

# Earth Engineering Technology Learnt from Low Temperature Serpentinization

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For our sustainable development, engineering technology in 21st century should be in safety, low-cost and environmentally friendly for human living together with the Earth. In such technology, not rare earth and platinum group elements but rather ubiquitous elements such as Si, Al, Mg, Fe should be used. Natural process is a physical, chemical and biological process existing in nature without the intent of human beings. Therefore, products and technology learnt from natural processes are available with low-cost and safety. In the natural processes, of course, ubiquitous elements play a key and major role. Not only civil and geological engineers but also engineering chemists and biologists are interested in natural processes for sustainable engineering technology. Especially, chemical processes at extremely alkaline environments have been attracted their attention for sustainable management of waste disposal used huge amount of concrete, recycling of alkaline materials such as cement, slag and fly ash, and so on. However, an understanding of the processes at such a hyperalkaline condition is not enough for safety assessment of the waste disposals and the recycling. In addition to this, many engineering chemists and biologists are also interested in the hyperalkaline processes for safety CO<sub>2</sub> geological storage, application of Fisher-Tropsch type reaction to natural system, and so on. Therefore, there are many contents to make lessons and be learnt from natural processes at hyperalkaline conditions. Fortunately, we can have the lessons at some ophiolites where occur low temperature present-day serpentinization.

Serpentinization has unambiguously been recognized as important geophysical and geochemical processes in mantle wedge and oceanic lithosphere. Serpentinized peridotite generally forms at reaction temperatures of 100–500°C as indicated by chemical, mineralogical and isotopic data. On the other hand, temperatures of present-day serpentinization observed at ophiolites and Lost City vents are considerably lower (40–75°C). This is in strong contrast to other known serpentinization systems. Thus, the temperature variability expressed by vent fluids from ultramafic-hosted hydrothermal systems on or slightly removed from mid-ocean ridge, is not altogether surprising. The low temperature hydrothermal field is characterized by a combination of extreme conditions never before seen in the marine environment. These conditions include venting of hyperalkaline and metal-poor hydrothermal fluids with high concentrations of dissolved H<sub>2</sub>, CH<sub>4</sub>. Huge amount of CO<sub>2</sub> gas is fixed into carbonate minerals observed in chimneys at the hyperalkaline vents and fissure filling of ultramafic rocks at the ophiolites. In this context, the previous studies on low temperature present-day serpentinization will be reviewed from the engineering points of view (hazardous anion migration, CO<sub>2</sub> geological storage, hydrogen and methane generation, abiogenic hydrocarbon production) in this presentation with introduction of our studies (lessons) at Oman ophiolite.

Keywords: Serpentinization, Hydrogen, Methane, Carbon dioxide storage, Hyperalkaline

## Carbonate hosted talc deposits in Nangarhar Province, Afghanistan

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Talc deposits in the E-W trending Spin-ghar fault block, southeastern part of Afghanistan, are hosted by Paleoproterozoic carbonate rocks. There are two types of talc mineralization in the study area, one is hosted by magnesite and the other by dolomite marbles. The objective of this study is to describe the talc mineralization on the basis of field observation, microscopic observation, XRD, XRF, ICP-MS and EPMA analyses.

In the study area, talc ore bodies are parallel to sub parallel to magnesite rocks and dolomite marble. The ore bodies are cross cut by intrusive rocks of diabase. Schistosity/foliation of quartz chlorite schist and quartz mica schist are parallel to sub parallel to talc ore bodies. Massive layers of tremolite were observed with most of the talc veins. Thin layers of talcose quartz have been marked within talc veins at places. Quartz veins follow the schistosity/foliation of gneiss all over the study area and cross cut by intrusive rocks at places. Mineral assemblages in the study area are (a) talc + tremolite + calcite, (b) talc ± cordierite, (c) talc + dolomite + calcite ± quartz ± apatite, (d) talc + dolomite + calcite and (e) dolomite + tremolite + calcite. Talc was formed by alteration of tremolite and magnesite in most of the studied areas, while in some deposits talc was formed by alteration of dolomite. Total REE contents of talc bodies, magnesite and dolomite marbles are 0.9, 5.3 and 13.0 ppm, respectively. The SiO<sub>2</sub> contents of carbonates and talc bodies range from 1.6 to 33.3 wt% and from 52.9 to 65.1 wt %, respectively, while MgO contents of carbonate and talc bodies range from 18.4 to 48.1 wt% and from 29.4 to 34.0 wt%, respectively. The CaO contents in talc bodies and magnesite are less than 1 wt%, while that of dolomite marbles ranges from 18.0 to 26.0 wt%. EPMA analysis of carbonates shows that dolomite and magnesite compositions are close to the ideal composition with Fe ranges from 0.04 to 0.17 wt % and 0.18 to 0.39 wt % respectively, while Mn ranges from 0 to 0.07 wt % and 0 to 0.04 wt % respectively. The concentrations of Al, Ta, Hf, Zr, Th and total REE in talc ores and carbonates rocks are very low and inconsistent with a felsic igneous rock protolith, whereas the low concentrations of Cr, Ni, and Co are inconsistent with a mafic igneous rock protolith. Therefore, the Mg-rich carbonate rock was likely the protoliths of talc ores. Magnesium has been derived from pre-existing Mg-rich carbonate host rocks, i.e., magnesite and dolomite marbles.

