

# Main Components of Geochemical Reservoirs of the Silicate Earth

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**Abstract**—Mass balance of incompatible elements was analyzed for different inferred reservoirs of the bulk silicate Earth. It was shown that the lower mantle, as well as the primitive mantle, includes an MORB-source depleted mantle component and material with a high content of incompatible elements. Contribution of the continental crust was found to be subordinate. The predominant part of the enriched mantle formed through differentiation of the mantle itself. Enriched material was supplied into the deep-seated zones of silicate shell through delamination of subcontinental lithospheric blocks affected by mantle metasomatism and their subsequent involvement in the mantle convective system. The osmium isotope composition of the plunged lithospheric material is modified in the lower mantle by the infiltration of sulfide melts.

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## INTRODUCTION

The chemical composition of the Earth is a cosmochemical and geochemical problem. The concept of the chondritic Earth was formulated by Vinogradov [1]. The pyrolite model of Ringwood used this concept in considering petrogenic components, suggesting that the primitive mantle is a mixture of depleted mantle peridotites and supposedly complementary magmas in proportions giving the chondritic Ca/Al ratio [2]. The chondritic model of the silicate Earth was extended later to trace elements. This approach is based on the fact that elements produced by high-temperature nebular condensation (for which calculated temperatures of 50% gas-to-solid transition are higher than 1400 K) occur in different types of chondrites approximately in equal proportions. Since the Earth was accreted from the same material as the parental bodies of chondritic meteorites, the bulk silicate Earth should show almost chondritic ratios of lithophile elements of high-temperature condensation. This principle, together with geochemical data on mantle rocks and magmas, was used to estimate the bulk composition of the Earth's primitive mantle [3, 4].

Some researchers accept more extreme versions of the chondritic model, assuming that the Earth is compositionally identical to a certain chondrite type [5, 6]. Covariations of indicator elements in meteorites and the Earth led them to conclude that the Earth's composition corresponds to carbonaceous chondrites, in particular, to their hypothetical type poor in volatile contents [5, 6].

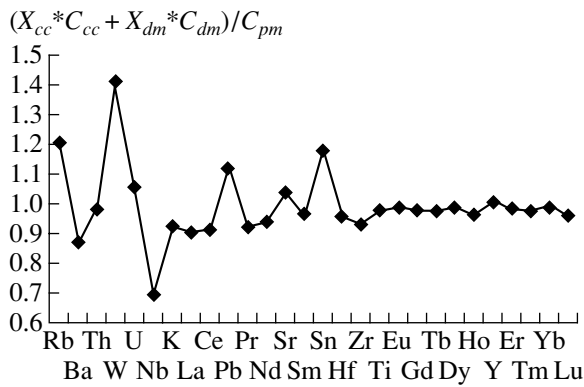
The chondritic proportions of components in the Earth are not exactly proved yet. For example, they could have been shifted at early stages by the collision of a partially differentiated Earth with a large cosmic

body and the consequent loss of a part of the outer shell [4]. The chondritic model is tested by the comparison of deduced conclusions with data on the abundances of non-volatile lithophile elements and their isotopes in mantle rocks and magmas. The most important criterion is provided by the Sm–Nd and Lu–Hf isotope systems, since all these elements belong to the lithophile elements of high-temperature condensation. Recent isotope data on different chondrites show a close positive correlation between  $^{143}\text{Nd}/^{144}\text{Nd}$  and  $^{176}\text{Hf}/^{177}\text{Hf}$  in the mantle rocks. At the same time,  $^{176}\text{Lu}/^{177}\text{Hf}$  and  $^{176}\text{Hf}/^{177}\text{Hf}$  ratios are somewhat more widely scattered than is seen in the Sm–Nd system. The average  $^{176}\text{Hf}/^{177}\text{Hf}$  value for carbonaceous chondrites lies within the mantle correlation trend in the Hf–Nd isotope diagram [7]. In general, data on these isotope systems and many elemental ratios in the mantle rocks indicate that the chondritic model is a good approximation for the bulk Earth composition.

