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Zirconium and Hafnium Fractionation in Differentiation of Alkali Carbonatite Magmatic Systems

L. N. Kogarko

Vernadsky Institute of Geochemistry and Analytical Chemistry, Russian Academy of Sciences,
ul. Kosygina 19, Moscow, 119991 Russia

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Abstract—Zirconium and hafnium are valuable strategic metals which are in high demand in industry. The Zr and Hf contents are elevated in the final products of magmatic differentiation of alkali carbonatite rocks in the Polar Siberia region (Guli Complex) and Ukraine (Chernigov Massif). Early pyroxene fractionation led to an increase in the Zr/Hf ratio in the evolution of the ultramafic–alkali magmatic system due to a higher distribution coefficient of Hf in pyroxene with respect to Zr. The Rayleigh equation was used to calculate a quantitative model of variation in the Zr/Hf ratio in the development of the Guli magmatic system. Alkali carbonatite rocks originated from rare element-rich mantle reservoirs, in particular, the metasomatized mantle. Carbonated mantle xenoliths are characterized by a high Zr/Hf ratio due to clinopyroxene development during metasomatic replacement of orthopyroxene by carbonate fluid melt.

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INTRODUCTION

Zirconium and hafnium are very valuable metals referred to the group of strategic mineral resources. Over 50% of the world's Zr and Hf reserves are concentrated in alkali rocks (nepheline syenite, alkali granite, and carbonatite), and about 45% are characteristic of exogenous zircon placers. More than 250 kt Zr and 70 kt of more valuable Hf are mined and used every year. As for alkali rocks, the highest concentrations of these elements are noted in agpaitic nepheline syenite genetically related to ultramafic carbonatite provinces, for example, on the Kola Peninsula, in Greenland, and in South Africa. The Zr content reaches a few percent in eudialyte lujavrite and 6–7 wt % in eudialyte, while Hf attains up to several tenths of a percent in the same rocks. Potential Zr and Hf resources in agpaitic nepheline syenite reach tens of millions of tons (eudialyte ore). The uniqueness and practical significance of eudialyte ore is related to its complex nature: it is also a source of rare earth and many other trace elements. In carbonatite, Zr and Hf are largely concentrated in baddeleytte ore actively developed, for example, in the Kovdor region (Kola Peninsula).

In the course of magmatic differentiation, Zr and Hf, as typical lithophilic elements, accumulate at the latest stages, culminating in the formation of alkali rocks and carbonatites. Zr and Hf make up the lattice of oxygen-bearing minerals only. Zircon, baddeleytte, and eudialyte are major commercially important Zr and Hf concentrators in the magmatic processes. Meanwhile, there are about 70 intrinsic minerals of these elements in nature, mostly observed in alkali rocks and carbonatites. As isomorphic impurities, Zr and Hf are included in the range of rock-forming minerals, replacing titanium, niobium, tantalum, rare earth, iron, and calcium due to similarity in size of ionic radii (Zr^{4+} (0.74); Y^{3+} (0.98); Ti^{4+} (0.69); Nb^{5+} (0.72); Ta^{5+} (0.72), Hf^{4+} (0.75). Zr and Hf concentrations of a few percent are characteristic of pyrochlore, columbite, xenotime, and pitchblende, replacing titanium, niobium, yttrium, uranium, and thorium. The Zr concentration occasionally reaches tenths of a percent in ilmenite, titanomagnetite, rutile, and titanite.

GEOCHEMISTRY AND FRACTIONATION OF ZIRCONIUM AND HAFNIUM IN THE EVOLUTION OF ALKALI CARBONATITE MAGMATIC SYSTEMS

Zirconium and hafnium, as well as niobium, tantalum, light and heavy rare earths, uranium, and thorium are referred to the group of analog elements, which behave identically in magmatic and many other processes. Meanwhile, magmatic systems involve fractionation of these pairs, reflecting variations in the physical and chemical conditions under which they are separated. In this regard, the study of fractionation of analog elements is of great interest for assessing such parameters as temperature and pressure, state of volatiles, oxygen fugacity, crystallization of mineral phases characterized by different distribution coefficients due to differences in their structures, etc.

