Determination of picomolar of zirconium, hafnium, niobium and tantalum in seawater using chelating resin and subsequent ICP-MS determination

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It has been known that Zr, Hf, Nb and Ta are high field strength elements (HFSE) belonging to group IV and V in the periodic table. Among these elements, Zr-Hf and Nb-Ta are geochemical twin elements who have similar chemical properties (i.e., ionic charge and radius) in crustal materials and rocks. Contrastingly, the ratios of Zr/Hf and Nb/Ta in seawater are strongly fractionated, and can be used as chemical tracers for the movement of water masses in the modern ocean and as a proxy for paleo-ocean circulation (Firdaus et al., 2011; Frank, 2011). However, for example, the average Zr concentration is 250 pmol/kg in deep seawater, which is more than 6 order of magnitude lower than those in rock materials. It is still challenging for us to determine sub-picomolar to picomolar of HFSE in seawater.

In this study, we developed a simple method to determine sub-picomolar to picomolar of dissolved Zr, Hf, Nb and Ta in seawater using chelating resin column preconcentration and ICP-MS. With mini-columns filled with commercially available chelating resin, HFSE were preconcentrated by 50 times. We obtained low blank values and good recovery enough to determine HFSE in open ocean surface waters. The detection limits, calculated from the procedural blank values, were 0.15 pmol/kg for Zr, 0.03 pmol/kg for Hf, 0.06 pmol/kg for Nb and 0.03 pmol/kg for Ta, respectively.

Using the new method, we revealed distributions of Zr, Hf, Nb and Ta in open ocean, the North Pacific Ocean, North Atlantic Ocean, Indian Ocean and in the marginal sea, Andaman Sea and Gulf of Thailand. We will discuss the fractionations of Zr–Hf and Nb–Ta in the marine environments.

Keywords: Zr, Hf, Nb and Ta, high field strength elements, seawater

