

## Metal Flux of Ferromanganese from Northwest and Equatorial Pacific

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The hydrogenetic ferromanganese crust is a slowly-growing chemical sedimentary rock composed iron and manganese oxides, with minor heavy metal elements, for example, Co, Ni, Pt, and REEs. We selected some seamounts on the Pacific plate and equatorial seamount for two typical model areas. We carried out occurrence observation of the crusts in a slope of the seamounts at water depths of 1000m to 3000m continually with high-vision camera equipped with ROV, and took intact and unbroken samples with the manipulator at Takuyo-5th seamount. We described substrate rocks, mineralogy and chemistry, and microstructures on fine-microscopic scales with radiometric dating (I. Graham, GNS).

The chemical analysis and calculation of metal flux indicated that, the Mn, the major component has concentrated continuously and fairly constantly in all areas and the depths, while the accumulation of Co depends mainly on water depth. On the other hand, elements which are of clastic origin including Fe and Al greatly reflect the distance from the continental source. Thus the hydrogenetic ferromanganese crusts are probably regarded as useful paleoceanographic archive.

Keywords: ferromanganese crusts, metal flux, northwest pacific, equatorial pacific

## Comparing rare earth elements in the surface layers of ferromanganese crusts and ambient seawater from the Takuyo Daigo

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Hydrogenetic ferromanganese (Fe-Mn) crusts are strongly enriched relative to the Earth's lithosphere in many rare and precious metals, including Co, Te, Mo, Bi, Pt, W, Zr, Nb, Y, and rare earth elements (REEs) (e.g. Hein et al., 2013). Accumulation of these trace metals from seawater is generally controlled by sorption (Koschinsky and Halbach, 1995; Koschinsky and Hein, 2003). REEs, except for Ce, behave as a dissolved trivalent cation in seawater and concentrated in the solid phase by adsorption (Nakada et al., 2013). Although a set of REE concentrations in Fe-Mn crusts is frequently used as a proxy to distinguish formation processes (e.g. Usui and Someya, 1997; Hein et al., 2000), it is not certain if REE concentrations in Fe-Mn crusts are correlated to those in surrounding seawater. In order to verify the correlation, REE concentrations in the outermost surface of Fe-Mn crusts and the surrounding seawater were directly compared at various depths (957-2987 m) on the Takuyo Daigo Seamount. We normalized the REE concentrations in the outermost surface of Fe-Mn crusts with its formation age, as the relative age of Fe-Mn crusts can be determined using osmium isotopic ratio (e.g. Klemm et al., 2005; 2008). For measurement of REE concentrations in seawater, inductively coupled plasma mass spectrometry (ICP-MS) was applied and solid phase extraction (SPE) techniques using chelating resins were conducted as pretreatment (Zhu et al., 2013). In this study, we compare depth profiles of the normalized REE concentrations in the outermost surface of Fe-Mn crusts and the REE concentrations in surrounding seawater.

Keywords: ferromanganese crust, seawater, Os isotope, rare earth elements, geochemistry

## Iron isotopic composition of seawater recorded in ferromanganese deposits

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Iron isotopic composition of marine ferromanganese deposits could be a useful tool to understand the biogeochemical cycle of iron in the ocean. In this study, we measured the iron isotopic compositions ( $\delta^{56}\text{Fe}$  relative to IRMM-14) of hydrogenetic and diagenetic ferromanganese deposits from the Pacific Ocean (1400-6000 m water depth). The hydrogenetic ferromanganese crusts and nodules had a consistent average Fe isotopic composition of  $-0.32 \pm 0.12$  ‰ (2SD). The consistent  $\delta^{56}\text{Fe}$  values imply homogenous Fe isotopic composition of modern deep seawater in the central to northwestern Pacific. Despite differences in mineralogy and chemistry, the  $\delta^{56}\text{Fe}$  values of diagenetic nodules ( $-0.34$  to  $-0.20$  ‰) were indistinguishable from those of hydrogenetic origin. These observations suggest that dissolution and re-precipitation of Fe in sediments resulted in no significant Fe isotope fractionation. These values are apparently lower than the  $\delta^{56}\text{Fe}$  values of seawater from  $<900$  m in the central Pacific ranging from  $+0.01$  to  $+0.58$  ‰ (Radic et al., 2011), implying that deep water is enriched in isotopically light iron. We also reconstructed the temporal variations of iron isotopic compositions in three hydrogenetic ferromanganese crusts from different water depths (1440, 2239, 2987 m) in the northwest Pacific. Regardless of water depth, the  $\delta^{56}\text{Fe}$  values of these crusts showed essentially constant ( $-0.31 \pm 0.13$  ‰, 2SD) throughout the past  $\sim 20$  Ma. This is remarkably consistent with the constant iron isotopic compositions of ferromanganese crust ( $-0.31 \pm 0.10$  ‰, 2SD) in the central Pacific over the last 10 Ma (Chu et al., 2006). Thus, it is suggested that the Pacific deep water has remained constant in iron isotopic composition for long time scale.