The primary chondrite Zr/Hf ratio is 37–34.2 (McDonough and Sun, 1995; Jochum et al., 1986;

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[1] Corresponding author: L.N. Kogarko. E-mail: kogarko@geokhi.ru

Weyer et al., 2002) and was previously considered as virtually constant in global reservoirs. Advanced analytical methods and new factual data on Zr and Hf geochemistry made it possible to identify high variations in the Zr/Hf ratio not only in different magmatic series, but also in mantle material observed as deep xenoliths and peridotite massifs, which are considered mantle substrate outcrops on the Earth's surface. Some works stated a considerable difference in the Zr and Hf distribution in basaltic series (Gast, 1968; Schilling, Winchester, 1967). Tholeiitic basalts of mid-ocean ridges, whose genesis is related to partial melting of upper mantle material, are characterized by poor Zr and Hf fractionation and a Zr/Hf ratio close to 37, i.e., to chondrite. Meanwhile, the Zr/Hf ratio is highly variable in basalts related to plume activity (basalts in ocean islands such as OIB) likely due to crystallization differentiation, fractional melting of the mantle source, or mantle metasomatism (Pfänder et al., 2007; David et al., 2000). Therefore, it is appropriate to note the pioneering work by Engel (Engel et al., 1965), who was the first to relate the Zr and Hf fractionation in ocean island basalts to the fluid phase migration in magma formation areas. These ideas were further developed by Dupuy (Dupuy et al., 1992), who suggested the carbonate metasomatism effect on fractionation of these metals. Variable-depth equilibrium and fractional melting of the mantle substrate also leads to noticeable fractionation of analog elements (Gast, 1968). According to some authors, The Zr/Hf ratio is controlled mainly by the clinopyroxene–melt equilibrium in shallow areas of partial mantle melting corresponding to spinel lherzolite facies due to the fact that Hf is a more compatible element in pyroxene (Green et al., 2000; Kogarko 2015a). With an increase in depth, the garnet stability region is marked by higher fractionation of Hf with respect to Zr (Hf distribution coefficient in garnet is higher compared to Zr), while an increase in pressure results in a much higher Hf distribution coefficient (Grassia et al., 2012). As a result, deep melts with a higher Zr/Hf ratio with respect to chondrite are formed, while the Zr/Hf ratio decreases dramatically in restite. The real nature of this process is confirmed by a very high Zr/Hf ratio (up to 87) in a number of deep alkali basalts of nephelinite series (Dupuy et al., 1992), and this ratio increases with melt alkalinity. A geochemical consequence of this process was reduction in the Zr/Hf ratio in depleted mantle restite lost higher alkalinity melts in the course of partial melting, which developed under garnet facies conditions. For example, a very low Zr/Hf ratio (up to 10) in depleted mantle peridotite of Ivrea (Balmucha Massif) and other areas also confirms the important role of partial melting under deep conditions (Weyer et al., 2002).

According to our research data (Kogarko, 2015b), the formation of Zr–Hf deposits is related to fractional crystallization differentiation of alkali-supersaturated magmas accompanied by intense fractionation of these elements; the Zr/Hf ratio increases from 38 in early rocks to 51 in later magmatic occurrences. The increase in this ratio is largely due to the wide magmatic crystallization field of alkali pyroxene (and amphibole), where the Hf distribution coefficient (0.58) is higher with respect to Zr (0.40) (Kogarko, 2015a, 2015b). As follows from the experimental data on the Zr and Hf distribution coefficients in pyroxene of magmatic systems with variable composition, the difference between these values is even twice as high (Hill et al., 2000; Green et al., 2000).

Zr and Gf are also highly fractionated in the differentiation of alkali carbonatite rocks related to the plume magmatism that developed in continents and ocean islands. One of the research objectives was to investigate the geochemistry and fractionation of Zr and Hf in the differentiation of alkali carbonatite complexes with thr example of the largest Mesozoic province in the Polar Siberia region (Maimecha–Kotuy Province) and the Proterozoic complex in Ukraine (Chernigov Massif).

