

Marine Chemistry of Zirconium, Hafnium, Niobium and Tantalum

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ABSTRACT

Here, we present the first simultaneous preconcentration and determination of ultratrace (pmol/kg level) Zr, Hf, Nb, Ta and W in seawater, both in the form of dissolved and acid-dissolvable species. 8-Hydroxyquinoline (8HQ) bonded covalently to a vinyl polymer resin, TSK-8HQ, was used in a chelating adsorbent column to concentrate the metals. The greatest advantage of this resin is its endurance to 5M HF, since this is an effective eluent for all five metals. The analytes were successfully concentrated from 250 mL seawater with a 50-fold concentration factor through the column extraction and evaporation. The detection limit was 0.009–0.15 pmol/kg. The procedure blank determined using ultra pure water as a sample was 0.005–0.37 pmol/kg. The five metals were quantitatively recovered from seawater with good precision (2–4%). The effect of sample pH, sample flow rate, eluent composition and sample pretreatment were carefully studied. This method was applied to seawater.

Keywords: Zr, Hf, Nb, Ta, Seawater

1. Introduction

Extensive information of trace metals in seawater is important for our understanding of the marine system. Since Zr, Hf, Nb and Ta in seawater are dominated by hydroxide species, they have the potential to be used as tracers of external sources, physical mixing and scavenging removal processes in the ocean. However, due to its analytical difficulties, Zr, Hf, Nb and Ta have been rarely studied. Earlier study found that fractionation of Zr-Hf and Nb-Ta occurs in aquatic environment, and the largest fractionation takes place in seawater. The concentration of Zr and Hf was 70–180 pmol/kg and 0.4–1.1 pmol/kg in the northeastern Atlantic Ocean, and was 25–366 pmol/kg and 0.20–1.02 pmol/kg in the subarctic North Pacific, respectively. The vertical profiles for Zr and Hf were indicative of a nutrient-like scavenging-regeneration behavior [McKelvey, 1998]. Although the concentration of Nb and Ta in seawater have been estimated to

be less than 50 pmol/kg and 14 pmol/kg, respectively, the exact concentration in the ocean was not known until recently [Godfrey, 1996]. In the same way as Mo, W has a conservative vertical profile in the Pacific Ocean. The W concentration in seawater was found to be around 50 pmol/kg. Kishida *et al.* found an anomalously high concentration of W in submarine hydrothermal fluids. It suggests that W has the potential to be used as an indicator to detect hydrothermal activity on the seafloor. A detailed analytical method for Nb and Ta in seawater has not been reported, whereas a few methods have been reported for Zr, Hf and W. Determination of these metals in seawater faces two major difficulties: (1) the ultra low concentration (100–0.05 pmol/kg) requiring a sensitive instrument with a low detection limit in addition to an appropriate preconcentration, (2) a high matrix concentration (35 g/kg major ions concentration of seawater at salinity = 35) that could severely interfere with the determination [Chester, 2000].

Solid-phase extraction is one of the fastest, economic and clean preconcentration methods to separate and concentrate trace metals from seawater matrix [Dierssen, 2001]. In a previous study, we used MAF-8HQ, the support of which is fluorinated silica gel, to concentrate Zr, Hf, Nb, Ta and W from seawater [Sohrin, 1998]. However, it was difficult to reduce the blanks and to elute the metals quantitatively. 8-HQ attached to a vinyl polymer, TSK-8HQ, has been used widely as a stationary phase in the solid-phase extraction. This resin has several advantages compared to the other chelating adsorbents; i.e., it is stable to acid or base hydrolysis, it does not exhibit volume changes with changes in pH, and the polymer itself (the solid support) has no cation exchange capacity and does not concentrate dissolved organic species [Firdaus, 2007]. In this presentation, we will show the distribution of ocean section study along 170° and 180°W in the Pacific basin.

