

Strong elemental fractionation of Zr–Hf and Nb–Ta across the Pacific Ocean

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Understanding the circulation of water masses in the world's oceans is critical to our knowledge of the Earth's climate system. Trace elements and their isotopes have been explored as tracers for the movement of water masses¹. One type of candidate elements² are the high-field-strength elements zirconium (Zr), hafnium (Hf), niobium (Nb) and tantalum (Ta). Here we measure the distributions of dissolved Zr, Hf, Nb and Ta along two meridional sections in the Pacific Ocean that extend from 65° to 10° S and from 10° to 50° N. We find that all four elements tend to be depleted in surface water. In the deep oceans, their concentrations rise along our transects from the Southern Ocean to the North Pacific Ocean, and show strong correlations with the concentration of silicate. These results indicate that terrigenous sources are important to the budget of Zr, Hf, Nb and Ta in sea water, compared with hydrothermal input. Unexpectedly, the weight ratios for Zr/Hf fall between 45 and 350 and those for Nb/Ta between 14 and 85 in Pacific sea water, higher than the ratios observed in fresh water, in the silicate Earth or in chondritic meteorites. We conclude that the fractionation of Zr/Hf and Nb/Ta ratios will be useful for tracing water masses in the ocean.

In the modern ocean, deep water is formed in the northern North Atlantic and the Southern oceans and flows to the Indian and the Pacific oceans. This thermohaline circulation results in an oceanic mixing time in the range 500 to 1,000 years. Silicate ($\text{Si}(\text{OH})_4$), a major nutrient, is taken up by diatoms from surface sea water to form siliceous tests, and remineralized from the sinking tests in deep water³. The silicate concentration increases with the age of the deep water. Such a biogeochemical cycle is important in controlling the biological productivity in the ocean. An international research collaboration program, GEOTRACES, has been launched recently to determine the global distribution of trace elements and their isotopes (TEIs) and to characterize more completely their biogeochemical cycles¹. Refractory elements have a low supply to the oceans relative to their abundance in the Earth's crust². They are also rapidly removed from sea water by adsorption on sinking particles, a process referred to as scavenging. These factors result in large variations in the oceanic distributions that typically reflect their sources, making them potential tracers of water masses. For this purpose, rare earth elements (REEs), which occur as carbonate complexes of a trivalent (+3) state, with exception of cerium (Ce^{4+}) and europium (Eu^{2+}), have been studied extensively⁴. Studies of high-field-strength elements (HFSEs), such as Zr, Hf, Nb and Ta, have been very limited so far because of the difficulty in their analysis with conventional methods. One of these HFSEs, Hf, possesses a radiogenic isotope ^{176}Hf from the decay of lutetium ^{176}Lu . Fractionation of the daughter/parent isotopes leads to large variations in the isotope ratios ($^{176}\text{Hf}/^{177}\text{Hf}$, expressed as ε_{Hf}). The Hf isotope ratios have

been measured in iron–manganese (Fe–Mn) crusts and nodules, sediments, and rocks^{5–9}. The first dissolved seawater Hf isotope data were recently published^{10,11}. Together with neodymium isotope ratios ($^{143}\text{Nd}/^{144}\text{Nd}$, expressed as ε_{Nd}), the Hf–Nd isotope system is used as an excellent proxy to elucidate the past change in continental weathering and/or hydrothermal sources to the ocean. It is now well known that for a given ε_{Nd} , sea water and precipitates, such as iron–manganese (Fe–Mn) crusts and nodules, have a more radiogenic ε_{Hf} than terrestrial materials. The reason of this decoupling has been under debate, with two hypotheses being offered: (1) incongruent release of Hf during continental weathering^{6–8} and (2) significant hydrothermal input of mantle-source Hf (refs 5,9). Therefore, elucidating the oceanographic distributions of HFSEs is also important in establishing a firm proxy in paleoceanography.

Here we report meridional ocean sections of dissolved Zr, Hf, Nb and Ta along 170° W (65° S–10° N) and 160° W (10° S–50° N; Fig. 1). The sampling stations are given in Supplementary Fig. S1. All data for HFSEs, nutrients and oceanographic properties are given in Supplementary Table S1. In general, the distributions of HFSEs are similar to that of silicate, except that 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 HFSEs against silicate show significant linearity (Supplementary Fig. S2).