The world's largest alkali ultramafic province, Maimecha–Kotuy, is about 74300 km^2 in area and is located northeast of Siberian plateau basalts. It is composed of 32 alkali ultramafic intrusions, a large number of alkali lavas and dikes, and a few carbonatite bodies (Egorov, 1991). In the north of the province is the Guli intrusion, which is the world's largest ultramafic–alkali carbonatite complex. The massif is oval in shape and 35 × 45 km in size; it consists of rocks overlapped by Quaternary sediments; and it is 1500–1600 km^2 in area (Egorov, 1991).

According to the geophysical data, this massif has almost vertical contacts and is likely tubular in shape (Egorov, 1991). Host rocks include alkali effusive rocks composed of meimechite flows. The Guli Massif, as well as other alkali ultramafic massifs in the province, was formed in a few phases (Table 1). The most common rocks include dunite (about 60% of the studied area) and ultramafic–alkali rocks (approximately 30%). All other varieties, including melilitolite, ijolite, alkali syenite, and carbonatite make up only 10% of the massif.

The central part of the intrusion is composed of two carbonatite massifs, which, in our opinion, constitute a single large complex that formed at several stages starting with intrusion of phoscorite, then calcite carbonatite, and ending with dolomite carbonatite. We investigated the Zr and Hf distribution pattern in all rocks of the Guli ultramafic–alkali carbonatite complex. Zr and Hf analyses were performed by ICP-MS with a Finnigan Element mass spectrometer and by neutron activation based on BEN and IFG international standards.

The analysis results are given in Tables 2 and 3. We identified higher Zr and Hf concentrations, reaching 0.7–0.19% Zr and a few tenths of a percent of Hf in rocks of the deeply differentiated Guli Massif. The

Table 1. Main intrusion phases, subphases, and rock types in Guli Massif

Intrusion phase	Subphase	Rock
7	4	Dolomite carbonatite
	3	Fine-grained calcite carbonatite
	2	Coarse-grained calcite carbonatite
	1	Phoscorite and ore phoscorite
6		Granite
5	2	Microshonkinite
	1	Agpaite syenite and quartz syenite
4		Ijolite and ijolite--pegmatite
3	3	Jacupirangite and melteigite
	2	Nephelinite and olivine nephelinite, nepheline picrite, and mica pyroxene picrite
	1	Melteigite, malignite, and shonkinite
2		Melilite rocks
1	2	Ore pyroxenite (kosvite), olivine pyroxenite, and peridotite
	1	Dunite

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average contents of these elements for variable rocks were assumed as the arithmetic mean values. High Zr and Hf contents in ultramafic alkali complexes in many regions were noted by Fersman (1939), Wedepohl (1969), Gerasimovsky et al. (1966), etc.