2. Research Methodology

2.1. Analytical Methods Seawater samples were collected during two cruises of KH-04-5 (December 2004–March 2005; stations SX) and KH-05-2 (August–September 2005; stations ST) of R/V Hakuho Maru (Figure 1). Clean technique was adopted throughout the procedure. A CTD Carousel equipped with 12 liter Niskin-X samplers was submerged using a titanium armed cable to collect seawater samples. Seawater was transferred from the sampler to low-density polyethylene bottles (Nalge Nunc) on deck using a silicon tube and filling bell to avoid

contamination by airborne particles. Samples were immediately brought into a clean room laboratory (class 100) on the vessel, passed through a 0.2 μm Nuclepore filter (Costar) using a closed filtration system, and acidified to pH 2.2 with HCl and HF. These samples were stored at ambient temperature until analysis. Zr, Hf, Nb and Ta were preconcentrated in 1 M HNO_3 with a concentration factor of 50, through solid-phase preconcentration using chelating resin immobilized-8-hydroxyquinoline and evaporation. The four elements were quantitatively recovered; the recovery of spiked metals was $100\pm 4\%$. Concentrations of Zr, Hf, Nb and Ta in the final solution were determined by HR-ICP-MS (Element II, Thermo Fischer). Measured isotopes were ^{90}Zr , ^{91}Zr , ^{177}Hf , ^{178}Hf , ^{93}Nb and ^{181}Ta . Standard solutions were used for calibration. Detection limit was 0.084, 0.006, 0.072 and 0.006 pmol/kg for Zr, Hf, Nb and Ta, respectively. Procedure blank was 0.25, 0.008, 0.078 and 0.009 pmol/kg, respectively. The precision was about 5% for each element. The seawater samples for dissolved Mn and Fe were obtained from the same samplers, filtered as described above, and acidified to pH 2.2 with HCl. Mn and Fe were preconcentrated using a column of Nobias Chelate-PA1 resin (Hitachi High-Technologies) and determined by a calibration curve method using an ELAN DRC II ICP-mass spectrometer (Perkin Elmer) [Warnken, 1999].

2.2. Calculation of the Oceanic Residence Time

The residence time (τ) of HFSEs in the ocean can be calculated from:

$$\tau = \frac{C_{\text{sw}} M_{\text{sw}}}{F_{\text{total}}} = \frac{C_{\text{sw}} M_{\text{sw}}}{F_{\text{riverine}} + F_{\text{atmospheric}} + F_{\text{hydrothermal}}}$$

where C_{sw} is the concentration of the element in seawater, M_{sw} is the total mass of seawater (1.35×10^{21} kg), and F_{total} , F_{riverine} , $F_{\text{atmospheric}}$ and $F_{\text{hydrothermal}}$ are total, riverine, atmospheric and hydrothermal flux of the element, respectively. The results are given in Table 1. C_{sw} of HFSEs used here is the average concentration of 163 deep water samples (>1,000 m) on the Pacific section. The resulting τ of HFSEs is comparable with or slightly longer than the oceanic mixing time of 500–1,000 years, and shorter than τ of silicate. The τ that has been estimated from scavenging models is 800–5,600 years for Zr and 650–1,300 years for Hf. The τ that has been estimated from riverine input is 5,000 years for Zr and 1,500 years for Hf. On the data from the Hudson River estuary, τ of Hf is estimated between 1,500 and 7,500 years. Using a

weighted average river concentration of 33 pmol/kg and variable f , it was argued that τ of Hf is in a range of 435–1,500 years. On the other hand, it has been proposed that τ of Hf is only a few hundred years, because Hf does not increase along the deep ocean conveyor. Thus, our estimates of τ for Zr and Hf seem to be acceptable. No other data of τ for Nb and Ta are available [Firdaus, 2011].

