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BBG21-P01

Room:Convention Hall

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## Experimental constraints on hydrogen generation and their linkage to the eco-system in ridge system

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Deep-sea hydrothermal vents were discovered in the late 1970s (Corliss et al., 1979; Edmond et al., 1979). Since then, they have been considered as a possible environment for the origin and early evolution of life on Earth (e.g., Yanagawa and Kojima, 1985; Russell and Hall, 1997). In addition, some researchers proposed that microbial ecosystems in the hydrothermal vents are primary producers which sustain most of the lives in the ocean (Jannasch et al., 1985 and our TAIGA project [http://www-gbs.eps.s.u-tokyo.ac.jp/~taiga/en/index.html]). It is important, therefore, to figure out the hydrothermal reactions in the ocean floor for better understanding of the ecosystems in the ocean. Especially hydrogen generation is one of the most crucial processes in the hydrothermal systems, because multidisciplinary studies suggest that the most ancient microbial ecosystems were originated and maintained in the vicinity of H<sub>2</sub>-rich hydrothermal fluids (Russell and Hall, 1997; Sleep et al., 2004; Kelley et al., 2005; Canfield et al., 2006). Such communities are possibly composed of hyperthermophilic subsurface lithoautotroph methanogene (Takai et al., 2006).

The supply of abundant hydrogen to power such primary producers is the most likely coupled to hydrothermal serpentinization of ultramafic rocks. In the modern ocean, H<sub>2</sub>-enriched hydrothermal fluids are commonly associated with slow-spreading midocean ridge (MOR) setting dominated by peridotite (Kelley et al., 2001; Fruh-Green et al., 2004). The serpentinization of abyssal peridotite has been well investigated both experimentally and theoretically. The investigations indicate that the peridotite-water reaction provides an extraordinarily high concentration of H<sub>2</sub> in the fluids (e.g., Seyfried et al., 1979; Allen and Seyfried, 2003; McCollom, 2007; McCollom and Bach, 2009). In the Hadean and early Archean ocean, however, it is believed that peridotite would be scarce in the ocean floor, and komatiite - hydrothermal reactions are the possible mechanism of hydrogen generation in the ocean floor. Yoshizaki et al. (2009) experimentally revealed that abundant H<sub>2</sub>, equivalent to H<sub>2</sub> abundance in the peridotite-hosted hydrothermal solutions, was produced in komatiite alteration. On the other hand, the fault-related H<sub>2</sub> generation has been found by the gas monitoring along surface trace of the active Yamasaki fault (Wakita et al., 1980) and more from the drilling cores near hypocenters of micro-earthquakes along the San Andreas Fault (Erzinger & Wiersberg, 2008). Recently, we showed using our friction experiment system that abundant H<sub>2</sub> generation in the fault systems readily occurs (Hirose et al., 2011).

In this contribution, I will briefly introduce the results obtained in our laboratory experimental systems, both hydrothermal and simulated fault types.

Keywords: experiment, hydrogen generation, hydrothermal system, ecosystem, ridge

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BBG21-P02

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### Electrical resistivity structure of the upper mantle beneath the southern Mariana Trough

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In the Southern Mariana Trough, the seafloor spreading rate is 45km/Myr at present (Kato et al., 2003) that is relativity slow, but there are characteristics of the fast spreading ridge. Specifically, the southern Mariana region has an axial topographic high (Martinez et al., 2000) and a low-gravity region under the spreading axis in associated with high magmatic activity as well as a sheet-like mantle upwelling (Kitada et al., 2006). In this study, we carried out an electromagnetic experiment along a profile across the spreading axis to estimate an electrical resistivity structure and hence the physical property like temperature, water and melt content in the upper mantle beneath the Southern Mariana Trough. The experiment was carried out with 11 Ocean Bottom Electro-Magnetometers (OBEM), which were deployed on a 126km length survey line across the spreading axis. Time-variation of electric and magnetic fields are obtained from recoverd 10 OBEMs. The observation period is from August 2010 to November 2010, the data was record for "85 days in two OBEMs and for "60 days in the rest of the OBEMs. In this presentation, we show a result of an investigation of a 2-D electrical resistivity structure using OBEM data with good quality at 8 sites. The magnetotelluric(MT) method is a base for the data analysis. We performed an inversion analysis of the electrical resistivity structure by using an upper boundary of the subducted slab inferred from a seismic research (Gudmundsson and Sambridge, 1998) as a prior constraint. This structure show that the resistivity gradually decreases with distance from the Mariana Trough. Especially, at depths less than 40km the trenchward region has higher resistivity (300 Ohm-m) than the opposite side (30 Ohm-m). The less resistive region prevails below the spreading center.