The Guli Massif is characterized by an increase in the Zr and Hf contents from primary magmas (picrite, nephelinite, and meimechite) and earlier rocks (dunite, kosvite) to intermediate differentiation products, such as melteigite, ijolite, and latest products, such as phoscorite and nepheline syenite (Table 2). Agpaitic nepheline syenite is distinguished by very high Zr and Hf concentrations, close to commercial values, taking into account the elevated contents of radioactive and rare earth elements in these rocks (Kogarko, 2014). The accumulation of Zr and Hf in the evolution of the Guli magmatic system was undoubtedly related to a very low distribution coefficient of these elements in early minerals, such as olivine and pyroxene, whose crystallizations fields are very large. The Zr and Hf contents are minor in these minerals: hundredths and tenths of g/t. Enrichment of the final differentiation products in Zr and Hf resulted in the formation of their own minerals; for example, eudialyte containing 12% ZrO_2 and 0.25% HfO_2 appears in nepheline syenite. Carbonatites include zirconolite, baddeleytte, and other minerals containing tens of percent of Zr, while the Hf content reaches a few percent. It should be noted that the development of the carbonatite complex is accompanied by depletion in Zr and Hf in the latest rocks of the massif: Zr and Hf contents fall from 1941 g/t Zr and 61 g/t Hf in early phoscorite to 8 g/t Zr and 1 g/t Hf in dolomite carbonatite (Table 2). This specific feature of the Guli carbonatite system is related to the very wide crystallization fields of such accessory minerals as zirconolite, zirkelite, and baddeleytte, which are achieved in phoscorite and noticeably concentrate not only Zr and Hf, but, as we have established earlier (Kogarko, 2012, 2014), also radioactive and rare earth metals. The irregular distribution of Zr and Hf in Guli carbonatites is primarily due to the accumulation of rock-forming—and more importantly for Zr and Hf—accessory minerals that are principal Zr and Hf concentrators, such as abundant baddeleytte, zirconolite, zirkelite, and sporadic pyrochlore and perovskite containing only a few percent of Zr and tenths of a percent of Hf (Williams and Kogarko, 1996).

According to our research data, the Guli rocks are marked by Zr and Hf fractionation. The Zr/Hf ratio increases regularly from early dunite, kosvite, meimechite, and nephelinite to later melteigite, ijolite, and it reaches from 33 to 51 (on average) at the final stages of differentiation in syenite and phoscorite (Table 2). The Zr/Hf ratio is much higher in the Guli carbonatite complex than in chondrite and increases in the course of evolution from 51 in early phoscorite to 72 in calcite carbonatite and 65 in dolomite carbonatite. On average, the Zr/Hf ratio is 63 throughout the Guli carbonatite complex, which is much higher than in chondrite (37), earlier intrusive phases, and primary magmas (Table 2). This evolution of the Guli alkali carbonatite magma is mainly related to the crystallization of pyroxene fractionating Hf to a greater extent with respect to Zr.

We used the Rayleigh equation to calculate variations in microconcentrations in the melt in the course of fractional crystallization and the mass balance equation to describe the equilibrium and fractional crystallization:

$$C^L = C^0(F^L)^{K-1}$$

(fractional crystallization)

Table 2. Zr and Hf distribution in Guli rocks

Dunite, kosvite				Olivine nephelinite			
No.	Zr	Hf	Zr/Hf	No.	Zr	Hf	Zr/Hf
1	108	3	35	1	134	3	50
2	128	4	34	2	177	4	43
3	89	2	37	3	300	7	44
4	137	4	38	4	337	8	45
5	46	2	31	5	310	9	42
6	108	4	28	***Average***	***252***	***6***	***45***
7	92	3	29	**Melilitite**			
8	106	3	31	No.	Zr	Hf	Zr/Hf
Average	***102***	***3***	***33***	1	75.0	2	37
Phonolite, syenite				2	59	2	32
No.	Zr	Hf	Zr/Hf	3	56	2	24
1	236	4	55	***Average***	***63***	***2***	***31***
2	631	8	79	**Ijolite**			
3	179	4	42	No.	Zr	Hf	Zr/Hf
4	722	13	56	1	357	9	40
5	7236	135	54	2	192	4	52
Average	***1801***	**33**	***57***	***Average***	***275***	***6***	***46***
Phoscorite				**Calcite carbonatite**			
No.	Zr	Hf	Zr/Hf	No.	Zr	Hf	Zr/Hf
1	220	7	31	1	164	3	55
2	342	8	41	2	210	3	73
3	66	2	34	3	179	3	60
4	12383	411	30	4	15	0.3	50
5	1945	62	31	5	55	0.4	147
6	63	1	49	6	35	2	23
7	189	2	94	7	47	0.4	107
8	321	3	99	8	106	2	62
Average	***1941***	***62***	***51***	***Average***	***102***	***2***	***72***
Dolomite carbonatite							
No.	Zr	Hf	Zr/Hf				
1	3	0.1	44				
2	145	0.2	87				
Average	***8***	***0.1***	***65***				

