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Preface: Front edge of submarine mineral resources research in Japan (Part 2)

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As we mentioned in the preface of the last special issue (Suzuki *et al*., 2015), greater interests in submarine resources have been generated recently because many people have realized their high potential. However, exploration methods for submarine mineral resources have not been well developed yet. This is partly because the genesis of the resources is poorly understood. To solve this problem, geochemical investigation possibly plays an important role in elucidating the genesis of submarine mineral resources. Based on such scientific investigation, many technologies used in underwater environments such as autonomous underwater vehicles (AUV) and electromagnetic survey tools have been significantly improved. In this situation, we realized that progress of scientific research on submarine resources should be well organized and be published in a special issue of *Geochemical Journal*. Therefore, we briefly summarize the essence of the papers in the two special issues (Vol. 49, No. 6 and this issue).

Solid methane hydrate is one of the potential energy resources in the ocean. It contains a large amount of methane within the crystal structure of water under the low-temperature and high-pressure condition in sub-seafloor environment. As the primary source of methane in the hydrate is of methanogenic origin, investigation on the methanogens distribution leads to better understanding of the generation processes of methane hydrate. Kaneko *et al*. (2014) recently developed the highly sensitive technique to estimate methanogenesis by quantification of coenzyme F430 in marine sediments. In this issue, Kaneko *et al*. (2016) applied this method and estimated the methanogenic biomass and activities based on the F430 content in marine sediments below seafloor off the Shimokita Peninsula and at the Nankai Trough.

As for mineral resources, four types closely associated with each tectonic setting are so far known. The discovery of hydrothermal vents in the late 1970s (Corliss *et al*., 1979; Edmond *et al*., 1979) has promoted the investigation and exploration of hydrothermal deposits. Ore deposits consist of sulfide minerals enriched in base and precious metals such as Cu, Pb, Zn, Au and Ag are precipitated from hydrothermal fluid. Hydrothermal fluid circulation system beneath the seafloor is driven by a heat source magma, where the fluid is evolved from seawater by various processes of fluid-mineral interactions. The other three types of mineral resources are formed in oxidative environments on the seafloor. Ferro-manganese crusts with high concentration of Co, Ni, Te, rare earth elements (REEs) and Pt with a thickness of a few cm to 20 cm are ubiquitously located on the slopes of seamounts with a depth of 500 to 5500 m (JAMSTEC press release, 2016). Ferro-manganese nodules with a size of a few mm to a few ten cm, consisting of Fe and Mn oxy-hydroxide with high concentration of Co, Cu and REEs, are found on the deep-sea floor (typically > 5000 m). The REY (rare earth elements and Y)-rich mud is also distributed on the deep-sea floor in the Pacific Ocean (Kato *et al*., 2011).

Survey of active hydrothermal plumes is one of the ways to find potential hydrothermal deposits. In the previous issue, Nakamura *et al*. (2015) utilized on-board

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wide-area multi-beam echo-sounding system (MBES) and found several acoustic anomalies in the water columns in the Okinawa Trough area. Observation of ocean floor and sub-seafloor using instruments mounted on AUV has been attempted because of the possible wide application of recent AUV. Kasaya *et al*. (2015) used the high-frequency MBES system mounted on AUV and obtained more precise images of the hydrothermal plumes than those acquired by on-board MBES in the Iheya North Knoll, the Okinawa Trough. Asada *et al*. (2016) also in this issue observed the hydrothermal area using the integrated high-resolution acoustic observation equipment consisting of multibeam echo sounder (MBES), sidescan sonar (SSS) and sub-bottom profiler (SBP) systems on the AUV *Urashima* (JAMSTEC). They indicate extension of the ore area on caldera floor and shallow sub-seafloor of the Bayonnaise Knoll, an actively rifted part of the Izu-Bonin volcanic arc. They claim that acoustic investigations along with appropriate interpretation are very useful to determine the detailed distribution of hydrothermal ores on the seafloor and at shallow subsurface. Komaki *et al*. (2016) also used AUV to measure the echo intensity (EI) with an acoustic Doppler current profiler (ADCP) over three hydrothermal vent fields (Snail, Archean and Pika) within the South Mariana Trough and found clear EI anomalies over the Pika and Archean vent fields. The characteristics of the higher EI anomalies were carefully examined and described in their work in terms of their relationship with turbidity. Chemical survey is also an effective way to find and identify hydrothermal vents. Okamura *et al*. (2015) in the previous issue developed the deep-sea hydrogen sulfide ion (HS^-) sensors based on linear sweep voltammetry with three electrodes. Yamamoto *et al*. (2015) developed a Hg sensor based on an anodic stripping voltammetry method. They have successfully detected the hydrothermal plumes in the South Mariana and Okinawa Trough and in the Iheya North hydrothermal field in Okinawa Trough, respectively.