Keywords: resistivity structure, the sourthern Mariana, upper mantle, subduction zone

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BBG21-P03

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## Decay of natural remanent magnetization of oceanic basalt on the back-arc spreading axis in the southern Mariana

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Magnetic anomaly high on a spreading axis has been a well-known character of the magnetic anomalies in the ocean, which is mainly related to magnetization intensity reduction of oceanic basalt due to alteration (low-temperature oxidation of titanomagnetite). For a better understanding of natural remanent magnetization (NRM) of oceanic basalt, we studied NRMs of basaltic rocks in the back-arc spreading axis in the southern Mariana. One to four meter cores were drilled from the seafloor by using a BMS in the cruise of TAIGA project (Taiga10M). Block samples were also collected during the dives of SHINKAI6500 in the cruise YK10-11. NRM intensities of these samples show a clear decrease within 2 km from the ridge axis. This value is consistent with a reported value in East Pacific Rise. These data suggest that the alteration has completed within 2 km distance from the ridge axis. Consistent scales from different ridges suggest that the NRM intensity reduction, which can be also observed as magnetic anomaly variation, may be related to the structure of ridge axis, for example, active hydrothermal circulation zone. Discussions of previous studies assume that the alteration process of ocean basalt is associated with age.

Keywords: oceanic basalt, natural remanent magnetization, magnetic anomaly, Mariana, hydrothermal circulatioin, TAIGA project

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BBG21-P04

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### Crustal magnetic structure around the hydrothermal fields in the Southern Mariana Trough

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Seafloor hydrothermal systems are important in relation to global heat and chemical fluxes as well as habitat of microbial communities. Circulation of fluids within oceanic crust depends on the geometry of heat source, the composition of rock as permeable medium and seawater. The substantial variation of hydrothermal systems active in various tectonic setting has important implications for the magnetic structure of oceanic crust.

It has been very difficult to detect the geophysical signature of hydrothermal systems based on crustal properties because the small scale of hydrothermal systems compared to distance between surface and bottom imposes limitation of resolution on the sea surface observation. The advance of near-bottom survey methods using a submersible, deep-tow, ROV and AUV has made possible high resolution geophysical mapping around hydrothermal areas. Near-bottom magnetic survey can provide direct information on the magnetization of shallow part of oceanic crust, implying the hydrothermal alteration both in active and fossil vent sites.

Near-bottom three component magnetic measurements on submersible Shinkai 6500 were carried out at three hydrothermal fields in the Southern Mariana Trough, the slow spreading backarc basin. We investigated the magnetic structure of three hydrothermal systems (Pica, Snail and Archean) to clarify how the geophysical and geological setting controls the fluid circulation in the small scale here.

The 14 dive surveys ware conducted successfully during R/V Yokosuka YK11-10 and YK10-11 cruise. A fluxgate magnetometer was attached to Shinkai 6500. Four dives (dives 1218, 1220, 1227 and 1228) were devoted to the Snail site located in nearest to the backarc spreading axis. Among those dives, dive 1227 crossed the axial volcanic zone, providing a ~2km long NW-SE transect. The other five dives (dives 1216, 1217, 1221, 1223 and 1224) were conducted around the Archean site, forming a ~60m high mound at the foot of ridge crest. The remaining four dives (dives 1214, 1219, 1222, 1225 and 1226) were done at an off-axis seamount where the Pica site was located. Dives 1214 and 1219 mainly cover the northern slope of this seamount and lead to the discovery of a new vent site (Urashima Site).

The observed data were first corrected for the effects of induced and permanent magnetizations of the submersible, based on Isezaki [1986]. To find plausible correction coefficients, we adopted the dumped least-square method (Honsho et al., 2009). The International Geomagnetic Reference Field (IGRF) is subtracted from the corrected data to obtain the geomagnetic anomalies. The crustal magnetization will be estimated using the AUV-collected high resolution bathymetry.

Keywords: Southern Mariana Trough, backarc basin, hydrothermal system, near-bottom magnetic measurement, crustal magnetization

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## U-Th radioactive disequilibrium dating of hydrothermal sulfide minerals from Okinawa and South Mariana Trough

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The time scale for a hydrothermal activity is an important factor controlling the size of hydrothermal ore deposits (Tivey, 2007) and the evolution of chemosynthesis-based communities in a submarine hydrothermal system (Watanabe et al., 2005). Many dating techniques using radioactive disequilibria of 235U, 238U, and 232Th decay series have been applied for hydrothermal submarine ore deposits (Lalou et al., 1993, Kadko, 1996). As one of several possible decay systems, 230Th-234U disequilibrium dating uses the increase of (230Th/234U) (parentheses denote activity ratios), which starts from zero in hydrothermal deposits. The maximum dating range of this method is up to 450 kiloyears (kyr). The system has been applied for massive sulfide mounds from Transatlantic Geotraverse (TAG) deposit on the mid-Atlantic Ridge using a thermal ionization mass spectrometer (TIMS), which yields a wide range of 230Th-234U ages: 2.6?38 kyr. Results show that episodic activities lasting more than 30 kyr in the TAG area which is positioned on a slow spreading ridge.

