Physical properties of rock samples of seafloor massive sulfide

*Yusuke Ota[1], Tada-nori Goto[2], Weiren Lin[2], Osamu Tadai[2], Takafumi Kasaya[2], Toshiya Kanamatsu[2], Hideaki Machiyama[2]

1.Kyoto University, 2.Japan Agency for Marine-Earth Science and Technology

Geophysical surveys around submarine hydrothermal areas are conducted to investigate new seafloor mineral resources. However, the information related to the volume of metallic material cannot be directly obtained from the geophysical surveys. As one of ways to solve this problem, construction of an appropriate rock-physical model of target area is helpful to interpret the geophysical results. For development of a rock model in a submarine hydrothermal area, we carried out the fundamental research about various physical properties and mineral component of rock samples collected from two hydrothermal areas; the Izena hole and the Noho site at the Okinawa Trough, Japan. We discussed the correlation between physical and chemical parameters.
In this research, we measured electrical conductivity, porosity, density, natural remanent magnetization (NRM), and metal element content of rock samples. The electrical conductivity, with measurement under the various conductivity of pore water, was interpreted using the modified Archie’s law (the parallel circuit model), and the surface conductivity and formation factor were determined. For porosity and density measurement, we used the buoyancy method. For NRM, we used the superconducting quantum interference device (SQUID) magnetometer. The metal composition ratio was measured with the X-ray fluorescence (XRF) analysis.

The rock samples including relatively large amount of conductive (> 25 wt. %) could not be explained by the simple parallel circuit model since the formation factor was unrealistic. We corrected the parallel circuit model in which the surface conductivity is a function of the pore-water conductivity. As a result, a positive correlation was found between the surface conductivity and Iron abundance ratio. Positive correlation was also observed between NRM and Iron. In conclusion, the rock model can include the metal abundance as a function of excess conductivity and NRM.

Keywords: seafloor massive sulfide ; Archie’s law; electrical conductivity; models

Keywords: seafloor massive sulfide, Archie’s law, electrical conductivity, models

Mineralogical and Geochemical Study of Hydrothermal Deposits from the Noho Site in the mid-Okinawa Trough

*Shuhei Totsuka[1], Jun-ichiro Ishibashi[2], Tatsuo Nozaki[3], Kazuhiko Simada[2]

1.Department of Earth and Planetary Sciences, Graduate School of Sciences, Kyushu University, 2.Department of Earth and Planetary Sciences, Faculty of Science, Kyushu University, 3.Research and Development Center for Submarine Resources, JAMSTEC

The mid-Okinawa Trough is recognized as an area with extensive hydrothermal activity. The Noho site is located in graben a few km south of the Iheya Small Ridge. Water depth of the Noho site is around 1600 m, which is deeper than many of other active hydrothermal fields in the Okinawa Trough. Temperature of vent fluids was recorded as high as 338 ℃ at the Yubikuwae Chimney Vent, which is the highest temperature in the Okinawa Trough. Since its discovery in 2014, the Noho site has been investigated by some dive expeditions. This is the first scientific report for mineralogy and geochemistry of hydrothermal deposits (chimneys and mound ores) obtained from the Noho Site.

Most part of the seafloor in the Noho site is covered with sediment, whereas outcrops of lava flow were observed in the Hitoshi Site that is adjacent to the northern side of the Noho Site. Mound structures sometimes higher than 10 m are recognized as aligned along three parallel lines in the direction of northeast-southwest. Many chimneys at the top of the mounds are characterized by "flange structure", which extends laterally as if overlapping eaves. It is often observed that vent fluids emanated from chimney walls formed a pool below the flanges and overflowed from the rim. One giant complex chimney structure called Yakushiji Chimney associated with several layers of flange towered up at ~45 m high from the sediment basin.

Samples we studied were recovered during NT15-02 and NT15-13 cruises. Because most of the samples were fragile, we made polished sections after infiltrating epoxy resin. Identification of ore minerals were conducted by observation with a reflection microscope. We conducted also EPMA (Electron Probe Micro Analyzer) and EDS (Energy Dispersive x-ray Spectroscopy) analysis for chemical analysis of major ore minerals and identification of minor minerals.

A typical mineral assemblage of chimneys was dominant pyrrhotite ($Fe_{1-X}S$) and sphalerite (ZnS), and minor galena (PbS), cubanite ($CuFe_2S_3$), barite ($BaSO_4$) and anhydrite ($CaSO_4$). Dendritic texture of sphalerite and galena was commonly recognized in chimneys, which is considered as evidence for rapidly cooling. Specific texture indicating pyrrhotite growth towards the fluid pool was recognized in the flange part of chimneys. Another common type of chimneys was a sulfate chimney that composed of mainly barite. This type of chimney included pyrite and As- and Sb-minerals as sulfide minerals. Mound breccia was composed mainly of sphalerite, and minor galena, chalcopyrite and cubanite. As sulfate minerals, anglesite ($PbSO_4$) was identified, which might be secondary occurrence. In the mound breccia, barite was rarely identified.

