

Relationships between the Chemical and Isotopic (Sr, Nd, Hf, and Pb) Heterogeneity of the Mantle

Yu. A. Kostitsyn

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

e-mail: kostitsyn@geokhi.ru

Received June 5, 2006

Abstract—The reasons for the isotopic heterogeneity of the mantle are analyzed in this paper on the basis of published isotopic data. It was shown that the observed variations in the Sr, Nd, Hf, and Pb isotopic compositions of oceanic basalts cannot be explained by mixing of a finite number of homogeneous reservoirs (components). The considerable variations in the contents of Rb, Sr, Sm, Nd, Lu, Hf, U, Th, and Pb and ratios of these and other trace elements in tholeiitic basalts indicate that the chemical heterogeneity of mantle-derived rocks is inherited in part from their sources. Oceanic tholeiitic basalts show a tight correlation between the variances of Nd, Hf, Sr, and Pb isotopic ratios and the variances of respective radiogenic additions that could be accumulated in these rocks over a time period of $\langle t \rangle = 1.8$ Gyr. This paradox clearly indicates that variations in all the mentioned isotopic systems in the mantle cannot be understood without the analysis of the geochemical heterogeneity of rocks.

The close to lognormal distributions of lithophile trace elements in oceanic tholeiitic basalts and the character of correlations between them suggest that magmatic differentiation was the major mechanism of the formation of chemical heterogeneity in the mantle. The role of metasomatism in the global transport of trace elements and formation of the geochemically heterogeneous mantle is probably rather limited. Intrusive processes within the mantle could result in the development of chemical and, after a period of time, isotopic anomalies in the mantle. Simple calculations show that long-lived geochemical anomalies related to alkaline magmatism could be responsible for EM-I type isotopic anomalies, and geochemical anomalies produced in the mantle by enriched tholeiitic melts could be sources of EM-II type isotopic anomalies. The analysis of the distribution of the isotopic compositions of mantle-derived igneous rocks in various “isochron” coordinates suggested that the formation of geochemical anomalies in the mantle is a long-term process lasting for hundreds of millions of years. Nonetheless, trends approaching 4.5 Ga were never observed in such diagrams, i.e., the mantle is in general rejuvenated in all isotopic systems. Both on global and local scales, there are no mantle domains that have remained geochemically closed and isolated since the Earth’s formation. The entire mantle is involved in material exchange processes.

The development of isotopic systems in the mantle was explored by means of statistical modeling accounting for the tendency of a continuous increase in the chemical heterogeneity of the mantle source and the tendency of obliteration of the isotopic heterogeneity owing to the convective mixing in the mantle. The modeling demonstrated that the character of the isotopic heterogeneity of the mantle is statistically consistent with the character of its chemical heterogeneity. The mantle isotopic anomalies HIMU, EM-I, and EM-II were generated by two simultaneous processes: the magmatic differentiation of mantle material and its not very efficient mixing.

DOI: 10.1134/S0016702907120014

INTRODUCTION

Several decades of isotopic investigations of various mantle-derived rocks have resulted in a clear understanding that the mantle is heterogeneous with respect to the isotopic compositions of strontium, neodymium, hafnium, lead, and other elements whose isotopic ratios change owing to radioactive decay. The determination of the reasons for and mechanisms of formation of this heterogeneity is one of the most intriguing problems of geochemistry, because it is closely related to our knowledge on the geodynamics of the mantle as a whole and its interaction with other geospheres, the Earth’s crust, and core.

According to the most popular current concept of the isotope geochemical evolution of the Earth’s mantle, the depleted mantle (DM) is a residue after the extraction of the continental crust from the primitive mantle [1–3], and various enriched mantle reservoirs, components, or anomalies (EM-I, EM-II, HIMU, and DUPAL) were produced by crustal recycling. During the past three decades, there appeared dozens of studies directly addressing the global modeling of this scheme in various isotope systems (Sm–Nd, Rb–Sr, U–Th–Pb–He, and Lu–Hf) and many hundreds of publications that used this model as a basis for particular petrogenetic reconstructions.