We will analyze several fractions of a sulfide crust collected from the South Mariana Trough and Okinawa Trough using 230Th-234U method by MC-ICP-MS.

The samples used in this study contain high amounts of sulfide and barite. Pb and Ba causes analytical interferences for U and Th isotope analyses, thus a good separation of the two elements is necessary. A two stage column chromatography was therefore used for the separation process.

The sulfide mineral from Izena hole of Okinawa Trough yielded ages ranging from 700 to 1000 years. Archean site of Mariana Trough yielded ages ranging from 0 to 2450 years with high U/Th ratio. Pika, Urashima and Snail site yielded ages ranging from 250 to 5000 year.

Keywords: hydrothermal vent, U-Th radioactive disequilibrium dating, Okinawa Trough, South Mariana Trough

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## Distribution of hydrothermal clay minerals in cores obtained by TAIGA 11 cruise from the Middle Okinawa Trough

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Intense hydrothermal fluid-sediment interactions are expected to occur below seafloor of active hydrothermal fields in the Middle Okinawa Trough, since these fields are covered with thick volcanic sediment which consists mainly of hemipelagic mud and pumiceous sediment. We investigate distribution of hydrothermal clay minerals in the sediment layer at these areas, in order to discuss physical and chemical environment below the seafloor.

In June 2011, the TAIGA 11 cruse was conducted using the R/V Hakurei-maru No.2 (Japan Oil, Gas and Metals National Corporation (JOGMEC)). We drilled 7 holes using the Benthic Multicoring System (BMS) and collected 2 cores using a large-diameter gravity corer (LC) in the Iheya North Knoll and the Izena Cauldron. Sub-samples were collected from the obtained cores at 5 to 10 cm intervals. Mineralogy of the samples was studied by analyses using XRD (X-ray diffraction) and EPMA (Electron Probe Micro Analyzer). Clay fractions (< 2 micrometer) were obtained from suspending bulk samples in distilled water and analyzed in detail. Oxygen and hydrogen isotope composition of the clay minerals was determined for some samples.

At the Iheya North Knoll, we drilled one hole using BMS (BMS-I-4. Drilling depth was 453 cmbsf). BMS-I-4 core comprised grayish white hydrothermal altered mud below 10 cmbsf. XRD and EPMA analysis indicated that the core was mainly composed of kaolin mineral. In addition to kaolin mineral, sphalerite and galena were found below 240 cmbsf, and sphalerite and dolomite were found in sediment plugged in a core catcher.

Occurrence of kaolin mineral has not been common in other seafloor hydrothermal active area and reported only at the Jade hydrothermal field in the Izena Cauldron by Marumo and Hattori (1999). However recently, kaolin mineral was dominantly found in a shallow depth at the Iheya North Knoll by drilling during the Integrated Ocean Drilling Program (IODP) Expedition 331 (Miyoshi et al, Clay Science Forum, 2011). These results suggest that kaolin mineral distributes laterally in a shallow depth below the seafloor at the Iheya North Knoll. Occurrence of kaolin mineral is rather common in onland geothermal areas, especially around acid springs caused by steam heating that is considered to be related with boiling of the deep hydrothermal fluid. In the Iheya North knoll, venting fluid chemistry was explained by boiling of deep hydrothermal fluid beneath the seafloor (Kawagucci et al., 2011). Based on this analogy, occurrence of kaolin mineral at the Iheya North Knoll would be attributed to acid condition caused by vapor-rich component deriving from boiling of deep hydrothermal fluid below the seafloor.

At the Izena Cauldron, we drilled one hole using BMS (BMS-J-2. Drilling depth was 530 cmbsf) and collected one core using LC (LC-J-2. 330 cmbsf) near the Biwako Vent site (BV site), which is located in the lower part of the slope in the Jade hydrothermal field. BMS-J-2 core comprised grayish white or gray hydrothermal altered mud below 380 cmbsf and XRD analysis found chlorite and sericite. LC-J-2 core comprised grayish gray hydrothermal altered mud below 280 cmbsf and was mainly composed of K-feldspar and chlorite below 300 cmbsf.

