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Marine geochemistry of Zr, Hf, Nb, Ta, Mo and W

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1. Introduction

In geochemistry, incompatible elements are unsuitable in size and/or charge to the cation sites of minerals, and therefore concentrated in a liquid phase during the fractional crystallization of magma. Among incompatible elements, Zr, Hf, Nb, Ta, Mo and W that have large ionic valences are classified as high field strength elements (Rudnick and Gao, 2005). Due to their similar chemical characteristics (e.g. ionic charge and ionic radius), Zr-Hf, Nb-Ta and Mo-W are known as 'geochemical twin elements'. In contrast to terrestrial environment, they have been scarcely studied in aquatic environment. In seawater, Zr, Hf, Nb and Ta are classified as 'refractory metals' (Orlans and Merrin, 2001), and are dominated by hydroxide species of $\text{Zr}(\text{OH})_4^-$, $\text{Hf}(\text{OH})_4^-$, $\text{Nb}(\text{OH})_4^-$ and $\text{Ta}(\text{OH})_4^-$, respectively. They are readily removed from solution by interaction with sinking particles, a process referred to as 'scavenging'. Mo and W are dominated by oxyacid species of MoO_4^{2-} and WO_4^{2-} , which are more soluble than hydroxide species (Turner *et al.*, 1981). The distribution and behavior of these metals in the ocean are reviewed in this paper.

2. Zirconium and Hafnium

We have analyzed seawater samples taken from stations K1 (51°N, 165°E), K2 (47°N, 160°E), KNOT (44°N, 155°E) and 35N (35°N, 160°E) in the western North Pacific (Figure 1). Dissolved (D)-Zr and Hf increased with depth. The concentration range of Zr and Hf was 31-275 pmol/kg and 0.14-0.95 pmol/kg, respectively (Figure 2). The deep water enrichment may result from regeneration of scavenged Zr and Hf, deep water sources such as hydrothermal and benthic flux, and lateral advection of deep water masses.

We found that the average D-Zr/Hf ratio was 341 ± 34 in deep water of the western North Pacific. Godfrey *et al.* (1996) reported that the D-Zr/Hf ratio in the northeastern Atlantic varied between 164 and 250. These data imply that the D-Zr/Hf ratio increases with the deep water circulation. D-Zr is enriched in the Pacific Deep Water compared to the North Atlantic Deep Water. D-Hf is less enriched in the Pacific Deep Water. This could be attributable to the fact that

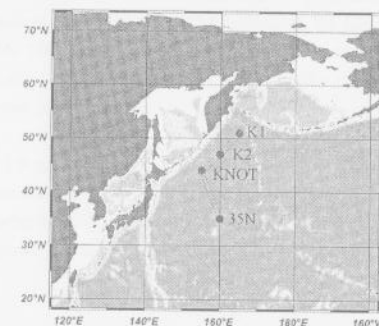


Figure 1. Sampling location

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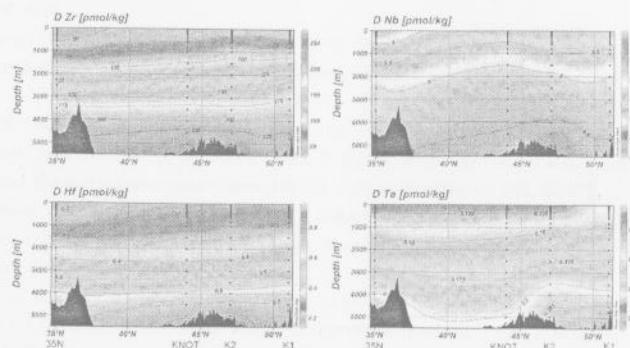


Figure 2. Sectional distribution of dissolved Zr, Hf, Nb and Ta in western North Pacific Ocean

Hf is more intensively scavenged in deep water than Zr (Firdaus *et al.*, 2008). Recently, Zimmermann *et al.* (2009) determined the concentration and isotope composition of D-Hf in the western North Pacific. The D-Hf concentration from the surface to 3,500 m depth agrees well with our data. In deep water below 3,500 m, our determination shows higher D-Hf concentration. It is probably due to the difference in sample pretreatment. We acidified seawater samples to pH 2.2 with HCl and small amount of HF (2×10^{-3} M). Therefore it is likely that the addition of HF is effectively preserves D-Hf in higher concentration.

