

On the Enigma of Nb-Ta and Zr-Hf Fractionation—A Critical Review

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ABSTRACT: Elemental ratios Zr/Hf and Nb/Ta are expected to be constant and of chondritic value (~36.30 and ~17.57, respectively) in mantle and mantle-derived rocks. Studies in recent years have shown, however, that these two ratios do vary in some of these rocks. For example, MORB-like seamount lavas from flanks of the East Pacific Rise (EPR) show a correlated Zr/Hf (~25–50) and Nb/Ta (~9–18) variation. These two ratios are also correlated with ratios of more incompatible over less incompatible elements (e.g., La/Sm, Rb/Cs, Th/U, Nb/U, Sm/Yb) and with radiogenic isotope ratios (e.g., $^{87}\text{Sr}/^{86}\text{Sr}$, $^{143}\text{Nd}/^{144}\text{Nd}$). Furthermore, abyssal peridotites, which are melting residues for MORB, also show a huge correlated variation between Zr/Hf (~2.5–335) and Nb/Ta (~1–170). All these observations plus a correlated variation between Zr/Hf (~22–48) and Nb/Ta (~10–23) in lunar rocks are consistent with the Zr-Hf and Nb-Ta fractionation being of magmatic origin. This contrasts with the common view that geochemical processes cannot readily fractionate them. As charges and ionic radii are the principal factors in the general theory of elemental fractionation, this theory cannot explain the fractionation of these two element pairs with the same charges (i.e., 5^+ for Nb and Ta, and 4^+ for Zr and Hf) and essentially the same ionic size (i.e., $R_{\text{Nb}}/R_{\text{Ta}}=1.000$, $R_{\text{Zr}}/R_{\text{Hf}}=1.006$ to ~1.026 for coordination numbers of 6, 7, 8 and 12). We explore the possibilities of other factors and processes (e.g., mass-dependent fractionation during magmatism) that may cause the observed Nb-Ta and Zr-Hf fractionation. We emphasize that understanding the correlated Nb-Ta and Zr-Hf fractionation “known” to take place during magmatism is fundamental for improved understanding of elemental fractionations through other earth processes

in various tectonic environments, including the origin and evolution of continental crust, which has a characteristic subchondritic Nb/Ta value of ~11–12.

KEY WORDS: Nb/Ta, Zr/Hf, correlated variation, magmatic process, mass-dependent fractionation.

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INTRODUCTION

The refractory element pairs such as Zr-Hf and

Nb-Ta have the same charges (e.g., Zr^{4+} and Hf^{4+} ; Nb^{5+} and Ta^{5+}) and effectively the same ionic radii (e.g., $r_{CN-6}^{Zr} = 0.72$, $r_{CN-6}^{Hf} = 0.71$, $r_{CN-6}^{Nb} = 0.64$, $r_{CN-6}^{Ta} = 0.64$) (Shannon, 1976) in mineral structures under known geological conditions. These common chemical properties determine that these element pairs have the same geochemical properties (Goldschmidt, 1937). That is, Zr-Hf and Nb-Ta should not fractionate from each other in geological processes. Therefore, Zr/Hf and Nb/Ta ratios in all earth materials should be constant and should be the same as the most undifferentiated Type 1 carboniferous chondrite (or CI chondrite) with Zr/Hf \approx 36.3 and Nb/Ta \approx 17.6 (McDonough and Sun, 1995; Sun and McDonough, 1989). Indeed, for many years, the nearly chondritic Nb/Ta and Zr/Hf ratios in oceanic basalts and in many other rocks have led to the general acceptance that Zr-Hf and Nb-Ta elemental pairs indeed do not fractionate in earth processes (e.g., Sun and McDonough, 1989; Hofmann, 1988; Hofmann et al., 1986; Jochum et al., 1986; Bougault et al., 1979). While this notion had been widely accepted, we did note that the bulk continental crust has Nb/Ta \approx 11–12 (Rudnick and Fountain, 1995; Taylor and McLennan, 1985; Taylor, 1977, 1967), which is far lower than the chondritic value of \sim 17.6. However, no effort was expended to explain the subchondritic Nb/Ta ratio in the continental crust.

The high-quality data obtained using ICP-MS on seafloor basalts (Niu and Batiza, 1997; Niu and Hekinian, 1997) demonstrated for the first time that Nb/Ta ratio in MORB melt is not constant, but varies from \sim 9 to \sim 18, nor is Zr/Hf ratio that varies from \sim 25 to \sim 50. Importantly, these two ratios correlate with each other. These new observations were entirely unexpected, but prompted our re-thinking and pointed out that our previous knowledge needs revision. As a result, why the bulk continental crust has subchondritic Nb/Ta ratio becomes an important problem to consider as its understanding may lead to new perspective on the origin of continental crust (Foley et al., 2002). With the further development and popularity of the ICP-MS analytical technique, non-chondritic Nb/Ta ratios have been observed in island-arc basalt (IAB) and back-arc basin basalt (BABB) (e.g., Elliott et al., 1997) and ocean island basalts (e.g., Pfaender et al., 2007). The observation that average mantle de-

rived melts, including mid-ocean-ridge basalt (MORB), ocean island basalt (OIB), BABB and IAB have subchondritic Nb/Ta ratios indicates that the mantle sources for these basalts must have subchondritic ratios (e.g., Rudnick et al., 2000). This, plus the subchondritic Nb/Ta ratio of the bulk continental crust, has led to the effort to search for a superchondritic Nb/Ta reservoir in the earth (e.g., Niu, 2004; Wade and Wood, 2001; Rudnick et al., 2000). The purpose of this article is not to solve the Nb-Ta fractionation problem as attempted by many because it is possible that Nb-Ta fractionation could be caused by a variety of processes, including magmatic, metamorphic and even perhaps sedimentary processes (i.e., Zr/Hf-rich mineral and Nb/Ta-rich mineral separation etc.), and the speculated causes of Nb-Ta fractionation are unconstrained and hence cannot be formulated into valid hypotheses to be tested. Therefore, in this article, we focus on correlated Zr-Hf and Nb-Ta fractionation as observed in MORB melts (Niu and Batiza, 1997), in abyssal peridotites (Niu, 2004) and also in lunar samples (Waenke et al., 1975). The Nb/Ta-Zr/Hf correlation, or coupled Zr-Hf and Nb-Ta fractionation, places the best constraints that their fractionation must be caused by magmatic processes because these ratios are also correlated with ratios such as La/Sm, Sm/Yb (Niu and Batiza, 1997) and with radiogenic isotopes (Niu et al., 2002). This will form a logical basis for understanding coupled Nb/Ta-Zr/Hf fractionation. We consider that this is the most logical starting point towards ultimate understanding of fractionation processes between element pairs that have otherwise identical or very similar chemical properties such as ionic sizes and charges.