There have been many attempts to construct a balanced model describing the observed isotopic heterogeneity of the mantle [4–11]. All these studies developed, in one way or another, the reservoir model, which considers the crust–mantle system as consisting of a finite number of homogeneous reservoirs, such as the lower mantle (primitive mantle), the upper mantle (depleted mantle), the oceanic crust, and the continental crust, which is further subdivided in some models into the lower and upper continental crust. In addition, subduction zones [7, 8] and the lower part of the lower mantle (D'' layer) [12] may be considered as independent reservoirs. By definition, each reservoir is considered in such models as chemically and isotopically homogeneous, and the observed heterogeneity of mantle-derived igneous rocks is attributed to the mixing of materials from various reservoirs, primarily, to the input of the materials of the Earth's crust into the upper mantle. In the recent years, some studies considered the mantle as a statistical assemblage of depleted material with various enriched components [13, 14], but these authors supposed that the isotopically enriched material is delivered to the mantle primarily by the subduction of continental crustal material.

Subduction is one of the most conspicuous manifestations of the convective mixing of mantle materials. Obviously, this is why most of the aforementioned geochemical models invoked subduction to explain the formation of various geochemical anomalies in the mantle. Not denying the possibility of mixing materials from various sources, including in subduction zones, I believe that the intrinsic chemical heterogeneity of the mantle is an obvious factor of the generation and development of its isotopic heterogeneity. In order to evaluate this factor, the following questions will be addressed considering suboceanic mantle as a source of oceanic basalts.

(1) To what extent may the sources of mid-ocean ridge basalts (MORB) and intraplate oceanic basalts (OIB) be chemically heterogeneous, primarily with respect to the Rb/Sr, Sm/Nd, Lu/Hf, and U/Pb ratios?

(2) Which is the character of this heterogeneity, and is it possible to determine the mechanism of its generation?

(3) To what extent can the chemical heterogeneity of these mantle sources be responsible for their isotopic heterogeneity?

To answer these questions, we will analyze the available published isotopic and geochemical data, consider the results of the statistical simulation of a gradual transformation from an initially homogeneous mantle to a chemically heterogeneous reservoir, and discuss the isotopic consequences of such a process. Before considering these problems, we will briefly review current geochemical concepts on the structure of the mantle and reasons for its isotopic heterogeneity. It is worth noting that these concepts were developed during a prolonged period of the meticulous accumula-

tion of isotopic data, initially under conditions of their strong deficiency. It cannot be excluded that, had these data been acquired within a shorter time period, the modern geochemical paradigm might have been different.

CURRENT CONCEPTS ON THE REASONS FOR THE ISOTOPIC HETEROGENEITY OF THE MANTLE

The development of modern ideas on the isotopic geochemistry of the mantle and the existence of geochemically different mantle components began from the pioneering studies of DePaolo and Wasserburg [1, 17], who reported the first data on the neodymium isotopic composition of mantle-derived rocks and revealed a negative relationship between the $^{87}\text{Sr}/^{86}\text{Sr}$ and $^{143}\text{Nd}/^{144}\text{Nd}$ isotope ratios. During the following years, the amount of available isotopic data¹ has increased by several orders of magnitude (Fig. 1), and the initial seemingly rigorous relationship transformed to a weaker correlation; nonetheless, the general approach to its interpretation has not changed: it is assumed that the isotopic heterogeneity of the mantle is controlled by the mixing of different more or less homogeneous components [1–3, 9, 10, 18, etc.]. There is a general consensus among most geochemists on the origin of the DM and EM components (Fig. 1). The former is considered as a source depleted by the extraction of the crust, and the latter is the same source contaminated by crustal materials as a result of subduction. The origin of the EM-I component with low strontium isotope ratios is attributed to mantle contamination with lower crustal materials, whereas the higher strontium isotope ratios in the EM-II component are related to the contribution of the upper crust containing sedimentary materials [2].