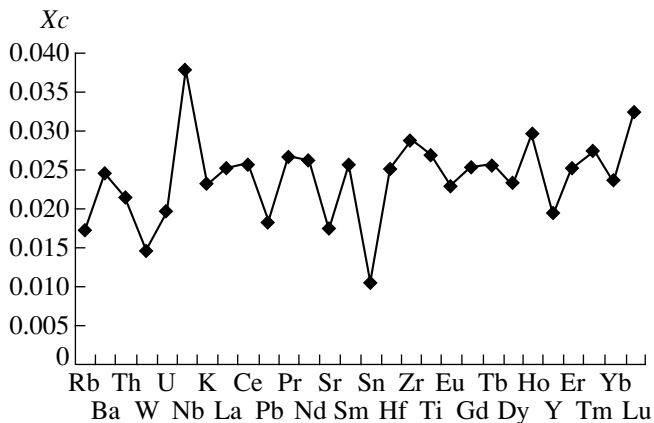
Composition of the bulk silicate Earth with chondritic ratios of non-volatile lithophile elements was estimated in [3, 4]. The global differentiation of the Earth produced geochemical reservoirs depleted (depleted mantle as a MORB source) and enriched (for example, continental crust) in incompatible elements. As a result, most mantle rocks and magmas lost the geochemical characteristics of the chondrite Earth.

## THREE-COMPONENT MODEL OF THE SILICATE EARTH

The composition of the depleted mantle was estimated by modeling of the generation of primary mag-



**Fig. 1.** Primitive pyrolite-normalized [4] calculated contents of incompatible elements in a mixture of continental crust and depleted mantle with weight proportions of the continental crust and mantle above 660-km seismic boundary.



**Fig. 2.** Values  $X_c = X_{cc} / (X_{cc} + X_{dm})$ , where  $X_{cc}$  and  $X_{dm}$  are fractions of continental crust and depleted mantle in the silicate Earth, as calculated for incompatible elements.

mas and their differentiation, which produced typical mid-ocean ridge basalts [8]. The average composition of the continental crust was obtained from data on various sedimentary and metamorphic rocks and lower crustal xenoliths in alkali basalts and kimberlites [9].

The simplest model of the differentiated Earth suggests that continental crust and depleted mantle compose the outer shells of the Earth to the boundary with the lower mantle, while the latter is identical to the undifferentiated bulk silicate Earth. However, mixing between continental crust (according to [4]) and depleted mantle (according to [8]) yields a composition significantly different from the primitive mantle in the chondritic model [4] (Fig. 1). The two components were mixed in weight proportions of continental crust and upper mantle. Thus, this simplest model failed the quantitative test.

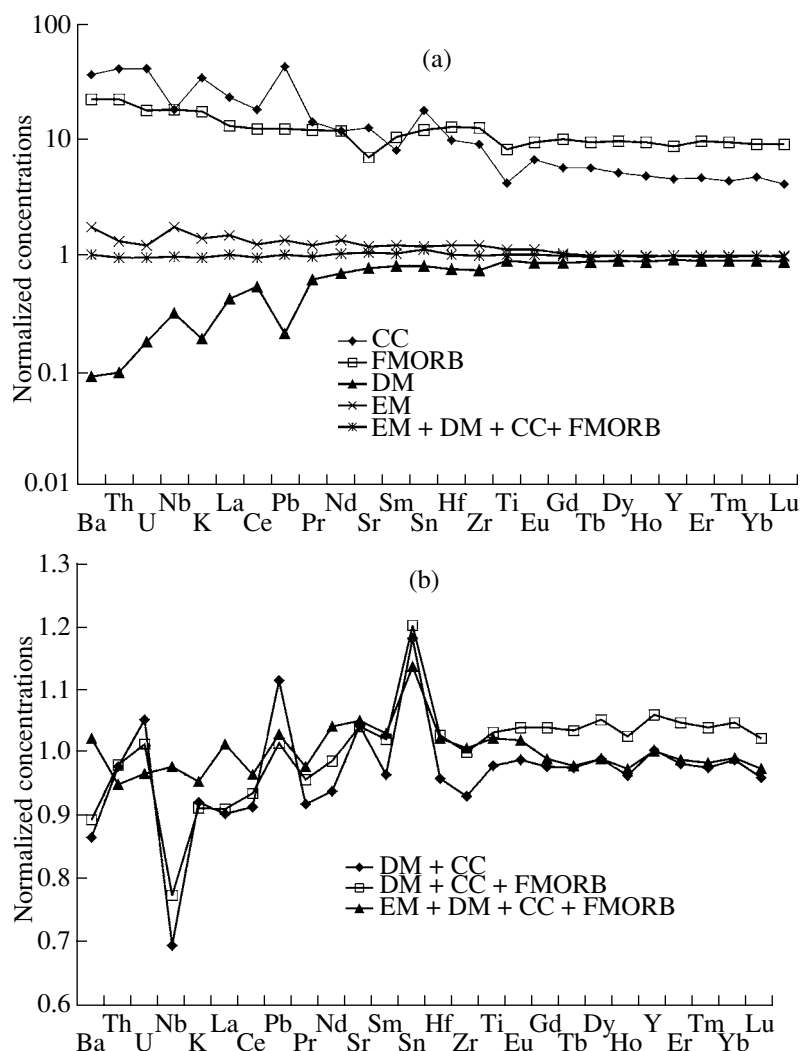
In the considered three-component model of the silicate Earth (continental crust + depleted mantle + prim-