In addition to the papers regarding survey of the hydrothermal plume mentioned above, Toki *et al*. (2016) discussed in this issue the chemical characteristics of the hydrothermal fluids from the Hatoma Knoll in the Okinawa Trough. They found a single source of the fluid which possibly underwent the phase separation beneath the seafloor. The hydrothermal fluids from the Hatoma vent possess the similar chemical feature to those of the other hydrothermal fluids in the Okinawa Trough. Based on the lower He isotopic compositions and the lowest carbon isotopic compositions of CH_4 in the fluids, Toki *et al*. (2016) suggested that the Hatoma hydrothermal system is the most significantly influenced by the sediments in the recharge zone among the Okinawa Trough hydrothermal systems.

The chemical compositions of ferromanganese crusts (Fe-Mn crusts) are discussed in this issue by Nozaki *et al*. (2016). They report major and trace element compositions of Fe-Mn crusts collected from the Takuyo Daigo Seamount, northwestern Pacific Ocean. They found that the elements enriched in the Fe-Mn crusts such as Co, Ni, Mo, Te, W, Pt and REEs are positively correlated with either Fe or Mn concentrations. They also estimate the reserve of Fe-Mn crusts around the Takuyo Daigo Seamount based on some assumptions.

A dense field of spherical ferromanganese (Fe-Mn) nodules with 5–10 cm in diameter was found approximately 300 km east of the Minamitorishima Island in the western North Pacific (Machida *et al*., 2016). They report that high acoustic reflectivity observed by the onboard acoustic system is related to this dense occurrence of the nodules. They found elements such as Fe, Ti, Co, As, REEs are concentrated in the nodule rim, while elements such as Al, P, Ca, Ni, Zn, Y, Mo, Ce and W are concentrated in the center, and decrease toward the rim. They suggest that Fe-Mn nodules in the area have high potential for metals of economic interest, especially Co, Ni, Mo and W. These Fe-Mn nodules can also serve as sources of information on paleoceanographic events since early Oligocene time.

Following the findings of REY-rich mud in the eastern South Pacific and central North Pacific Ocean (Kato *et al*., 2011), a REY-rich mud layer was also reported in the eastern Indian Ocean, and that enrichment of REY in this area is controlled by the sedimentation rate (Yasukawa *et al*., 2014, 2015). In the present issue, Iijima *et al*. (2016) report the discovery of deep-sea mud extremely enriched in REY around the Minamitorishima Island in the western North Pacific. The maximum total REY concentration in this area reaches approximately 7000 ppm, which is much higher than that reported for conventional REY deposits on land and other known potential REY resources in the ocean. Fujinaga *et al*. (2016) describe the detailed lithological and chemical characteristics of REY-rich mud similar to those investigated by Iijima *et al*. (2016) and the surrounding sediments around the Minamitorishima Island in this issue. The REY-rich mud layers are characterized by abundant grains of phillipsite, biogenic calcium phosphate and manganese oxides, and are widely distributed in relatively shallow depths beneath the seafloor in the southern part of the area around the Minamitorishima Island.