When the lead isotope system was involved into the consideration (Fig. 2), a new component, HIMU, was discovered. It is manifested in basalts with high $^{207}\text{Pb}/^{204}\text{Pb}$ and $^{206}\text{Pb}/^{204}\text{Pb}$ values, which indicate a high U/Pb ratio in the source. In U–Pb isotope geochemistry, the $^{238}\text{U}/^{204}\text{Pb}$ ratio is traditionally designated as μ , which explains the name of the HIMU component. In the $^{207}\text{Pb}/^{204}\text{Pb}$ – $^{206}\text{Pb}/^{204}\text{Pb}$ diagram (Fig. 2), mantle-derived rocks form a linear array, which is usually attributed to the mixing of the DM and HIMU components (in contrast to Fig. 1, two-component mixing in these coordinates is described by a straight line). It was supposed [3, 19, 20] that the HIMU component was formed owing to the subduction of oceanic crust, and most of the lead present in the descending blocks was removed by island-arc magmas into the continental crust, which resulted in the formation of local areas with high U/Pb ratios in the mantle.

¹ All the neodymium isotope ratios reported in this paper are renormalized to $^{146}\text{Nd}/^{144}\text{Nd} = 0.7219$.

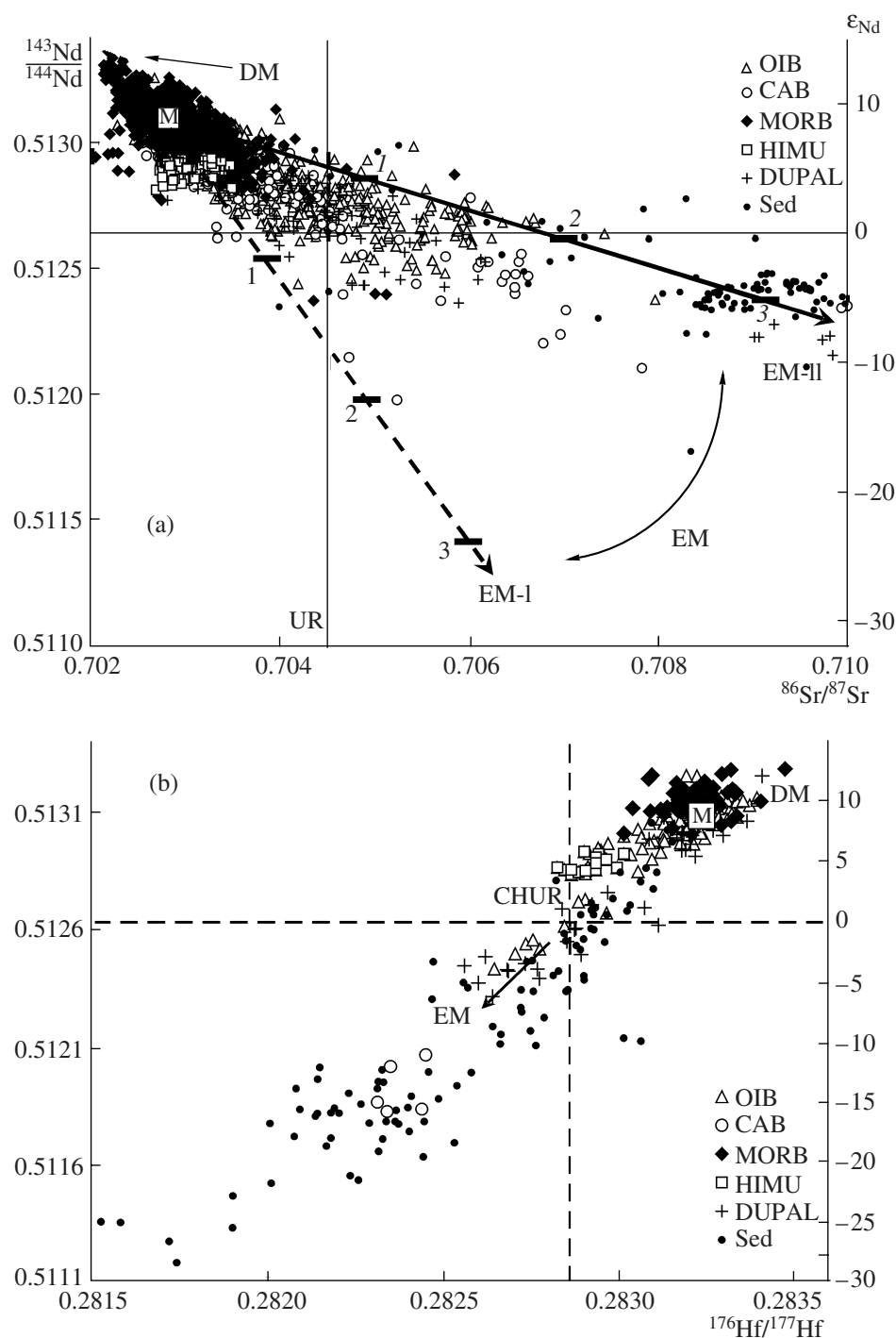


