

Fractionation of Zirconium and Hafnium during Processes of Mantle Metasomatism

Academician L. N. Kogarko

Received December 23, 2015

Abstract—For the first time, fractionation of zirconium and hafnium in carbonatized mantle xenoliths from the eastern Antarctic has been studied. An elevation relative to the chondrite values of Zr/Hf in the metasomatized xenoliths has been revealed. The main reactions of the carbonate metasomatism lead to replacement of primary orthopyroxene by secondary clinopyroxene. A substantial broadening of the clinopyroxene crystallization field results in an increase of Zr/Hf in an equilibrated melt due to a higher partition coefficient of Hf in clinopyroxene, relative to that of Zr. Migration of reaction-active carbonate and carbonate–silicate melts, equilibrated to metasomatic wehrlite, causes an increase in the Zr/Hf value in the carbonatized mantle substrate.

DOI: 10.1134/S1028334X16060076

Carbonatite melts are active agents of mantle metasomatism [1–3]. Percolation of melt–fluids, enriched with incompatible elements, forms enriched reservoirs, sources of alkaline–carbonatite magmas and related deposits of valuable metals. According to the experimental results, partial melting of the mantle substrate in the presence of CO₂ produces melts of dolomite composition, whose migration produces metasomatic zones by the following reactions: $2\text{Mg}_2\text{Si}_2\text{O}_6 + \text{CaMg}(\text{CO}_3)_2 = 2\text{Mg}_2\text{SiO}_4 + \text{CaMgSi}_2\text{O}_6 + 2\text{CO}_2$, $3\text{CaMg}(\text{CO}_3)_2 + \text{CaMgSi}_2\text{O}_6 = 4\text{CaCO}_3 + 2\text{Mg}_2\text{SiO}_4 + \text{CO}_2$ [1, 4].

Despite the limited body of information on the geochemistry for the elements and counterparts in the mantle substrate, the partition of Zr and Hf during processes of carbonate metasomatism has already been noted in abyssal xenoliths from Northern Tanzania [3], Spitsbergen [2], and other areas. These studies demonstrated that in carbonatized mantle nodules Zr/Hf rises substantially, sometimes reaching values above 100 [3].

Our studies of carbonate metasomatism in mantle xenoliths from some regions [1] have also revealed a notable separation of Zr compared to Hf.

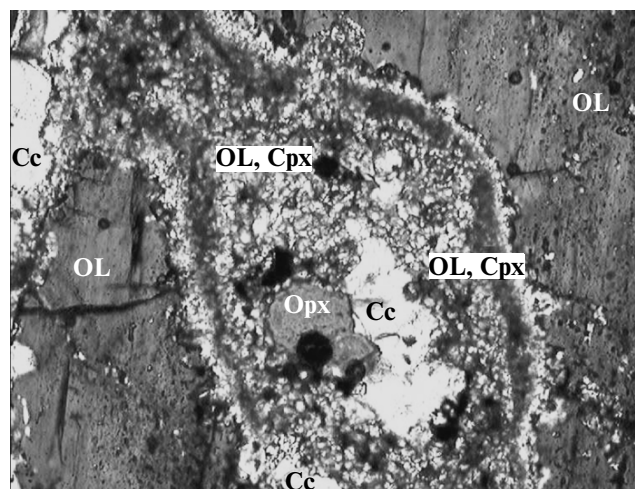
This regularity has been observed particularly well in the metasomatized mantle xenoliths from Oasis Jetty, East Antarctica, located in the Palaeozoic Beaver rift system. The latter stretches for 400 km north–northwestward. The age of the olivine mela–nephelinite host rock, according to K–Ar analysis, is Early