BACKGROUND

Composition of Bulk Earth and Its Silicate Portion

It has been assumed that the bulk earth should have chondritic (CI-like) composition in terms of refractory (non-volatile) lithophile elements (not lost during earth's accretion) such as the more abundant major elements like Al, Ca and Ti, and elements of low and ultra-low abundances including rare earth elements (REEs, i.e., La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb and Lu), high field strength elements (HFSEs, e.g., Zr, Hf, Nb and Ta) and some

other refractory elements like Sr, Y, Ba, Th and U (McDonough and Sun, 1995). Because of their lithophile nature, these elements are concentrated in the silicate portion of the earth (i.e., the mantle and crust), which is altogether called bulk silicate earth (BSE) or primitive mantle (PM) after core separation in the very early history of the earth (McDonough and Sun, 1995).

Elemental Fractionations in the Silicate Earth—The Crust and Mantle

Processes of magma generation and evolution are the most effective mechanisms that have led to the chemical fractionation of the earth from the presumably uniform PM to the present day heterogeneous earth. Magma generation, regardless of the nature of the source rock, is the result of partial melting with two products: the melt and the residue (e.g., Niu, 2005). When the source rock undergoes partial melting, elements that prefer to enter the melt phase are called incompatible elements, whereas those that prefer to stay in the residual minerals are called compatible elements. That is, partial melting of a fertile mantle source is the process that transforms the mantle material into two compositionally different products: (1) the melt, which is more felsic, enriched in the incompatible elements, and finally evolved into igneous rocks of varying mineral assemblages in the crust; and (2) the residue, which is left in the mantle, more mafic (or ultramafic), more refractory, and depleted in the incompatible elements.

Figure 1 compares average compositions of mantle-derived melts from different tectonic settings and model compositions of mantle “reservoirs”. Crustal rocks (e.g., MORB, OIB, BCC and IAB) have overall elevated abundances of REEs compared to the primitive mantle. The bulk continental crust (BCC) that represents a very low-degree melt phase extracted from the PM (i.e., Hofmann, 1988) is enriched in incompatible elements and contains probably ~30% of earth’s Ba, Rb, Th, U, K, Pb budget (Hofmann, 1997; Rudnick and Fountain, 1995). The DMM (depleted MORB mantle) as a result of BCC extraction is thus highly depleted in incompatible elements (e.g., Hofmann, 1988). So, N-MORB (normal mid-ocean-ridge basalt) melts derived from the DMM inherit the

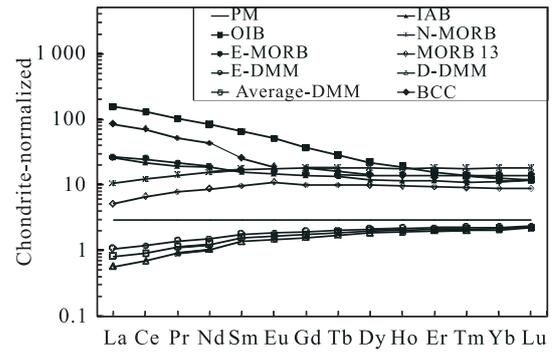


Figure 1. Chondrite-normalized rare earth element (REE) diagram showing that these average earth rocks are all different from the ideal composition of the primitive mantle (PM). Values for the PM, average compositions of ocean island basalts (OIB), N-type and E-type mid-ocean-ridge basalts (MORB) are from Sun and McDonough (1989). Average composition of island-arc basalts (IAB) is from Elliott (2003). Highly depleted MORB (MORB 13) is from Niu and O’Hara (2009). Average bulk continental crust (BCC) is from Rudnick and Gao (2003). Depleted, enriched and average compositions of the DMM are from Workman and Hart (2005).

depleted signature in the progressively more incompatible elements (e.g., $[La/Sm]_{CN} < 1$) despite the overall higher abundances of incompatible elements (i.e., REEs) than both the PM and DMM. The source region for E-MORB (enriched MORB) may have derived from a mantle source with an enriched component such as metasomatized lithologies (e.g., Niu and O’Hara, 2003).

Factors Controlling Elemental Fractionation and Partition Coefficients

The fact that melts have elevated REE abundances over the mantle compositions (e.g., the PM and DMM) (Fig. 1) means that these elements are incompatible during magmatism (magma generation and evolution), i.e., their bulk distribution coefficient $D < 1$ (defined as $D = \sum_{j=1, j \neq l}^{j=m, j \neq n} x_j k_d^{i,j}$, where $k_d^{i,j}$ is called the partition coefficient, which is the concentration ratio of element i in mineral j and in the coexisting liquid l , and x_j is the weight proportion of mineral j among all the minerals involved). Most incompatible elements do not form their own minerals because of

their very low abundances, but reside in crystal structures of silicate minerals primarily by means of substituting major elements. It has long been known since the pioneering work by Goldschmidt (1937) that there are two primary factors (there are others such as types of chemical bonds etc. following Ringwood (1955)) which determine the ability of an element to substitute major elements: the similarity of (1) charge and (2) size of the substituting element to those of elements to be substituted (Onuma et al., 1968; Nagasawa, 1966; Goldschmidt, 1937).

Figure 2 uses REEs to show the concept that different minerals have different k_d values for a given element and the same mineral can have different k_d values for different elements. For example, heavy REEs are in general less incompatible than light REEs for most of these minerals in Fig. 2. For the peridotite-basaltic melt system, clinopyroxene (cpx) and garnet are in general better hosts of incompatible elements than other phases although these elements are also incompatible in clinopyroxene and garnet except heavy REEs which are compatible in garnet (Fig. 2).

It follows that for a suite of incompatible elements, if their charges are the same, the larger its size is, the more incompatible it is. For example, in most cases, REEs are progressively larger in size from the heaviest Lu to the lightest La. Hence, REEs (mostly 3^+ under geological conditions/processes) are progressively more incompatible with increasing size from Lu to La. So, during partial melting LREEs prefer to enter the melt than HREEs, showing $[LREEs/HREEs]_{PM} > 1$ (Fig. 1). For example, the BCC represents a low-degree melt extracted from the PM (e.g., Hofmann,

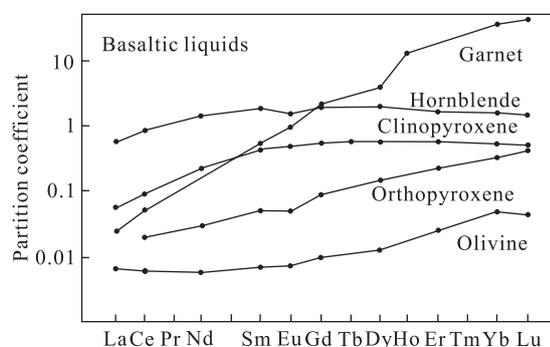


Figure 2. Partition coefficient of REEs between these given minerals and basaltic melts (data from the compilation of Rollinson, 1993).