itive mantle), the mixing proportions of continental crust and depleted mantle can be changed to obtain primitive mantle with chondritic ratios of non-volatile lithophile elements. This corresponds to the case when the depleted mantle and continental crustal components are present not only in the outer part of the Earth, but also in the lower mantle, where they can be mixed with primitive mantle. This is a more realistic model, which suggests a mixture of depleted and primitive mantles with isotope characteristics of most intraplate oceanic island basalts, whose source is depleted in incompatible elements (PREMA [10], FOZO [11], or PHEM [12]), but to a lesser extent than the MORB source. This model implies that

$$(1 - X_c)C_{dm} + X_c C_{cc} = C_{pm},$$

where  $X_c = X_{cc} / (X_{cc} + X_{dm})$ ,  $X_{cc}$  and  $X_{dm}$  are respective fractions of continental crust and depleted mantle in the silicate Earth,  $C_{cc}$  and  $C_{dm}$  are respective concentrations of an element in these reservoirs, and  $C_{pm}$  is the concentration of the element in the primitive mantle. Hence,  $X_c = (C_{pm} - C_{dm}) / (C_{cc} - C_{dm})$ . This formula was applied to calculate  $X_c$  on the basis of the contents of different incompatible elements in the continental crust and depleted and primitive mantles. Results of these calculations are shown in Fig. 2. The optimal  $X_c$  for a group of elements was calculated by the least square method as 0.021. Figure 2 shows that the  $X_c$  values for some elements significantly differ from this optimal value, which may indicate either imperfection of the applied model or uncertainty in the estimated average contents of these elements in components of the silicate Earth.

Figure 3b demonstrates a primitive mantle-normalized multielement diagram for a mixture of depleted mantle (97.9%) and continental crust (2.1%) with the optimal mixing proportions obtained by the least square method. There are significant deviations for the elements which behave differently in processes of basaltic mantle magmatism (magmatism of mid-ocean ridges and intraplate oceanic islands) and formation of the continental crust (average composition of the continental crust and calc-alkaline magmas). These are Nb and Ta, whose abundances in the continental crust are lower than those of their analogues in the basaltic systems (e.g., U for Nb), as well as fluid-mobile components (e.g., Pb, Sn, and others), which are abundant in the continental crust and calc-alkaline magmas [13]. Thus, the considered model (Fig. 3b) demonstrates a negative deviation for Nb and a positive deviation for Pb and Sn, from the accepted composition of the primitive mantle. Thus, calculated optimal proportions of the depleted mantle and continental crust show excess crustal geochemical signatures. Hence, the material enriched in incompatible elements without distinct negative anomalies of Nb and Ta and positive anomalies of fluid-mobile components is required, in addition to the continental crust, to solve the problem of global geochemical reservoirs.