Keywords: Afghanistan, Spin Ghar, Talc, Dolomite, Magnesite, Tremolite

## Pb isotope ratios of the Nansatsu gold deposits, Kagoshima, Japan: Implication for gold mineralization

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Elucidating the origin of metals constituting the deposits can provide a crucial key constraint in exploration for new mineral deposits. It is previously considered that the epithermal deposits, one of the most important types of gold deposits, are formed by ore-forming fluids originated from magmatic water discharged from hydrous magmas and/or meteoric water evolved by circulation and reaction within the shallow crust. The fluids extract metals from magmas and/or host rocks and then move to the shallower part of the crust, resulting in deposition of valuable metals due to reduction of pressure and temperature [1]. The previous mineralization model has been proposed on the basis of isotopic study of relatively light elements (e.g., H and O) in the ore-forming fluids. However, recent isotopic studies on heavy metals (e.g., Pb, Sr and Nd) suggest the involvement of another important component, i.e., slab-derived fluid, to the formation of epithermal ore deposits [2].

To detect the source of metals contributing to the formation of epithermal gold deposits, Pb isotopes can provide direct and useful information. Our previous study of the Pb isotopic compositions of sulfide ores from the Akeshi gold deposit (one of the Nansatsu-type gold deposits) demonstrated that the ore samples show three different trends in  $^{206}\text{Pb}/^{204}\text{Pb}$ - $^{207}\text{Pb}/^{204}\text{Pb}$ - $^{208}\text{Pb}/^{204}\text{Pb}$  isotopic compositional space [3]. Two of these trends were interpreted as influences of the bed rock and the slab-derived fluid from the Philippine sea plate. The results suggest that both the bed rock and the slab-derived fluid could have contributed to mineralization of the Akeshi gold deposit. The third trend, however, could not be explained by any geochemical end-member near the deposit.

In the present study, to cover a spatial variation in geochemical signatures, we newly analyzed the samples including bed rocks, host rocks, and sulfide ores from the Kasuga and Iwato gold deposits both in Kagoshima prefecture, which are also among the typical Nansatsu-type gold deposits. We will show the new analytical results, and discuss the origin of the Nansatsu-type gold deposits more comprehensively.

### References

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Keywords: Nansatsu-type gold deposits, slab-derived fluid, Pb isotopic ratio, ore-forming fluid, epithermal deposits

## Relationship between high-grade gold mineralization and fluid pressure in the Yamada sub-deposit, Hishikari Epithermal Gold Deposit, Japan

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The Hishikari deposit is a world-class low sulfidation epithermal deposit hosting the most productive gold mine in Japanese mining history. It is composed of the Honko, Sanjin and Yamada sub-deposits. Mixed Bingham distributions have been fitted to the orientation of the ore veins for the clustering of Yamada sub-deposit in order to unravel the paleostress conditions. Furthermore, the relationship between fluid pressure and high-grade gold mineralization has been investigated. Two paleostress states A (of strike-slip faulting regime) and B (intermediate between reverse-faulting and strike-slip faulting regime) were identified. The subsequent analysis of high-grade ore bands (gold grade > 100 g/t) shows that although most of Yamada veins were formed by ore fluids with low driving pressures, the high grade veins among them were formed by those with higher driving pressures. This reveals a close association between high-grade gold mineralization and higher driving pressures. If the principal stress magnitudes are assumed to be constant over the sub-deposit, provided that the data were collected at the same elevation, the result also means that high-grade gold mineralization in the Yamada sub-deposit is related to higher fluid pressures. This is further supported by the fact that the high-grade ore bands deposition is controlled by the stress state A which is more likely to be associated with the main hydrothermal activity (thus higher fluid pressure).