1988), hence showing large $[LREEs/HREEs]_{PM} > 1$. Because extraction of the BCC has led to the depletion of the upper most mantle (i.e., the DMM; e.g., Hofmann, 1988) as the source for MORB, the latter imparts MORB melts with $[LREEs/HREEs]_{PM} < 1$.

On the other hand, if the charge is the same and the size is similar, the two elements can behave very similarly even though their chemical properties may be different. One of the best examples is Eu, an REE that could occur as Eu^{2+} , whose size is very similar to Sr^{2+} , hence both behave very similarly as manifested by MORB data (see Niu and O'Hara, 2009).

Consequently, elemental pairs Zr^{4+} - Hf^{4+} and Nb^{5+} - Ta^{5+} , which have the same charge and essentially identical size, should behave the same in magmatic processes or perhaps in all the geological processes. It follows that Zr/Hf and Nb/Ta ratios should be the same in all earth materials and earth reservoirs with bulk earth or chondritic values, i.e., Zr/Hf ~ 36.3 and Nb/Ta ~ 17.6 respectively (Palme and O'Neill, 2003; McDonough and Sun, 1995; Sun and McDonough, 1989). Indeed, Nb/Ta and Zr/Hf ratios in oceanic basalts and in many other rocks have long been accepted to be constant and to be of chondritic value as summarized in Table 1 (e.g., Sun and McDonough, 1989; Hofmann, 1988; Hofmann et al., 1986; Jochum et al., 1986; Bougault et al., 1979).

Table 1 reflects the state of our knowledge for many years prior to 1990s. The Nb/Ta and Zr/Hf ratios stay constant with chondritic (except in CC) values regardless of actual abundances of these elements in various mantle-derived basalts. It further implies that magmatic processes cannot fractionate Nb-Ta and Zr-Hf. Therefore, we had considered that partition coefficients for Nb and Ta and for Zr and Hf between all minerals and melts and among these minerals are the same and no geological process can effectively fractionate these paired elements (Palme and O'Neill, 2003; McDonough and Sun, 1995; Sun and McDonough, 1989; Hofmann, 1988; Hofmann et al., 1986; Jochum et al., 1986; Bougault et al., 1979), in particular in the processes of mantle melting and melt evolution of mantle-derived melts beneath ocean ridges, island arcs and intra-plate ocean islands.

Nevertheless, it has been noted for some time that Nb/Ta in continental crust is ~ 11 (Green, 1995;

Rudnick and Fountain, 1995; Taylor and McLennan, 1985), yet there was no attempt to explain such significant subchondritic value until Niu and Batiza (1997) and Niu and Hekinian (1997) showed correlated Zr/Hf- Nb/Ta variations in seafloor basalts using high-quality ICP-MS data (see below). Then, Foley et

al. (2002) attempted to explain the subchondritic Nb/Ta ratio in the CC by invoking amphibole-involved melting processes that can fractionate Nb-Ta and that may be responsible for the proto-type continental crust in early history of the earth.

Table 1 Ratios of element pairs in different rocks (data from Sun and McDonough, 1989)

Element	C1	PM	N-MORB	E-MORB	OIB	CC
Nb (ppm)	0.246	0.713	2.33	8.3	48	12
Ta (ppm)	0.014	0.041	0.132	0.47	2.7	1.1
La (ppm)	0.237	0.687	2.5	6.3	37	18
Sm (ppm)	0.153	0.444	2.63	2.6	10	3.9
Zr (ppm)	3.87	11.2	74	73	280	123
Hf (ppm)	0.106 6	0.309	2.05	2.03	7.8	3.7
Yb (ppm)	0.17	0.493	3.05	2.37	2.16	2
Nb/Ta	17.57	17.39	17.65	17.66	17.78	10.91
Zr/Hf	36.30	36.25	36.10	35.97	35.90	33.24
La/Sm	1.6	1.6	1.0	2.4	3.7	4.6
Sm/Yb	0.90	0.90	0.86	1.10	4.63	1.95

OBSERVATIONS

As discussed above, it has been recognized for some time that the BCC has a subchondritic Nb/Ta ratio of ~11–12 (Rudnick and Fountain, 1995; Taylor and McLennan, 1985). It has also been noted that the Zr/Hf ratio in some OIB varies and may be genetically associated with mantle source metasomatism by carbonatite melts (Dupuy et al., 1992). But no correlated Zr/Hf-Nb/Ta fractionations have been observed.

Nb-Ta and Zr-Hf Fractionation in Seafloor Basalts

The high-quality ICP-MS data for 80 seamount basalt glasses (trace elements were determined by ICP-MS at the University of Queensland) show large Nb/Ta (~9–18) and Zr/Hf (~25–50) variations (Fig. 3; after Niu and Batiza, 1997), which differ significantly from the chondritic values (shaded band). We know that in a plot of X/Y vs. X , if the data trend with the slope >0 , then $D_X < D_Y$, i.e., the element in the numerator is more incompatible than the one in the denominator (Niu and Batiza, 1997; Sun and McDonough, 1989; Hofmann, 1988). So, Fig. 3 demonstrates $D_{Zr} < D_{Hf}$ (Fig. 3a) and $D_{Nb} < D_{Ta}$ (Fig. 3b) during the petrogenesis of these basalts, which means that Zr is more incompatible than Hf and Nb is more

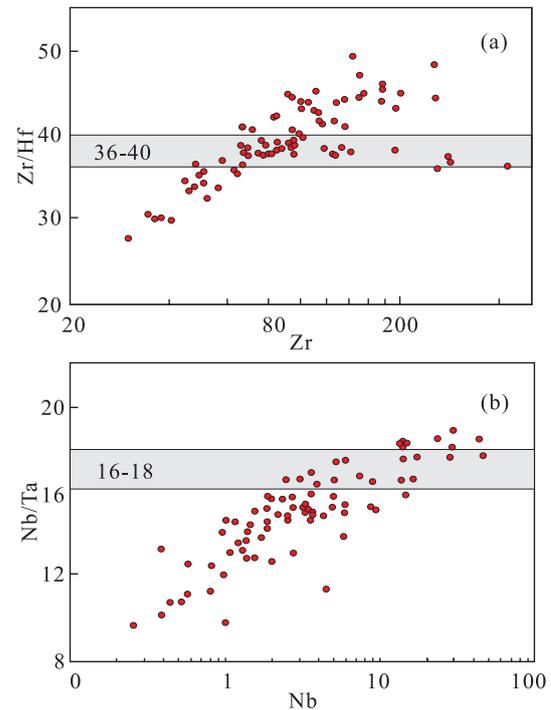


Figure 3. Plots of Zr/Hf vs. Zr and Nb/Ta vs. Nb for the seamount data (Niu and Batiza, 1997). The positive slope of the trend defined by the data indicates $D_{Zr} < D_{Hf}$ and also $D_{Nb} < D_{Ta}$, where D refers to bulk partition coefficients of a given element as indicated.

incompatible than Ta.