Iron content in sphalerite was determined to discuss chemical condition for sulfide minerals precipitation. The chimneys of the Noho site showed Fe content in sphalerite as high as 18.30 mol%, whereas the mound breccia showed 8.95 mol %. These high Fe content suggest sphalerite precipitation in reductive environment. According to a compilation of Fe content among hydrothermal deposits in the Okinawa Trough, most of them were in a range from 0 to 5 mol %, and only few samples showed such high ratios.

Another specific characteristic of mineralogy of hydrothermal deposits from the Noho site is occurrence of pyrrhotite and cubanite. In hydrothermal deposits from other hydrothermal fields in the Okinawa Trough, chalcopyrite and pyrite were commonly observed as Cu-Fe-S minerals. The mineral assemblage of pyrrhotite and cubanite suggests low sulfur fugacity and reductive precipitation

environment, which is in accordance with the high Fe content in sphalerite. As well as the reductive precipitation condition, high temperature fluid as 338℃ could be favorable for formation of Cu, Pb, Zn -rich sulfide deposits in the Noho Site.

Keywords: Iheya Small Ridge, Seafloor hydrothermal deposit, Flange structure, NT15-02 Cruise, NT15-13 Cruise

Arsenic Occurrence and Its Origin in Sulfides Deposits of the Hokusetsu Area, Osaka, Japan

*Emilie Even[1], Harue Masuda[1], Takafumi Hirata[2]

1.Osaka City University, 2.Kyoto University

Arsenic contamination in the river and ground waters of the Hokusetsu area, Osaka Prefecture, Japan, have been chronically reported since 1994. The dissolution of pyrite contained in the host rocks is thought to be responsible for the As contamination. Our geochemical investigation of the As origin and the sulfur isotopic data suggested that two kinds of sulfide ore deposits would be responsible for the As contamination: one from the Late Paleozoic intensive submarine volcanisms that lead to the formation of stratiform Cu and bedded Mn deposits, and the other from the Late Cretaceous igneous activities that lead to the formation of the myriad ore deposits that constitute the W-Cu-Sn Province of Southwest Japan.

In order to confirm the origin of As, sedimentary rocks collected in highly contaminated areas and sulfides ores from in several mines were chemically analyzed. The sulfides minerals assemblages were optically observed under reflected light. As and associated trace elements were analyzed with Laser Ablation-Inducted Coupled Plasma-Mass Spectrometry (LA-ICP-MS) to document the genetic relationships among host rocks and ore deposits to the As origins.

Weathered sulfides along calcite veins, related to the Paleozoic volcanogenic ore deposits contained important levels of As, together with Pb, Cu and Zn, implying that the sulfides were the cause of the As contamination of hydrosphere of the study area. Others sulfides found in the contact-metamorphosed sedimentary rocks by the granitic intrusion, were mostly pyrite with some minor chalcopyrite and sphalerite. These sulfides contained As plausibly substituting sulfur as arsenopyrite. Heavy metals such as Ni, Co were found in the sulfides from hydrothermal ore deposits and in contact-metamorphosed rocks related to granitic activities, suggesting the As-enrichment in these rocks was induced by the igneous intrusion during Late Cretaceous.

Level of As in rivers and ground waters were generally higher in areas hosting sedimentary rocks rather than in area hosting metamorphosed rocks or closed to deposits related to granitic magma. This implies that the diffuse distribution of As-bearing sulfides and its dissolving rate, likely controlled by the crystalinity and/or the size of crystals, are important to factors contributing to the As contamination of the studied hydrosphere.

Keywords: Arsenic, Igneous Intrusion, Ore Deposit, Sulfide

Mantle potential temperature in Ordovician estimated from ultramafic dikes in the Hayachine-Miyamori Ophiolite

*Takafumi Kimura[1], Kazuhito Ozawa[1]

1.Department of Earth and Planetary Science, The University of Tokyo

Estimation of the secular variation of thermal state of the Earth’s mantle is imperative to understand the evolution of the solid Earth. One of the key proxies of the thermal state is mantle potential temperatures (McKenzie and Bickle, 1988) estimated from chemical compositions of magmas erupted at particular tectonic settings: spreading centers or non-arc environments (Herzberg et al. 2010). This restriction of tectonic setting is necessary to guarantees that the estimated potential temperatures represent that of the entire mantle. In this regard, an arc environment is avoided to estimate potential temperature because of its complex tectonics and strong influence of water dehydrated from subducting slab for magmas genesis. However, we must use even arc environment to estimate mantle potential temperature to achieve a dense distribution of potential temperature over the wide age span of the Earth’s history.