Keywords: mixed Bingham distribution, Hishikari, Yamada, orientation, driving pressure, fluid pressure

# Subsurface Lithologic and Alteration Mapping and Modelling of the Kay Tanda Epithermal Gold Deposit, Lobo, Batangas, Philippines

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The Kay Tanda epithermal gold deposit is located at the southern flank of Mt. Lobo in the Batangas mineral district, Philippines. It contains approximately 4.9 M metric tonnes of indicated and measured resources at 1.09 g/t Au and 2.15 g/t Ag at 0.5 g/t Au cut-off grade. Situated outside established and well-studied gold districts in the Philippines, its deposit characteristics are among the least studied in the country. This study aims to generate a three-dimensional lithologic and alteration model of the deposit using the data gathered from geologic logging and detailed petrographic and X-ray diffraction analyses.

The deposit is mainly hosted in the Middle Miocene Looc Volcanic Complex (locally named as Talahib Andesite) which is composed of andesitic to dacitic volcanoclastic sequences. Based on the regional mapping conducted by the Bureau of Mines and Geosciences (BMG) in 1980, andesitic sequences dominate the upper sequences of the formation while the lower sequences are dominantly dacitic in composition. Geologic logging showed intertonguing and alternating sequences of the dacitic and andesitic sequences in the deposit. The dacitic sequences are mainly composed of dacitic lapilli tuff. They are composed of strongly hydrothermally altered dacitic fragments with quartz phenocrysts exhibiting embayed to resorbed textures. The andesitic sequences are composed of andesite lava flows. They are hydrothermally altered and exhibit characteristic trachytic and porphyritic textures. The plagioclase phenocrysts are completely altered to clay but their euhedral lath-like habit is still preserved. The Looc Volcanic Complex is intruded by a local multi-facies intrusion called the Balibago Intrusive Complex. It is composed of diorite, quartz diorite and andesite porphyry. The diorite and quartz diorite are phaneroporphyritic while the andesite porphyry exhibits aphanoporphyritic textures. Overlying the Looc Volcanic Complex is the Late Miocene to Early Pliocene Calatagan Formation, a complex sedimentary sequence of sandstones, siltstones, shales, conglomerates, and limestone lenses with minor andesitic tuffs. Weak mineralization was found in some sandstones and limestones of the Calatagan Formation. Overlying the deposit is a post-mineralization Balibago Andesite. It is composed of a slightly to moderately weathered andesitic lapilli tuff.

X-ray diffraction was used to determine the specific alteration mineral assemblages of the samples. The Looc Volcanic Complex is affected by advanced argillic and argillic alteration. The advanced argillic alteration zone is composed of pyrophyllite and kaolinite with minor illite. Argillic alteration zone is composed of illite and smectite with minor amounts of kaolinite. The mineralized portions of the Calatagan Formation are also argillic altered. The intrusive rocks of the Balibago Intrusive Complex are mainly affected by propylitic alteration which is composed of chlorite and illite.

A three-dimensional lithologic and alteration model was generated using the Leapfrog Geo Software. Also, assay values for gold, silver, lead, zinc and copper were inserted in the model to determine the location of the high grade zones of the deposit. The model shows that the gold and silver mineralization are mainly hosted in the dacitic volcanoclastic sequences of the Looc Volcanic Complex which are strongly affected by advanced argillic alteration. Base-metal mineralization is mostly found at the deeper levels of the deposit.