**Fig. 3.** (a) PM-normalized [4] contents of incompatible elements in different hypothetical reservoirs of the silicate Earth. (CC) continental crust [9]; (FMORB) early basaltic crust; (DM) depleted mantle [8], (EM) enriched peridotite mantle; (DM + CC + FMORB + EM) is a mixture of depleted mantle (68.58%), continental crust (1.05%), early basaltic crust (0.19%), and enriched peridotite mantle (30.18%). (b) Simulation of incompatible element contents in primitive mantle by estimate of optimal proportions in a mixture of different depleted and enriched materials. A criterion of minimization of squared deviations for calculated and initial contents was used. The values were normalized to primitive mantle [4]. (DM + CC) mixture of depleted mantle (97.9%) and continental crust (2.1%); (DM + CC + FMORB) mixture of depleted mantle (97.46%), continental crust (1.60%), and early basaltic crust (0.94%); (DM + CC + FMORB + EM) is a mixture of depleted mantle (68.58%), continental crust (1.05%), early basaltic crust (0.19%), and enriched peridotite mantle (30.18%).

### EARLY BASALTIC CRUST

Concepts of three-component composition of the silicate Earth (continental crust + depleted mantle + primitive mantle) are also not consistent with U and Th geochemistry. The Th/U ratio is practically the same in the primitive mantle (3.83) and the continental crust (3.85), and almost two times lower (2.1) in the depleted mantle (MORB source). At such Th/U ratios, the primitive mantle cannot be represented as a mixture of continental crust and depleted mantle. One more component with higher Th/U ratio as compared to that in the primitive mantle is required.

The oceanic crust, which formed at the earliest stages of the Earth's evolution, can be inferred as a possible enriched reservoir, in addition to the continental crust. The early basaltic crust enriched in incompatible elements was proposed to be at least temporarily isolated from the upper mantle to explain rapid changes in Nd and Hf isotope ratios in the depleted mantle. In the upper mantle depleted in Nd and Hf relative to Sm and Lu, the  $^{143}\text{Nd}/^{144}\text{Nd}$  and  $^{176}\text{Hf}/^{177}\text{Hf}$  ratios significantly increased during the first several million years of the Earth's history [14]. It was also proposed that the early basaltic crust might be a significant component of the lowermost lower mantle (below 1600 km), which could

Contents of incompatible elements (in ppm) in different hypothetical reservoirs of the silicate Earth

Element	PM	DM	CC	FMORB	EM
Rb	0.605	0.055	32	13.9	1.06
Ba	6.75	0.61	250	154	11.8
Th	0.083	0.008	3.5	1.9	0.11
W	0.016	0.002	1	0.29	0.021
U	0.022	0.004	0.91	0.4	0.027
Nb	0.6	0.19	11	10.7	1.06
K	260	49	9100	3492	364
La	0.686	0.29	16	8.6	1.03
Ce	1.785	0.96	33	22.4	2.2
Pb	0.185	0.039	8	2.3	0.25
Pr	0.27	0.17	3.9	3.2	0.3
Nd	1.327	0.93	16	9.4	1.8
Sr	20.3	16.05	260	217.6	24.4
Sm	0.431	0.35	3.5	5.3	0.5
Sn	0.138	0.113	2.5	1.8	0.17
Hf	0.3	0.23	3	3.8	0.37
Zr	10.8	8.14	100	89.5	13.2
Ti	1282	1168	5400	12225	1441
Eu	0.162	0.14	1.1	1.6	0.18
Gd	0.571	0.5	3.3	5.5	0.59
Tb	0.105	0.092	0.6	1.03	0.1
Dy	0.711	0.64	3.7	6.8	0.7
Ho	0.159	0.14	0.78	1.4	0.16
Y	4.37	4.06	20	43.1	4.4
Er	0.465	0.42	2.2	4.4	0.47
Tm	0.072	0.065	0.32	0.67	0.07
Yb	0.462	0.42	2.2	4.3	0.46
Lu	0.072	0.064	0.3	0.66	0.072

Note: (PM) primitive mantle [4]; (DM) depleted mantle [8]; (CC) continental crust [9]; (FMORB) early basaltic crust (this paper); (EM) enriched peridotite mantle (this paper).

be partially isolated from the overlaying convective system of the silicate Earth [15].

To estimate the composition of the early basaltic crust, the ancient magma generation was assumed to be similar to the magma generation in the modern mid-ocean ridges; however, the source of the magmas was primitive pyrolite material rather than the depleted mantle of present-day composition. Consistently with this assumption, the average contents of incompatible elements in the N-MORB were multiplied by the ratios of their contents in the primitive mantle [4] to those in the depleted upper mantle [8] (table, Fig. 3a).