Keywords: iron isotope, ferromanganese crust

## Fractionation of Hafnium-Zirconium in ferromanganese crusts

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The couples of High Field Strength elements (HFS elements), e.g. Zirconium (Zr)-Hafnium (Hf) and Niobium (Nb)-Tantalum (Ta), are called Twin-element due to the consistency of their valences and ionic-radii in the environment. As a consequence, these couples must show uniform ratio, which is theoretically same as that of chondrite meteorite. However, the significant fractionations among HFS elements in natural samples have been found, and it was proposed as enigma of Zr-Hf and Nb-Ta fractionation (Niu et al. 2012). The large fractionation of these elemental couples has also been found in the ferromanganese crust (FMC) (Bau 1996). In this study, we attempted to clarify the accumulation mechanism of HFS elements in FMCs with some methods including X-ray absorption fine structure (XAFS) technique for synthesised and natural samples to serve as an aid to approach to this enigma.

Six FMC samples were collected from the Takuyo-Daigo and Ryusei seamounts, from 950 m (summit) to 3000 m water depth, with hyper-dolphin (remotely operated vehicle) equipped with live video camera and manipulators. Near urface layer (less than 1 mm) of all FMC was analysed with XRD and XAFS to confirm the mineral composition and speciation of Zr together with chemical reagents, Zr minerals and rock samples as standard materials. The concentrations of Zr and Hf in these samples were also measured by ICP-MS after appropriate treatments. Furthermore, to serve as an aid to clarify the fractionation mechanism between Zr and Hf in FMCs, distribution coefficients (Kd) and chemical states were determined through the co-precipitation experiments of Hf and Zr with ferrihydrite and  $\delta$ -MnO<sub>2</sub>. To analyse the chemical states on the solid phase, XAFS was employed.

The major mineral composition of Fe and Mn had no significant variation with the water depth of these seamounts. The concentrations of Zr and Hf were increased with depth, and their ratios were varied without showing any trends. However, these ratios were totally fractionated from that in the seawater (Firdaus et al., 2011). For all samples, Hf was enriched in FMC compared to Zr. The chemical state of Zr in FMCs through the depth showed, 1) coprecipitation with ferrihydrite, 2) coprecipitation with  $\delta$ -MnO<sub>2</sub>, and 3) basalt-like composition, and the rate of basalt-like composition of Zr was increased with water depth. The concentrations of Zr in the fraction between ferrihydrite and  $\delta$ -MnO<sub>2</sub> were uniform through with the depth. Furthermore, the concentration of Zr in these fraction was also uniform, that is, the increased-concentration of Zr in the samples from deeper seamounts could be explained by the increase in basalt-like fraction. From the results of co-precipitation experiments of Zr and Hf with ferrihydrite and  $\delta$ -MnO<sub>2</sub>, it was found that the Hf-DFO was more precipitated compared with Zr-DFO. In this case, the bond length of Hf-O was significantly shorter than that of Zr-O.

Keywords: Zirconium, Hafnium, Ferromanganese crust

## Paleoceanographic Record on the Dual Structure of Hydrogenetic Ferromanganese Crusts

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Most Hydrogenetic ferromanganese crusts in the Pacific consist of two growth generations: a phosphatized older growth generation and a non-phosphatized growth generation. This study attempts some detail analyses such as macroscopy, microscopy, chemistry, mineralogy, age and growth rate determination to consider how the dual structures are formed. As a result of age growth rate determinations supported by GNS, the boundary of two growth generations concentrates approximately 15-10 Ma regardless of water depth and region. In the middle to late Miocene, the climate was prominently cold by Antarctic glaciation. As a result, a phosphogenesis of ferromanganese crusts may have occurred because the dissolves phosphate rich and oxygen rich deep water were redistributed to the intermediate water depths by upwelling at the seamounts.

Keywords: ferromanganese crust, marine environment, pacific, seamount

## Proposed valid description of ferromanganese crusts and the significance of this method

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This study shows valid description of ferromanganese crusts for acid solution method. Before this, we used some detail analyses such as chemistry, mineralogy and microscopy. This method can extract the dissolution fragments from ferromanganese crusts and is more useful than the method used up, until now. The fragments consists of several kinds of minerals, for example, quartz, magnetite and clay mineral. These fragments, possibly, can be classified into detrital, biogenetic, volcanic and hydroge-netic origins.

Keywords: Ferromanganese crusts, Microstratigraphy, Paleoceanography

## Comparative analysis of microbial community on hydrogenetic ferro-manganese crusts from North-West Pacific Ocean

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Ferro-manganese crust (Mn crusts) is rock covered with iron and manganese oxides, and present on the boundary layer between hydrosphere and lithosphere. Mn crusts grow with sedimentation of these oxides from seawater. Growth rate is 1-10 mm/Myr, estimated by radiometric dating and magnetic stratigraphy (Usui and Someya, 1997). Mn crust is widely distributed on outcrop of seamount and sea plateau with slow sedimentation rate.

