Preface

Preface for Ore Geology Reviews Special Issue: Marine mineral deposits: New resources for base, precious, and critical metals

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International activities directed toward deep-ocean mining are accelerating at an amazing pace, with more than 2.5 million square kilometers under contract for exploration and that number is increasing monthly. Global metal markets, establishment of regulatory frameworks by coastal nations and the International Seabed Authority, and technology developments are driving this global endeavor. Technology now exists for the mining of deep-ocean seafloor massive sulfides, manganese nodules, and phosphorite, and is in the final stages of development for cobalt-rich ferromanganese crusts. Within the next few years, the first deep-ocean mines will have begun operations and a new industry will have been born. Since exploration for economically viable deposits on the vast seafloor at great depths is expensive, better understanding of the origin of these deposits is essential for efficient exploration and extraction.

Consequently, this is a perfect medium to address current research accomplishments, present new research on various deposit types and genetic models, and evaluate the best ways forward for research and development. Research is essential on the contributions of deep-ocean mineral deposits to the global minerals wealth of critical metals including rare earth elements. These metals are common in deep-ocean mineral deposits and will be needed for the rapid development of high-tech, green-tech, and energy applications, and to support the rapidly growing middle class in high-population countries with expanding economies. Articles in this Special Issue were derived from presentations given during Marine Minerals Sessions at the 2015 and 2016 Goldschmidt Conferences in Prague and Yokohama, respectively. These papers focus on seafloor massive sulfides, hydrothermal manganese-oxide deposits, ferromanganese (Fe-Mn) crusts and nodules, and rare earth-rich sediment.

A brief introduction to the Special Issue Papers

P. Josso et al. (this issue) propose a new discrimination scheme for oceanic ferromanganese deposits based on high field strength and rare earth elements. This new scheme places hydrothermal manganese deposits with high trace element concentrations into a hydrothermal field rather than in hydrogenetic or diagenetic fields as in other discrimination diagrams. They also provide a general discrimination that can be used onboard ship to direct exploration activities. That scheme uses elements that can be easily determined with shipboard analytical instruments.

Typically Be and Os isotopes have been used to date Fe-Mn crusts and nodules, but these techniques are generally expensive and require an accelerator for Be. Because of these limitations, new dating techniques are welcome in order to diversify the number of dating tools that can be used. **A. Noguchi et al.** (this issue) describe a new technique that uses magnetostratigraphy to determine growth rates and thereby date five ferromanganese crusts recovered from the northwest Pacific. They found a consistent reversal pattern in all five crusts that were collected at different locations. The ages are consistent with those determined using $^{10}Be/^9Be$ ratios.

Hydrogenetic Fe-Mn crusts from open-ocean environments have been well studied, but fewer studies have evaluated continent-proximal deposits. **T. Conrad et al.** (this issue) show that Fe-Mn crusts formed within the California continental-margin environment have significantly different mineralogy and chemical compositions compared to crusts formed in open-ocean environments. Many of these characteristics are related to higher Fe/Mn ratios and to lower redox conditions in the continental-margin environment. Redox cycling on continental shelves and slopes contribute the additional Fe that increases the Fe/Mn ratios in the crusts.

Fe-Mn crusts from Pacific Ocean seamounts and ridges are moderately well known, but studies of crusts from the Atlantic and Indian Oceans are less common. **E. Marino et al.** (this issue) describe Fe-Mn crusts from four Cretaceous seamounts in the Canary Island Seamount Province, northeast tropical Atlantic. These crusts are among the thickest recovered from the global ocean and may also be among the oldest. These crusts have higher contents of Fe, Ti, Pb, and REY, and lower Mn, Co, Ni, and PGE contents than Pacific and Indian Ocean crusts. Temporal changes in chemical composition can be related to changes in ventilation of the North Atlantic Oxygen Minimum Zone and changes in Sahara dust input.

The older parts of thick Fe-Mn crusts were commonly phosphatized during several Cenozoic events before the younger layers precipitated. Little information is available as to the timing of those events. **K. Nishi et al.** (this issue) determined the age range using Be isotopes of the non-phosphatized layer of a large number Fe-Mn crusts collected from across the western and central equatorial Pacific. They extended the Be age model using paleomagnetic stratigraphy and micropaleontology. They further calculated the base of the non-phosphatized layer to vary from about 17 Myr to 10 Myr, much younger than previous results for ages of phosphatization of the seamounts.

In situ ROV geological mapping and sampling are scarce in the study Fe-Mn crusts on seamounts from the summit to the lowermost flank. **A. Usui et al.** (this issue) completed just such a study, from about 800 to 5500 m water depths on Takuyo-Daigo Seamount, northwest Pacific. They found that Fe-Mn crusts up to 105 mm thick cover all rock substrates. Be isotope dating and extrapolations of those dates indicate that the crusts have been growing apparently continuous at all water depths for the past 17 Myr, including in the Oxygen Minimum Zone.