Keywords: Kay Tanda deposit, epithermal, Lobo, Batangas, Philippines, hydrothermal alteration, geologic modelling

# Mineralogical and oxygen isotope studies of skarn type tungsten deposit at the Date-Nagai, NE Japan

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The Date-Nagai skarn type tungsten deposit locates at the Abukuma Mountain. The Idateyama body, an ilmenite series granodiorite (102-106 Ma), distributes widely in the area and lenticular hornfels are accompanied as roof pendant. Small limestone layer is included in hornfels. Skarn develops between hornfels and limestone as a thin layer. Three types of skarn, garnet-vesuvianite skarn, green skarn and fine-grained skarn are distinguished from their appearance and mineral assemblage. Scheelite is accompanied in all these skarns. Paragenetic study suggests that mineral assemblage in skarn differed between early and late stages. Early stage garnet is optically isotropic, whereas that of later stage shows anisotropy. Scheelite precipitated in relatively later stage of mineralization.

Chemical compositions of skarn minerals were examined by EPMA. Garnet of early stage has compositions near grossular, whereas those of later stage contain pyrospite moles up to ~70%. Andradite mole in both garnets is very low (<8.0 mole %), which suggests reduced environments since Fe<sup>3+</sup> in skarn-forming solution was very low. Chemical composition of clinopyroxene is approximately middle between diopside and hedenbergite. Powellite mole in scheelite is very low (<1.4 mole %).

Oxygen isotope compositions of minerals were analyzed by means of CO<sub>2</sub>-laser ablated BrF<sub>5</sub> technique. Garnet and scheelite have variable  $\delta^{18}\text{O}$ , 4.6-8.2 ‰ and 0.8-2.9 ‰, respectively. Temperature of skarn formation was calculated using oxygen isotope fractionation factor between quartz and scheelite, and T=283°C was obtained. Using this temperature,  $\delta^{18}\text{O}$  of skarn-forming solution was calculated. Early stage solution had  $\delta^{18}\text{O}$  values of 6-8 ‰ and most garnet precipitated from this solution. While later stage solution had lighter  $\delta^{18}\text{O}$  values 1-5 ‰, and this solution was responsible for precipitation of scheelite and quartz. Origin of skarn-forming solution of early stage was mostly magmatic water, while contribution of meteoric water increased in later stages.

Keywords: tungsten skarn, oxygen isotope, garnet

# Characteristics and Ore Genesis of the Clifton Porphyry Copper-gold Prospect, Northern Luzon, Philippines

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The Clifton prospect is one of the priority prospects identified by the renewed exploration campaign of Philex Mining Corporation (PMC), the mining company that has been operating the Sto. Tomas II orebody, an auriferous porphyry copper deposit located in the southern tip of the Baguio District since 1957. Mineralization in Clifton is porphyry copper type associated with a quartz diorite complex emplaced along a ENE-WSW structure. In this study, we investigated the intrusive rocks from the viewpoints of cross-cut relations, alteration and associated vein types, mineral paragenetic sequence, fluid inclusions and sulfur isotopes to reveal the condition of mineralization.

Corelogging and petrographic analyses recognized at least intrusive rocks intruding through the basement consisting of volcanic rocks of the Pugo Formation (PMV): (1) the Early Andesite Porphyry (EAP), (2) the Intra-mineral Diorite Porphyry (IMD), and (3) the Late Andesite Porphyry (LAP). The intrusive rocks have similar mineralogical compositions, and are distinguished via texture of the groundmass, degree of alteration and density of veinlets. The emplacement of the multiple intrusive rocks introduced several alteration types: (1) K-silicate alteration is well-developed in the EAP and its contacts with the PMV. It is characterized by pervasive hydrothermal biotitization, and is accompanied by abundant chalcopyrite, bornite and magnetite with ilmenite-hematite and sphene as disseminated grains. Associated wavy quartz veinlets cross-cut the host rocks. (2) Quartz-dominated K-silicate alteration, occurring within the "Stockwork Zone" ("SQZ"), introduced addition of silica accompanied by chalcopyrite-pyrite-magnetite-hematite with rare gold. It is accompanied by sheeted quartz, quartz-magnetite, and chalcopyrite-rich quartz veinlets. (3) Chlorite-sericite overprint accompanied by chalcopyrite-pyrite affects the bottom portion of the "SQZ", and cross-cuts the earlier quartz veinlets. Chalcopyrite grains appear to be rimmed by an unidentified silver-bearing mineral. Lastly, (4) propylitic alteration, characterized by chlorite-actinolite, in the IMD and LAP.