$$C^L = C^0/(F^L + K(1 - F^L))$$
(crystallization equilibrium),

where C^L is the current concentration in the melt; C^0 is the concentration in the melt prior to crystallization; F^L is the portion of remaining melt; and K is the distribution coefficient. Based on these equations and the Zr and Hf distribution coefficients estimated in the equilibrium of pyroxene–alkali melt (Kogarko, 2015a, 2015b), we calculated the clinopyroxene content, which should be fractionated to provide an increase in the Zr/Hf ratio from 31 in the Guli primary magmas to 51 in the final products such as phoscorite. The values of 0.26 obtained for the case of equilibrium crystallization and 0.21 for the fractional crystallization differentiation are consistent with petrographic studies confirming the reality of this value, especially at the middle stages of evolution of the alkali carbonatite system during melteigite and ijolite formation. Hence, crystallization differentiation was the major process caused the Zr and Hf accumulation and and increase in the Zr/Hf ratio in later differentiation products of primary magmas in the Polar Siberia region.

As follows from our studies of the geochemical characteristics of carbonatite in the Proterozoic complex of the Ukrainian Shield, such as the Chernigov carbonatite massif, carbonatites are also characterized by elevated Zr and Hf contents and a high Zr/Hf ratio (Table 3). The Proterozoic Chernigov Massif, as well as the Mesozoic Guli Complex, is distinguished by deep differentiation. The massif is composed of silicate alkali rocks (alkali syenite, nepheline syenite, alkali pyroxenite, and melteigite) and carbonatites. The geological structure of the massif is described in (Sheremet et al., 2011). The average Zr and Hf contents in Chernigov calcite carbonatite are higher with respect to Guli sóvite, while the Zr/Hf ratio is lower (Table 3); in the Chernigov Massif, the Zr and Hf contents and the Zr/Hf ratio in calcite carbonatites is also higher compared with late dolomite carbonatites. The average Zr/Hf ratio in Chernigov calcite and dolomite carbonatites is higher than in chondrite (like in the Guli Complex). This geochemical feature is also likely due to more intensive Hf fractionation in early pyroxenes in the Chernigov Massif. The development of pyroxenite at the earlier formation stages of this massif is consistent with the proposed mechanism. As follows from our data and those obtained by other researchers (Chakhmouradian, 2006) on Zr and Hf fractionation, the Zr/Hf ratios in many of the world's carbonatite massifs are higher than in chondrite and are quite similar to each other, which is likely due to the specific features of their geochemical evolution.

As follows from a comparison of the data on the Zr and Hf distribution in Mesozoic and Proterozoic alkali carbonatite complexes (Table 4), the earliest manifestations of carbonatite magmatism in the Polar Siberia region are characterized by much higher contents of not only these elements, but also of radioactive and rare earth metals. which makes these rocks very valuable sources of strategic raw materials. The Guli carbonatite complex formed synchronously with Siberian traps (Kogar and Zartman, 2008) and thus was a part of the Siberian superplume. Plumes are known to be related to large magmatic chambers, whose differentiation, owing to active convective phenomena, can lead to substantial accumulation of ore material. Large deposits and valuable mineralization of strategic metals observed in South America, East Africa, and on the Kola Peninsula developed in plume series of alkali rocks.

Table 3. Zr and Hf distribution in (1) Chernigov and (2) Cape Verde rocks

Calcite carbonatite (1)

No.	Zr	Hf	Zr/Hf
1	588	7	85
2	55	2	36
3	70	2	38
4	45	2	26
5	630	11	59
6	396	5	82
7	301	3	100
8	32	1	28
9	378	7	55
Average	***277***	***4***	***57***

Dolomite carbonatite (1)

No.	Zr	Hf	Zr/Hf
1	93	2	44
2	55	1	41
3	36	0.9	40
4	563	14	41
5	112	3	45
6	7	0.3	27
7	73	0.9	80
Average	***134***	***3***	***45***

Carbonatite (2)

No.	Zr	Hf	Zr/Hf
1	475	10	48
2	56	0.9	59
3	123	0.9	137
4	304	8	39
5	9	0.1	73
6	350	3	115
7	125	2	80
8	173	4	42
9	67	0.9	75
Average	***187***	***3***	***74***

FRACTIONATION OF ZIRCONIUM AND HAFNIUM DURING MANTLE METASOMATISM

It is assumed today that some carbonatites are products of partial melting of metasomatized and carbonated mantle.