Fig. 1. Relationships between the isotopic compositions of neodymium, strontium, and hafnium in mid-ocean ridge basalts (MORB), oceanic intraplate basalts (OIB), HIMU basalts, basalts of the Indian Ocean and the South Atlantic belonging to the DUPAL anomaly [15], continental alkali basalts (CAB), and detrital silicate sediments (Sed). The sources of the isotopic data are given in [16].

Both diagrams (Figs. 1, 2) reveal another anomalous group of rocks represented by the mid-ocean ridge basalts from the South Atlantic and the Indian Ocean. They show elevated $^{87}\text{Sr}/^{86}\text{Sr}$ and $^{207}\text{Pb}/^{204}\text{Pb}$ values compared with other nonanomalous MORB. The

source of this rock group was termed the DUPAL anomaly by Hart [21] in honor of its discoverers Dupre and Allegre [22]. Its origin is explained by the multi-component mixing of DM, HIMU, EM-I, and EM-II materials [15].

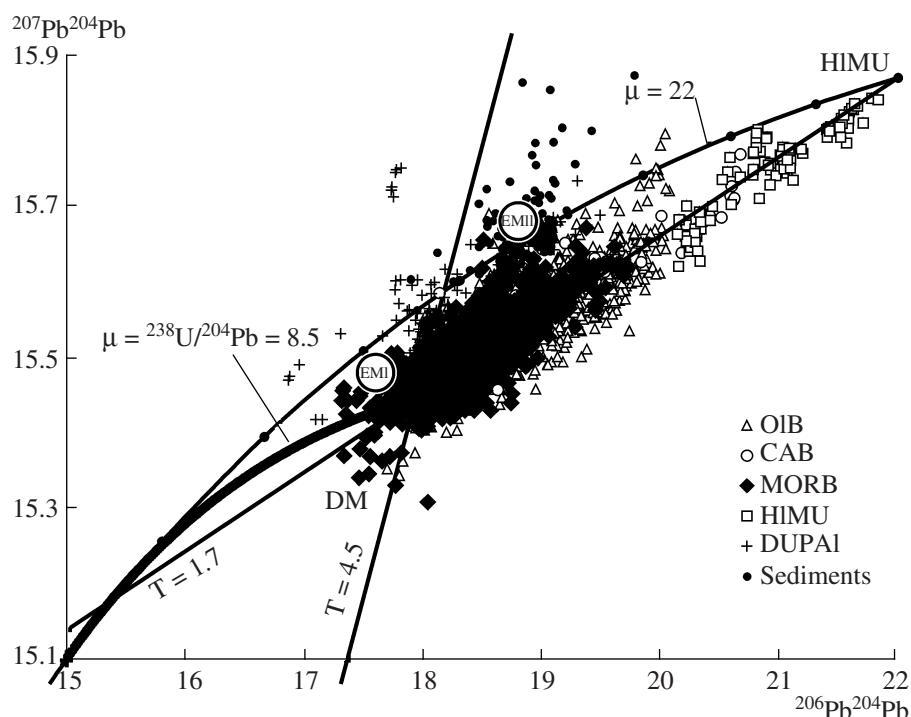


Fig. 2. Lead isotope compositions of the same groups of rocks that are shown in Fig. 1. The slope of the general trend for mantle rocks corresponds to about 1.7 Ga. The HIMU basalts are distinguished from the total set of OIB by the arbitrary boundary $^{238}\text{U}/^{204}\text{Pb} > 20$. Also shown are the compositions of the enriched suboceanic mantle of the EM-I and EM-II types estimated by Hart [15].