As in Fig. 3, the samples show relatively large variations in Nb/Ta and Zr/Hf, which is also true for Nb/U (Fig. 4b), Rb/Cs (8–98) (Fig. 4c), Th/U (1.4–3.8) (Fig. 4d) and La/Sm (Figs. 4e–4f). And they show significant correlations with each other and with La/Sm (note that plots involving La/Sm show curved data arrays). Such correlated variations indicate that the Nb-Ta and Zr-Hf fractionation is of magmatic origin due to mantle melting, melt evolution or perhaps mantle source formation or modification in its histories genetically associated with earlier melting events. More importantly, these plots confirm that Zr and Nb are more incompatible than Hf and Ta, respectively. Also, Th and Nb are similar and both are more in-

compatible than U and Ta (Niu and Batiza, 1997).

Figure 5 shows significant correlations of Sr-Nd isotopic ratios with Zr/Hf and Nb/Ta. The correlations of Zr/Hf and Nb/Ta with Sr-Nd isotopes are not expected until Niu et al. (2002). This finding indicates that (1) the elements in the numerator are indeed more incompatible than the elements in the denominator; (2) the geochemical process is a magmatic process and is best explained by melting-induced mixing of a two-component mantle with the enriched one and a depleted one. The high Nb/Ta and Zr/Hf end member is associated with high $^{87}\text{Sr}/^{86}\text{Sr}$ and low $^{143}\text{Nd}/^{144}\text{Nd}$ (an enriched high Rb/Sr and low Sm/Nd source), and the low Nb/Ta and Zr/Hf end member is associated with low $^{87}\text{Sr}/^{86}\text{Sr}$ and high $^{143}\text{Nd}/^{144}\text{Nd}$ (a depleted low

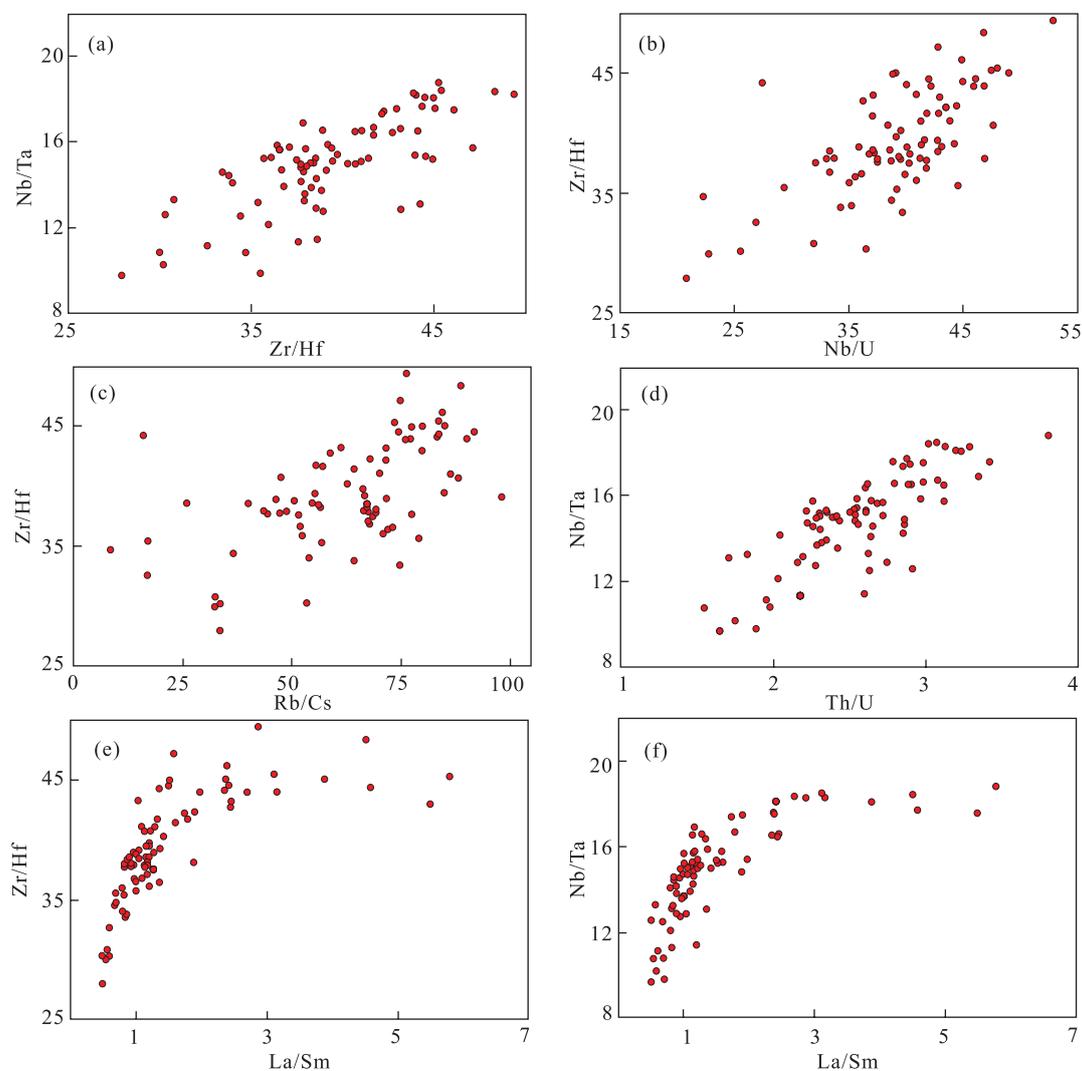


Figure 4. Trace element ratio-ratio plots of seamount data (Niu and Batiza, 1997) showing the correlations of Nb/Ta and Zr/Hf with other commonly used ratios of geochemical significance that confirms that Nb-Ta and Zr-Hf do fractionate and Nb and Zr are more incompatible than Ta and Hf, respectively.