A direct correlation of copper and gold concentration is evident in the early stage biotite-dominated K-silicate alteration. Higher concentrations of copper in the quartz-dominated K-silicate alteration are associated with the later chalcopyrite-rich mineralization. Higher silver contents correspond to the higher silver content of the electrum,  $\text{Ag}/(\text{Au}+\text{Ag}) = \text{c.a. } 46.7$  atomic% was measured in a minute gold globule found in the later chalcopyrite-rich mineralization.

Abundance ratios of vapor-rich fluid inclusions to polyphase hypersaline fluid inclusions vary from 18% to 47% and from 95% to 287%, for the veins related to the "SQZ" and the later quartz veins at the shallower parts, respectively. The significant increase in the vapor to brine ratio at the shallower depth compared to the deeper portions indicates the transport of vapor in the shallower part.

Formation depth of Clifton is shallow, estimated to be 2.2 km, 58MPa at 650°C, 58 MPa during the earliest stage, and uplifted to 1.5 km, 38.5MPa at 525°C, during the chalcopyrite-rich stage, based on fluid inclusion microthermometry.

Sulfur isotope analyses measured  $+1.0$  to  $+6.0$   $\delta^{34}\text{S}_{\text{CDT}}$  (‰) indicating that the source of sulfur is enriched in  $^{34}\text{S}$  similar to the other hydrothermal ore deposits in the western Luzon arc.

Keywords: Clifton prospect, Baguio District, porphyry copper-gold mineralization





## Mineralization of Ag-rich Sulfide Minerals in Chimney Samples at Bayonnaise Knoll, Izu-bonin Arc.

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The Bayonnaise Knoll is located in the Izu-Bonin Arc, which forms an arc-trench system. In this study, the growth process of chimneys formed by hydrothermal fluid ejecting from hydrothermal vents, and mound ore formed around chimneys, is clarified based on geochemistry and mineralogy. Measured value for precious and base metals for the studied samples show Au (4.635 ppm), Ag (354 ppm), Cu (0.406 wt%), Pb (0.252 wt%), Zn (11.841 wt%) contents and used to compare with the average Kuroko-ore. In addition, the grade of Au and Ag are larger than that average value.

Chimney has a tubular structure and the growth axis is perpendicular to the chimney length. A manganese oxide is covered to the surface, 1) a white sulfate rich portion (G1), 2) followed by a gray portion containing sulfide (G2) and 3) a black porous portion containing sulfide (G3). This similar classification can be also observed in the Kuroko-ore. Ba distribution are evenly confirmed in G1-G2 but only confirmed in G3 as a large crystalline portion in vug. It is known from previous studies that the formation temperature of barite (G1) is mainly estimated as 150-215 °C and the formation temperature of sphalerite (G2-G3) is around 205-225 °C. Sphalerite, galena and chalcopyrite, which belongs to Kuroko-ore, were mainly observed in G2-G3. These similar mineralization can be obtained Kuroko-ore. From EPMA measurements, Ag-rich portion is distributed mainly on the outside of G2 and Ag-Cu-Pb, in which sulfide minerals were confirmed. It is presumed that Ag-rich-sulfide minerals were formed at around 200 °C because of the formation temperature of barite and sphalerite and that Ag-rich-sulfide distribution. Therefore, from the above point, chimney and mound ore in the Bayonnaise Knoll, is Au and Ag rich, but characterized by a similar concentration of major elements (Cu, Pb, Zn) to the Kuroko ores. And it was found that Ag-sulfide minerals were distributed in G2.

Keywords: Bayonnaise Knoll, Chimney, Ag-sulfide Minerals

## Resistivity Structure around Off-Okinawa Hydrothermal Area Using Two-Dimensional Inversion of Marine DC Resistivity Survey