Assuming similar formation conditions for the early and modern basaltic crust, we accepted that the temperature of the convective upper mantle was mainly defined by parameters of the transition of peridotite material from rigid to plastic state and practically did not vary with time. Significantly higher global heat flow in the first several million years after accretion owing to the significantly higher contents of heat-generating elements led to the lower average thickness of the lithosphere and significant increase of thermal convection. As a result, magma production was significantly more intense than in the present day. However, the thin lithosphere universally defined low partial

melting pressures, which were similar to those in the shallow magma-generating systems beneath modern mid-ocean ridges.

The least square estimate of the optimal proportions of depleted mantle, continental crust, and hypothetical early basaltic crust (FMORB) on the basis of incompatible elements yields 97.46, 1.60, and 0.94%, respectively. This three-component mixture is compared in Fig. 3b with generally accepted composition of primitive mantle. This model is somewhat better than the previous one; however, it still shows significant negative Nb and Ta anomalies, and positive, Pb and Sn. This indicates overestimated amount of the continental crust in the latter model and requires the involvement of an additional enriched geochemical reservoir.

### ENRICHED PERIDOTITE MANTLE

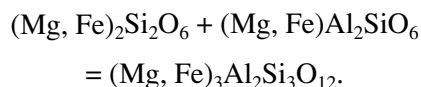
Estimates of EM sources of intraplate oceanic islands were used as an enriched geochemical reservoir [10]. Data on the chemical composition of lavas from Tristan da Cunha Island were taken for calculations.

Suggesting that the considered magmas were derived by the partial melting of mantle lherzolites, we calculated the parameters of this process taking into consideration that the contents of moderately incompatible elements, including HREE, in different early peridotites practically depend neither on the addition of a minor intergranular melt (mantle metasomatism) nor on the previous removal of such a melt (generation of depleted MORB-source mantle from primitive mantle). These contents of moderately incompatible elements are close to those in the primitive mantle and significantly differ from contents of strongly incompatible elements (LREE, U, Th, and others).

Assuming that HREE contents in the oceanic basalt source were similar to those in the primitive mantle prior to melting, we can subsequently calculate the parameters controlling the generation of primary magmas and the contents of strongly incompatible elements, including LREE, in the magma source. To solve this problem, we used the above calculation procedure suggesting the magma formation by the model of aggregate fractional melting.

Fractional melting caused by adiabatic decompression of the ascending mantle primarily depends on the initial mineral composition of source and the degree of melting at the end of the process. Depending on the depth of protolith solidus, the melting material initially contains certain amounts of garnet.

Garnet is generated from enstatite, diopside, and tschermakite components of pyroxenes by the following scheme:



The simulation of the phase composition of primitive pyrolite with a PARMEL program [8] shows that garnet-free two-pyroxene pyrolite under near-liquidus conditions (at pressure of about 2.6 GPa) can be represented as a mixture of respective 0.26, 0.14, and 0.6 weight fractions of clinopyroxene, orthopyroxene, and olivine, the amount of which decreases after garnet appearance (weight fraction  $F_{Grt}$ ) according to the following equations:

$$F_{Cpx} = 0.26 - 0.2F_{Grt},$$

$$F_{Opx} = 0.14 - 0.3333F_{Grt},$$

$$F_{Ol} = 0.6 - 0.4667F_{Grt},$$

which define the initial mineralogic composition of pyrolite prior to melting.

Discretization of continuous fractional melting was attained by segmentation of the total (aggregate) fraction of generated melt into small intervals (taken as 0.001 of total weight of the system).

Within each interval, the proportions of crystalline phases vary owing to different extent of resorption (or crystallization) during melting, as well as pressure decrease during adiabatic decompression decreasing mainly the garnet fraction. Modeling of pyrolite melting during adiabatic decompression at 2.8 GPa with a PARMEL program shows that the appearance of a unit weight of the melt decreases garnet and clinopyroxene contents by respective factors of 0.97 and 1.08 and increases olivine and orthopyroxene contents by respective factors of 0.63 and 0.42. These proportions taken as constant for the considered process were used to calculate the mineralogic composition of pyrolite at all stages of fractional melting. The mineral composition is required to estimate combined (bulk) distribution coefficients. Distribution coefficients for individual minerals were taken from [16–18].