Chlorite and/or sericite were found in the BMS-J-2 and LC-J-2 cores collected near the BV site. This clay mineral assemblage near the BV site is different from that in the Black Smoker Chimney site (BSC site) which is located in the higher part of the slope in the Jade field. In the BSC site, kaolin mineral, smectite and sericite were found in surface sediment (Miyoshi et al., the Blue Earth Symposium, 2011). This different assemblage of clay minerals may reflect different physical and chemical environment below the seafloor of these two sites; for example low temperature and acid environment in BSC site and high temperature and alkaline environment in the area around BV site.

Keywords: Seafloor hydrothermal system, Iheya North Knoll, Izena Cauldron, Benthic Multicoring System (BMS), Hydrothermal alteration, Kaolin mineral

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# Growth rate determination of ferromanganese crusts from the Takuyo Daigo Seamount using an osmium isotope stratigraphy

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A ferromanganese crust (Fe-Mn crust) is widely distributed on the seamount slopes and is recognized on the ocean floor at various depths throughout the world. Since a Fe-Mn crust precipitates from ambient seawater at an extremely slow rate, one thick Fe-Mn crust sample solely records paleocean environmental changes through the Cenozoic period. In order to unravel paleocean environmental changes using a Fe-Mn crust, the sedimentary age of a Fe-Mn crust is required. Previous studies proposed that the Os isotope stratigraphy is a reliable dating method for a Fe-Mn crust throughout the Cenozoic period (e.g., Klemm et al., 2005, 2008). In this study, we determined the Os isotope profile of Fe-Mn crusts from the Takuyo Daigo Seamount (#5 Takuyo Smt) to estimate its growth rate. Our samples were systematically collected from the seamount outcrops using ROV Hyper Dolphin / RV Natsushima during the NT09-02 Leg.2 Cruise.

The Os isotope compositions of three Fe-Mn crusts collected from different depths (1424, 1440 and 2987 mbsl) show a similar trend and coincide very well with that of marine Os isotope record from present (187Os/188Os ~1.02) to 12 Ma (187Os/188Os ~0.77). These results indicate that the growth rates of Fe-Mn crusts in the #5 Takuyo Smt are uniform (ca. 3 mm/My) regardless of water depths which is consistent with the age constraints of the Be-10 dating method. However, in the older part (bottom part near the basement rock) of the two Fe-Mn crusts collected from 1424 and 1440 mbsl, the Os isotope compositions have large deviations from the seawater Os isotope record reconstructed from metalliferous sediment cores (Ravizza & Peucker-Ehrenbrink 2003). Moreover, the Fe-Mn crust collected from 2987 mbsl totally lacks the section older than 12 Ma. These large deviations can be explained either by the occurrence of growth hiatus or secondary geochemical modifications by phosphatization.

It is turned out that Fe-Mn crusts of the #5 Takuyo Smt. are appropriate material to reconstruct the paleocean environmental changes continuously from present to 12 Ma. In this presentation, we also discuss the secular and temporal variations in the major and trace element geochemical compositions of the Fe-Mn crusts together with the Os isotope compositions.

Keywords: ferromanganese crust, growth rate, osmium isotope, Takuyo Daigo Seamount, geochemistry, paleoceanography

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## Reactivity of chromate, molybdate, and tungstate on ferrihydrite by XAFS and molecular orbital calculation

ARIGA, Daisuke1\*

<sup>1</sup>Daisuke Ariga, <sup>2</sup>Masato Tanaka, <sup>3</sup>Teruhiko Kashiwabara, <sup>4</sup>Yoshio Takahashi

Hexavalent Chromium (Cr(VI)) has serious toxicity and carcinogenicity with high mobility in aquatic system. Therefore, fundamental understanding of the adsorption mechanism of chromate to ferrihydrite, an important adsorbent in natural systems, is essential to discuss their scavenging behavior. Although molybdenum (Mo) and tungsten (W) are congeners with Cr, the adsorption mechanisms (inner- or outer-sphere complexation) on ferrihydrite are different: molybdate forms outer-sphere complex, but tungstate forms inner-sphere complex (1). However, adsorption mechanisms of Cr(VI) on ferrihydrite is unknown. In this study, we performed extended X-ray absorption fine structure (EXAFS) analysis and *ab initio* molecular orbital (MO) calculations to reveal adsorption mechanisms of chromate and the results were compared with those for molybdate and tungstate.

