報　告

Determination of Zr, Hf, Nb, Ta, Mo and W in seawater

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Comprehensive information of trace elements in seawater is important for understanding the marine system. Zr, Hf, Nb, Ta, Mo and W are adjacent elements in the periodic table. In seawater, Zr, Hf, Nb and Ta are dominated by hydroxide species such as $Zr(OH)_5^-$, $Hf(OH)_5^-$, $Nb(OH)_6^-$ and $Ta(OH)_6^-$, while Mo and W are present as MoO_4^{2-} and WO_4^{2-}. The hydroxide dominated elements are more reactive than the oxyacid dominated elements and thought to have potential as oceanographic tracers of external sources, physical mixing, and scavenging removal processes.

We have developed a solid-phase extraction method using TSK-8HQ as chelating resin to concentrate these elements in seawater (Figure 1)[1]. The greatest advantage of this resin is its endurance to 5M HF, since this is an effective eluent for the six metals. The analytes were quantitatively concentrated from 250mL seawater with a 50 fold concentration factor through

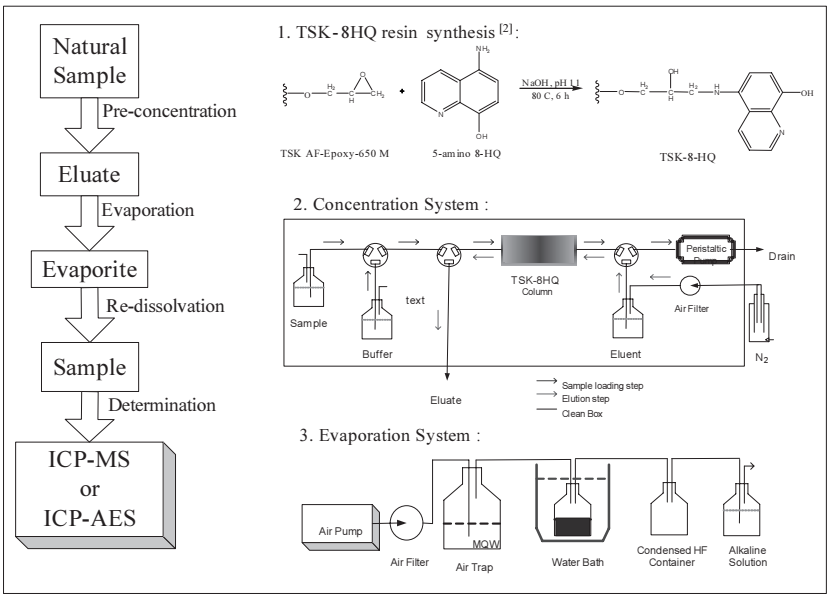

Figure 1. Analytical method

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本研究の一部は，㈶海洋化学研究所の研究委託「太平洋，南極海における微量元素の断面観測」により行われた．

the column extraction and evaporation. Seawater samples were collected from the western North Pacific during the MR05-K01 cruise of R/V Mirai using a CTD carousel, on which Niskin-X samplers were mounted. The interior of the samplers was coated with Teflon and cleaned with detergent and HCl. A portion of seawater for dissolve species (D) was filtered through a 0.2μm Nuclepore filter and acidified to pH 2.2 with HCl and HF. A portion of seawater for acid-dissolvable species (AD) was acidified without filtration. The acid-dissolvable element includes dissolved species and a labile particulate fraction dissolved during storage. It would contain species, such as iron hydroxides, adsorbed on clay minerals and incorporated in organisms.

At station K1 (51°N 165°E); K2 (47°N 160°E); 35N (35°N 160°E) and KNOT (44°N 155°E) in the North Pacific Ocean, Zr and Hf show systematic enrichment with depth, Nb shows slight depletion in surface water, Ta shows enrichment in bottom water, whereas Mo and W show conservative vertical profiles. The concentration range of dissolved Zr, Hf, Nb, Ta and W are 31−275, 0.14−0.95, 4.0−7.2, 0.08−0.29 and 40−51pmol kg^{-1}, respectively, whereas that of Mo is 97−105 nmol kg^{-1}. The range of Zr/Hf, Nb/Ta and Mo/W mole ratio are 156−394, 24−64 and 1940−2600. AD to D ratio for Zr, Hf, Nb and Ta are higher in the surface and bottom water compared to mid-depth, whereas concentrations for Mo and W show no significant difference between D and AD. It means particulate Zr, Hf, Nb and Ta exist in surface and bottom waters. We also determined the dissolved concentrations in river, rain water etc. Average Zr/Hf ratio in crust, river water and rain water is 36, 131 and 114, respectively. Average Nb/Ta ratio is 13, 17 and 23, respectively. Average Mo/W ratio is 0.58, 61 and 51, respectively. Thus, Zr/Hf, Nb/Ta and Mo/W ratios increase in the order of continental crust < river water < seawater, and the variation of Mo/W in seawater is much larger than that of Zr/Hf and Nb/Ta.

References:

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[2]. H. Dierssen, W. Balzer and W.M. Landing (2001) *Mar. Chem.* 73. 173–192.