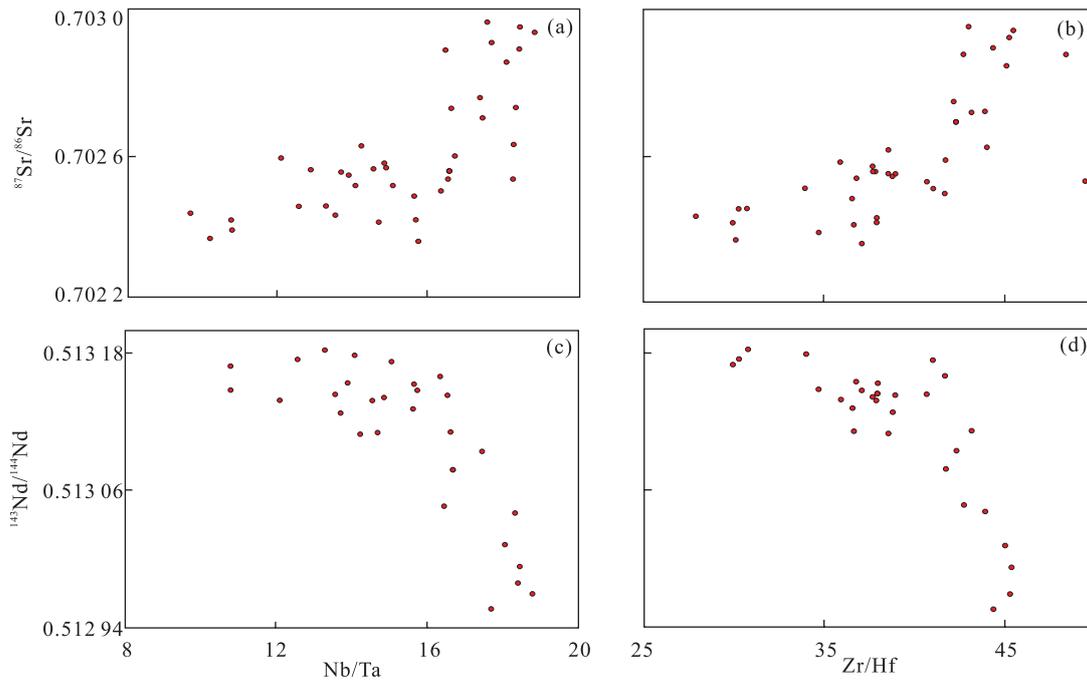


Figure 5. Seamount data (Niu et al., 2002; Niu and Batiza, 1997) showing the significant correlations of isotopic ratios with Zr/Hf and Nb/Ta.

Rb/Sr and high Sm/Nd source), which requires a long time to produce the isotopic variations; (3) while the most recent melting event(s) may cause Zr/Hf-Nb/Ta fractionation, the mantle source materials must have experienced magmatic processes in their long histories, likely in excess of 1 Ga (Niu et al., 2002).

Nb-Ta and Zr-Hf Fractionation in Abyssal Peridotites

Plate separation at ocean ridges causes the mantle beneath to rise and partially melt by decompression. MORB are evolved equivalent of the melt whereas the abyssal peridotites are melting residues. We have seen above that MORB melts show correlated variation between Zr/Hf and Nb/Ta (Fig. 4). Figure 6 shows that the abyssal peridotites (~130 samples) also define a correlated variation between Zr/Hf (~3–300) and Nb/Ta (~1–200) (Niu, 2004). The seamount basalt samples are also plotted for comparison. We should note that these data are of high quality after the most careful disposal with the least contamination (see details in Niu, 2004). The ~2 orders of magnitude Nb/Ta and Zr/Hf variations in abyssal peridotites emphasize the urgent understanding of the origin of Nb-Ta and Zr-Hf fractionation. Note that Nb/Ta and Zr/Hf ratios are also correlated with ratios of the more incompati-

ble over less incompatible elements such as La/Yb, Ce/Y, Ce, Be/Tb (Niu, 2004). All these observations not only confirm that Nb is more incompatible than Ta and Zr is more incompatible than Hf, but also are consistent with the notion that the fractionation of Nb-Ta and Zr-Hf is a magmatic process.

Nb-Ta and Zr-Hf Fractionation in Lunar Samples

If the samples of seafloor basalts and abyssal peridotites can tell us information about the mantle-crust differentiation, the lunar samples may imply the history of the cosmogony. These lunar samples are carefully analyzed using the method of 14 MeV INAA (instrumental neutron activation analysis) for Zr, Y, Nb and Ni and of RNAA (radiochemical NAA) for other trace elements. Waenke et al. (1975) reported that Zr/Hf and Nb/Ta are also correlated with each other in lunar samples including mare basalts and incompatible elements highly enriched KREEP (rich in K, REE and P, Fig. 7). Mare basalts and KREEP both are related to the melting and melt evolution, which imply that the correlation between Zr/Hf and Nb/Ta is a magmatic process. This process clearly took place in the very early history of the moon (>3.8 Ga). Also, Fig. 7 is consistent with the notion that Zr is more incompatible than Hf and Nb is more incompatible than Ta.

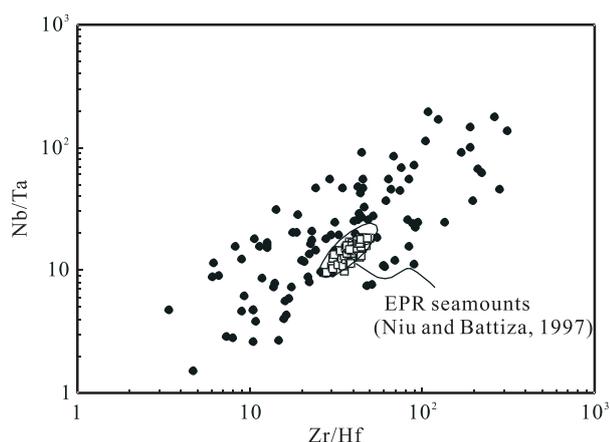


Figure 6. Abyssal peridotite data (Niu, 2004) showing the significant correlation between Zr/Hf and Nb/Ta that exhibits over two orders of magnitude variation. The seamount basalt data (open squares; see Fig. 4a) are plotted for comparison.

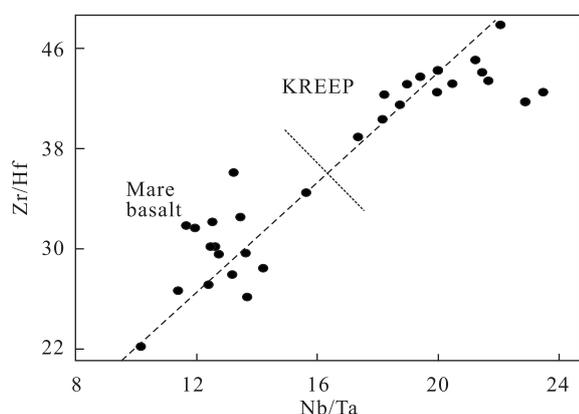


Figure 7. Zr/Hf vs. Nb/Ta correlation of lunar samples (Waenke et al., 1975).