Based on the adsorption experiments, adsorption amount of chromate was determined using inductively coupled plasma mass spectrometry (ICP-MS). EXAFS analysis was used to clarify coordination environment of chromate on ferrihdyrite measured at BL-12C in Photon Factory (Tsukuba, Japan). In addition, *ab initio* MO calculations were performed for the oxyanions (chromate, molybdate, tungstate) with Fe-(oxyhydr) oxide cluster model to obtain adsorption energy of outer-sphere complex and hydration energy of these oxyanions.

From the EXAFS analysis, Cr-Fe shell was observed for chromate on ferrihydrite in pH 4 and pH 6 spectra, while the spectrum at pH 8 was almost identical to that of chromate solution. However, the contribution of Cr-Fe shells at pH 4 and pH 6 are considered small degree because of low coordination number (CN) value. Hence, it is suggested that chromate mainly forms outer-sphere complex on ferrihydrite. Adsorption amount of chromate decreased as the ionic strength increased, which can be regarded as another evidence of the formation of outer-sphere complex. From *ab initio* MO calculations, stabilities of hydration complex in water and outer-sphere complex on ferrihydrite decreased in the order of chromate > molybdate > tungstate. Based on these results, it is suggested that it is relatively less stable for tungstate to form hydration and outer-sphere complexes, which allows us to conclude that chromate and molybdate prefer to form outer-sphere complexes, whereas tungstate to inner-sphere complex.

(1) Kashiwabara et al (2011) Geochim. Cosmochim. Acta 75, 5762-5784.

Keywords: Chromium, Ferrihydrite, Adsorption, XAFS, Molecular orbital calculation

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# Mineralogy and geochemistry of hydrothermal ores collected from active hydrothermal fields in shallow water depth

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Since boiling is inhibited by hydrostatic pressure, hydrothermal fluid circulates below the seafloor in a liquid phase that can dissolve much amount of elemental species. Metal elements transported by the hydrothermal fluid precipitates near the seafloor due to cooling, which results in formation of seafloor massive sulfide ore deposits. If hydrothermal activity develops at shallower water depth, the boiling point is limited to lower temperature. Since solubility of metal elements is strongly controlled by fluid temperature, the limitation of fluid temperature would affect mineralogy of hydrothermal ores precipitated at rather shallow water depth. In order to find this influence in natural systems, we studied mineralogy and geochemistry of hydrothermal ores collected from two active hydrothermal field in the Okinawa Trough, both are located at water depth shallower than 1000 m.

Hydrothermal ore samples were collected during NT11-20 expedition using ROV Hyper-Dolphin (JAMSTEC), from Minami-Ensei Knoll at water depth around 700 m, and from Yoron Knoll at water depth around 600 m. Dominant minerals in the ores were determined by XRD (X-ray diffraction) analysis. To identify minor minerals and to determine chemical composition of the representative minerals, EPMA (Electron Probe Micro Analyzer) analysis was conducted. Neutron activation analysis was conducted to determine bulk content of some trace elements.

Major sulfide and sulfate minerals commonly found in the hydrothermal ores were barite, sphalerite, galena, pyrite, chalcopyrite, stibnite, orpiment, tetrahedrite and Pb-Ag-Sb sulfide mineral. A few ores included covellite and Ag-S sulfide mineral as trace mineral. The tetrahedrites showed diversity in chemical composition. Ag content of the tetrahedrites was 0 to 2.8 atm% for the ores from Minami-Ensei Knoll and 2.6 to 9.5 atm% for those from Yoron Knoll. It is well known that higher Ag content in a tetrahedrite is related with relacement of As by Sb in higher proportion. This tendency was confirmed among the ores we studied. FeS content in ZnS is known as an indicator for oxidation-reduction environment during ore formation. FeS/ZnS ratio was 0 to 3.2 mol% for the ores from Minami-Ensei Knoll and 0 to 2.7 mol% for those from Yoron Knoll. The low FeS content would reflect formation under rather oxidative circumstances.

Keywords: Seafloor massive sulfide, tetrahedrite, sphalerite, Okinawa Trough

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### Ecological effect of hydrothermal plume on deep sea environment

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Seafloor is one of the largest interface of the biosphere in the earth. Interfaces among the subsystem of the earth, e.g. atmosphere, land, sea, and subseafloor, produce energy potential that harbors life. Hydrothermal plume assume the major flux of heat and chemicals between sea and subseafloor. In the TAIGA project, we investigated ecology in the hydrothermal plumes. We found that 1.) the microbial population was closely correlated with the chemical composition of hydrothermal fluid and 2.) the major microbes in the plume were putative sulfur oxidizer SUP05 and methane oxidizer Methylococcos. On the other hand, hydrothermal plume of Hakurei site at Izena hall and Pika site at southern Mariana trough harbors fewer microbial populations, which expected by their chemicals in hydrothermal fluid. Based on these microbial information, we will discuss the variety of hydrothermal systems in subduction zone.