3. Results and Discussion

Generally Zr and Hf increase with depth. Nb and Ta show depletion in surface water (0 – 300m depths) and enrichment in bottom water. Results of the ocean section showed that the concentration of Zr, Hf, Nb and Ta in surface water is high in the Southern Ocean and Subarctic Pacific Ocean. In deep water (2,000m – bottom), Zr shows lowest concentration in Southern Ocean and gradually increase toward northern stations, coincidence with the flow of deep thermohaline circulation [Sarmiento, 2006]. In contrast, Hf, Nb and Ta show less pronounced increase toward northern stations. We found that water masses in Pacific basin are characterized by unique Zr/Hf and Nb/Ta ratio. Characterized water masses are Circumpolar Deep Water, Antarctic Bottom Water, Antarctic Intermediate Water, Eastern South Pacific Central Water, Pacific Equatorial Water, Eastern North Pacific Central Water, North Pacific Intermediate Water and North Pacific Deep Water.

Zirconium (Zr) and hafnium (Hf) belong to group 4 forming tetravalent (+4) ions, and niobium (Nb) and tantalum (Ta) belong to group 5 forming pentavalent (+5) ions. Because of their high field strength, they are not readily incorporated into silicate minerals and classified as incompatible elements. Variations of Zr/Hf and Nb/Ta ratios are critical for understanding crust-mantle differentiation and evolution of the Earth-Moon system. They are classified as refractory elements in oceanography, because they form hydroxide species and are not very soluble in seawater. Here we show the first basin-scale sectional distributions of dissolved Zr, Hf, Nb and Ta in the Pacific Ocean. These elements are generally depleted in surface water and increase from the Southern Ocean to the North Pacific Ocean in deep water, showing strong correlations with silicate ($R > 0.8$). The distributions indicate importance of terrigenous sources to the budget of Zr, Hf, Nb and Ta in seawater compared to hydrothermal input (Figure 2). The weight ratios are 45–350 for Zr/Hf and 14–85 for Nb/Ta in the Pacific Ocean seawater, which are generally

higher than those in fresh water, the silicate Earth and chondrite. The Zr/Hf and Nb/Ta ratios are useful to trace water masses and their fractionation in the ocean is very unique.

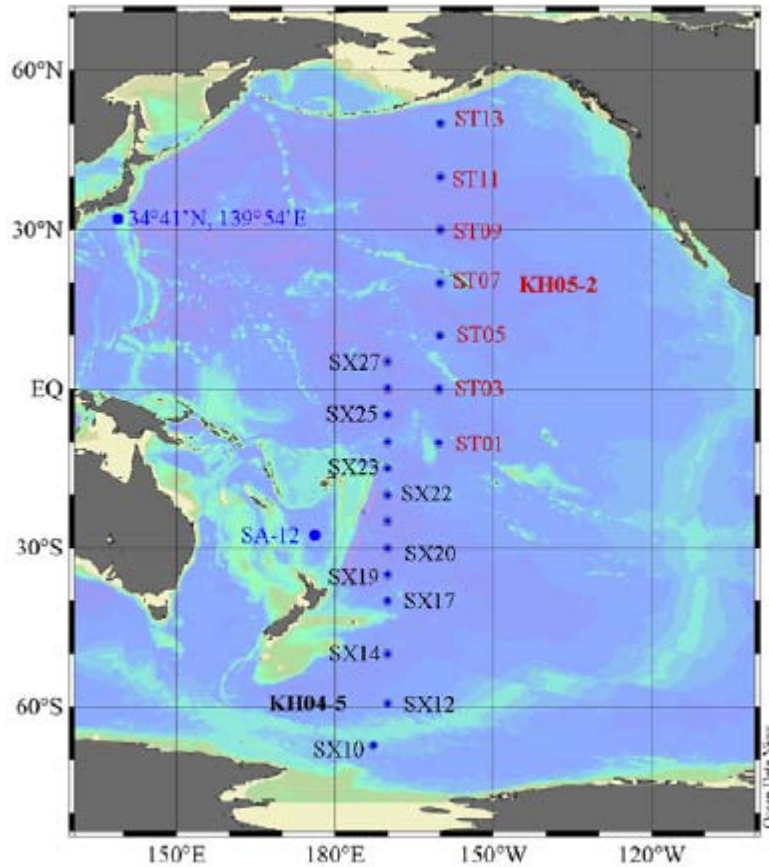


Figure 1. Location of sampling stations in the Pacific Ocean.