An ophiolite is a rock body having a mantle section overlain by oceanic crust exhumed to the Earth’s surface at various ages at leat from the Paleoproterozoic time to the very recent past (Stern, 2005). Moreover, ophiolite pulses, in which a large number of ophiolites were formed and exhumed in a confined period, are thought to reflect the mantle thermal state (e.g., Abbate et al., 1985). Ophiolites thus provide very useful information on magma generation in the mantle and thus have large potential for elucidating secular variation of mantle potential temperature. However, accumulated studies on ophiolites have revealed that many ophiolites were formed in subduction zones, from fore-arc to back-arc basin (Dilek and Furnes, 2011).

In this study, we estimate a mantle potential temperature at ~500Ma from an Ordovician arc ophiolite: Hayachine-Miyamori Ophiolite located in the South Kitakami Massif, northern Japan, which is shown to have been formed in an arc environment on the basis of extensive geological, petrological, and geochemical studies (Ozawa et al., 2015). We use porphyritic ultramafic dikes intruded into near the base of the cumulate members (Ozawa, 1984). The dikes, which intrude orthopyroxene-bearing dunite, have phenocrysts of euhedral –subhedral olivine (~5 mm in size and ~30 vol%) and minor clinopyroxene (~3 mm in size and ~2 vol%) set in finer matrix consisting of pargasite, orthopyroxene, clinopyroxene, and plagioclase. Some dikes show multiple branching, and shape-preferred orientation of phenocrysts and concentration of olivine phenocrysts in the middle of the dikes suggesting operation of flow differentiation. From these field observations, it is inferred that dikes were solidified rapidly in closed system after intrusion at a liquid state in order to keep the suspension of olivine crystals in the middle of the dikes. We obtained chemical composition of rocks with variable amounts of phenocrysts. Effects of alteration, metamorphism, and diffusional elemental exchange with the host peridotite are subtracted to obtain compositional variation right after the solidification of dikes. A linear trend of the bulk composition plotting on Harker diagram is obtained through this procedure, indicating that a two-component mixing took place with one end component of the trend extending toward the olivine composition. Subtracting the estimated average composition of olivine in an amount of the phenocryst mode for each rock sample, the compositions are plotted in a restricted region of the Harker diagram. This suggests that the composition represents that of melt intruded into the host peridotite as a crystal-loaded magma. The water content of the magma is estimated to be ~1.5 wt% from the amount of amphibole in the dikes. After correcting fractional crystallization, a primary melt composition is obtained, from which melting temperature and pressure, partial melting degree, and mantle potential temperature

are estimated.

Keywords: arc ophiolite, mantle potential temperature, partial melting degree, primary melt

Formation mechanism of spherulite in welded tuff: devitrification induced by volatile components

*Takuya Echigo[1], Yoichiro Saito[2], Mitsuyoshi Kimata[3], Masahiro Shimizu[3], Norimasa Nishida[4], Shigeru Takizawa[5]

1.Faculty of International Resource Sciences, Akita University, 2.Master's Program in Science and Engineering, University of Tsukuba, 3.Doctoral Program in Earth Evolution Sciences, Graduate School of Life and Environmental Sciences, University of Tsukuba, 4.Chemical Analysis Division, Research Facility Center for Science and Technology, University of Tsukuba, 5.National Research Institute for Earth Science and Disaster Prevention

This study reports detailed mineralogical and geochemical descriptions of the spherulite occurring in welded tuff from Aga town, Niigata prefecture, Japan, and also discussed its formation process. Powder X-ray diffraction showed that this spherulite mainly consists of cristobalite and Na-rich sanidine without any secondary minerals such as clay and zeolite minerals produced by hydrothermal alteration. Both bulk chemical analyses of spherulite and groundmass and microprobe analyses of plagioclase phenocrysts included in spherulite and groundmass revealed that the present spherulite crystallized from the same pyroclastic deposits as the host rock (strongly welded rhyolite tuff). The rare earth elements (REE) contents obtained by ICP-MS are slightly enriched in spherulite rather than in the host rock, indicating that the precursor of spherulite contained volatile components that induced the REE diffusing from the surrounding pyroclastic deposits into spherulite precursor. Textural observation using back-scattered electron image and micro-Raman spectroscopy showed that the present spherulite has three layers structure: rim (dense texture), mantle (porous texture) and core (fan-shaped aggregates of fibrous crystals). The distribution of elements within spherulite was examined using electron-microprobe analyzer with wave-dispersive spectrometer (EMPA-WDS). These results demonstrated that both Ca and Na are enriched in both the rim and core of spherulite, suggesting that Na-rich plagioclase is crystallized in these parts. In addition, detailed observation by secondary electron microscopy showed that fibrous microcrystals (~ 1 μm) of both feldspar minerals and cristobalite were intergrown to constitute fan-shaped aggregates in the core and porous aggregates of larger crystals (~ 5 um) in the mantle. These chemical and textual evidences suggested that the present spherulite is formed in a series of steps: (1) Non-crystalline precursors of spherulite were generated by local concentrations of volatile components in pyroclastic deposits. (2) Ca ion migrated to the boundary between the precursor of spherulite and the host rock and resulted in crystallization of plagioclase-rich rim. (3) Rapid intergrowth of cristobalite and plagioclase occurred in the core of spherulite and can be made up into the fan-shaped aggregate. (4) From the residual volatile-rich glass, fine crystals of Na-rich sanidine and cristobalite were intergrown and resulting volume shrinking generated pores in the mantle. (5) Euhedral crystabalite precipitated on the pore wall due to degassing of volatile components.