DISCUSSION

We have demonstrated that it is magmatic processes that have produced the correlated Nb/Ta-Zr/Hf variation. Thus, in search of a superchondritic Nb/Ta reservoir in the earth, we also need to consider Zr/Hf so as not to ignore magmatism as a fundamental process fractionating Nb from Ta and Zr from Hf.

Current Interpretation

Since the work by Niu and Batiza (1997) and with the popularity of ICP-MS, Nb-Ta fractionation has been observed in island-arc and back-arc basalts (e.g., Elliott et al., 1997) and OIB (e.g., Pfaender et al., 2007). As rutile is a necessary mineral in eclogite of subducting ocean crust and is one of the major hosts

for Nb and Ta, it is predicted that rutile in subducting ocean crust must have superchondritic Nb/Ta and may cause the significant Nb/Ta variations in arc lavas (e.g., Klemme et al., 2002; Foley et al., 2000; Elliott et al., 1997), which would help explain Nb/Ta fractionations in oceanic basalts as a result of crustal recycling. Rudnick et al. (2000) suggested that a superchondritic reservoir with rutile-bearing eclogites must be hidden in the lower mantle. But Aulbach et al. (2008) showed that Nb/Ta varies significantly in rutile and high Nb/Ta correlates with the low $^{176}\text{Hf}/^{177}\text{Hf}$, which is associated with metasomatism. If so, deeply subducted eclogites may not be the suspected superchondritic Nb/Ta reservoir and the proposed fractionation effect of rutile cannot explain the Zr/Hf fractionation and the overall coupled Nb/Ta-Zr/Hf fractionation in seafloor basalts (Niu and Batiza, 1997), abyssal peridotites (Niu, 2004), and lunar rocks (Waenke et al., 1975). On the other hand, Nb is proposed to be moderately siderophile at very high pressures, and the missing Nb in the silicate earth may be in the core (Muenker et al., 2003; Wade and Wood, 2001). While this idea is interesting, it cannot be proven as yet because of the inability to sample the core, and the earth's core would not, preferentially take Zr (vs. Hf), La (vs. Sm), Rb (vs. Sr), and Nd (vs. Sm) (see Fig. 5). The experiments by Tiepolo et al. (2000) show that partial melting of amphibolites in the subducting ocean crust will give rise to the subchondritic Nb/Ta in the melt. Foley et al. (2002) proposed a model that the early continental crust formation was controlled by melting of amphibolites because amphiboles (vs. rutile) have characteristically high superchondritic Nb/Ta (>17.3), and amphibole as a residual phase during melting will result in melts with subchondritic Nb/Ta, thereby explaining the low Nb/Ta of the continental crust. On the basis of abyssal peridotite study, Niu (2004) speculated that the superchondritic Nb/Ta reservoir could be in the recycled oceanic lithosphere. Also, Niu and O'Hara (2009) observed excess Nb, Ta, Eu, Sr and Ti in most primitive MORB, implying that these elements also are excessive in the DMM, supporting the notion that the DMM and BCC are complementary in terms of overall abundances of incompatible elements (Hofmann, 1988). Their model of partial melting of the ocean crust under amphibolite facies conditions in

zones of continental collision explains the key characters of the bulk continental crust (see Fig. 8 of Mo et al., 2008) much better than the island arc model (see Table 2 of Niu and O'Hara, 2009). However, all the above models cannot explain the correlated (or coupled) Nb-Ta-Zr/Hf fractionation.

It has also been noted that Zr/Hf in some intra-plate basaltic rocks fractionated and may be genetically associated with mantle source metasomatism by carbonate melts (Dautria, 1992; Dupuy, 1992), but again this cannot explain the correlated fractionation

of Zr/Hf and Nb-Ta.

Factors Controlling Nb-Ta and Zr-Hf Fractionation in Magmatic Processes

Mass-dependent fractionation

Table 2 shows that the two pairs of elements Zr-Hf and Nb-Ta hold the same charge and the same or similar ionic size but a factor of two differences in their respective atomic masses. Therefore, they have been generally considered to behave the same in geological processes in the past.

Table 2 Relevant parameters of Zr, Hf, Nb, Ta, Rb and Sr (Klein and Hurlbut, 1999)

Element	Z	Structure valences	Ionic radius (Å)				Atomic mass	CI-chondrite (ppm)	PM (ppm)	
			CN=6	CN=7	CN=8	CN=12				
Zr	40	[Kr]4d ² 5s ²	4	0.72	0.78	0.84	1.6	91.22	3.870	11.2
Hf	72	[Xe]5d ² 6s ²	4	0.71	0.76	0.83	1.59	178.49	0.107	0.309
Zr/Hf			1.000	1.014	1.026	1.012	1.006	0.511	36.29	36.25
Nb	42	[Kr]4d ⁴ 5s ¹	5	0.64	0.69	0.74	1.47	92.91	0.246	0.713
Ta	73	[Xe]5d ³ 6s ²	5	0.64	0.69	0.74	1.47	180.95	0.014	0.041
Nb-Ta			1.000	1.000	1.000	1.000	1.000	0.513	17.571	17.395
Rb	37	[Kr]5s ¹	1	1.52		1.61	2.5	85.47	2.32	0.635
Cs	55	[Xe]6s ¹	1	1.67		1.74	2.72	132.91	0.188	0.032
Rb/Cs			1.000	0.910		0.925	0.919	0.643	12.340	19.845

If $D_{Zr}/D_{Hf} < 1$ and $D_{Nb}/D_{Ta} < 1$ are correct as observed, Nb-Ta and Zr-Hf fractionations can take place in magmatic processes. However, it is not straightforward why $D_{Zr}/D_{Hf} < 1$ and $D_{Nb}/D_{Ta} < 1$ should be the case in terms of the known theory of elemental fractionation. It is also difficult for $D_{Zr}/D_{Hf} \sim 0.5$ and $D_{Nb}/D_{Ta} \sim 0.5$ (e.g., Green et al., 2000; Green, 1994) to explain the huge Nb-Ta and Zr-Hf fractionations in abyssal peridotites (Fig. 6) because abyssal peridotites are not simple residues, but residues with olivine accumulation and incompatible element refertilization (Niu, 2004; Niu and Batiza, 1997; Niu and Hekinian, 1997), and much of the Nb, Ta, Zr and Hf is associated with melt refertilization in the thermal boundary layer atop the mantle beneath the ridge axis.