For the dissolved Nb-Ta system, the slope is close to the mole ratio of Nb/Ta = 22 in continental crust. This may suggest the insignificant fractionation between Nb and Ta in deep water, reflected in the comparable (2.7×10^3 y for Nb and 1.3×10^3 y for Ta). It should be noted that the regression line has a positive Nb intercept, which is distinct from the general proportionality between Nb and Ta in the lithosphere and sediments. The unique fractionation in the ocean may be attributed to incongruent inputs of Ta or preferential removal of Nb from surface seawater, deserving further study.

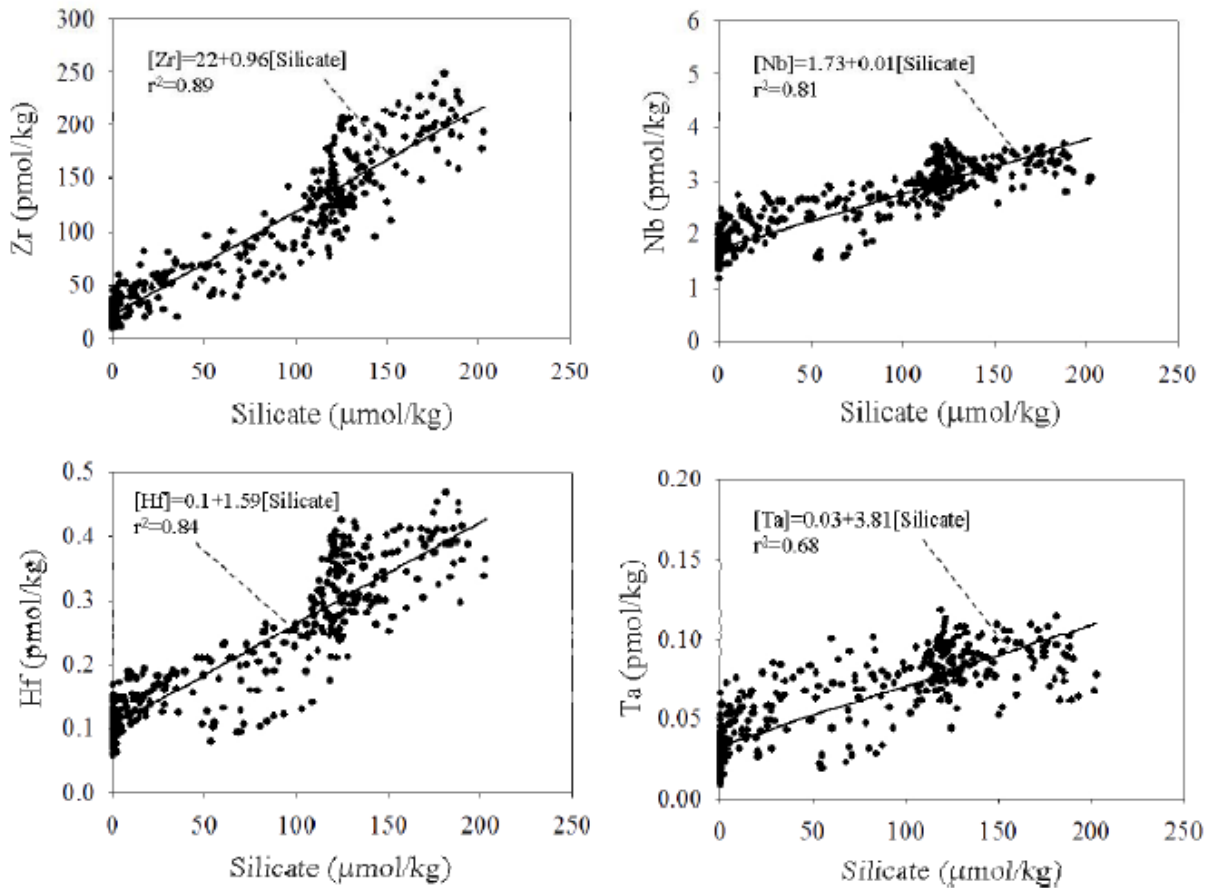


Figure 2. Scatter plots of dissolved HFSE versus silicate in seawater. (a) Zr, (b) Hf, (c) Nb and (d) Ta. Regression lines are calculated using the data from the North Pacific.

Seawater data of dissolved Hf versus Zr plot above the mole ratio of $Zr/Hf = 71$ in continental crust. The slope is markedly higher than that for the Atlantic. The intercept of the regression line is close to zero in the Atlantic and becomes negative in the North Pacific. These trends indicate the inter-ocean fractionation of the Zr-Hf system. A comparison with this work and the previous observations [Firdaus, 2008] reveals that Hf concentration does not increase progressively along the pathway of the deep circulation, in contrast to Zr and to Nd. Hafnium should be scavenged from deep water more promptly than Zr and Nd. Strong scavenging of Hf onto opal in the Southern Ocean has been proposed. On the basis of our new data, we have reassessed the budget and residence time (τ) of dissolved Zr, Hf, Nb and Ta in the ocean (Table

1). The τ for Hf of 8.7×10^2 years is roughly one quarter that for Zr of 3.7×10^3 years, which is consistent with the previous observations.

Table 1. Residence time of HFSEs in the ocean