Chakhmouradian (2006) previously drew attention to elevated Zr/Hf ratios of up to 60 in phoscorite of different carbonatite complexes in the world. Using the fractional crystallization model of the Kola Peninsula ultramafic–alkali series, Chakhmouradian theoretically showed a significant decrease in Zr and Hf contents in the final differentiation products,such as carbonatites. Meanwhile, according to geochemical data, the Zr and Hf concentrations, on the contrary, increase in phoscorite; hence, it was concluded that phoscorites were independent melts of the mantle substrate. A similar example is likely carbonatites from the Cape Verde Islands, which are the most ancient igneous rocks there (CA complex, Mazarovich et al., 1990) and are not directly related to ultramafic–alkali rocks. The results of (Hoernle et al., 2002) are consistent with our data: the average Zr/Hf ratio in calcite carbonatites of Cape Verde Islands is higher than that in chondrite (60), while it increases to 111 in dolomite (Table 3).

Carbonatite melts are active agents of mantle metasomatism (Ivanov et al., 1993; Kogarko et al., 1995; Kogarko et al., 2007; Rudnick et al., 1992; Downes, 2001; Yaxley, 1991). Infiltration of fluid

Table 4. Zr and Hf distribution in carbonated mantle xenolith and metasomatic clinopyroxene

Carbonated mantle nodules				Clinopyroxene			
No.	Zr	Hf	Zr/Hf	No.	Zr	Hf	Zr/Hf
1	20	0.13	153	1	27	1	Center 25
2	10	0.04	227	1	26	0.4	Rim 71
3	12	0.15	80	2	678	8	80
4	15	0.17	88	3	367	8	46
5	31	0.21	147	4	627	10	66
Average	***18***	***0.14***	***125***	***Average***	***345***	***5***	***58***

melts enriched in incompatible elements leads to the occurrence of enriched reservoirs, sources of alkali carbonatite magmatism. According to the experimental data, partial melting of the mantle substrate when there is CO_2 is accompanied by the formation of dolomite melts, whose migration results in the development of metasomatic zones according to the following reactions:

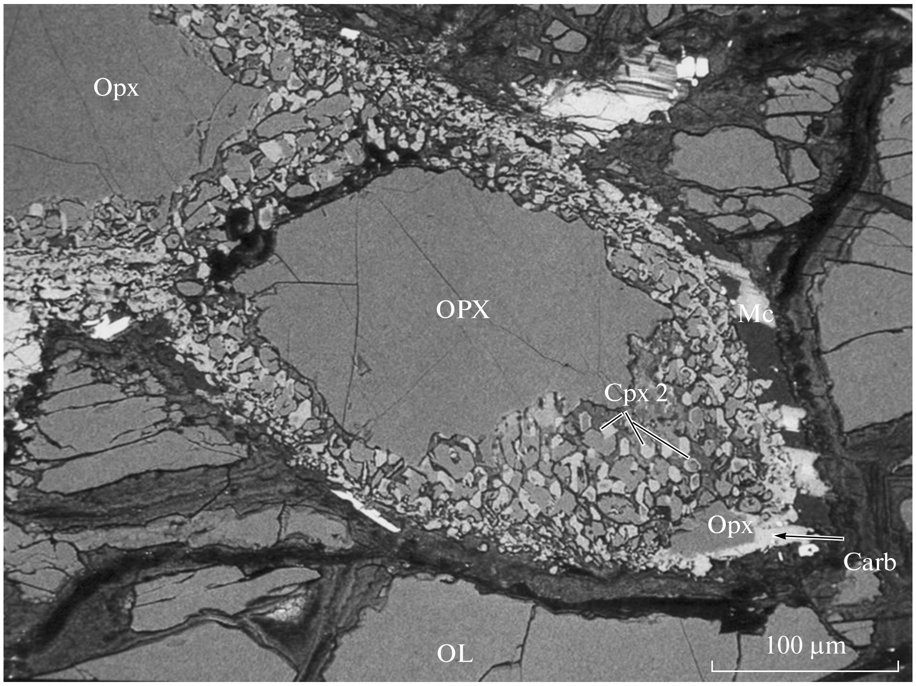
$$2Mg_2Si_2O_6 + CaMg(CO_3)_2$$
$$= 2Mg_2SiO_4 + CaMgSi_2O_6 + 2CO_2,$$
$$3CaMg(CO_3)_2 + CaMgSi_2O_6$$
$$= 4CaCO_3 + 2Mg_2SiO_4 + 2CO_2$$