Keywords: spherulite, welded tuff, volatile component

Crystallization mechanism of groundmass nanolites inferred from the crystal size distribution of the Shinmoedake 2011 eruption

*Mayumi Mujin[1], Michihiko Nakamura[1], Akira Miyake[2]

1.Division of Earth and Planetary Materials Science,Department of Earth Science,Tohoku University, 2.Department of Geology and Mineralogy, Graduate School of Science, Kyoto University

Groundmass nanolites in pyroclastic rocks have a potential to indicate the physicochemical conditions of conduit magmas at transition points of eruption styles. Generally, the decompression and resulting degassing of ascending magmas produce the effective undercooling of hydrous melts, which drives crystallization of groundmass microlites (decompression-induced crystallization; e.g. Cashman and Blundy, 2000). Mujin and Nakamura (2014) reported presence of nanolites in the quenched products of the 2011 eruption of Shinmoedake, Kirishima volcanic group, Kyusyu Japan. They defined the nanolites of plagioclase and pyroxene in the dense juvenile fragments of the Vulcanian explosion on the basis of change of their crystal size distribution (CSD) slopes. They also found a gap in the CSD of Fe-Ti oxide and defined the finer nanometer-scale crystals as nanolite. In this study, we further define “ultrananolites” of pyroxenes and Fe-Ti oxide in the same sample as that investigated by Mujin and Nakamura (2014) based on a gap in CSD from the nanolites: between 300 and 30 nm for pyroxenes and between 10 and 2 nm for Fe-Ti oxide. The crystals in these size ranges were rare. In the present study, we present a theoretical interpretation for these observations by considering decompression-induced crystallization of solid solution minerals in order to investigate the development of undercooling in the course of magma ascent leading to various eruption styles.

In the framework of classical CSD theory, in which straight CSD represents constant nucleation density (N_0) and crystal growth rate (in length, G), two explanations can be applied for steepening of CSD slope: a sudden increase of undercooling and crystallization delay leading to rapid recovering. The constant G can be assumed when the undercooling is constant. If crystallization differentiation of the melt catches up with the increase of the liquidus temperature by decompression, the degree of undercooling is kept constant and thus the kink of CSD slope is not formed. Assuming that N_0 and G are proportional to the degree of undercooling, the kink of CSD requires a sudden change of undercooling. The change from phenocrysts to microlites is usually caused by onset of magma ascent from a magma chamber. The increase of undercooling from the crystallization stage of microlite to that of nanolite may be caused by the rapid decrease of water solubility in melts and resulting sharp increase of the liquidus temperature. When crystallization differentiation of melt does not catch up with the increase of the liquidus temperature, the crystallization delays and the degree of undercooling increases gradually. If such magmas with large undercooling are emplaced in the shallow level, crystal nucleation is facilitated and thus the kink of CSD slope may form.

The gap of CSD requires nucleation pause for a certain period of time in the course of crystallization. This may occur when activation energy for nucleation exceeds undercooling with decreasing water content (Dowty, 1980). The observed gap in the CSD of the Shinmoedake eruption may be caused by accelerating decrease of water solubility in the magmas as they approaches to the surface.

Keywords: nanolite, microlite, decompression, crystallization, undercooling

Formation of Sodium-rich, High-Mg# Melt by Reaction of Felsic Melt with Peridotite: Implications from Felsic Veins Observed in the Magarisawa Peridotite, Hidaka Mountains, Northern Japan

*Kohei Yamashita[1,2], Jinichiro Maeda[3], Masako Yoshikawa[4], Tomoyuki Shibata[4], Toru Yamasaki[2]

1.Department of Natural History Sciences, Graduate School of Science, Hokkaido University, 2.Research Institute of Geology and Geoinformation, Geological Survey of Japan, AIST, 3.Department of Natural History Sciences, Faculty of Science, Hokkaido University, 4.Beppu Geothermal Research Laboratory, Kyoto University

Origin of Na-rich felsic veins and pools which are rarely found in sub-arc mantle xenoliths (e.g., Shimizu et al., 2004) has been controversial. Some authors have suggested that they are trapped Na-rich slab melt (e.g., Kepezhinskas et al., 1995), whereas others suggest that their Na-rich nature is attributed to reaction of felsic melt and mantle peridotites (e.g., Prouteau et al., 2001).