For each interval of fractional melting which generates additional melt fraction,  $\Delta F^L$ , variations of trace element abundance in a crystalline residue were calculated from the following formula based on the mass balance for equilibrium partial melting:

$$C_n^S = \frac{C_{n-1}^S(1 - F_n^L + \Delta F^L)}{\Delta F^L/K + 1 - F_n^L},$$

where  $C_n^S$  is the content of trace element in the crystalline residue at the end of an interval of fractional melting,  $C_{n-1}^S$  is the content of trace element in a crystalline residue at the end of the previous interval of fractional melting,  $F_n^L$  is the weight fraction of the melt from the total weight of the system for the interval of fractional melting, and  $K$  is the combined (weighted average) distribution coefficient.

After completion of the entire cycle of fractional melting ( $F_n^L = F^L$ , where  $F^L$  is the melt fraction after completion of partial melting), the content ( $C^L$ ) of a trace element in an aggregate melt (mixtures of all melts produced during individual intervals with  $F_n^L$  increment equal to  $\Delta F^L$ ) was calculated from  $C^S$  using the following mass balance formula:

$$C^L = \frac{C^0 - C^S(1 - F^L)}{F^L},$$

where  $C^0$  is the element content in the source prior to the partial melting.

At given concentrations of trace elements in source and primary magma, deviations of the calculated  $C^L$  from the observed contents in magmatic rocks (with correction for olivine fractionation) were minimized by SIMPLEX algorithm [19] with variations of  $F^L$  and  $F^{Grt}$ , thus providing optimal estimates of these parameters.

The estimated  $F^L$  and  $F^{Grt}$  were then used together with distribution coefficients to estimate the contents of strongly incompatible elements in an aggregate melt, assuming that their contents in the source were identical to those in pyrolite. Deviations of thus calculated contents from those observed in primary magma (in magmatic rocks with correction for olivine fractionation) could be explained by differences between real source and model pyrolite. Therefore, the contents of these elements in the initial protolith were calculated from the formula  $C^{PR} = C^{pyr}C^{obs}/C^{calc}$ , where  $C^{PR}$  is the element content in protolith,  $C^{pyr}$  is its content in pyrolite,  $C^{obs}$  is the observed element content in the magmatic rock (with correction for olivine fractionation), and  $C^{calc}$  is the calculated element content in the aggregate melt assuming pyrolite composition of the source.

Calculations of the peridotite source for volcanic rocks from Tristan da Cunha Island using the described procedure yield a composition significantly enriched in strongly incompatible elements as compared to primitive pyrolite:  $(La)_N = 1.5$  (table and Fig. 3a). Least-square calculations showed that the primitive mantle can be represented as a mixture of 1.05% continental crust, 0.19% early basaltic crust, 68.58% depleted mantle, and 30.18% model enriched mantle.

The comparison of the calculated mixtures with modeled composition of the primitive mantle (Fig. 3b) shows that the addition of enriched mantle as a hypothetical reservoir, accompanied by a decrease in amount of the continental crust and hypothetical early basaltic crust, significantly improved the model: the Nb and Pb anomalies almost disappeared, while the positive Sn anomaly somewhat decreased.

The mass balance calculations for the chondritic model of the primitive mantle raise two questions: (1) which are the proportions of the proposed compo-

nents, in addition to primitive pyrolite, in the lower mantle and (2) which mechanism is responsible for the generation of enriched mantle?

Assuming that the material of the continental crust in the silicate Earth accounts for 0.65%, i.e., is equal to the fraction of the continental crust, the lower mantle should consist of 50.99% primitive mantle, 23.14% depleted mantle, and 24.85% enriched mantle. In this hypothetical case, the continental crust is absent in the lower mantle, while the proportion of primitive material is the highest. Early basaltic crust is estimated to account for only 0.15%.

On the other hand, assuming that the lower mantle does not contain primitive pyrolite, it should consist of 58.70% depleted mantle, 40.64% enriched mantle, 0.41% continental crust, and 0.25% hypothetical early basaltic crust. In this case, the contribution of continental crust to the lower mantle composition is the highest.