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Global demands for metal resources have increased interest to development of deep-ocean hydrothermal ore deposit called as SMS (Seafloor Massive Sulfide). SMS deposits, including rare and precious metals, have been often found out around hydrothermal active areas; for example in the Okinawa and Izu-Bonin areas, located in the Japanese Exclusive Economic Zone, and in the mid-Atlantic ridge. Geophysical explorations with electromagnetic (EM) methods are recently carried out around the SMS deposits because the SMS deposits are known as low resistivity material and the resistivity distribution below the seafloor can be a good indicator for the buried SMS deposits. However, the resistivity structure below hydrothermal active areas has not been clearly investigated. In this study, I developed a two-dimensional inversion of a marine deep-towed DC resistivity survey as an effective tool to exploration of SMS deposits. Marine deep-towed DC resistivity survey system was originally developed as a sensitive tool to gas hydrate, but the numerical simulations how the survey is sensitive to the SMS deposits have never been conducted. The inversion developed in this study is based on the model space Occam's inversion method and the finite-difference method is applied in the forward modeling calculation to solve potential difference between electrodes at the electric-current injection to the seawater. We tested the system using the synthetic data and found that the inversion can estimate the buried SMS deposits effectively. The first test is based on newly-developed inversion with smoothness constraint, frequently used to solve ill-posed inverse problems. Although the ordinary constraint assuming a smooth model can detect the low resistivity anomalies, the real distributions of SMS deposits are concentrated at narrow (thin) zones, and cannot be treated as the smooth model. In order to obtain sharp-change of resistivity matching the petrophysical information, I add a guided Fuzzy C-Means (FCM) clustering constraint into the objective function in the inversion procedure. Two balance parameters in this objective function should be controlled in the inversion, but the optimal ways to adjust these parameters have not been proposed. Therefore, I propose an algorithm to choose these parameters properly. The new algorithm is based on the two stages; the first stage with the ordinary Occam scheme, then the second stage with the FCM constraint where the inverted model and parameter in the first stage are the initial model and the fixed parameter. The other parameters are decided with the scaling scheme. The refined inversion results show that the inversion with the FCM constraint can produce sharp boundaries in resistivity structure, which can handle with the realistic petrophysical information. Finally, I applied the inversion code to the field data obtained at the Okinawa Trough; the inverted resistivity anomalies are consistent with the known geological investigations of hydrothermal fluid flows and the observed distributions of seafloor venting sites.

Keywords: Direct Current resistivity survey, Seafloor massive sulfide deposits, Inversion

## Evaluation of metal dissolution from fresh hydrothermal core samples collected at Izena Hole during CK16-05 and rapid detection of their toxicity on marine phytoplankton community

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Environmental impact assessment is essential to reduce loads of seafloor metal-mining operations to marine environments. Accidental leakage of crushed hydrothermal ores from mining vessel is one of the possible concerns. Metals and metalloids could be released from mineral particulates and damage marine phytoplankton communities, the primary producers at the base of the marine food chain. Our previous study found that high amounts of metals can be released from fine particulates of oxidized hydrothermal ores into seawater, and they inhibit the growth of a marine phytoplankton species. In this study, metal leaching potential of deoxidized (fresh) ores was evaluated using whole round core (WRC) samples collected from Izena Hole, Okinawa Trough, by *D/V Chikyū* (CK16-05). Also, the toxicity of the leachates on marine phytoplankton was estimated onboard using delayed fluorescence (DF)-based bioassay method which is a useful tool to estimate rapidly and easily toxic metals (Yamagishi et al., 2016). Four whole round core samples (C9025A 6H-2, C9026A 7X-CC, C9027B 1X-CC, and C9028A 7S-CC) were taken from sulfide mineral rich sections and powdered manually with agate mortars. Approximately 3 g of each powdered sample was mixed with 30 mL of artificial seawater, and then the mixture was shaken at room temperature for 6 h. After shaking, the solid phase was separated by centrifugation and filtered. Dissolved metals and metalloids in the liquid phase is quantified using an inductively coupled plasma-mass spectrometry.

A newly developed bioassay technique was applied to evaluate the toxicity of the core-leachates onboard. A test organism for the bioassay was a marine Cyanophyceae of *Cyanobium sp.* (NIES-981), which had been cryopreserved and was resuscitated onboard just before the bioassay test. The inhibition effect of the leachates on the algal photosynthetic activity or growth was quantitatively determined by a custom made ultra-weak luminescence detector system (Type 7600, Hamamatsu Photonics) at 15 min, 1, 3, 6, 9, 12 and 24 h after the exposure to those leachates.

Zn (4–15 ppm), Pb (2–16 ppm), Cd (20–130 ppb), and Mn (130–160 ppb) were detected from the leachates of samples C9025A 6H-2, C9027B 1X-CC, and C9028A 7S-CC. These metal contents in the leachate from the core samples were 2–3 order of magnitude lower than in the leachates from the oxidized ore samples. On the other hand, the contents of these elements in the leachate from sample C9026A 7X-CC was significantly low.