Felsic veins of various widths (microscopic order to ca. 50–60 cm) and lithologies are observed in the Magarisawa Peridotite (the MP) which is composed mainly of Pl lherzolite, northern Hidaka Mountains, Hokkaido (Yamashita et al., 2015, JpGU abstract). We discuss chemical modification process, particularly Na-enrichment of the felsic melts due to reaction with the MP.

The felsic veins are subdivided into four facies: 2Px Granite (Qz+Kfs+Pl+Opx+Cpx); Opx Monzodiorite (Qz+Kfs+Pl+Opx); Norite (Pl+Opx); Pl-veinlet (Pl+Opx), which is branched from 2Px Granite or Opx Monzodiorite. Microscopic characteristics and whole rock compositions suggest that 2Px Granite and Opx Monzodiorite preserve melt compositions and that Norite and Pl-veinlet represent Pl-Opx cumulates.

Sr and Nd initial ratios of all these veins are similar and correspond to those of the pelitic granulite/anatexite surrounding the MP (Maeda and Kagami, 1996). It suggests that all felsic veins have formed from partial melt of the pelitic granulite.

It is noted that the Opx Monzodiorite is characterized by especially high-Na_2O content and -Mg# (6-7 wt% and 74-82, respectively). It also shows relatively high-SiO_2 content (62-64 wt%). Experimental partial melt of pelitic granulites opposed at southern Hidaka Mountains (Osanai et al., 1997 in Japanese), which is expect to have similar compositions to the initial melt forming the Opx Monzodiorite, show much lower Na_2O content and Mg# than the Opx Monzodiorite. It suggests that partial melt of the pelitic granulite have experienced marked chemical modification within the MP. Possible chemical modification processes are fractional crystallization of Pl+Opx (i.e., Norite or Pl-veinlet) and the initial melt-peridotite reaction. However, because the Opx Monzodiorite shows no Eu anomaly, it seems to have never experienced fractional crystallization of Pl. Thus, latter process is probable.

Opx-wall, reaction zones (ca. 1 mm in width) composed of secondary Opx is always formed along vein-peridotite boundary. Phl is characteristically formed between the Opx Monzodiorite vein and Opx-wall. On the other hand, between Opx-wall and Pl-veinlet which is branched from the Opx Monzodiorite, high-Ca# Pl (Ca#~90) + vermicular Opx±Phl with ca. 1 mm in width (vermicular zone) is always formed.

Based on the results of this study, we propose the process how Na-rich, high-Mg# (Opx Monzodioritic) melt have formed by reaction between felsic melt and peridotite, occurred within the MP:

(1) Initial SiO_2-rich melt (melt1) intrudes into peridotite, followed by the formation of Opx-wall along melt1/peridotite boundary;

(2) Concurrently with (1), because of diffusion of Mg and Fe from peridotite into melt1, relatively SiO_2-poor melt (melt2) is locally formed between melt1 and peridotite;
(3) When diffusion between SiO_2-rich melt and SiO_2-poor melt occurs, alkalis diffuse from latter to former (uphill diffusion: e.g., Sato, 1975). By this process, Na (and K) may diffuse from SiO_2-poor melt2 to SiO_2-rich melt1 against concentration gradients of alkalis (melt1 > melt2). Elements except for Na and K (e.g., Si, Mg, Fe and Ca) diffuse according to the concentration gradient;
(4) Finally, Na_2O (and K_2O) contents and Mg# of melt1 become higher than initial melt. Vermicular zone, including high-Ca# Pl, may represent the composition of melt2 which become lower Na_2O than initial composition.

Keywords: felsic melt-peridotite reaction, uphill diffusion, Hidaka Magmatic Belt

Crystallization history and petrogenesisi of the Hikami granitic rocks, south Kitakami Mauntains, Japan

Jun Sasaki[1], *Nobutaka Tsuchiya[1], Tatsuro Adachi[2], Nobuhiko Nakano[2], Ippei Kitano[2], Yasuhito Osanai[2], Yoshiko Adachi[3]

1.Department of Geology, Faculty of Education, Iwate University, 2.Department of Earth Sciences, Faculty of Social and Cultural Studies, Kyushu University, 3.Center for Transdisciplinary Research, Niigata University

Hikami granitic complex are divided into next ten rock types; hornblend-bearing granodiorite-tonalite (A-1, A-2, A-3 and A-4), hornblend-free granodiorite-tonalite (B, C, and D), and granodiorite associated with the Tsubnosawa metamorphic rocks (E, F and G). Zircon U-Pb ages were determined with laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) for each rock type, and solidification age of the Hikami granitic rocks are Ordvician age of around 450 Ma. Petrogenesis of felsic rocks B and C in the Hikami granitic complex can be explained by the fractional crystallization model from the common parental magma of rock type A-2. Difference between the trends of A-2 to B and C can be explained by the slightly different conditions of fractional crystallization. Source material of the Ordovician granites including Hikami granitic rocks is considered to be a basaltic to andesitic material in lower continental crust, which has Sr-Nd isotopic composition more depleted compared with the Tsubonosawa metamorphic rocks and more enriched conpared with the amphibolites in teh Kurosegawa belt (Osanai et al., 2000).

