

## 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 (MnO<sub>2</sub>) (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