The reported vertical profile of dissolved Zr at 16° 28' N, 168° 50' W closely resembles our profile at station ST07 (20° N, 160° W), except the former shows a higher bottom concentration of 295 pmol kg^{-1} (ref. 12). Our previous observations in the northwestern North Pacific also show high concentrations of dissolved Zr ($262\text{--}275 \text{ pmol kg}^{-1}$) in bottom water, where labile-particulate Zr also increases with depth, showing bottom maxima ($72\text{--}84 \text{ pmol kg}^{-1}$; ref. 13). The vertical profiles of dissolved Hf in the North Pacific in this study match well with those observed at stations 39°–24° N, 170° E (ref. 11). Our previous observations in the northwestern North Pacific again show high concentrations of dissolved Hf ($0.79\text{--}0.95 \text{ pmol kg}^{-1}$) and labile-particulate Hf ($0.21\text{--}0.28 \text{ pmol kg}^{-1}$) in bottom water¹³. In surface water, the concentrations of Zr and Hf significantly increase at coastal stations^{2,12}. This is also confirmed by our data. All these results indicate that there are bottom and coastal sources of Zr and Hf. For Nb and Ta, there are no distribution data other than ours¹³. Our previous and present data suggest that Nb and Ta are more uniformly distributed than Zr and Hf, and they also have both bottom and coastal sources. The most probable origins of these sources are rivers and terrigenous dust particles^{6,14}. HFSEs have higher concentrations in granites (continental crust) than in basalts (oceanic crust)^{15,16}, and the dust flux from the continents is 100 times higher in the North Pacific than in the South Pacific¹⁷.

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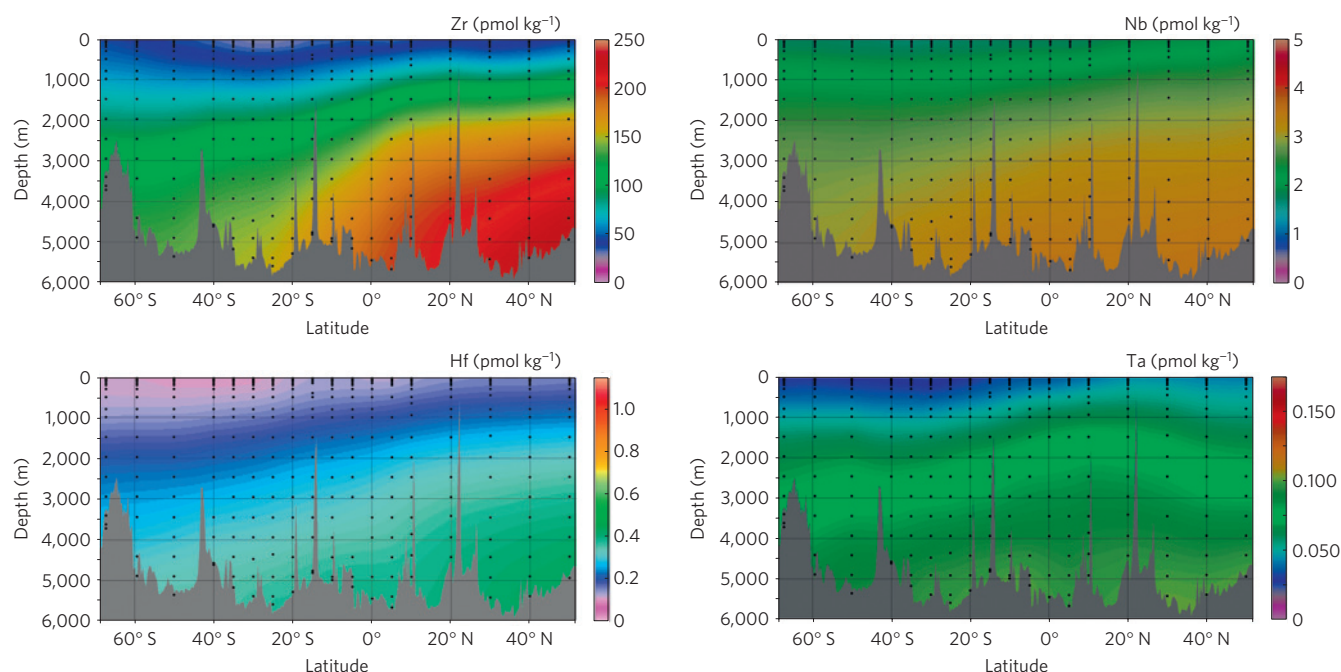


Figure 1 | Sectional distributions of dissolved Zr, Hf, Nb and Ta in the Pacific Ocean along 170° W and 160° W. The black dots indicate the point of sampling. The plots were made using ODV (<http://www.awi-bremerhaven.de/GEO/ODV>).