Cretaceous. There, the mantle xenoliths constitute up to 20–25% of the rock volume, ranging in size from a few cm up to 0.7 m. The rock association of the xenoliths includes all the rocks entrained by the melt from the upper mantle and crust of the eastern Antarctic: garnet-bearing spinel lherzolite, habsburgite, dunite, and fragments of crustal matter. The majority of xenoliths have a protogranular texture, according to Mercier and Nicolas [5]. The main rock-forming minerals of the xenoliths are olivine, clinopyroxene, orthopyroxene, spinel, and garnet. Many xenoliths have irregularly shaped zones and veins of carbonate: calcite, dolomite, and magnesite. Texturally, these patches are later formations: carbonate veins cut the main primary minerals and form reaction zones in which orthopyroxene is mainly altered (figure). The metasomatized zones, as has been found, contain some accessory minerals: apatite and micas along with first find of henrymeyerite [4] in a mantle rock: $(\text{Ba}_{0.97}\text{Ca}_{0.03}\text{K}_{0.03}\text{Na}_{0.11})\Sigma_{1.14}(\text{Fe}_{0.92}\text{Mg}_{0.17}\text{Al}_{0.02})\Sigma_{1.11}(\text{Ti}_{6.66}\text{Si}_{0.25})\Sigma_{6.91}\text{O}_{16}$. The latter mineral was found previously in the Kovdor carbonatite (Kola Peninsula) [6]. By applying neutron-activation and XRF analyses along with LA–MC–ICP–MS, the compositions of some mantle xenoliths have been determined, as has the distribution of Zr and Hf in some minerals (Table 1). All the studied mantle nodules have experienced processes of partial melting, which is supported by lower concentrations of Ca and Al in comparison to the primitive mantle: CaO–3.65 % wt, Al₂O₃–4.49% wt [7]. In the process of partial melting, a melt will, first of all, intake the incompatible, including Zr and Hf elements in accordance with the values of their mineral–melt partition coefficients, which in conditions of equilibrium mantle melts are very low, in the order of thousands of parts. At the degree of partial melting of the mantle substrate of 1%, the incompatible ele-

Vernadsky Institute of Geochemistry and Analytic Chemistry,
Russian Academy of Sciences, ul. Kosygina 19, Moscow,
119991 Russia
e-mail: kogarko@geokhi.ru

ments (Zr, Hf) virtually entirely pass into the equilibrium melt [8]. The bulk coefficients of Ca and Al partition during partial melting in the mantle are considerably higher by some tenths of a percent. Consequently, it is possible to conclude that in the studied xenoliths (Table 1) all Zr and Hf are gained during process of metasomatism, at least in nodules nos. 1, 5, and 6, which are notably depleted in Ca and Al: their matter experienced partial melting to some degree. Thus, the significant partition of Zr and Hf in the studied xenolith samples is a result of metasomatically induced intake by the already molten matrix. On the other hand, all metasomatized xenoliths without exception contain glass of mainly phonolite or quartz syenite compositions. This means that the evolution of the studied mantle matter was quite complex and that carbonatized mantle matter, in turn, was melted as a result of a significant decrease in the solidus temperature during metasomatic introduction of volatiles. Earlier [1] in mantle nodules from Montaña Clará Island (Canary archipelago), partial melting of the carbonatized mantle substrate was studied; it resulted in formation of three immiscible fluids—siliceous of syenite composition, carbonate resembling the composition of calcite carbonatite, and sulfide.

One of the major geochemical consequences of the carbonatization of mantle matter is the reaction of substitution of orthopyroxene by clinopyroxene and wehrlitization of the altered substrate. In our opinion there is a significant broadening of the crystallization field of clinopyroxene, which has a higher partition coefficient for Hf than that of Zr; this leads to formation of carbonate–silicate liquids with a higher Zr/Hf ratio, which may explain the notable deviation of this value in many carbonatites, relatively to chondrite [9–11]. Our studies have demonstrated quite high Zr/Hf in carbonatites of Polar Siberia, Ukraine, and the Cabo Verde Islands (Table 2). Uprise of such carbonate melts to higher crustal levels will trigger metasomatic reactions and forms carbonatized zones with elevated Zr/Hf, which has been observed in the East Antarctic mantle xenoliths. The orthopyroxene



Reaction zone in metasomatized mantle rock. OL, olivine; Cc, carbonate; Opx, orthopyroxene; OL, Cpx, reaction zone.

content in the mantle substrate exceeds 20%, so its substitution by clinopyroxene, which fractionates Zr from Hf, would significantly contribute to growth of the Zr/Hf value in molten carbonatite and carbonatite–silicate melts. The proposed model of Zr–Hf fractionation during carbonate metasomatism in the mantle is further corroborated by partition of these elements in the pyroxenes from the East Antarctic carbonatized mantle nodules. The first generation of clinopyroxene has lower Zr/Hf compared to that of pyroxene of the second generation, which is formed by metasomatic replacement of the primary pyroxene (Table 1). Notably, some of the metasomatic zones contain zoned pyroxene, which are a result of substitution of the primary phase by reaction products. From the pyroxene centers outwards, an increase in Zr/Hf has been identified (Table 1).

