mo and W in water-sediment system under various redox condition

ERIKO, Omori<sup>1</sup>, TAKAHASHI, Yoshio<sup>1\*</sup>, KAWAGUCCI, Shinsuke<sup>2</sup>, KASHIWABARA, Teruhiko<sup>2</sup>, YOKOYAMA, Yuka<sup>1</sup>, MIYOSHI, Youko<sup>3</sup>, ISHIBASHI, Jun-ichiro<sup>3</sup>

<sup>1</sup>Hiroshima University, <sup>2</sup>JAMSTEC, <sup>3</sup>Kyushu University

The concentration of W dissolved in the modern ocean is considerably lower than that of Mo, although Mo and W have similar chemical characteristics, since both elements belong to Group 6. It is considered that W is adsorbed significantly onto iron-manganese oxides, while in contrast Mo is difficult to adsorb on the iron-manganese oxide due to the difference in the surface complexes formed at the oxide surface (Kashiwabara et al., 2011). On the other hand, under the reductive ocean such as in the early earth, the concentration of these trace elements might be controlled by adsorption onto sulfides. In this system, it is assumed that Mo is adsorbed significantly onto the sulfide and is removed from seawater, while in contrast W is difficult to adsorb on the sulfide and dissolved in seawater. In other words, by the changes of redox condition due to the evolution of the atmosphere from low oxygen to high oxygen concentrations, the water solubilities of Mo and W in the primordial ocean are expected to be contrastive to the modern ocean. However, water solubilities of Mo and W under reductive ocean are not well known in particular from chemical process within the phenomena. Thus, purpose of this study is to clarify the solid-water distributions of Mo and W under reductive condition by adsorption experiments and analysis of marine sediments with their interstitial waters.

Based on the adsorption experiments, adsorption of Mo and W onto pyrite was larger at lower pH, possibly due to the larger positive charges induced at lower pH. However, it was found that adsorption distribution coefficient of Mo was about 8 times larger than that of W. XANES spectra showed that adsorption forms, or chemical species, of the both elements were also sulfide. However, the formation of Mo sulfide was not affected by pH, whereas formation of W sulfide did not proceed under high pH condition where W sulfide was not observed. Thus, the water solubility of W is most likely greater than that of Mo in the sediment under reductive condition.

The preference of formation of sulfur-bound species for Mo than W and larger affinity of Mo to the sulfide than W were the opposite result to what we found for their solid-water distributions under oxic condition. In the latter system, W forms more stable surface complex to iron-manganese oxides, which results in the larger solubility of Mo in water compared with W.

To confirm the suggestions from laboratory studies, abundances and speciation analyses were conducted for the hydrothermal water-sediment system in the mid-Okinawa Trough, especially for Mo. For the sediment samples, variation of chemical species of Fe and S estimated by their K-edge XANES indicates that redox condition became reductive at greater depth in the sediment. As a result of the distribution between sediment and interstitial water, a larger  $K_d$  values were obtained at deeper layer for Mo. In addition, XANES spectra indicated that dominant species of Mo was oxygen-bound species in oxidative shallow layer, while tetravalent sulfide was dominant in reductive deep layer.

Keywords: Molybdenum, Tungsten, Redox condition, Solubility, XAFS, Sediment