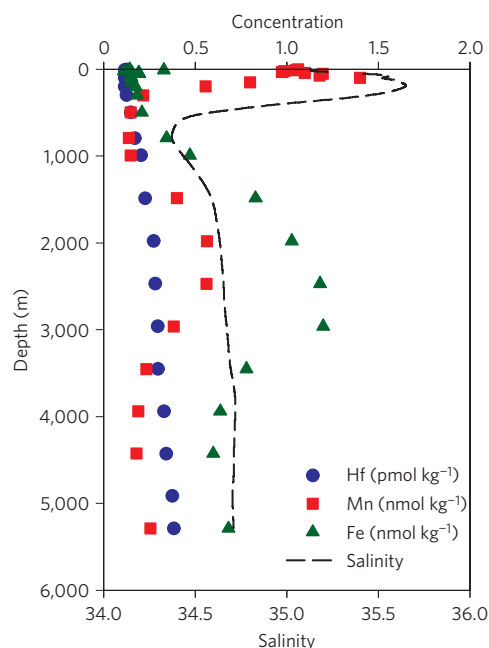


Figure 2 | Vertical profiles of dissolved Mn, Fe and Hf at station SX22 (20° S, 170° W).

The dust particles may be partially dissolved in surface water and find fast transport to bottom water by particulate settling and/or advection, resulting in the bottom source.

There are at least three areas on our section which are very close to the sites where hydrothermal plumes and activity have been reported. Multiple hydrothermal plumes have been found along the south Tonga arc and Valu Fa Ridge (21°–25° S, 177°–176° W; ref. 18) and along the two back-arc spreading centres of the NE Lau Basin (14°–18° S, 174°–175° W; ref. 19). Figure 2 gives the vertical profiles of dissolved Mn, Fe and Hf at a nearby station, SX22 (20° S, 170° W). It is most likely that the Mn maximum at

2,000–2,500 m depth originates from a hydrothermal plume. Iron shows a broader increase, with the maximum at a slightly greater depth (2,500–3,000 m), which may suggest that it is derived from hydrothermal activity as well as remineralization in the South Fiji and the Lau basins. However, there is no anomaly on the profile of Hf. This should be the direct data showing that a hydrothermal plume does not carry dissolved Hf. This is also true for the other three HFSEs. On the Pacific–Atlantic Ridge, potential hydrothermal plume sources were located at ~64° S, 168° W on the basis of mantle helium (He; ref. 20). During our cruise, a Mn anomaly which was five times higher than the ambient seawater concentration was detected above the Pacific–Antarctic Ridge at 65° S, where methane was also anomalously high (Tsunogai, personal communication). These anomalies can be attributed to a hydrothermal plume. Furthermore, hydrothermal plumes from the Loihi Seamount hydrothermal vents were detected as anomalies in Fe, Mn and isotopes of He at station ALOHA (22° 45' N, 158° W; ref. 21). These stations are also close to our stations for HFSEs. However, there are no hydrothermal plume signals on the ocean sections for HFSEs. It is likely that HFSEs, if any, released from hydrothermal sites are efficiently scavenged by Fe–Mn oxide particles in the vicinity of the sites and that hydrothermal input is insignificant to the budget of dissolved HFSEs in the ocean.

All seawater data of dissolved Hf versus Zr plot above the mole ratio of $Zr/Hf = 71$ in continental crust¹⁶ (Fig. 3a). For the North Pacific Ocean, a regression line is given by $[Zr] = -61 + 681 [Hf]$ with $r^2 = 0.97$ ($n = 158$). 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^{10,11,13,22,23} 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 proposed¹⁰. 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 (Supplementary Note and Table S2). The τ