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# Electrical resistivity structure of a seafloor hydrothermal system at the southern Mariana Trough spreading axis

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The electrical resistivity structure of the shallow crust is sensitive to the porosity of the crust and seawater temperature within the crustal pore. Therefore, by revealing the electrical resistivity structure of the shallow crust around a hydrothermal system, we can reveal the horizontal and depth distribution of seawater associated the hydrothermal system. In this study, we estimated the electrical resistivity structure around the southern Mariana Trough spreading axis (Snail site;12\_57'N, 143\_37.2'E) with the Magnetometric Resistivity (MMR) method which is effective to reveal the shallow (~1000m) electrical resistivity structure. The MMR survey was carried out during the KR03-13 cruise of R/V Kairei from Japan Agency for Marine-Earth Science and Technology (JAMSTEC). The vertical bipole source was applied between two electrodes near the sea-surface and just above the seafloor to generate an artificial electric current. Five Ocean bottom electro-magnetometers (OBEMs) were deployed as receivers around the active hydrothermal site to record variations of magnetic field induced by currents flowing into the crust. We determined the onedimensional crustal electrical resistivity structure by the method of least square by comparing the observed amplitude of induced magnetic field with the analytical solution of Edwards et al. (1981, 1984). Also, we determined the three-dimensional crustal electrical resistivity structure by the trial-and-error method using three-dimensional forward modeling (Tada et al., in prep.) to reproduce the distribution of the magnetic field anomaly. Magnetic field anomaly was calculated from differences in the amplitude between the observation and the prediction from the one-dimensional model determined by the method of least square. We determined the one-dimensional crustal electrical resistivity of 5.6 Ohm-m to a depth of 1500m. We estimated the temperature of crustal pore fluid between 0 and 390 deg C, and increases with depth, from 5.6 Ohm-m uniform structure, a crustal porosity profile at the Hole 504B (Becker, 1989), and Archie's law (Archie, 1942). We also estimated the three-dimensional crustal electrical resistivity structure around the hydrothermal site based on the uniform one-dimensional model. We found that there are four low crustal electrical resistivity regions around the hydrothermal site. These regions have the resistivity of 0.6 Ohm-m, expose at the seafloor, and these maximum depth is 200m. One low resistivity region is located near the Snail site and the others are away to northwest by ~350m from the Snail site. The low resistivity regions of 0.6 Ohm-m correspond to the temperature of crustal pore fluid of between 109 and 148 deg C, is constant at a depth of 200m from the seafloor. If the temperature of pore fluid in the region with the resistivity of 0.6 Ohm-m is supposed to be 0 deg C, which was estimated to be the temperature of pore fluid in the uniform 5.6 Ohm-m resistivity region, the porosity of this region is required to be approximately 60%. However, the crustal porosity of approximately 60% is not realistic because crustal porosity at a young crust is observed to be 34% (Pruis and Johnson, 2002). Therefore, the low crustal electrical resistivity regions suggest the existence of hot pore fluid because the highest porosity region can not have low crustal electrical resistivity. We conclude that there are four low crustal electrical resistivity regions which suggest the existence of hot pore fluid around the Snail site, one is near the Snail site and the others are away to northwest by ~350m from the Snail site.

Keywords: Southern Mariana Trough, seafloor hydrothermal system, Magnetometric Resistivity method

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### Evaluation of redox condition by selenium speciation coprecipitated with barite

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Barite (BaSO<sub>4</sub>) preserved in marine sediments can maintain its crystalline form at wide range of temperature, which can be present in hydrothermal vent. Barite crystals coprecipitated in seawater contain some elements that may reflect the physicochemical condition of the seawater from which they are formed. Selenium dissolves mainly as selenite ( $SeO_3^{2-}$ ) or selenate ( $SeO_4^{2-}$ ) in seawater, where the valence of selenium depends on the redox condition. Sulfate ion is stable in wide range in the Eh-pH diagram of sulfur, and the range include the Eh-pH boundary of selenite-selenate in the Eh-pH diagram. Therefore, the oxidation state of selenium in barite can provide information on the redox condition in the depositional environment. The purpose of this study is to establish a method to estimate the redox condition in the environment where barite is precipitated.