CONTRADICTIONS IN THE MODEL OF CRUSTAL RECYCLING

We briefly outlined above an elegant geochemical model explaining the isotopic heterogeneity of the mantle by mixing with crustal materials. In this section, we will analyze the contradictions of this model, which are sufficiently serious to claim that it is at least not universal if not inconsistent.

HIMU Component

It is believed that mantle sources of this type owe their existence to the subduction of oceanic crust. The U/Pb ratio of descending blocks increases at the expense of the preferential lead transportation into the continental crust with island-arc magmas [3, 19, 20, 23]. Such a behavior of lead is supported by the systematic difference in the Pb/Ce ratio between the basalts of mid-ocean ridges and island arcs. In the opinion of the authors cited above, the elevated Pb/Ce values in island-arc basalts compared with MORB indicate a lead loss from the descending slab, which resulted in a local increase in the U/Pb ratio in the mantle.

In order to check this hypothesis, let us consider Fig. 3. The data on island-arc basalts were taken from [23–30]. The list of other publications used in Fig. 3 can be found in [16]. As can be seen in Fig. 3a, the Ce/Pb ratio of island-arc basalts is systematically different from

those of MORB and OIB (by a factor of 6 on average), which may indicate a preferable influx of lead into island-arc melts compared with cerium. However, does this mean that the U/Pb ratio changes in the same fashion?

As can be seen in Fig. 3b, the island-arc basalts cluster along a line corresponding to $\mu = ^{238}\text{U}/^{204}\text{Pb} = 8$, i.e., the U/Pb value of island-arc basalts is in general similar to the average estimates for the mantle [11, 31]. This fact alone is sufficient to refute the possibility of lead-uranium fractionation during the formation of island-arc magmas and, correspondingly, the formation in such a way of high U/Pb ratios in the descending blocks of oceanic crust. A comparison of Figs. 3a and 3b suggests that the enrichment of island-arc magmas in lead relative to cerium is accompanied by their equivalent enrichment in uranium, while the U/Pb ratio remains essentially constant. Similar U/Pb values were observed in the normal (i.e., not enriched in lithophile elements, including uranium and lead) varieties of mid-ocean ridge basalts (N-MORB), which compose the major portion of the second layer of the oceanic crust. It is obvious that the removal of any amount of melts with $\mu \approx 8$ from a protolith with $\mu \approx 8$ will leave a residue with $\mu \approx 8$. This trivial statement demonstrates the inconsistency of the model of the formation of the source of HIMU basalts by the subduction of oceanic crust.

