

Why does the Pd/Pt anomaly cause for marine manganese crust ?

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In spite of the almost same concentration of Pt and Pd in deep ocean water, the Pt content in marine manganese crust, which distributes near the top of sea mount, is often 10~100 times higher than that of Pd[1]. This is called “Pt/Pd anomaly” in marine geochemistry, which has not been made clear even at present. The concentration of trace metals is considered to be controlled by the adsorption reaction on the surface of marine manganese crust whose main mineral is δ -MnO₂. In order to elucidate the Pd/Pt atomic ratio anomaly for marine manganese crust, we compared the adsorption behaviors Pt(II) and Pd(II) complex ions in artificial sea water on δ -MnO₂ and the chemical states of the adsorbed Pt and Pd.

(1) Adsorption behaviors of Pt and Pd

Pd adsorbed rapidly in early stage on δ -MnO₂, but the amount of Pd adsorbed approached slowly a constant value. On the other hand, Pt adsorbed slowly during the experiment. Therefore, the amount of Pt adsorbed exceeded the amount of Pd adsorbed after a certain time depending on the experimental conditions.

(2) Chemical states of Pt and Pd

The results of X-ray absorption spectroscopy showed that the sorbed Pt(II) was oxidized to Pt(IV) by Mn(IV) in the δ -MnO₂ and the isomorphous substitution of the Pt(IV) with the Mn(IV) occurred. On the other hand, Pd(II) was physically adsorbed, but no oxidation of the Pd(II) occurred.

(3) Cause of the Pt/Pd anomaly

“Pt/Pd anomaly” is considered to be due to difference of adsorption behavior of Pt(II) and Pd(II) complex ions onto marine manganese crust.

[1] J.R. Hein et al, *Ore Geology Reviews* **51** (2013) 1-14