Keywords: Hikami granitic rocks, petrochemistry, Ordovician, Kitakami Mountains

GANSEKI: Maintaining Accessibility of JAMSTEC Rock Samples and Associated Information

*Takayuki Tomiyama[1], Yasumi Toyoda[2], Hiroki Horikawa[1], JAMSTEC Data Sample Team

1.Japan Agency for Marine-Earth Science and Technology, 2.Marine Works Japan, Ltd.

Japan Agency for Marine-Earth Science and Technology (JAMSTEC) provides data and samples obtained by research cruises of JAMSTEC vessels for further public uses with research/educational purposes [1]. The GANSEKI database, an online-system which disseminates metadata, collection inventory, and geochemical data of JAMSTEC rock samples, has been operated for years since it was established 2006, though several improvements have been implemented during the period [2]. Not only curating JAMSTEC rock samples and associated information which were obtained by recent cruises, but we also curate those obtained by old cruises; those of down to 1980s are still available on GANSEKI. Some geochemical data of non-JAMSTEC rock samples are also gathered into GANSEKI for researchers' convenience, referring to literatures on ocean geosciences.

Most of rock samples are fairly durable for long-time archiving as a resource for scientific research. Even if decades have passed since a rock sample was collected, one can still utilize it to carry out a research using modern techniques. It is important for utilizing such old samples that there is abundant information, such as sampling date, location, surrounding geometry, geological occurrence, who was the initial user, how samples are collected, for what purpose they have done it, etc. If such information remains abundantly and maintained for easy access, public users, who were not in touch with sampling, can evaluate and utilize samples from a standpoint close to that of initial researcher who sampled them.

One of the strong points of JAMSTEC rock samples is that associated information such as metadata, video/photo data, geophysical observation data, cruise reports and so on were collected simultaneously with rock sampling and many of them are still accessible even for old cruises. These associated information is accessible at databases introduced in "NUUNKUI" data site, in which GANSEKI itself is also included [3].

Individual sample information on GANSEKI is directly linked to online information, which is selected for its importance for rock sample usability. Among NUUNKUI data site, cruise and dive information on DARWIN, video/photo data on J-EDI are especially important for GANSEKI [4, 5]. As for the visualization service of submersible dive tracks which used to be available on previous JDIVES virtual exploration system, JAMSTEC is now implementing similar functions into the J-EDI system.

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Keywords: Rock sample, On-line database, curation

Development of low-cost simple dead time correction system for accurate quantitative electron probe microanalysis (EPMA) of trace element

*Takenori Kato[1]

1.Institute for Space-Earth Environmental Research, Nagoya University

High-current and long-time X-ray sampling is required in quantitative electron probe microanalysis of trace elements. The X-ray count rate becomes extremely high in case of standard materials measurement at high-current. In this case, accuracy of dead time correction is an important factor to accurate quantitative EPMA of trace elements.

To achieve long-time maintenance-free stable dead time correction in quantitative EPMA, a simple pseudo-fixed dead time system has been developed. The mono-stable multivibrator is inserted after single-channel analyzer (SCA) / pulse-height analyzer (PHA). The dead time of this design can be considered to be a fixed value when the count rate is bellow 200kcps. The relative error in this system is smaller than 0.5%.

Keywords: Electron probe microanalysis (EPMA), Dead time correction, X-ray spectrometry, Wavelength dispersive spectrometer (WDS), Proportional counter

New occurrences of silica clathrate minerals in Sakhalin

*Koichi Momma[1], Kenichiro Tani[1], Ritsuro Miyawaki[1]

1.National Museum of Nature and Science

Silica clathrate minerals are rare minerals containing various gas molecules (CH_4, C_2H_6, CO_2, H_2S, N_2 etc.) in their cage-like framework structures constructed of pure silica. Three types of silica clathrate minerals have been hitherto known in nature. They are structurally analogous to gas hydrates. In fact, the three minerals, melanophlogite, chibaite, and bosoite are isostructural with three types of natural gas hydrates, i.e., sI, sII, and sH hydrates, respectively. The source of gas molecules in silica clathrate minerals is also considered to be common with one type of natural gas hydrates having thermogenic origin.

We recently noticed two specimens of quartz pseudomorphs from Sakhalin in old mineral collection of the National Museum of Nature and Science. They are labeled as quartz pseudomorphs after fluorite or apophyllite because they have truncated octahedral shape. However, they look identical to quartz pseudomorphs after chibaite occurred in Chiba and Nagano prefectures. These specimens motivated us to field investigation of Sakhalin. The two specimens are from “Souni misaki” (Kuznetsova) and “Bisyasan”, the most southwest part of Sakhalin where Miocene sedimentary rocks and volcanic rocks are exposed. Unfortunately, we could not approach these places during the field survey in 2015 but we discovered new locality of melanophlogite at Nevelsk. Melanophlogite is associated with fossils of various chemosynthetic shells in calcareous concretion of mudstone of Miocene age. The concretions are abundantly distributed as veins or pipes mostly parallel to the bedding plane, or some of them look like isolated nodules of diameters up to several meters. Among these concretions, melanophlogite only occurs in the one containing massive amount of shells and voids. Melanophlogite occurs in these voids as aggregates of cubic crystals of sizes up to 0.1 mm, associated with chalcedony and small quartz crystals.