Takahashi *et al*. (2015) investigated the detailed geochemical characteristics of the deep-sea sediments recovered from the ODP core collected from the northwestern Pacific based on the chemical compositions of the sediments, especially REE pattern, synchrotron X-ray absorption spectroscopy and chemical leaching method. They suggested that REE abundances in apatite (described as 'biogenic calcium phosphate' above), which is the key mineral in the processes of REY enrichment (Kashiwabara *et al*., 2014; Kon *et al*., 2014), in the sediment depend on the amount of REEs fixed in Mn (and Fe) oxides, and then apatite finally fixes the REEs during early diagenesis. They also mentioned the possibility and limitation of using apatite as a proxy of seawater chemistry. Ohta *et al*. (2016) analyzed the mineralogy and grain size distribution of the cores around Minamitorishima Island by microscopic observations. They found that the highly REY-enriched layers ($\sum$REY > ~2,000 ppm) contained significant amounts of calcium phosphate and phillipsite. The shapes of the calcium phosphate grains suggest that they were mostly biogenic in origin. Based on these results they claim that the bulk $\sum$REY content was mainly controlled by the amount of biogenic calcium phosphate, which is well known to concentrate REY. Increased accumulation of biogenic calcium phosphate was responsible for the REY enrichment, which is consistent with the above-mentioned abundant REY in apatite in the sediments (Kashiwabara *et al*., 2014; Kon *et al*., 2014). Takaya *et al*. (2015) proposed an appropriate method to extract REY from extremely REY-enriched sediment from northwestern Pacific Ocean. They reported that the highest extraction efficiency of REY other than Ce was over 95% using hydrochloric acid and over 80% using sulfuric acid.

Nakamura *et al*. (2016) propose a way to obtain information over a wide distribution of REY-rich mud around the Minamitorishima Island using acoustic characterization of pelagic sediments from sub-bottom profiler data. They found that three types of the acoustic facies can be distinguished: opaque (O), transparent (T) and layered (L). The O-type facies is acoustically opaque and highly reflective beneath the top surface. The T-type facies is acoustically transparent, with a basal reflector from the acoustic basement. The L-type facies is characterized by a layered sequence of multiple reflectors. Based on correlation of the acoustic facies types with lithological and geochemical data of sediment core samples, they showed that the T-type facies correspond to REY-rich mud and L-type facies correspond to non-REY-rich sediment covering REY-rich mud. These findings can lead to an appraisal of the rough distribution of REY-rich mud by ship survey.

Scientific research on submarine resources is getting more important both for better understanding of global material cycling and for their exploration. Our goal is to promote the research on submarine resources. We hope that our two special issues are useful for this purpose.

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References

Asada, M., Kasaya, T., Sayanagi, K. and Goto, T. (2016) Indication of hydrothermal deposits and ore area on caldera floor and shallow sub-seafloor of the Bayonnaise knoll, based on high-resolution acoustic investigation. *Geochem. J*. **50**, this issue, 461–475.

Corliss, J. B., Dymond, J., Gordon, L. I., Edmond, J. M., Von Herzen, R. P., Ballard, R. D., Green, K., Williams, D. A. B., Crane, K. and Van Andel, T. H. (1979) Submarine thermal springs on the Galapagos Rift. *Science* **203**, 1073–1083.

Edmond, J. M., Measures, C., McDuff, R. E., Chan, L. H., Collier, R., Grant, B., Gordon, L. I. and Corliss, J. B. (1979) Ridge crest hydrothermal activity and the balances of the major and minor elements in the ocean: The Galapagos data. *Earth Planet. Sci. Lett*. **46**, 1–18.