On the bioassay experiment for the leachates from C9025A 6H-2, C9027B 1X-CC, and C9028A 7S-CC, the DF-intensities of *Cyanobium sp.* greatly decreased at 24 h comparing to the control, i.e., without the leachate. On the other hand, the leachate from C9026A 7X-CC which contained low amounts of metals did not cause the significant inhibition effect on *Cyanobium sp.*

Our results clearly show that non-oxidized fresh hydrothermal ores can release various toxic metals into seawater as same as the oxidized hydrothermal ores (e.g., weathered chimney ores), and such contaminated seawater leachates could inhibit the growth activity of natural marine phytoplankton. Therefore, appropriate management systems for controlling the leakage and disposal of mining ores and

wastes to the marine surface area should be devised to preserve the natural marine ecosystem.

Keywords: hydrothermal ore, metal contamination, marine phytoplankton

## Fe isotope fractionations relating to the ore formation processes in volcanogenic massive sulfide deposits

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The Hokuroku district in Northeast Japan hosts many large volcanogenic massive sulfide (VMS) deposits called Kuroko deposits, which were formed around 15 Ma by ancient submarine hydrothermal activity. Because they are composed of sulfide minerals that are stable in a reducing environment, redox environment on the seafloor during the formation of Kuroko deposit may play an important role in the preservation of the sulfide ores. Furthermore, factors controlling the size and grade for VMS deposits have not been well understood. Previous studies have shown that Fe isotope ratios as well as Rare Earth Element (REE) patterns of ferruginous cherts that associated with Kuroko deposits may reflect the depositional environments. However, sulfides containing in the sedimentary rocks may affect the bulk Fe isotope ratio. Therefore, the objective of this study is to understand formation processes of a large and high-grade VMS deposit based on Fe isotope variations in the sulfide ores and ferruginous cherts with considering the effect of Fe mineralogy to the bulk Fe isotope ratios.

Studies samples were obtained from several VMS deposits from the Hokuroku district as well as Palmer deposit in Alaska, USA. Microscopic observations of the polished sections and the major element contents obtained by X-ray Florescence (XRF) analysis demonstrated that the samples are typical black ores, containing sphalerite and galena, yellow ores, containing chalcopyrite and pyrite, and ferruginous cherts, containing quartz and minute grains of hematite. Some ferruginous cherts also contains iron sulfide (e.g., pyrite, pyrrhotite) as it was concerned. Most ferruginous chert samples also show a distinct positive Eu anomaly in their REE patterns, suggesting that they are affected by high temperature hydrothermal fluids. Fe isotope ratios of sulfide minerals physically separated from ferruginous chert samples were not significantly different from those of the bulk samples, indicating that the presence of iron sulfides in the ferruginous cherts does not affect the bulk Fe isotope ratio. The bulk Fe isotope analysis of ferruginous chert samples from all the studied deposits using multi-collector inductively coupled plasma-mass spectrometry (MC-ICP-MS) shows large variations in the  $\delta^{56}\text{Fe}$  values (-1.55–+2.04‰). The variations in Fe isotope ratios suggest that partial oxidation of dissolved ferrous iron occurred by mixing ferrous iron-bearing anoxic water with oxygen-bearing seawater, and therefore that the sea-floor of the Hokuroku basin was likely anoxic during the formation of Kuroko deposits. Furthermore, while samples from some deposits (e.g., Matsumine, Kosaka) tend to show more negative  $\delta^{56}\text{Fe}$  values, those from other deposits (e.g., Fukazawa, Palmer) tends to show more positive  $\delta^{56}\text{Fe}$  values. The difference may be stemmed from their formation processes. Near equilibrium conditions between hydrothermal fluids and sulfides in the ore bodies by a long-term circulation may have lead to a steady  $\delta^{56}\text{Fe}$  value (e.g., -0.5‰) of dissolved iron in the hydrothermal fluids and negative values of ferruginous chert by a Raleigh-type fractionation. On the other hand, rapid precipitation of sulfides ore body under dynamic conditions may have caused a kinetic isotope fractionation, leading to shift  $\delta^{56}\text{Fe}$  value of both hydrothermal fluids and ferruginous cherts to more positive values.

Keywords: Fe isotope, VMS deposit, Chemical Sedimentary rock, Seafloor hydrothermal activity