Since the early work by Goldschmidt (1937), it has been well known that it is the size and charge that control element substitutions in mineral structures. There have been a number of models to improve this theory. The most important one is the Onuma plots

(Onuma et al., 1968). The "lattice strain" model (Wood and Blundy, 1997; Blundy and Wood, 1994), a further development of Onuma plots, is perhaps the most successful thermodynamic model in predicting partitioning behavior of an element during magmatic processes. However, the "lattice strain" model remains charge and size dependent. Therefore, strictly speaking, the lattice strain model does not apply to Zr-Hf and Nb-Ta fractionations because of the identical charges (5^+ for Nb and Ta, and 4^+ for Zr and Hf) and essentially the same ionic radius ($R_{Nb}/R_{Ta} = 1.000$ and $R_{Zr}/R_{Hf} = 1.006$ to ~ 1.026 for a given coordination number, i.e., CN=6, 7, 8 and 12) of the two elemental pairs (Klein and Hurlbut, 1999).

For element pairs Zr-Hf and Nb-Ta, they have relatively large differences only in the electronic structure (see below) and mass, so it is logical to reason that a factor of 2 mass differences ($M_{Zr}/M_{Hf} = 0.511$; $M_{Nb}/M_{Ta} = 0.513$) may exert influences on the observed fractionations (or the apparent relative incompatibil-

ity). Niu and Batiza (1997) first pointed out that, for two elements of similar or identical chemical properties the lighter element (e.g., $^{90-92}\text{Zr}$, ^{93}Nb) is more incompatible than the heavier one (e.g., $^{177-180}\text{Hf}$, ^{181}Ta), which is apparently the same for the trivalent REEs (i.e., LREEs are more incompatible than the HREEs) although it is unknown how much of the effect is due to mass difference and how much of the effect results from ionic size variation. These observations and inferences encouraged Niu and Hekinian (1997) to suggest mass-dependent fractionation, whether it is due to mass-dependent differential diffusion rates or differential mass transfer rates. While the ~50% mass difference for Zr-Hf and Nb-Ta is significantly greater than the mass difference between an LREE and an HREE and than the mass differences between commonly considered isotopic fractionations of light stable elements at relatively low temperatures, there is the possibility that mass fractionation of heavy metals at high-temperature mantle conditions may be possible (Niu, 2004). Niu (2004) suggested that mass-dependent fractionation (differential diffusion) may be expressed as $D_A/D_B=(M_B/M_A)^{1/2}$, where D_A and D_B represent diffusion coefficients of species with mass M_A and M_B , respectively. In the case of Nb-Ta and Zr-Hf, $M_{\text{Ta}}/M_{\text{Nb}}$ and $M_{\text{Hf}}/M_{\text{Zr}}$ ratios are ~2, so the diffusion coefficient ratio would be $D_{\text{Nb}}/D_{\text{Ta}}$ (or $D_{\text{Zr}}/D_{\text{Hf}}$)=1.414. That is, the lighter element would diffuse, under ideal situations, ~41% more efficiently than the heavy element. ~41.4% fractionation just from the mass-dependent diffusion coefficient is very attractive. This huge efficiency also contrasts with familiar per-mil level light isotope fractionations. For example, for ^{16}O and ^{18}O fractionation, $D^{18}\text{O}/D^{16}\text{O}=(16/18)^{1/2}=0.943$, there would be a 57‰ (or 5.7%) fractionation. Our future work is to find out if the mass fractionation of heavy metals can take place under mantle conditions.

Electron configuration-dependent Nb-Ta and Zr-Hf fractionations in melts

Table 2 shows that Nb-Ta and Zr-Hf elemental pairs have the same or similar electron configurations. However, this may not actually be true because all Hf and Ta are in period 6 whereas Zr and Nb are in period 5, and our current view on electronic structures is

based on the assumption that the chemical properties of elements are determined by valence electrons. But, it is yet unknown whether geologically electrons in “stable” interior shells participate in forming complexes in silicate melts. It is also possible that Nb and Ta may take valence of 4^+ as well as 5^+ in some geological environments and through some geological processes. Waenke et al. (1975) proposed, with the aim of explaining the correlation between Zr/Hf and Nb/Ta in lunar rocks, that Nb and Ta are more similar to those of Zr and Hf if they were in the 4^+ state. A lower oxygen fugacity in the source region could increase the $\text{Nb}^{4+}/\text{Nb}^{5+}$ (also $\text{Ta}^{4+}/\text{Ta}^{5+}$) and thus Nb and Ta may follow the behavior of Zr and Hf in melts. If this is true, there is thus the possibility that Nb-Ta fractionation may follow the fractionation of Zr-Hf although why Zr is more incompatible than Hf (hence Nb is more incompatible than Ta) in peridotite-basalt systems remains unresolved.

It is also possible that the similarity of Hf to Zr and Ta to Nb may be due to the familiar “lanthanide contraction effect”. As the crystal field theory has successfully explained the partition behavior of the transition metals (those in the 4th period elements), there could be the possibility that the crystal field theory may help explain the different partition behavior between Zr and Hf and between Nb and Ta. If so, a somewhat modified form of the crystal field theory would be necessary because for Zr^{4+} , Hf^{4+} , Nb^{5+} , and Ta^{5+} the participating *d* subshell valence electrons are on *N* and *O* shells (vs. *M* shell for transition metals). We anticipate that a theoretical exploration in this respect will be useful.

Other factors such as the coulomb force, electronegativity, and ionization enthalpy could have some effect, but their differences between the elemental pairs are significantly smaller than their mass differences. Therefore, they may be less significant in affecting their elemental fractionation although these factors will need to be considered in the development of improved crystal field theory for elements in 5th and 6th periods (see above).

Metasomatism process

Carbonatite metasomatism in the mantle source region may cause superchondritic Nb/Ta and fraction-

ated Zr/Hf ratios (Fábio et al., 2002; Dupuy et al., 1992) in subsequent basaltic melts, but cannot produce correlated Nb/Ta and Zr/Hf fractionation. Furthermore, it has been reported that there is no correlation between Zr concentration and Zr/Hf in carbonatite melt, implying that the varying Zr/Hf is unrelated to the crystallization of a particular mineral or minerals of non-chondritic value (Fábio et al., 2002). Thus, Fábio et al. (2002) extrapolated that the shifted Zr/Hf ratio is inherited from their heterogeneous mantle source. This notion is in accordance with the scenario observed in MORB (seafloor basalts) (Niu et al., 2002). Nb/Ta is reported (Weyer et al., 2003) to decouple from Zr/Hf in the mantle because Nb and Ta are more sensitive to the enrichment process than Zr and Hf. All these observations and inferences suggest that the coupled fractionations of Zr/Hf and Nb/Ta should not be caused by the aforementioned metasomatism processes although mantle metasomatism is in itself a low-degree melt magmatism (Niu and O'Hara, 2003).

