Distribution of zirconium, niobium, hafnium, and tantalum in the subarctic North Pacific Ocean and the Indian Ocean

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Zirconium (Zr), niobium (Nb), hafnium (Hf), and tantalum (Ta) are known as high-field strength elements (HFSE) since they form highly charged ions. Because the mole ratios of Zr/Hf and Nb/Ta in seawater change significantly depending on the water mass, they are considered to be useful as oceanographic tracers [1]. However, their concentrations in seawater are very low (< 300 pmol/kg) and their determination is still a challenge in analytical chemistry. We have improved our preconcentration method using TSK-8-hydroxyquinoline (TSK-8HQ) resin [2] and investigated the concentration profiles of the four elements in dissolved (d) and total dissolvable (td) fractions at five stations from 160° E, 47° N to 160° W, 51° N in the subarctic North Pacific Ocean and eleven stations from 40° E, 62° S to 86° E, 17° N in the Indian Ocean.

Recovery of Zr, Nb, Hf, and Ta from a seawater sample was evaluated via the determination of spiked (0.05-300 pmol/kg for each element) and unspiked seawater. The recovery was 100 ± 4 % for Zr, 100 ± 4 % for Nb, 101 ± 3 % for Hf, and 103 ± 6 % for Ta (mean \pm sd, n = 10). The concentration range of dZr, dNb, dHf, and dTa in the subarctic North Pacific Ocean was 30-276, 1.0-2.6, 0.09-0.78, and 0.006-0.026 pmol/kg, respectively. The concentrations of Zr and Hf increased from surface water to deep water, whereas those of Nb and Ta hardly varied from surface water to bottom water. Moreover, there were only small differences between td and d concentrations. The Zr/Hf mole ratio increased from ~180 in surface water to ~410 at a depth of 2000 m in the subarctic North Pacific Ocean. In contrast, the Nb/Ta mole ratio was nearly constant at ~150 throughout the water column. We will report new profiles from the subarctic North Pacific Ocean and the Indian Ocean to compare them with those of previous studies.

[1] Firdaus, M.L. *et al.* (2011) *Nature Geoscience*, **4**, 227-230.
[2] Firdaus, M.L. *et al.* (2007) *Analytica chimica acta*, **583**, 296-302.