Coprecipitation experiment of selenium with barite was conducted to clarify the relationship between selenate/selenite rates in synthetic seawater and in barite. After this experiment, the precipitates of barite and aqueous phase were separated by filtration with a 0.20 e micro-meter filter (mixed cellulose ester, Advantec). Total concentrations of selenium in the remaining solution and precipitates were measured by ICP-MS to determine the apparent distribution coefficient (Kd) of selenium between barite and seawater. The selenate/selenite ratios in the solution and in the precipitates were measured by HPLC-ICP-MS and X-ray absorption near-edge structure (XANES) at the selenium K-edge, respectively. Micrometer scale distribution and oxidation state of selenium in barite formed in marine sediments in Okinawa hydrothermal vent was determined by e micro-XRF- XAFS in natural samples.

The XANES results showed that selenite was preferentially incorporated into barite rather than selenite. Selenate can be incorporated only when the selenate/selenite ratio is over 0.9 in the aqueous phase. The apparent distribution coefficient of selenium was reduced by increasing selenate/selenite ratio in the aqueous phase. These results are caused by the preferential incorporation of selenite into barite due to the high stability of Ba-selenite complex compared with Ba-selenate complex.

Based on the relationship, the redox condition of the interstitial water in the sediment was estimated. The micro-XRF-XAFS result showed that selenate fraction was 60% for the barite in the sediment. The result suggests that the seawater from which barite was precipitated was under oxic condition. This result is consistent with the redox condition of the sediment suggested by iron and sulfur XANES results in the same sample, which showed that the environment was highly oxic.

Keywords: barite, selenite, selenate, redox condition

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## Geochemisty of pore fluids collected from active hydrothermal fields in the mid-Okinawa Trough

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TAIGA11 Expedition was conducted in June, 2011 to investigate subseafloor environment below active hydrothermal fields by direct access using a shallow drilling system. Three active hydrothermal fields at Iheya North Knoll (27 47'N, 126 54'E), at Izena Cauldron Jade site (27 16'N, 127 05'E) and at Izena Cauldron Hakurei site (27 15'N, 127 04'E) were selected as exploration targets. The expedition focused on a subseafloor hydrothermal fluid circulation system that develops in sediment consists of volcaniclastic and hemipelagic materials. In this presentation, we will report geochemistry of pore fluids extracted from the obtained core samples and discuss evidence for intrusion of the hydrothermal component and for hydrothermal interactions.

Shallow drillings during TAIGA 11 Expedition was conducted using a BMS (Benthic Multi-coring System) that was loaded on R/V Hakurei-maru No.2. In addition to the BMS drilling, we also conducted coring using a large diameter gravity corer (abbreviated as LC) during bad sea condition. Pore fluid extraction from sub-sampled sediment was conducted onboard as soon as possible after core recovery. Three to eight sub-samples of 20 to 50 cm<sup>3</sup> in volume were collected every one meter from the core samples. The extracted pore fluid were divided into sub fluid samples and provided for analysis of major elements, trace elements, organic species, and specific isotope measurements. Sub sediment samples for gas species analysis were collected directly from the obtained core, those were kept in a glass vial and provided for headspace gas analysis. Chemical analysis of major species was conducted in following methods; Onboard colorimetry (molybdene blue method) for Si, ICP-AES after 200 times dilution of an acidified sample for Na, Mg, Ca, atomic absorption spectrophotometry after 200 times dilution of an acidified sample for K, ion chromatography after 300 times dilution for SO4, silver titration (Mohr method) for Cl, onboard electrode measurement for pH, onbaord acid titration for alkalinity, and onboard colorimetry (indo phenol method) for NH4.

In the Iheya North Knoll hydrothermal field, one BMS drilling and one LC coring were conducted. Core of BMS-I-4 (drilling depth: 453 cm) comprised grayish white hydrothermal altered mud that was identified as kaolin mineral, below 10 cmbsf (Miyoshi et al., this meeting). Pore fluid from the corresponding depth showed enrichment in major cations (Na, K, Ca and Mg), which may be explained by leaching during the hydrothermal alteration. Pore fluid chemistry also showed evidence for sulfate reduction in the sediment layer, such as high alkalinity and existence of hydrogen sulfide.

In the Jade site in the Izena Cauldron, three BMS drillings and one LC coring were conducted. Core of BMS-J-2 (drilling depth: 529 cm) comprised grayish white or gray hydrothermal altered mud below 370 cmbsf (Miyoshi et al., this meeting). Unfortunately, pore fluid could not be extracted from this alteration layer. Pore fluid collected from the shallower layer showed similar major element composition to that of seawater.

In the Hakurei site in the Izena Cauldron, two BMS drillings were conducted. Core of BMS-H-1 (drilling depth: 610 cm) showed evidence for sulfide/sulfate mineralization below 223 cmbsf. Pore fluid from corresponding depth show enrichement in Si, K, Ca and NH4, which could be attributed to intrusion of the hydrothermal component. This result suggests the mineralization is related with fluid mixing between the hydrothermal component and seawater component within the sediment layer beneath the seafloor.