Metals	Seawater Concent. (pmol/kg)	Budget (mol)	River Concent. (pmol/kg)	River Flux (mol/yr)	Rain Concent. (pmol/kg)	Rain Flux (mol/year)	Hydrothermal Flux (mol/year)	Residence Time (years)
Zr	155	2.1E+11	4.3E+02	1.6E+07	1.1E+02	4.1E+07	0.0E+00	3.7E+03
Hf	0.33	4.5E+08	4.9E+00	1.8E+05	9.1E-01	3.3E+05	0.0E+00	8.7E+02
Nb	3.1	4.2E+09	1.8E+01	6.7E+05	2.5E+00	9.0E+05	0.0E+00	2.7E+03
Ta	0.087	1.2E+08	1.4E+00	5.2E+04	1.1E-01	4.0E+04	0.0E+00	1.3E+03
Si*		1.1E+17		5.6E+12		5.0E+11	6.0E+11	1.6E+04

*Data taken from Sarmiento (2006).

4. Conclusion

We report meridional ocean sections of dissolved Zr, Hf, Nb and Ta along 65°S–10°N, 170°W and 10°S–50°N, 160°W. Zr and Hf show gradual increase with depth. Surface concentration of Hf is low in the southern hemisphere. In deep water, Zr takes the lowest concentration at 67°S and increases toward northern stations. Hf shows a slight increase to the north. Nb and Ta show depletion in surface water and relatively uniform distributions in deep water. Surface concentration of Nb and Ta is low in the southern hemisphere as well as Hf. Again, the deep water concentration of Nb and Ta is the lowest at 67°S and increases to the north. These distributions are similar to that of silicate, whereas silicate is more depleted in surface water and has a maximum at 2,000–3,000 m depth in the North Pacific. The correlation coefficient (R) against silicate is 0.94, 0.92, 0.90 and 0.83 for Zr, Hf, Nb and Ta, respectively ($n = 409$). The plots of HFSE against silicate show fairly good linearity, whereas positive deviations from regression lines are apparent for Zr and Hf at high concentrations. These results imply that HFSE participate in biogeochemical cycling with silicate and that there is additional input of HFSE in the North Pacific deep water.

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