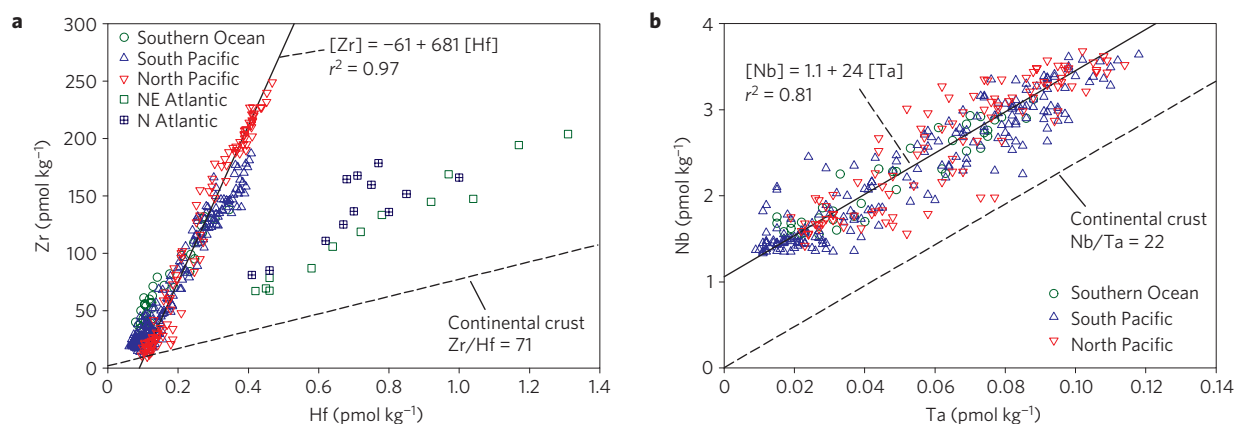


Figure 3 | Scatter plots of dissolved HFSEs in sea water. a, Hf versus Zr. b, Ta versus Nb. Regression lines are calculated using the data from the North Pacific (present study). The data of the Atlantic Ocean and continental crust are taken from refs 16,22,23.

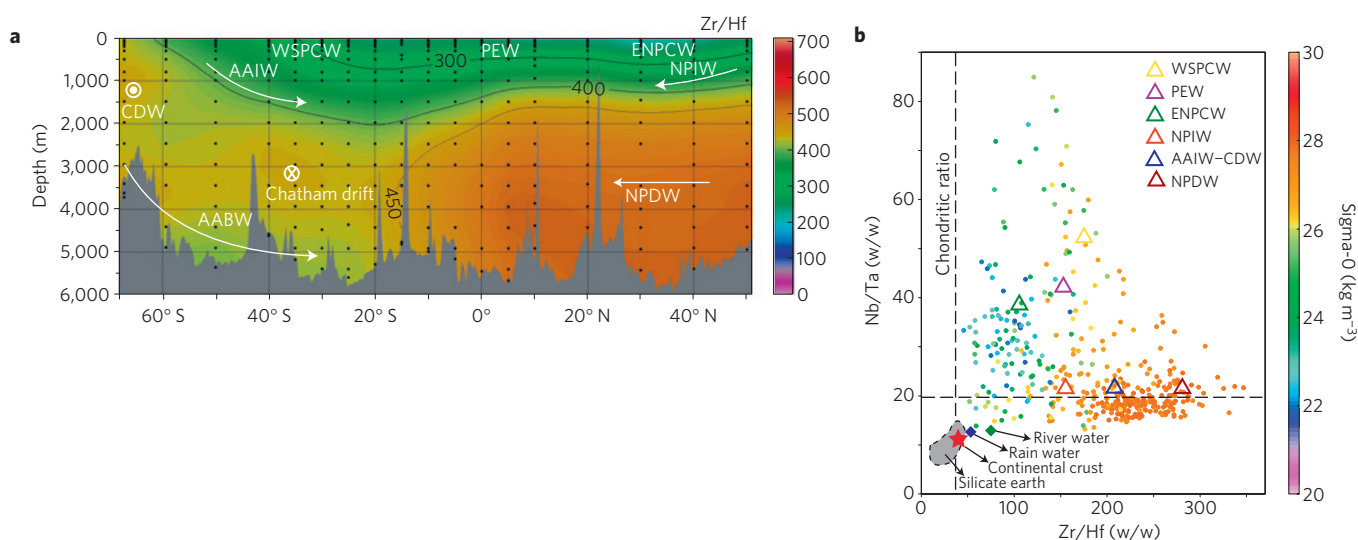


Figure 4 | Zr/Hf and Nb/Ta ratios as tracers of water masses. a, Sectional distribution of dissolved Zr/Hf mole ratio in the Pacific Ocean. Water masses indicated are Circumpolar Deep Water (CDW), Antarctic Bottom Water (AABW), Antarctic Intermediate Water (AAIW), Western South Pacific Central Water (WSPCW), Pacific Equatorial Water (PEW), Eastern North Pacific Central Water (ENPCW), North Pacific Intermediate Water (NPIW) and North Pacific Deep Water (NPDW). **b, Plot of Zr/Hf versus Nb/Ta weight ratios.** Colour gradation is for potential density ($\Sigma\text{-O}$). The core of water masses are shown as triangles. The data of the other reservoirs in the Earth and chondrite (dashed lines) are also shown^{13,16,24}.

for Hf of 8.7×10^2 y is roughly one quarter that for Zr of 3.7×10^3 y, which is consistent with the observations discussed above.