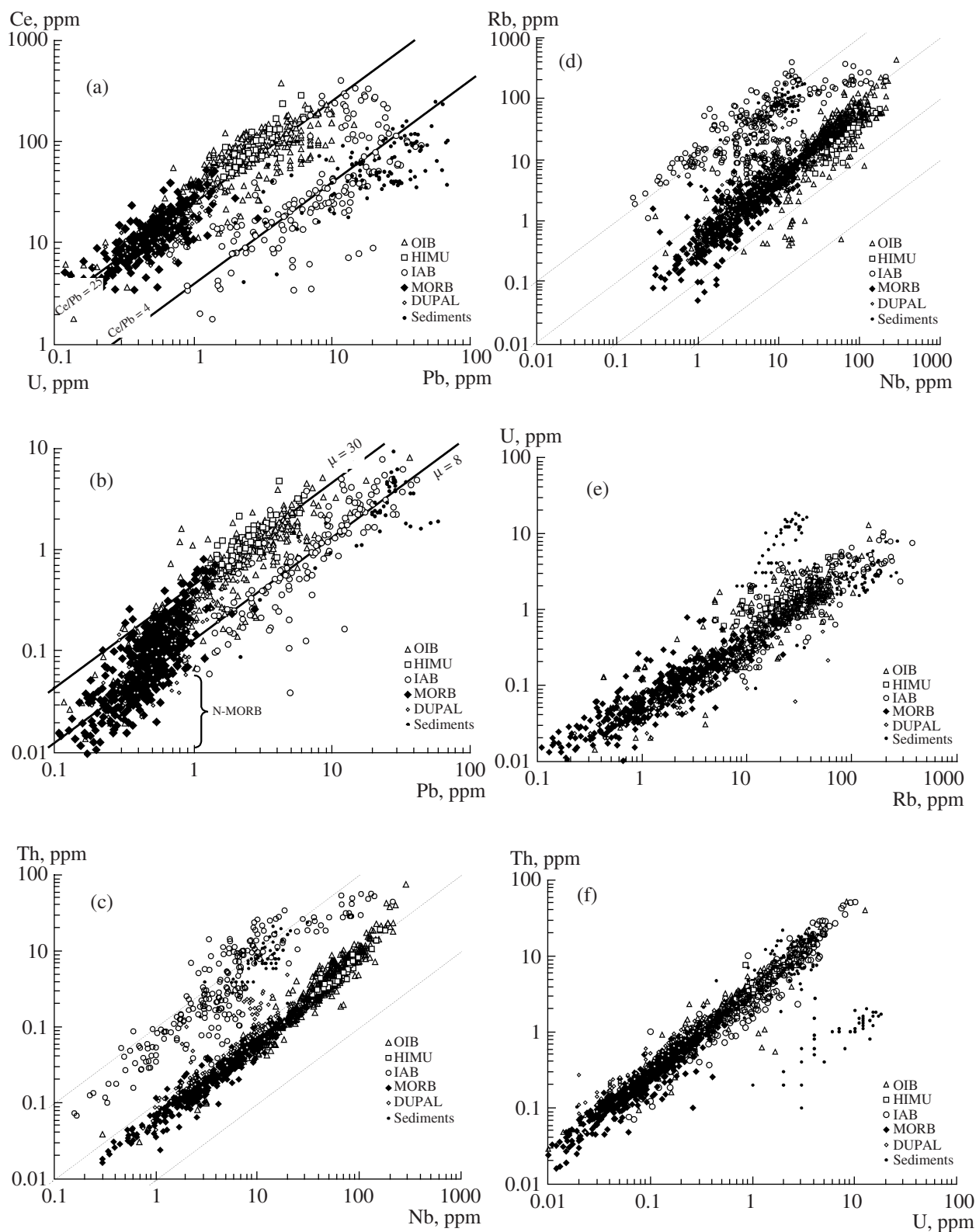


Fig. 3. Covariations of the contents of (a) Ce and Pb and (b) U and Pb in mid-ocean ridge basalts (MORB), intraplate oceanic basalts (OIB), HIMU basalts, island-arc basalts (IAB), and detrital silicate sediments. The island-arc basalts are significantly different from MORB in terms of (a) Ce/Pb, but (b) the U/Pb ratios of N-MORB and island-arc basalts do not differ significantly and are similar to the average estimate for the mantle composition ($\mu \approx 8$).

It is remarkable that the HIMU basalts show high uranium and lead contents and significantly elevated U/Pb ratios (Fig. 3b); their μ value is up to several tens. Thus, the enriched composition of these basalts is consistent with the enriched character of their source (Fig. 2). This is a very important observation, and it will be further discussed below in the constructive part of the paper.

EM-I and EM-II Components

The formation of enriched mantle sources, EM-I and EM-II, through the crustal contamination of the mantle material is nowadays a widespread and almost universally accepted assumption in geochemistry. The most convincing argument for this model is the negative correlation between the isotopic ratios of neodymium and strontium (Fig. 1a). The negative trend of mantle-derived rocks is continued by various crustal complexes, including granitoids and sedimentary rocks.

However, such a simple interpretation of Fig. 1a is in conflict with the fact that the supposed end-members (DM and crust) are not revealed in other isotopic coordinates. In particular, linear arrays must be observed for mixed systems in the $^{143}\text{Nd}/^{144}\text{Nd}$ –Sm/Nd coordinates (Fig. 4a), i.e., basic rocks, primarily tholeiitic basalts formed from the material of the depleted mantle and contaminated by crustal materials must in general be confined to the dashed line (Fig. 4a) connecting the estimated average compositions of the crust and the upper mantle [9] and passing through the CHUR point [16]. The fact that the compositions of tholeiites may correspond to the composition of their source in such coordinates will be shown in the next section. It is clearly seen that the real isotope data for mantle-derived igneous rocks do not form such linear trends and plot far from the model mixing line. This observation severely limits the petrogenetic significance of crustal recycling. Possible exceptions are some basalts from the Indian Ocean and the South Atlantic pertaining to the DUPAL anomaly [15].