Keywords: silica clathrate minerals, methane seep, chemosynthetic community

Thermoluminescence and impurities of quartz from Sambagawa metamorphic belt, central Shikoku

*Theeraporn Chuenpee[1], Osamu Nishikawa[5], Yoshiaki Kon[4], Kiyotaka Ninagawa[3], Shin Toyoda[3], Takeyuki Ogata[5], Takashi Uchida[5], Isao Takashima[2]

1. Faculty of Engineering and Resource Science, Akita University, 2.Mining Museum, Akita University , 3.Department of Applied Physics, Okayama University of Science, 4.National Institute of Advanced Industrial Science and Technology, 5.Faculty of International Resource Sciences, Akita University

Quartz is an essential constituent in igneous, sedimentary and metamorphic rocks and is a major phase in veins. The crystallization of quartz under various geological environments allows it to enclose a varirty of trace element impurities, which play an important role in its Thermoluminescence (TL) emission. The TL emission of quartz shows great variety in intensity and wavelength. Blue to green TL emission at high temperature range has been commonly detected in quartz originated from plutonic rocks and hydrothermal veins. The orange to red TL emission with high temperature peaks ranging between 300 to 350 °C has been generally observed in quartz extracted from volcanic ash layers and archaeological burnt materials. Nevertheless, characteristics of TL emission in metamorphic quartz, as well as its relation to trace element and metamorphism have been poorly understood. In order to clarify these issues, the TL emissions and trace element compositions in quartz grains extracted from samples of pelitic and siliceous schist and their associated quartz vein were studied. Samples from different metamorphic grades (e.g. chlorite zone, garnet zone, albite-biotite zone and oligoclase-biotite zone) were collected from the Sambagawa Metamorphic Belts in central Shikoku, Japan.

The purified quartz grains were irradiated with a ^{60}Co gamma irradiator, using a dose of 5 kGy. TL emissions were measured at Okayama University of Science and Akita University. Trace element concentrations in the grains were measured by Agilent 7500 Series LA-ICP-MS. Paramagnetic defects were determined using JEOL PX-2300 SER spectrometer at Okayama University of Science.

A high intensity of the peaks below 200 °C favors the lower metamorphic grade. On the other hand, TL emissions at above 200 °C tend to increase with the higher metamorphic grade. There is an obvious decreasing tendency in Al content with increasing metamorphic grade, while no significant difference in concentration of Ti. It was measured that Al center is presented in all samples, whereas E´ center and Peroxy center are commonly existed in the higher metamorphic grade samples. It is reasonable to consider that the declenation of Al content, and the existance of E´ center and Peroxy center with increasing metamorphic grade presumably influences the characteristics of the TL temperature peaks in the samples.

Keywords: Gamma radiation-induced thermoluminescence, Sambagawa Metamorphic Belt

ALCHEMI experiment for Al/Si-disordering of annealed sillimanite

*Yohei Igami[1], Shunsuke Muto[2], Masahiro Ohtsuka[3], Akira Miyake[1]

1.Graduate School of Science, Kyoto University, 2.Institute of Materials and Systems for Sustainability, Nagoya University, 3.Graduate School of Engineering, Nagoya University

The polymorphs of Al_2SiO_5 (andalusite, kyanite, sillimanite) have assumed a special significance for geologists as indicators of the pressures and temperatures experienced by metamorphic rocks. The structure of sillimanite consist of AlO_6 octahedra chains, which are linked with Si/Al tetrahedra double chains parallel to the *c*-axis. These tetrahedral Si/Al are normally ordered distribution, but the disordering at high temperature (HT) has been suggested by e.g. Greenwood (1997). Miyake et al. (2008) showed that sillimanite in Napier complex has the structure like anti-phase boundary (APB), and suggested the possibility of Al/Si-disordering and evidence of UHT metamorphism. Annealing experiments had been carried out to estimate the degree of Al/Si-ordering of sillimanite, but it had not been cleared quantitatively. The main problem is the difficulty of separating mullite phase from sillimanite sample. Tomba et al.(1999) showed that sillimanite heated at HT partly transform to mullite ($Al_2[Al_{2+2x}Si_{2-2x}]O_{10-x}$), which is very similar to sillimanite crystallographically. Thus, separating only sillimanite from experimental data obtained from bulk which contain sillimanite and mullite is very difficult. In addition, XRD which is generally used has the other difficulty to distinguish Al from Si caused by similar X-ray scattering factor.