The combination of mantle metasomatism under conditions of an increased regime of volatiles, mainly carbon dioxide, with variation of the partial melting

Table 1. Partition of Zr and Hf in carbonatized mantle xenoliths and metasomatic clinopyroxene, ppm

Carbonatized mantle nodules				Clinopyroxene			
no.	Zr	Hf	Zr/Hf	no.	Zr	Hf	Zr/Hf
1	20.0	0.13	153	1	26.7	1.07	Center 25
2	10.0	0.04	227	1	26.4	0.4	Edge 71
3	12.0	0.15	80	2	678	8.43	80
4	15.0	0.17	88	3	367	8.00	46
5	31.0	0.21	148	4	627	9.53	66
Average	17.6	0.14	125	Average	345.02	5.49	57.6

Table 2. Partition of Zr and Hf in carbonatite of the Chernigov Massif (1), Cabo Verde (2) and Guli Massif (3), ppm

Calcite carbonatite (1)				Dolomite carbonatite (1)			
no.	Zr	Hf	Zr/Hf	no.	Zr	Hf	Zr/Hf
1	588	6.9	85.1	1	93.2	2.1	44.2
2	55.1	1.5	36.2	2	55.1	1.4	40.5
3	69.5	1.8	37.7	3	36	0.9	39.7
4	44.9	1.7	25.9	4	563	13.9	40.5
5	630	10.8	58.6	5	112	2.5	44.9
6	396	4.8	82.4	6	7.1	0.3	27.4
7	301	3	100	7	73.1	0.9	80.1
8	32.3	1.1	28.2	Average	134	3.1	45.3
9	378	6.9	54.9	Carbonatite (3)			
Average	277	4.3	56.6	no.	Zr	Hf	Zr/Hf
Carbonatite (2)				1	219	7.2	30.7
no.	Zr	Hf	Zr/Hf	2	342	8.3	41.1
1	475	9.9	47.8	3	66	2	33.9
2	56	0.9	58.9	4	12383	411	30.1
3	123	0.9	137	5	1945	62	31.4
4	304	7.8	38.8	6	63.1	1.3	48.5
5	9.1	0.1	73.3	7	1891	2	93.8
6	350	3	115	8	321	3.3	98.7
7	125	1.6	80.2	9	164	3	54.7
8	173	4.2	41.5	10	210	2.9	73.3
9	66.8	0.9	75.3	11	179	3	59.7
Average	187	3.3	74.2	12	15	0.3	49.8
				13	55	0.4	147
				14	35	1.5	23
				15	47	0.4	107.2
				16	106	1.7	62.4
				17	2.6	0.1	44
				18	13.5	0.2	86.8
				Average	1003	28	62

parameters of the mantle substrate is undoubtedly the cause of significant geochemical differentiation in abyssal magma generation zones, and it triggers fractionation of rare elements with subsequent formation of enriched reservoirs, i.e., sources of carbonatite magmas and related deposits of valuable metals. This process evolves to a great degree in zones of melt generation of large magmatic provinces associated with mantle plumes.

ACKNOWLEDGMENTS

This study was supported by the Russian Science Foundation, grant no. 15-17-30019.

REFERENCES

1. L. N. Kogarko, C. M. B. Henderson, and H. Pacheco, *Contrib. Mineral. Petrol.* **121**, 267–274 (1995).

2. D. A. Ionov, C. Dupuy, S. Y. O'Reilly, M. G. Kopylova, and Y. S. Genshaft, *Earth Planet. Sci. Lett.* **119**, 282–297 (1993).
3. R. L. Rudnick, W. F. McDonough, and B. W. Chappell, *Earth Planet. Sci. Lett.* **114**, 463–475 (1992).
4. L. N. Kogarko, G. Kurat, and T. Ntaflos, *Can. Mineral.* **45** (3), 497–501 (2007).
5. S. C. C. Mercier and A. Nicolas, *J. Petrol.* **16**, 454–487 (1975).
6. R. H. Mitchell, V. N. Yakovenchuk, A. R. Chakhmouradian, P. C. Burns, and Y. A. Pakhomovsky, *Can. Mineral.* **38**, 617–626 (2000).
7. H. Palme and H. St. C. O'Neill, *Treatise Geochem.* **2**, 1–38 (2003).
8. A. V. Giris, V. K. Bulatov, G. P. Brey, A. Gerdes, and H. E. Höfer, *Lithos* **160/161**, 183–200 (2013).
9. K. Hoernle, G. Tilton, M. J. Le Bas, S. Duggen, and D. Garbe-Schoenberg, *Contrib. Mineral. Petrol.* **142**, 520–542 (2002).
10. A. R. Chakhmouradian, *Chem. Geol.* **235**, 138–160 (2006).
11. C. Dupuy, J. M. Liotard, and J. Dostal, *Geochim. Cosmochim. Acta* **56**, 2417–2423 (1992).

Translated by A.N. Larionov