Mobilization of Zr, Hf and Nb, Ta

As abyssal peridotites are mostly serpentinized, it could be possible that serpentinization may cause the coupled Zr/Hf-Nb/Ta fractionation. However, significant correlations of Nb, Ta, Zr and Hf with other incompatible elements indicate that the coupled fractionation is of magmatic origin (Niu, 2004). There is the suggestion that Nb and Ta could be mobilized during subduction zone metamorphism (Gao et al., 2007; Xiao et al., 2006), but experimental studies showed that the HFSEs are not mobilized during the serpentinization and dehydration processes (Kogiso et al., 1997; Tatsumi et al., 1986).

Melt structure

In a study of zircon and hafnon solubility in water-saturated granitic melts, Linnen and Keppler (2002) reported that the melt activity coefficient controlled by melt composition determines mineral-melt partition coefficients rather than the charge and ion radii in the crystal lattice (Blundy and Wood, 1994; Brice, 1975). When the melt composition varies from metaluminous to prealuminous, the ratio of D_{Zr}/D_{Hf} increases from 2 to 5. While melt structure may indeed be important, it remains unclear how melt struc-

ture can effectively affect partition coefficients of two elements with identical charges and ionic size (i.e., Zr-Hf and Nb-Ta). Importantly, for the peridotite-basalt system, major element compositions in basalts vary within a very limited extent, especially Al_2O_3 ; hence, melt structure varies very little and hence cannot be an important factor. Furthermore, in addition to aluminum content what else may control melt coefficient? Linnen and Keppler (2002) suggested that the oxygen atoms or electronegativities (1.4 for Zr, 1.3 for Hf) may play a role. But no studies have supported this speculation so far.

Zircon, hafnon and Nb-Ta oxides

Crystal structures of zircon and hafnon are nearly identical because the unit cell volume of hafnon is only 1.24% smaller than zircon (Speer and Cooper, 1982), indicating that Zr and Hf have essentially identical chemical properties as discussed above. Because Zr and Hf are extremely compatible and are, in fact, major elements in zircons, Zr-Hf fractionation, if any, should be recorded in zircons and zircon crystallization would be a major process of Zr-Hf fractionation. As Zr and Hf are chemically very similar, in theory, Zr/Hf in zircon should be the same as the natural abundances of the two elements (e.g., chondritic). In fact, the content of HfO_2 in zircon varies from 4 wt.%–8 wt.% to 35 wt.% in different crystals (Huang et al., 2002; Wang et al., 1996), and even in a single crystal zircon from the core to the rim (Zhang et al., 2004). The ability of zircon to fractionate Zr from Hf may be caused by melt composition (Linnen and Keppler, 2002) or supercritical fluids generated from the pegmatitic system (Norton and Dutrow, 2001) in which any sorts of complexes can form and fractionate these and other elements. But actually many zircons analyzed having nothing to do with pegmatite also cover a large range of Zr/Hf (Hei H., unpublished data). Studies of Zr/Hf in the zircon in granites (Wang et al., 2000) show that the large variation (95.14 to 30.44) probably also associated with a fluid phase, although we don't understand why Zr and Hf can fractionate in such fluids. Still, the same problem is that how do we explain the fractionation of Zr/Hf in such systems supposing that we can put aside Nb/Ta at this moment. Are the geochemical properties no longer

determined by charges and size? If so, what other properties? As for MORB, abyssal peridotites, and lunar rocks, there is unlikely such a supercritical fluid at work. Even if there is, this still cannot cause the coupled fractionation of Zr/Hf and Nb/Ta because fluids in the mantle (i.e., not in solid crystals under deep mantle high-pressure conditions) can not readily transport the HFSE (Brenan et al., 1995).

SUMMARY

(1) Coupled fractionation of Zr-Hf and Nb-Ta is convincingly a magmatic process. Assuming the correlated variation of Nb/Ta-Zr/Hf in lunar samples reflect a unique process in the early history of the magmatic differentiation in the solar system, then the observed correlated Nb/Ta-Zr/Hf variation in seafloor basalts and abyssal peridotites may be inherited from very early earth processes. That is, in the primary differentiation process of the uniform PM, Nb/Ta and Zr/Hf may be correlated. There is thus the possibility that the decoupled Zr/Hf-Nb/Ta fractionation may have been caused by a later (or more recent) process such as mantle metasomatism, partial melting associated with subduction zone processes (i.e., the involvement of a residual phase like rutile) and processes associated with the origin and growth of continental crust. It is also possible that lunar rocks, seafloor basalts and abyssal peridotites share some similar conditions such as the low oxygen fugacity when they formed; thus the Nb⁴⁺ may follow Zr⁴⁺ and Ta⁴⁺ may follow Hf⁴⁺ although it still needs understanding how Nb⁴⁺ may fractionate from Ta⁴⁺, and Zr⁴⁺ from Hf⁴⁺.

(2) Mass-dependent fractionation is the most promising explanation for the coupled variation of Nb/Ta and Zr/Hf. The issue is what mechanism may actually and effectively fractionate the twin elements and which processes may have caused the coupled fractionation. The classic “lattice strain” theory has difficulties in explaining the observations. So far, there is no known evidence that Nb and Ta can occur as 4⁺ in magmatic systems; we cannot entirely rule out the possibilities that “mass-dependent fractionation”, “low oxygen fugacity effect” and “melt activity coefficient control” may be all at work. All these need experimental testing. First, experiments under high tem-

peratures and pressures are needed to see whether the correlated Nb/Ta and Zr/Hf fractionations exist in magma differentiation processes systematically from basaltic to granitic although some observations have implied this (Zhang et al., 2004; Niu and Batiza, 1997; Niu and Hekinian, 1997), which requires understanding both the abundances and distribution of these elements in corresponding liquidus minerals (both major and accessory phases). Furthermore, we need precise and well-designed experimental studies and isotopic analyses of ‘serpentinization-resistant’ (or immobile) elements at different mass levels (e.g., ^{46,47,48,49,50}Ti, ^{90,91,92,94,96}Zr, ^{174,176,177,178,179,180}Hf) in abyssal peridotites to test the hypothesis of mass-dependent fractionation using MC-ICP-MS (Niu, 2004). This is because, so far, the largest correlated Zr/Hf and Nb/Ta fractionation is best documented in abyssal peridotites (Fig. 5; Niu, 2004).

(3) It is important to apply and further develop the crystal field theory for d-subshell electron behavior in *N* (for Zr and Nb) and *O* (for Hf and Ta) shells in forming complexes in silicate melt and in supercritical geological fluids. It is also worth to explore if f-shell electrons of Ta⁵⁺ and Hf⁴⁺ may participate in geological reactions because we usually considered that element pairs are identical on the basis of common principles in chemistry (i.e., the effects of valence electrons only), which may have limited our understanding of the geological processes.

(4) It is our intention that this review will help encourage more scientific efforts in understanding elemental behaviors in earth processes, which likely contain answers to many aspects of the general question of how the earth works.

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