On the other hand, Atom location by channeling-enhanced microanalysis (ALCHEMI) was carried out for Al/Si-disordering of orthoclase by Taftø & Buseck (1983). ALCHEMI method is basis of channeling-enhanced emission and has been used to determine the crystal structure by TEM-EDS. ALCHEMI can apply to ~1μm region, and can distinguish the elements which is generally difficult for XRD. Furthermore, HARECXS (High Angular Resolution Electron Channeling X-ray Spectroscopy) developed from ALCHEMI was carried out for ion-irradiated spinel by Yasuda et al. (2006, 2007), recently. HARECXS requires many measurements of the characteristic X-ray by varying the direction of incident electron beam, but this method provides quantitative information of atomic configurations. In this study, HARECXS experiment were carried out on sillimanite annealed in various temperature in order to determine the degree of Al/Si-ordering.

We annealed sillimanite in Rundvågshetta, Lützow-Holm, Antarctica in the range of 790-1530℃ and then cooled. These samples were examined by HARECXS using TEM-EDS (JEOL JEM-2100F+JED-2300T). X-ray signals of Al-K, Si-K and O-K were collected simultaneously as a function of electron beam direction between -80-8 and 808 Bragg conditions. This experiment was carried out at sillimanite region avoiding mullite or glass inclusions, observed in the annealed samples, same as the result of Tomba et al. (1999) or Holland & Carpenter (1986). The simulation program, ICSC, (Oxley & Allen, 2003) showed certainly that the HARECXS profile changes sensitively with the degree of Al/Si-ordering.

As the result, the HARECXS profiles of annealed samples were similar to the profiles simulated by Al/Si-disordered model. For quantitative information, we fitted the experimental profiles to the linear combination of two simulated profiles, simulated by ordered and disordered model. In each fitting result, the ratio of ordered profile to disordered profile, *x*, is the first-order approximation of the degree of Al/Si-ordering. We confirmed that the profiles simulated using *x* is also consistent to measured profiles. As the result of experiment of various samples using this method, we revealed that the degree of Al/Si-ordering decrease with increasing heating temperature. Thus this method can reveal the maximum metamorphic temperature from ~1μm size sillimanite. Furthermore, this HARECXS method cannot apply only to sillimanite but also to various minerals to determine site occupancies and estimate formation environment.

Keywords: ALCHEMI, sillimante, Al/Si-disorder

Grain size and cooling rate effect on phase taransition between proto- and clino-enstatite

Tatsuya Osako[1], *Akira Miyake[1], Shugo Ohi[2]

1.Department of Geology and Mineralogy, Graduate School of Science, Kyoto University, 2.Shiga University

[Introduction]

Protoenstatite (PEN, space groupe:*Pbcn*), one of the polymorph of enstatite($MgSiO_3$), is the stable phase at high temperature above 1000°C below 1557°C at atmospheric pressure. It is generally known that protoenstatite is the unquenchable phase. Actually, PEN has never been reported from natural specimens to date. However, Foster (1951), Lee and Heuer(1987), and so on reported PEN was observed at room temperature from experimental generative materials.

Smyth(1974) studied in detail the transformations among polymorphs of enstatite using high temperature single-crystal X-ray techniques. He showed that in rapid quench PEN transformed to clinoenstatite(CEN, *P*21/*c*) and in slow cooling rate PEN transformed to orthoenstatite(OEN, *Pbca*), and concluded that the rapid transformation between PEN and CEN occurs martensitically . On the martensitic transformation, in general, it is known that a parent phase stability is effected of grain size, cooling rates, shear stress and so on. On the PEN-CEN transformation, similar effects reported (e.g Huang et al., 1994), but few quantitative attempts concerning such effects have been made. The purpose in this study is to make clear the condition PEN can retain at room temperature associated with grain size and cooling rates.

[Experiments]

The starting material of experiments was OEN synthesized by the flux method according to Ozima (1982). All experimental specimens are analyzed by the XRD method. (1) Grain size effect: We crushed and assorted synthetic OEN as grain size (1.2, 5.2, 46, 87, 140, 180 um), and heated these samples by the box electric furnace at 1200°C for 20 hours, and after that cooling rate was 5°C/min. (2) Cooling rate effect: Unifying grain size 1.2 um, heated at 1200 °C for 20hr, and after that cooling rate was 6 patterns.(0.1, 1, 3, 5, 10 °C/min, water cooling)

[Results]

(1) Grain size effect: Only CEN peaks existed in the 180 um sample, on the other hand both CEN and PEN peaks existed in the smaller than 140 um. The smaller grain size was, the more PEN retained. It is shown that gran size particularly affects the PEN stability. (2) Cooling rate effect: In the case of a cooling rate was 3 °C/min, most PEN retained. And retained PEN decreased on both the faster and slower cooling than 3 °C/min.

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Keywords: protoenstatite, phase transition, size effect, cooling rate