Marine manganese deposits: Status, subjects, and perspectives.

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Marine manganese deposits, for example, crusts and nodules, occur mainly on the deep floors below the depth about 1000 meters. The deposits are noted as probable metallic ores for some useful metal elements. The distribution patterns, mechanism of formation and deposition, are recently intensively studied around the Japanese Islands in the Northwestern Pacific ocean. In this paper, the history of geoscientific study and resource exploration will be reviewed, in various aspects of geology, geochemistry, mineralogy, microbiology, and paleoceanography. The most important scopes of study on marine manganese deposits are, 1) chemical and mineralogical forms of manganese minerals, 2) mode and processes of deposition of useful metallic elements, 3) relationship of deposition of manganese oxides to marine geology, hydrological conditions, 4) characterization as nano material, 5) microbial effects on the deposition of manganese minerals, 6) correlation with terrestrial manganese and iron/manganese oxide deposits. A systematic joint scientific programs should be reactivated to veil the real occurrence of the deposits, using modern high-tech vehicle, sensors, analysis apparatus of fine, fast, and high-resolution. In the paper, recent results will be overviewed based on our cruises and analysis with joint collaboration with domestic and international institutions.

Keywords: marine manganese deposit, manganese nodule, manganese crust, Northwest Pacific, seamount, geoscience
Geochemistry of ferromanganese crust: recent scientific results

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Ferromanganese crusts (Fe-Mn crusts) are a kind of marine chemical sediment composed of iron and manganese oxides occurring on the surface of seamounts and oceanic plateaus at depths from 400 to 4000 meters below sea level (mbsl) (Hein et al., 2000). Fe-Mn crusts possess especially high concentrations of rare metals such as cobalt, tellurium, and rare earth elements, and are expected as submarine mineral resources. Occurrence, chemical compositions and growth patterns of Fe-Mn crusts are locally variable, and their genesis, growth rates and enrichment processes of elements are required to evaluate Fe-Mn crusts as mineral resources. Therefore, we have been conducting scientific research on genesis of Fe-Mn crusts.

The depositional ages of sublayers in a Fe-Mn crust sample have been determined by the Be-10 isotope system and ultrafine-scale magnetostratigraphy (Oda et al., 2011). Though these methods can provide precise age data of the young part of Fe-Mn crusts (up to 10 million years), development of the method to determine the age of the whole layers is required. Klemm et al. (2005) applied osmium (Os) isotope stratigraphy in which the Os isotopic composition of each Fe-Mn crust layer is measured and matched to the well-known marine Os isotope evolution of the past 80 Ma. We analyzed the Os isotope of the Fe-Mn crusts collected from the Takuyo-Daigo, Ryusei and MC10 (Micronesia) seamounts. The obtained results indicate that the Fe-Mn crusts from Takuyo-Daigo and Ryusei seamounts have the growth rate of approximately 3 mm/million years in the past 15 million years. Also, it is proposed that, though the Fe-Mn crust from MC10 seamount is likely to have grown continuously, those from the Takuyo-Daigo seamount encountered significant changes in growth rates, possibly a growth hiatus, between ca. 15 and 30 million years ago.

We have revealed through speciation of elements by synchrotron X-ray that element concentration in Fe-Mn crusts are well constrained by mode of adsorption on iron (ferrihydrite) and manganese oxides (MnO2) (Kashiwabara et al., 2008, 2011, 2013, 2014). As for homologous tungsten and molybdenum, for example, Fe-Mn crusts are distinctly more enriched with tungsten than molybdenum. Kashiwabara et al. (2013) conducted EXFS analyses and proposed its mechanism based on the chemical speciation data as follows: Tungsten forms an inner-sphere complex both on iron and manganese oxides, while molybdenum forms an inner-sphere complex on iron oxide and forms an outer-sphere complex on manganese oxide. Such difference in mode of adsorption leads to difference in concentrations of tungsten and molybdenum in Fe-Mn crusts. On the other hand, tungsten abundance of seawater is suggested to be low due to removal of tungsten in seawater driven by its adsorption on Fe-Mn crusts and other Fe-Mn oxides on the seafloor.

Keywords: ferromanganese crust, seamount, osmium isotope stratigraphy dating, rare metal, coordination complex
Fluctuations of seawater Sr isotope ratio have been actively reconstructed since the 1980s. The seawater Sr isotope curves are used widely as a tool of dating (Sr isotopic stratigraphy) and as a tracer to evaluate surficial circulation of materials in the Earth’s surface.

Futa et al. (1988) attempted to apply the Sr isotope stratigraphy to two Pacific manganese crusts and Ingram et al. (1990) applies the two-step sequential extraction method to leach original seawater Sr. Hein et al. (1992) observed fine-scale compositions in texture and chemistry of a Pacific manganese crust based on Sr isotopic ages. On the other hand, VonderHaar et al. (1995) assessed Sr isotopic dating for a manganese crust to conduct various leaching procedures. As the result, they pointed out the possibility of replacement of original Sr by later stage seawater Sr after growth. After that, Sr isotopic stratigraphy has not been actively applied as the dating method for marine manganese deposits.

In this study, various leaching procedures were tested to obtain basic data for Sr isotopic composition in marine manganese deposits. It was concluded that the two-step sequential extraction using acetic acid was the best way to minimize the effect of Sr from detrital silicates within manganese deposits.

Keywords: manganese deposits, manganese crusts, manganese nodules, strontium, isotope, growth rate
Paleomagnetic study on the ferromanganese crusts recovered from northwest Pacific

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We have conducted paleomagnetic measurements on the ferromanganese crusts recovered from five different locations in the northwest Pacific. The analyses were made on a series of the thin slices (0.5-1.0 mm in thickness) cut perpendicular to the growth layers of the crusts, from surface to the interior. We recognized 2-8 polarity reversals in the crusts, and the most surficial layers were commonly characterized by normal polarities. Assuming that these layers were grown constantly in Brunhes normal polarity chron (0-0.78 Ma), growth rates were estimated as 2.1-5.0 mm/Ma. These rates are consistent with those estimated by the $^{10}$Be/$^{9}$Be method except for one location.

Keywords: ferromanganese crust, paleomagnetic polarity, growth rate
Distribution of Co-rich ferromanganese crusts and evolution of the seamounts in the NW pacific

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Marine hydrogenetic ferromanganese crusts are known as potential mineral deposits for cobalt, nickel, platinum, rare earths and other metals of emerging economic interest.

The crusts show particularly high concentrations of rare metals for high-technology and green technology and usually cover stable rock outcrops in large areas of crests and slopes of seamounts where pelagic sedimentation is generally low or often lacking, thus the Northwest (NW) pacific seamount provinces are most promising sites for future deep-sea mining.

The ferromanganese crusts have been studied in this area by a number of scientific researchers from several countries. Japan Oil, Gas and Metals National Corporation (JOGMEC) commenced survey cruises for the crusts in 1987. In 2014, JOGMEC also obtained an exclusive license from the International Seabed Authority for the crusts in the high sea of NW pacific. The area located approximately 600 km offshore of south-east of Minami-tori-shima island in the EEZ of Japan.

However, our scientific knowledge for understanding the origin, nature, environments and economic potentiality is still limited.

The patterns of distribution, resource potential and the relationship to geological parameters were found to be characterized by the potentiality for the ferromanganese crusts little by little. In this presentation, the relationship between crust abundance and diversity in the geological evolution of the seamounts in the NW pacific is discussed on the basis of bathymetric, geological, geophysical and environmental data.

Keywords: cobalt-rich, ferromanganese crust, northwest pacific, seamount