They calculated that Fe and Mn fluxes were nearly constant throughout that time period.

Very little work has been published on the Fe-Mn deposits of the Arctic Ocean. **N. Konstantinova et al.** (this issue) provide new data on Fe-Mn crusts collected from a dredge haul (2770–2200 m water depth) taken on Mendeleev Ridge in the western Arctic Ocean. These crusts have a unique composition compared to crusts from the rest of the global ocean and are rich in Li, Th, Sc, As, and V. These crusts also have the largest Fe/Mn ratio and highest detrital mineral content, which both decrease with time. Another difference with open-ocean crusts is common occurrence of todorokite and birnessite in addition to vernadite, which makes these Arctic crusts more like the continental-margin crusts described by Conrad et al. (see above).

Deep-ocean sediment can contain relatively high contents of rare earth elements and yttrium (REY), with a growing interest in their resource potential as an alternative to land-based REY deposits. To better understand the processes that led to enrichment of the REY in deep-ocean sediments, **A. Menendes et al.** (this issue) provide a detailed geochemical study of Atlantic Ocean sediments. They show that REY contents are highest in slowly accumulating pelagic red clays, especially those that contain Fe-Mn micronodules. They also found that REY contents in these Atlantic samples are about four times lower than in Pacific deep-ocean sediments.

Marine hydrothermal manganese deposits have been well studied from dredged samples, but their geological context and ages are poorly known. They are assumed to be young because they mineralize the upper layers of sediments. **K. Yamoaka et al.** (this issue) use U-Th dating to identify both Holocene (~8.8 ka) and fossil (~4.4 Ma) hydrothermal Mn deposits collected from the Izu-Ogasawara arc in the West Pacific. The Holocene samples are typical of other such deposits, very low Fe/Mn ratios, low trace metals including REY. In contrast the fossil deposits showed enrichments in many minor metals, such as Ni, Cu, Zn, Pb, and REY, indicating post-depositional uptake of those metals from seawater.

Low-temperature hydrothermal Mn deposits commonly have low minor-metal contents, or enrichments of only 1 or 2 minor metals. **E. Pelleter et al.** (this issue) describe low-temperature Mn-oxide mineralization in the Wallis and Futuna back-arc system, southwest Pacific, with very high contents of Ni, Cu, and Co. These deposits might represent late-stage products of a specific type of hydrothermal system with the following characteristics: (i) lack of precipitation of high-temperature sulfides at depth that would typically sequester Ni, Cu, Co; (ii) capping of the hydrothermal system so that Ni, Co, Cu are not lost to the water column; (iii) the ability of the Mn minerals to strongly scavenge metals from the fluid.

One of the least known aspects of seafloor massive sulfide deposits is the temporal history including deposit age and duration of mineralizing episodes. **G. Cherkashov et al.** (this issue) address these issues through study of sulfide bodies along the northern equatorial Mid-Atlantic Ridge, an area that includes 18 hydrothermal fields. Dating shows relatively old ages for those deposits, averaging ~66 ka, with the oldest deposit being ~223 ka. They further determined that hydrothermal discharge has an episodic character alternating inactive and active phases. Statistical analyses of the ages show the superposition of several periods of activity with durations of ~15, 10, and 5 ka.

Sulfur and Pb isotopes of massive sulfides are important tools to determine the source of both elements and to understand the origin of hydrothermal ore deposits. Based on isotopic analyses of sulfide minerals in different hydrothermal fields from mid-ocean ridge and volcanic-arc systems, **Z. Zeng et al. (1)** (this issue) demonstrate that the source of S is both associated igneous rock S and seawater S. Isotopic ratios of Pb reflect mainly leaching from local basaltic rocks that host the sub-seafloor hydrothermal systems, with only limited contribution from seawater and/or pelagic sediments. The variability of S and Pb isotopic ratios is related to spreading rates, magmatic degassing, fluid-rock interaction, and fluid-seawater mixing.

Studies of the chemical characteristic of biota from seafloor hydrothermal fields are important for understanding mass fluxes and element partitioning from hydrothermal fluids into the biosphere, metal bioaccumulation in hydrothermal ecosystems, and the nature of chemical cycles. **Z. Zeng et al. (2)** (this issue) analyzed the mineral, chemical, and carbon and oxygen isotopic ratios of mussels and clams from Okinawa Trough hydrothermal fields. They concluded that (i) the metal contents and distributions in different organs vary significantly among locations and among individuals within the same hydrothermal field; (ii) the incorporation of REE from the hydrothermal fluid into the tissues produces different Eu/Eu* ratios than found in the hydrothermal fluid.

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