Fujinaga, K., Yasukawa, K., Nakamura, K., Machida, S., Takaya, Y., Ohta, J., Araki, S., Liu, H., Usami, R., Maki, R., Haraguchi, S., Nishio, Y., Usui, Y., Nozaki, T., Yamazaki, T., Ichiyama, Y., Ijiri, A., Inagaki, F., Machiyama, H., Iijima, K., Suzuki, K., Kato, Y. and KR13-02, MR13-E02 Leg 2 and KR14-02 Cruise Members (2016) Geochemistry of REY-rich mud in the Japanese Exclusive Economic Zone around Minamitorishima Island. *Geochem. J*. **50**, this issue, 575–590.

Iijima, K., Yasukawa, K., Fujinaga, K., Nakamura, K., Machida, S., Takaya, Y., Ohta, J., Haraguchi, S., Nishio, Y., Usui, Y., Nozaki, T., Yamazaki, T., Ichiyama, Y., Ijiri, A., Inagaki, F., Machiyama, H., Suzuki, K., Kato, Y. and KR13-02 Cruise Members (2016) Discovery of extremely REY-rich mud in the western North Pacific Ocean. *Geochem. J*. **50**, this issue, 557–573.

JAMSTEC press release (2016) Cobalt-rich Ferromanganese Crust Extended beyond 5,500 m Depth in Ocean—A big leap for elucidation of genesis—. http://www.jamstec.go.jp/e/about/press_release/20160209/

Kaneko, M., Takano, Y., Chikaraishi, Y., Ogawa, O., N., Asakawa, S., Watanabe, T., Shima, S., Krüger, M., Matsushita, M., Kimura, H. and Ohkouchi, N. (2014) Quantitative analysis of coenzyme F430 in environmental samples: a new diagnostic tool for methanogenesis and anaerobic methane oxidation. *Anal. Chem*. **86**, 3633–3638.

Kaneko, M., Takano, Y., Ogawa, N. O., Sato, Y., Yoshida, N. and Ohkouchi, N. (2016) Estimation of methanogenesis by quantification of coenzyme F430 in marine sediments. *Geochem. J*. **50**, this issue, 453–460.

Kasaya, T., Machiyama, H., Kitada, K. and Nakamura, K. (2015) Trial exploration for hydrothermal activity using acoustic measurements at the North Iheya Knoll. *Geochem. J*. **49**, 597–602.

Kashiwabara, T., Toda, R., Fujinaga, K., Honma, T., Takahashi, Y. and Kato, Y. (2014) Determination of host phase of lanthanum in deep-sea REY-rich mud by XAFS and μ-XRF using high-energy synchrotron radiation. *Chem. Lett.* **43**, 199–200.

Kato, Y., Fujinaga, K., Nakamura, K., Takaya, Y., Kitamura, K., Ohta, J., Toda, R., Nakashima, T. and Iwamori, H. (2011) Deep-sea mud in the pacific ocean as a potential resource for rare-earth elements. *Nat. Geosci.* **4**, 535–539.

Komaki, K., Furushima, Y. and Yamamoto, H. (2016) 3D characteristics of ADCP echo intensity anomaly observed over the Snail, Archean, and Pika hydrothermal vent fields in the South Mariana Trough. *Geochem. J.* **50**, this issue, 477–492.

Kon, Y., Hoshino, M., Sanematsu, K., Morita, S., Tsunematsu, M., Okamoto, N., Yano, N., Tanaka, M. and Takagi, T. (2014) Geochemical characteristics of apatite in heavy REE-rich deep-sea mud from Minami-Torishima area, southeastern Japan. *Resour. Geol.* **64**, 47–57.

Machida, S., Fujinaga, K., Ishii, T., Nakamura, K., Hirano, N. and Kato, Y. (2016) Geology and geochemistry of ferromanganese nodules in the Japanese Exclusive Economic Zone around Minamitorishima Island. *Geochem. J.* **50**, this issue, 539–555.