Keywords: Seafloor hydrothermal activity, hydrothermal component, hydrothermal fluid interaction, ocean floor drilling, pore fluid

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## Hydrothermalreaction between NaCl fluid and felsic rock collected from the Hatoma knoll, Japan

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Many active hydrothermal fields exist in the Okinawa trough, Japan, where the seafloor is spreading due to a rifting activity of back-arc basin. The trough is covered with both hemipleagic and volcanic sediments and hosts a number of hydrothermal sites that form black smoker type metal-rich sulfide chimneys.

To clarify the generation mechanism of high-temperature hydrothermal fluid in the felsic rock-hosted system, we are conducting a hydrothermal experiment simulating the water/rock reaction under an elevated temperature/pressure condition. As a starting material, we use a volcanic rock collected from the Hatoma knoll hydrothermal vent field during the NT11-20 cruise. The rock sample and a NaCl fluid are reacted at 325 degree C and 300 bars over 1,080 hours. Although the experiment is still continuing, we will present the preliminary results such as the time variation of the composition of the reacted hydrothermal fluid.

Keywords: Hydrothermal alteration experiment, Hatoma knoll, Felsic rock

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### Comparative analysis of microbial community on ferro-manganese crusts from Takuyo-Daigo seamount and Ryusei seamount

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#### Purpose

Ferro-manganeese crusts (Mn crusts) are the rocks covered with iron and manganese oxides and are widely distributed on the seafloor. Due to rapidly depleting land-based mineral resources, oceanic mineral deposits gain greater significance. Mn crusts are known for enrichment of several transition metals like Cu, Ni, Fe, Co, Pt etc. They are abundant in the seafloor and it is expected that they contribute greatly to the material circulation between hydrosphere and lithosphere. The microbes inhabiting the surface of the crusts may have a major role in the material circulation, especially on carbon and nitrogen. Previous electron microscopic observations demonstrated the existence of microbes on Mn crusts. However, there is a lack of molecular studies on species diversity and abundance. Thus, a comparative study was undertaken to analyze the diversity and abundance of microbes on the Mn crusts from Takuyo-Daigo seamount and Ryusei seamount

#### Method

Mn crusts, ambient sediments and seawater were collected from four sampling points at Takuyo-Daigo Seamount NT09-02 cruise in Feb 2009. The water depth of each sampling point was 1200 m, 1419 m, 2209 m and 2991 m, respectively. Mn crusts, ambient sediments and seawater were collected from two sampling points at Ryusei seamount on KY11-02 cruise in Feb 2011. The water depth of each sampling point was 1194 m, 2079 m, respectively. DNA was extracted from each sample, followed by amplification of 16S rRNA gene and *amoA* (ammonia monooxygenase, subunit A) gene using universal primers and bacterial/archaeal *amoA* specific primers respectively. Clone libraries were constructed and nucleotide sequences were determined. The microbial community compositions and diversity were analyzed by phylogenetic and statistical analysis. Copy numbers of the 16S rRNA and amoA genes of bacteria and archaea were estimated by quantitative PCR.

#### Result and Discussion

Quantitative PCR estimated that both bacterial and archeal abundance in the ferro manganeese crust from the Takuyo-Daigo were about  $10^6$  to  $10^7$  cells/g, respectively. Archaea was dominated in the three of four Mn crust samples ( $50^83$  % of total cell numbers) analyzed.

Comparing the microbial community of Mn crusts, sediment and seawater it is evident that Mn crusts consist of a significantly different microbial composition from the others, suggesting the uniqueness of the ecosystem.

Phylotypes closely related to Marine crenarchaeota Group I (MGI) were detected from six Mn crust samples, collected from the two seamounts. MGI includes ammonia oxidizing archaean which is distributed ubiquitously in the ocean. Phylotypes closely related to *Nitrosospira*, an ammonia oxidizing bacteria were present in four Mn crusts sample collected from the Takuyo-Daigo seamount. Abundance of the ammonia oxidizers were confirmed by sequencing and quantitative PCR analysis of bacterial and archaeal amoA gene. The copy number of bacterial and archaeal amoA gene was estimated as 10 <sup>5</sup> to 10<sup>6</sup> copy/g.

This study demonstrated a high abundance of ammonia oxidizers in ferro-manganeese crusts, which signifies the possible role of ammonia oxidizers as the primary producers in ferro-manganeese crusts.

Keywords: ferro-manganese crusts, microbial ecosystem, 16S rRNA gene