TO WHAT EXTENT IS THE UPPER MANTLE CHEMICALLY HOMOGENEOUS?

This question is very important for isotope geochemistry on the whole, because, in principle, the appearance in the past of long-lived geochemical heterogeneities in the distribution of the Rb/Sr, Sm/Nd, U/Pb, Th/Pb, and Lu/Hf ratios is sufficient for the formation of Sr, Nd, Pb, and Hf isotopic heterogeneities in the mantle. The chemical heterogeneity of mantle-derived igneous rocks is evident in Figs. 3–6 and 10. However, do these rocks reflect the heterogeneity of their mantle sources? The composition of melt depends on the degree of melting of source rocks, and the ultimate composition of volcanics depends on the degree of melt differentiation during fractional crystallization.

Let us consider if these processes can account for the observed trace element variations in mid-ocean ridge basalts.

As can be seen in Fig. 5, the mid-ocean ridge basalts with MgO contents typical of tholeiites (about 8 wt %) are very heterogeneous with respect to the contents of uranium (two orders of magnitude) and rubidium (2.5 orders of magnitude). This observation indicates that the fractional crystallization of parental melts is not one of the major processes responsible for the formation of the chemical heterogeneity with respect to these trace elements. Indeed, the extensive fractionation of olivine and clinopyroxene from basic melts would have inevitably resulted in considerable variations in MgO correlated with trace components. Figure 5 shows the compositions of island-arc and intraplate oceanic basalts, many of which could be explained by the influence of fractional crystallization; however, about two-thirds of 1500 MORB points fall within a narrow range between 7 and 9 wt % MgO (shown by dashed lines), which corresponds to the standard composition of these rocks. It is evident that the heterogeneity of this sample set with respect to rubidium and uranium is not related to the fractional crystallization of parental melts.

Similar reasoning leads us to the conclusion that variable degrees of partial melting of a chemically homogeneous peridotite could not be responsible for the variations in trace element contents observed in Figs. 3, 5, and 6: this would require 2–3 orders of magnitude variations in the degree of melting [32, 33] for rocks with very similar petrochemical properties.

We are forced to conclude that the chemical heterogeneity of MORB (Figs. 3, 5, 6) is inherited to a large extent from their source. It is noteworthy that lherzolites show the same degree of trace-element heterogeneity coupled with rather small variations in MgO (Fig. 5).

The formation of such heterogeneities could be due to magmatic activity and metamorphic or metasomatic reactions in the mantle not only in the zone of depletion but also in magma conduits, where ultramafic rocks could be contaminated by the enriched melts; in magma chambers, where extensive melt differentiation could occur; and, finally, at the expense of formation of intrusive bodies in the mantle. It is obvious that the deep-seated melt may not be always fully extracted from the mantle, leaving no trace. This is physically impossible. Consequently, magmatic processes may result in the formation of mantle domains both depleted and enriched in lithophile elements.

Another mechanism for the formation of geochemically enriched zones in the mantle is the subduction of oceanic crust, primarily the eclogitized rocks of its second layer [34]. However, with respect to geochemical consequences, this mechanism is in essence closer to two-component mixing, which, as can be seen in Fig. 6, is not in agreement with the character of the chemical heterogeneity of MORB.