Labile particulate (LP)-Zr and Hf, which represents a chemically labile fraction of particulate species, were nearly constant from surface to 3,500 m at stations K1 and K2, and increased to the bottom. The increase of LP-Zr and Hf started at a depth of 1,500 m at station 35N. LP-Zr/Hf showed a larger variation in the upper water column. The LP-Zr/Hf ratio was 319 ± 76 in the Pacific Deep Water. Although this value is close to the D-Zr/Hf ratio, it is much higher than the Zr/Hf ratio of 91 in pelagic clay. These results suggest that LP-Zr and Hf originate from the scavenging of the dissolved species in deep water.

3. Niobium and Tantalum

We found that D-Nb showed a slight depletion in surface water and enrichment in bottom water, while Ta showed a slight increase near the bottom (Figure 2). The range of D-Nb and Ta was 4.0-7.2 and 0.08-0.29 pmol/kg, respectively. LP-Nb was enriched in both surface and bottom water. LP-Ta was almost constant from the surface to 3,000-4,500 m depths and showed enrichment in bottom water. The LP-Nb/Ta ratio was high and variable in surface water than deep water. The LP-Nb/Ta value in bottom water is close to that in pelagic clay. Therefore, it is probable that the mechanism controlling the LP mole ratio is different between Nb/Ta and Zr/Hf. It is likely that the increase of LP-Nb and Ta in bottom water can mainly be attributed to resuspension of sediment.

Both Zr-Hf and Nb-Ta are lithophile and refractory, and the chondritic ratio is $Zr/Hf = 19.9$ and $Nb/Ta = 34.3$ (Munker *et al.*, 2003). The Zr/Hf ratio is 5-70 in the silicate Earth. However, all the

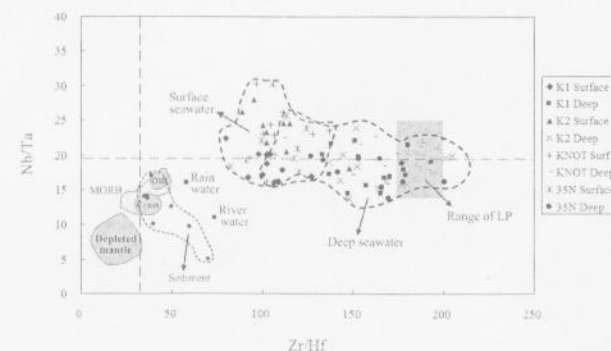


Figure 3. Plot of Zr/Hf vs Nb/Ta weight basis ratio in Earth's system. Surface seawater data are from 10 to 300m depth, deep seawater data are from 400m to bottom water. Broken lines represent the chondritic ratio. Terrestrial reservoir data are taken from Munker *et al.* (2003). Sediment data are taken from Li (2000)

major reservoirs of the silicate Earth display subchondritic Nb/Ta ratio of 3-18 (Figure 3), which is known as 'Nb Paradox'. Hence, mass balance considerations require a reservoir(s) on the Earth that has a superchondritic Nb/Ta. In previous results (Firdaus *et al.*, 2008), we observed the first superchondritic values of Nb/Ta on the Earth in the western North Pacific waters (Figure 3). Thus, it is possible that the ocean has a key to solve the Nb Paradox.

4. Molybdenum and Tungsten

The distribution of D-Mo and W were uniform both vertically and horizontally. LP-Mo and W were negligible. The average concentration (normalized to S=35) was 103 ± 3 nmol/kg for Mo and 47 ± 3 pmol/kg for W. The long residence time of Mo (760,000 y) and W (61,000 y) leads to complete mixing of Mo and W in the world ocean (Firdaus *et al.*, 2008). The completely mixed Mo creates a uniform $^{98/96}\text{Mo}$ isotope composition in various water masses and ocean basins (Nakagawa *et al.*, 2008).

The crustal abundance of Mo and W is 1.1 and 1.9 ppm, respectively (Rudnick and Gao, 2005). In seawater, however, Mo shows much higher concentration than W (~2,000 times). These results imply that W is removed from seawater much faster than Mo, probably by adsorption onto suspended particulates (e.g. iron oxyhydroxide, manganese oxide and clay minerals).

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