(Kogarko et al., 1995; Kogarko et al., 2007) .

Separation of Zr and Hf during carbonate metasomatism was noted in the mantle substrate (deep nodules) in northern Tanzania (Rudnick et al., 1992), Svalbard (Ionov et al., 1993), and other regions. According to the investigation results, the Zr/Hf ratio significantly increases and occasionally reaches values exceeding 100 in carbonated mantle nodules (Rudnick et al., 1992).

Our studies of carbonate metasomatism in deep mantle xenoliths (Kogarko et al., 1995; Kogarko et al., 2007) in a number of regions also revealed the evident separation of Zr and Hf.

This trend is well defined in metasomatized mantle xenoliths in the east Antarctica region, in the Jetty Oasis confined to the Paleozoic Beaver rift system. The rift zone, 400 km in length, extends north and northwest. The age of host olivine melanephelinite was estimated by the K–Ar method as Early Cretaceous (Andronikov, 1990). Deep xenoliths occupy 20–25% of the east Antarctica region and vary in size from a few centimeters to 0.7 m. The mantle xenolith assemblage reflecting an extended section of the upper mantle and crust in the east Antarctica region is composed of garnet-containing and spinel lherzolite, harzburgite, dunite, and fragments of crustal material. Most xenoliths have a protogranular structure, according to the classification by Nicolas and Mercier (1975). The major rock-forming minerals of mantle xenoliths include olivine, clinopyroxene, orthopyroxene, spinel, and garnet. Many xenoliths contain irregularly shaped zones, veinlike segregations of carbonate material observed as calcite, dolomite, and magnesite. These zones are later in their structural features; carbonate veinlets cross major rock-forming minerals and form reaction zones, which are mainly developed and replace orthopyroxene (figure). We identified a number of accessory minerals in metasomatic zones, such as apatite and mica; henrymeyerite was found for the first time in the mantle substrate: $(Ba_{0.97}Ca_{0.03}K_{0.03}Na_{0.11})\Sigma_{1.14}(Fe_{0.92}Mg_{0.17}Al_{0.02})\Sigma_{1.11}(Ti_{6.66}Si_{0.25})\Sigma_{6.91}O_{16}$ (Kogarko et al., 2007); it was previously identified in Kovdor carbonatites (Kola Peninsula) (Mitchell et al., 2000). We determined the compositions of a number of mantle xenoliths, the Zr and Hf distribution in them, and some minerals by neutron activation and X-ray fluorescence analysis (Tables 1, 2). All studied nodules underwent partial melting, because their Ca and Al concentrations are lower than the contents of these elements in the primitive mantle: 3.65 wt % CaO and 4.49 wt % Al_2O_3 (Palme and O'Neill, 2003). In the course of partial mantle melting, such incompatible elements as Zr and Hf are the first to pass into the melt, and their distribution coefficients in the equilibrium of melt–minerals are very low, a few thousandths of a percent. At a degree of mantle substrate melting of 1%, incompatible elements (Zr and Hf) almost completely pass into the equilibrium melt (Girnis et al., 2013). The bulk distribution coefficients of Ca and Al are much higher, a few tenths of a percent, during partial mantle melting. Hence, it can be concluded that Zr and Hf were supplied almost completely as a result of metasomatic processes in the studied mantle xenoliths (Table 3), at least in nodules 1, 5, 6 with much lower Ca and Al contents (less than 1% CaO and Al_2O_3), the material of which was subjected to partial melting by a few percent. On the other hand, all metasomatized xenoliths contain phonolite and quartz–syenite glass. This means that the history of the investigated mantle material is very compelx, and the carbonated mantle material, in turn, likely melted due to a significant decrease in the solidus temperature during metasomatic supply of volatiles. We investigated the partial melting processes of carbonated mantle material in Montana Clara Island (Canary Archipelago) nodules (Kogarko et al., 1995); these processes result in the formation of three immiscible liquids, such as silicate liquid with a syenite composition, carbonate liquid