Nakamura, K., Kawagucci, S., Kitada, K., Kumagai, H., Takai, K. and Okino, K. (2015) Water column imaging with multibeam echo-sounding in the mid-Okinawa Trough: Implications for distribution of deep-sea hydrothermal vent sites and the cause of acoustic water column anomaly. *Geochem. J.* **49**, 579–596.

Nakamura, K., Machida, S., Okino, K., Masaki, Y., Iijima, K., Suzuki, K. and Kato, Y. (2016) Acoustic characterization of pelagic sediments using sub-bottom profiler data: Implications for the distribution of REY-rich mud in the Minamitorishima EEZ, western Pacific. *Geochem. J.* **50**, this issue, 605–619.

Nozaki, T., Tokumaru, A., Takaya, Y., Kato, Y., Suzuki, K. and Urabe T. (2016) Major and trace element compositions and resource potential of ferromanganese crust at Takuyo Daigo Seamount, northwestern Pacific Ocean. *Geochem. J.* **50**, this issue, 527–537.

Ohta, J., Yasukawa, K., Machida, S., Fujinaga, K., Nakamura, K., Takaya, Y., Iijima, K., Suzuki, K. and Kato, Y. (2016) Geological factors responsible for REY-rich mud in the western North Pacific Ocean: Implications from mineralogy and grain size distributions. *Geochem. J.* **50**, this issue, 591–603.

Okamura, K., Sugiyama, T., Noguchi, T., Fukuba, T. and Okino, K. (2015) Development of a deep-sea hydrogen sulfide ion sensor and its application for submarine hydrothermal plume exploration. *Geochem. J.* **49**, 603–611.

Suzuki, K., Ishibashi, J., Kato, Y. and Nozaki, T. (2015) Preface: Front edge of submarine mineral resources research in Japan. *Geochem. J.* **49**, 575–577.

Takahashi, Y., Hayasaka, Y., Morita, K., Kashiwabara, T., Nakada, R., Marcus, M. A., Kato, K., Tanaka, K. and Shimizu, H. (2015) Transfer of rare earth elements (REE) from manganese oxides to phosphates during early diagenesis in pelagic sediments inferred from REE patterns, X-ray absorption spectroscopy, and chemical leaching method. *Geochem. J.* **49**, 653–674.

Takaya, Y., Fujinaga, K., Yamagata, N., Araki, S., Maki, R., Nakamura, K., Iijima, K. and Kato, Y. (2015) Chemical leaching of rare earth elements from highly REY-rich mud. *Geochem. J.* **49**, 637–652.

Toki, T., Itoh, M., Iwata, D., Ohshima, S., Shinjo, R., Ishibashi, J., Tsunogai, U., Takahata, N., Sano, Y., Yamanaka, T., Ijiri, A., Okabe, N., Gamo, T., Muramatsu, Y., Ueno, Y., Kawagucci, S. and Takai, K. (2016) Geochemical characteristics of hydrothermal fluids at Hatoma Knoll in the southern Okinawa Trough. *Geochem. J.* **50**, this issue, 493–525.

Yamamoto, M., Kodamatani, H., Kono, Y., Takeuchi, A., Takai, K., Tomiyasu, T. and Marumo, K. (2015) Development of a deep-sea mercury sensor using *in situ* anodic stripping voltammetry. *Geochem. J.* **49**, 613–620.

Yasukawa, K., Liu, H., Fujinaga, K., Machida, S., Haraguchi, S., Ishii, T., Nakamura, K. and Kato, Y. (2014) Geochemistry and mineralogy of REY-rich mud in the eastern Indian Ocean. *J. Asian Earth Sci.* **93**, 25–36.

Yasukawa, K., Nakamura, K., Fujinaga, K., Machida, S., Ohta, J., Takaya, Y. and Kato, Y. (2015) Rare-earth, major, and trace element geochemistry of deep-sea sediments in the Indian Ocean: Implications for the potential distribution of REY-rich mud in the Indian Ocean. *Geochem. J.* **49**, 621–635.