Mn crust contains several metals (ex. Cu, Co, Ni, Pt and Rare Earth Element etc. Hein, 2000). Considering content of rare metals and rare earth element, and abundance of Mn crust on seafloor, it is expected to use of Mn crust as a resource.

Our knowledge about microbes on surface and inside of Mn crust is limited. We analyzed the microbial community on the surface of Mn crust from Takuyo-Daigo Seamount at the depth of 2991 m. We show that high abundance of microbes and highly diversified microbial community on the surface of Mn crust and microbial community on Mn crust is different from that of sediment or seawater (Nitahara et al., 2011). However, it is not clear that these characteristics are general between Mn crust on different area or different depth. So we collected and analyzed Mn crust from several seamounts including Takuyo-Daigo seamount using 16S rRNA gene phylogeny.

We compared microbial communities of Mn crust from Takuyo-Daigo seamount and Ryusei seamount, there is a little difference. Comparative analysis between Mn crust, sediment and seawater from Takuyo-Daigo seamount and Ryusei seamount shows that microbial community composition of Mn crust and sediment are similar, while that of seawater is different from that of Mn crust and seawater.

In this presentation, in addition to Takuyo-Daigo seamount and Ryusei seamount, we will discuss about comparative analysis including Mn crust from Daito Ridge and Ogasawara sea plateau.

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## On-site deposition and exposure experiments at a low-temperature hydrothermal area

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An on-site deposition and on-site adsorption experiments were carried out at a possible hydrothermal area in the Izu-Bonin arc, NW Pacific. The mineralogical and chemical analyses on the exposed glass, ceramics and on the artificial busserite samples suggested a new precipitation during 12 years and positive accumulation of some transitional metals. This finding was the first evidence of modern active precipitation of manganese oxide from normal sea water/ hydrothermal waters in the ocean floors.

Keywords: low-temperature hydrothermal activity, bayonaise hill, manganese mineral, busserite, todorokite, adsorption



## Uranium isotope composition in ferromanganese crusts: Implications for the paleoredox proxy

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Variations of the  $^{238}\text{U}/^{235}\text{U}$  ratio ( $d^{238}\text{U}$ ) in sedimentary rocks have been proposed as a possible proxy for decoding the paleo-oceanic redox conditions, although the marine U isotope system is not fully understood (Stirling et al., 2007 GCA; Weyer et al., 2008 EPSL).

Here we investigate the spatial variation of  $d^{238}\text{U}$  in modern ferromanganese crusts by analyzing U isotopes in the surface layer (0-3 mm depth) of 19 samples collected from 6 seamounts in the Pacific Ocean. The  $d^{238}\text{U}$  values in the surface layers show little variation and range from -0.59 to -0.69 permil. The uniformity of  $d^{238}\text{U}$  values is consistent with the long residence time of U in modern seawater (Dunk et al., 2002 Chem. Geol.), although the  $d^{238}\text{U}$  values are lighter than that of present-day seawater by  $\sim 0.24$  permil (Stirling et al., 2007 GCA; Weyer et al., 2008 EPSL). The light  $d^{238}\text{U}$  is consistent with the isotope offset found during the adsorption experiment of U to birnessite (Brennecke et al., 2011 ES&T). Our results suggest that removal of lighter U from seawater to ferromanganese crusts is responsible for the second largest uranium isotopic fractionation in the modern marine system and could provide a source of heavy U to seawater.

Depth profiles of U isotopes ( $d^{234}\text{U}$  and  $d^{238}\text{U}$ ) in two ferromanganese crusts were investigated to reconstruct the evolution of oceanic redox state during the Cenozoic. The depth profiles of  $d^{238}\text{U}$  show very limited ranges, and have similar values with those of the surface layer samples. The absence of any resolvable variations in the  $d^{238}\text{U}$  depth profiles suggests that the relative proportions of oxic and reducing uranium sinks have not varied significantly over the past 40 Myr. However, the  $d^{234}\text{U}$  depth profiles in the same samples suggest the possible U redistribution after deposition. Therefore, the  $d^{238}\text{U}$  values may have been overprinted by secondary mobilization with pore-water or seawater. These results suggest that careful evaluation of secondary disturbance is required before applying chemical and isotope depth profiles of ferromanganese crusts to understand paleocean environmental changes.

To assess the potential effect of U removal by Mn oxides on seawater  $d^{238}\text{U}$ , we calculated the seawater  $d^{238}\text{U}$  under different fractions of U removal by Mn oxides using a simple isotope balance model. This calculation suggests that seawater  $d^{238}\text{U}$  could have varied significantly throughout the Earth's history along with the changes of the Mn oxides accumulation rate.

Keywords: Uranium,  $^{238}\text{U}/^{235}\text{U}$ ,  $^{234}\text{U}/^{238}\text{U}$ , paleoredox, ferromanganese crust, isotope geochemistry