## Adsorption structure of vanadium in marine ferromanganese oxides and its relation to host phase and isotope ratio of vanadium

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Marine ferromanganese oxides contain various trace elements and are used as a geochemical tool. Molybdenum (Mo) shows a lighter isotope enrichment in marine ferromanganese oxides. This is the result of isotope fractionation of V between sea water and ferromanganese oxides. It is confirmed that the host phase of Mo in ferromanganese oxide is manganese (Mn) oxides with distorted Oh adsorbed structure by X-ray absorption fine structure (XAFS) analysis (e.g. Kashiwabara et al., 2011). Thus, it is thought that the isotope fractionation is caused by the geometrical change of Mo from Td in dissolved form, i.e.,  $MoO_4^{2-}$ , to distorted Oh adsorbed structure on Mn oxide. Recently, we found that to form the distorted Oh adsorbed structure of Mo, it is necessary to have two elemental properties, i.e. d<sup>0</sup> electron configuration and appropriate ionic radius (Tanaka et al., 2018). Vanadium (V) has these properties, i.e., similar ionic radius to Mo(VI) and d<sup>0</sup> electron configuration at V(V) state. Thus, it is expected that V(V) behaves in marine ferromanganese oxides are similarly to Mo, i.e., exhibiting distorted Oh adsorption structure on Mn oxide and a large fractionation during the adsorption. In the same way to Mo, XAFS analysis can be applied to the determination of the V behavior in ferromanganese oxides. However, ferromanganese oxides include titanium (Ti) and lanthanum (La), which can affect to V XAFS measurement with fluorescence mode due to their similar fluorescence energy to V. Therefore, Transition Edge Sensor (TES), which has high energy sensitivity and energy resolution, was adopted to XAFS measurements to avoid the interferences by Ti and La. The TES-XAFS method was applied to the analysis of V in hydrogenetic (HG) and diagenetic (DG) ferromanganese oxides. We found that the host phase of V in HG is Fe-(oxyhydr)oxide, while that in DG is Mn oxide. Thus, the V behavior in ferromanganese oxides is somewhat different from Mo. The adsorption structures of V in these ferromanganese oxides are also different, and tetrahedral (Td) in HG and distorted octahedral (Oh) in DG. From the adsorption structures, it is expected that V isotope ratio in HG is similar to that in seawater, while that in DG is enriched in lighter isotope due to the isotope fractionation during adsorption like Mo.

Keywords: marine ferromanganese oxide, vanadium, Transition Edge Sensor (TES), XAFS