For the dissolved Nb–Ta system, a regression line is given by $[\text{Nb}] = 1.1 + 24 [\text{Ta}]$, with $r^2 = 0.81$ ($n = 158$), in the North Pacific Ocean (Fig. 3b). The slope is close to the mole ratio of $\text{Nb}/\text{Ta} = 22$ in continental crust¹⁶. This may suggest insignificant fractionation between Nb and Ta in deep water, reflected in the comparable τ (2.7×10^3 y for Nb and 1.3×10^3 y for Ta). It should be noted, however, that the regression line has a positive Nb intercept, which is distinct from the general proportionality between Nb and Ta in sediments and rocks^{24,25}. The unique fractionation in the ocean may be attributed to incongruent inputs of Nb or preferential removal of Ta from surface sea water.

The main water masses in the Pacific basin²⁶ are characterized by a different Zr/Hf ratio (Fig. 4a). We can attribute the maximum in Zr/Hf at 1,000 m depth, 67° S to the core of Circumpolar Deep Water (CDW) that flows from west to east. The observed high Zr/Hf ratios at 3,500 m depth $\sim 35^\circ$ S are probably owing to the introduction of the Deep Western Boundary Current (DWBC) that flows west over the North Chatham Drift²⁷. Dissolved REEs have attracted attention as unique tracers of water masses⁴. When we

compare the vertical profiles of dissolved mole ratio for Zr/Hf and La/Lu at $\sim 30^\circ$ S and $\sim 30^\circ$ N in the Pacific (Supplementary Fig. S3), the variation range is 5.5 for Zr/Hf and 1.8 for La/Lu. Thus, the variations in Zr/Hf are much greater than those in REEs, which implies HFSEs would be more sensitive and robust tracers given that the analytical uncertainty is comparable between HFSEs and REEs. The ocean section of dissolved Nb/Ta mole ratio is given in Supplementary Fig. S4. The Nb/Ta ratio is fairly uniform in deep water. In surface water, the ratio is high, particularly at 40° – 25° S and 50° N, where Western South Pacific Central Water (WSPCW) and Eastern North Pacific Central Water (ENPCW) exist.

The ranges of Zr/Hf and Nb/Ta weight ratios in sea water are 45–350 and 14–85, respectively (in Fig. 4b conversion factors from weight ratios to mole ratios are 1.957 and 1.948, respectively). The water masses are characterized by a unique set of Zr/Hf to Nb/Ta ratios. Therefore, the combination of Zr/Hf and Nb/Ta ratios gives a new and promising tool to trace water masses in the ocean. Furthermore, it is clear from Fig. 4b that both the ratios of twin elements in sea water are generally higher and more variable than those in river and rain water. The fractionation of HFSEs occurs as soon as they are introduced into surface water and continues during

the ocean circulation. The change in dissolved Zr/Hf from terrestrial to seawater values has been observed in the Hudson River estuary²⁸. In the lithosphere, Zr/Hf and Nb/Ta ratios normally show limited variations, with a few exceptions such as abyssal peridotites²⁹ and late-stage rocks from a Proterozoic anorthosite complex³⁰. Also there is a general linearity between Zr/Hf and Nb/Ta ratios. The fractionation in the lithosphere is mainly controlled by the charge and radius of ions, resulting in a strong correlation between Zr/Hf and Nb/Ta ratios^{24,29,30}. In contrast, the fractionation of HFSEs in the ocean is unique and deserves further study.

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Author contributions

M.L.F. and Y.S. designed the research. M.L.F. carried out the determination of HFSEs. K.N. contributed to sample collection and T.M. determined Mn and Fe. All authors contributed to data interpretation and preparation of the manuscript.

Additional information

The authors declare no competing financial interests. Supplementary information accompanies this paper on www.nature.com/naturegeoscience. Reprints and permissions information is available online at <http://npg.nature.com/reprintsandpermissions>. Correspondence and requests for materials should be addressed to M.L.F.