BSE image of carbonation zone and orthopyroxene replacement. (Cpx) Metasomatic clinopyroxene; (Opx) orthopyroxene; (Mc) mica; (OL) olivine; (Carb) carbonates (calcite and dolomite).

similar in composition to calcite carbonatite, and sulfide liquid.

One of the main geochemical consequences of the mantle material carbonation process is the replacement of orthopyroxene by clinopyroxene andthe development of deep substrate wehrlitization. In our view, the crystallization field extension of clinopyroxene characterized by a higher Hf distribution coefficient with respect to Zr leads to the formation of carbonate–silicate melts with a higher Zr/Hf ratio, which explains the considerable deviation of this ratio to higher values in relation to chondrite in many carbonatites (Hoernle et al., 2002; Chakhmouradian, 2006; Dupuy, 1992). Movement of such carbonate melts to upper structural floors cause metasomatic reactions and the formation of carbonated zones with higher Zr/Hf ratio observed in deep xenoliths in the East Antarctica Region. The mantle substrate contains more than 20% orthopyroxene, so the replacement of this mineral by clinopyroxene, which fractionates Zr and Hf, will undoubtedly contribute to an increase in the Zr/Hf ratio in the melting out of carbonatite melts. The proposed model of Zr and Hf fractionation during carbonate mantle metasomatism is confirmed by the nature of the distribution of these elements in pyroxene of carbonated nodules. First-generation clinopyroxene is characterized by a lower Zr/Hf ratio with respect to second-generation pyroxene, which forms in the course of metasomatic replacement of primary orthopyroxene (Table 3).

The combination of mantle metasomatism for a higher content of volatiles, mainly carbon dioxide, and variations in the partial melting parameters of mantle material, is certainly a cause of deep geochemical differentiation of abyssal magma generation zones, which leads to fractionation of rare elements and the occurrence of rare element-rich reservoirs, which are sources of carbonatite magmatism and related rare metal deposits.

CONCLUSIONS

The evolution of large magma chambers of ultramafic–alkali magmas is accompanied by intense accumulation of Zr, Hf, and other strategic metals (radioactive and rare earth elements) up to the achievement of crystallization fields of concentrating minerals, such as eudialyte in nepheline syenite, and zirconolite, baddeleytte, and zirkelite in Guli carbonatites. The contents of these elements pass through a maximum in the development of the magma chamber, and we have identified a considerable drop in the Zr and Hf concentrations in the latest products of the carbonatite system, such as dolomite carbonatites. Crystallization differentiation was the leading process controlling the geochemistry of Zr, Hf, and other strategic metals in the Guli magmatic system. Early pyroxene fractionation led to an increase in the of Zr/Hf ratio in the evolution of the ultramafic–alkali magmatic system due to a higher Hf distribution coefficient in pyroxene with respect to Zr.

The sources of high Zr and Hf concentrations in primary alkali magmas in the Polar Siberia region are enriched mantle reservoirs that formed under the metasomatic supply of lithophilic strategic metals to the magma generation zone.

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