Actually, the lower mantle composition can be intermediate between the considered extreme cases. Thus, according to our estimate, the lower mantle consists of 0–51% primitive mantle, 23–59% depleted mantle, 25–41% enriched mantle, 0–0.4% continental crust, and 0.15–0.25% early basaltic crust. As mentioned above, these components are not universally present in pure state in the lower mantle. Real lower-mantle rocks presumably present mixtures of different materials. As estimated by Allegre from isotope data, the lower mantle contains  $20 \pm 10\%$  depleted mantle, [20]. It is seen that our lower limit for this value coincides with the upper limit estimated by Allegre.

According to the data in [21], which were obtained based on Ar isotopic evidence, the contribution of continental material to the lower mantle does not exceed 0.24%, a value that also lies within our estimated range of the possible percentage of continental crustal material in the lower mantle (0–0.4%).

Several hypotheses have been advanced to explain the origin of the material enriched in incompatible elements, which is traced in the isotope signatures of the magmas of some intraplate ocean islands. A very popular viewpoint is that the geochemical features of these magmas are caused by subsidence of continental material enriched in incompatible elements, probably in the form of abyssal sediments subducted together with oceanic plates, into the deep-seated mantle horizons. For some volcanic complexes, this hypothesis is confirmed by the correlation between continental signatures, for example, between the size of Nb mining and the  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio [22]. The mass balance calculations presented in this work are consistent with the possible contribution of a few tenths of a percent of continental material in the lower mantle processes. However, the predominant part of the enriched mantle bears no signatures of continental material, and presumably originated owing to differentiation of the mantle itself.

A very attractive idea is that the enriched material is transported into deep-seated zones owing to break-off (delamination) of subcontinental lithospheric blocks, which were influenced by the low-degree melts enriched in incompatible elements, i.e., silicate or carbonate melts penetrated into the lithosphere from the underlying convective mantle [23]. Accumulation of Re–Os isotope data cast some doubts on this hypothesis, since the residual material that predominates in the lithosphere has very low Re/Os ratios, which resulted in time-integrated low radiogenic  $^{187}\text{Os}/^{188}\text{Os}$  ratio. At the same time, ocean-island magmas bearing Sr and Nd isotope signatures of enriched mantle typically show no anomalously low  $^{187}\text{Os}/^{188}\text{Os}$ . We suggest that this fact is not decisive. Actually, the subsidence of lithospheric blocks in the lower mantle can significantly affect their Os isotope characteristics owing to the percolation of sulfide melts. This explanation can be substantiated by the fact that temperatures in the upper mantle are higher than cotectic temperatures in the Fe–Ni–S system, i.e. sulfide melts can be universally present in the interstices between crystalline silicates and oxides. New geochemical data indicate that the infiltration of sulfide melts in the mantle rocks can significantly affect Os isotope composition [24].

The considered model of the mass balance of enriched and depleted reservoirs in the primitive mantle cannot be taken as final. The crystallization products of the global magmatic ocean, including predominant magnesian silicate perovskite with subordinate calcium silicate perovskite and ferripericlasite have to be added to the enriched components [25]. Such a mineral assemblage can be significantly enriched in incompatible elements owing to their high distribution coefficients for calcium silicate perovskite. The presence of such a material in the lowermost third part of the lower mantle, which is supposedly isolated from the global convective system of the silicate Earth, was inferred from data on the planetary heat flow [15].

## CONCLUSIONS

(1) Mass balance calculations of incompatible elements for different possible reservoirs of the bulk silicate Earth show that the lower mantle, in addition to primitive mantle material, contains a depleted MORB-source mantle component and domains enriched in incompatible elements.

(2) Only an insignificant part of the enriched material in the lower mantle can be represented by the continental crustal component. The predominant part of the enriched mantle resulted from differentiation of the mantle itself.

(3) The enriched material was presumably supplied into the deep-seated zones of the silicate shell owing to delamination of subcontinental lithospheric blocks affected by mantle metasomatism and their subsequent involvement in mantle convective system.

(4) Variations of Os isotope composition in the subsided lithospheric material are caused by the infiltration of sulfide melts.

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