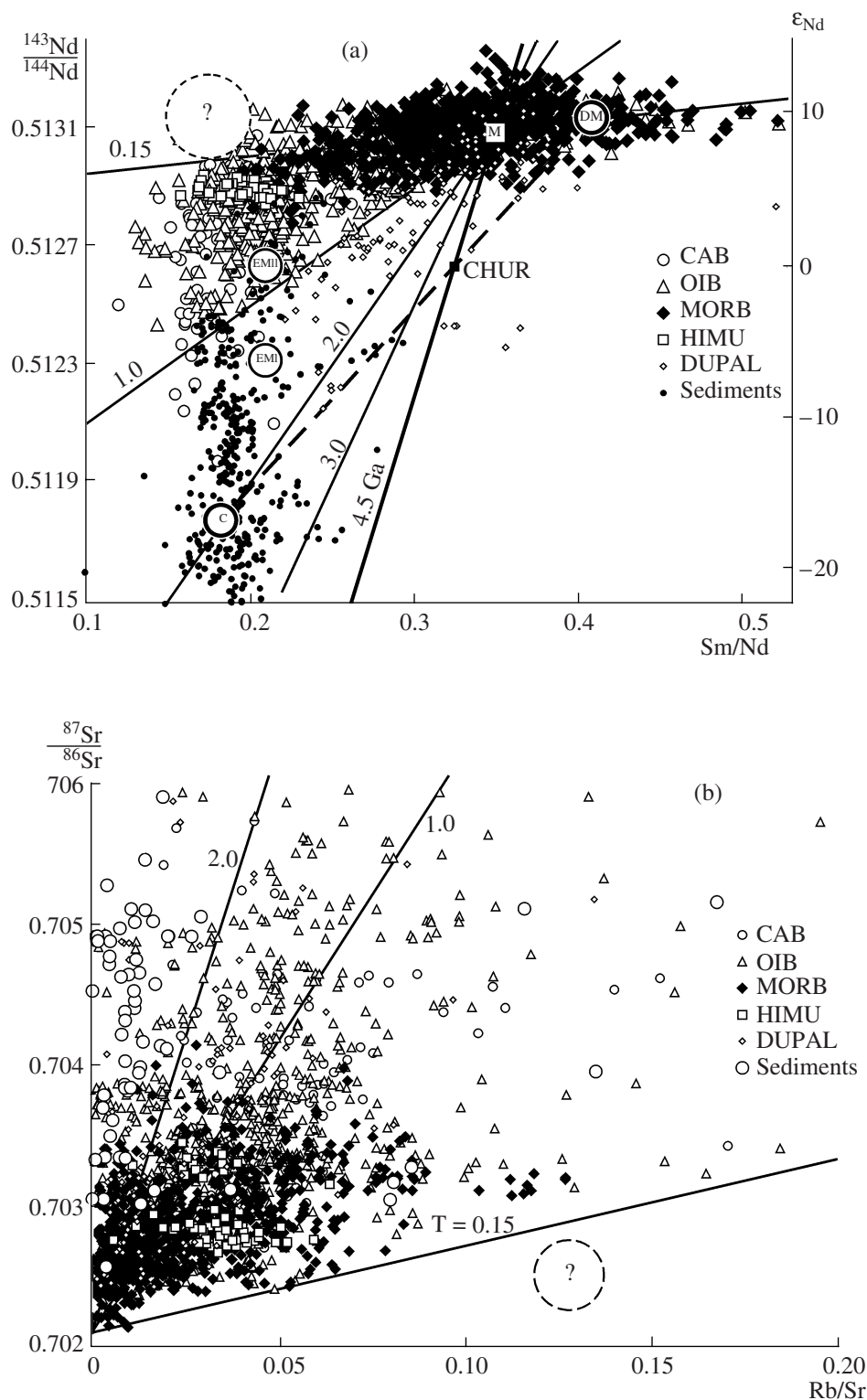


Fig. 4. Relationships between (a) neodymium isotope composition and Sm/Nd and (b) strontium isotope composition and Rb/Sr for mid-ocean ridge basalts (MORB), intraplate oceanic basalts (OIB), HIMU basalts, DUPAL basalts from the Indian Ocean and the South Atlantic [21], and continental alkali basalts (CAB). Also the upper diagram shows the 4.5 Ga geochron passing through the CHUR point. The geochron also comprises the supposed composition of the primitive mantle (point M) [16]. The dashed line connects the model compositions of the continental crust (C) and the depleted mantle (DM) [9]. Also shown are the compositions of the enriched suboceanic mantle of the EM-I and EM-II types estimated by Hart [15]. The lines of model ages of 0.15, 1.0, 2.0, and 3.0 Ga (corresponding to T_{DM}) are shown in both diagrams.

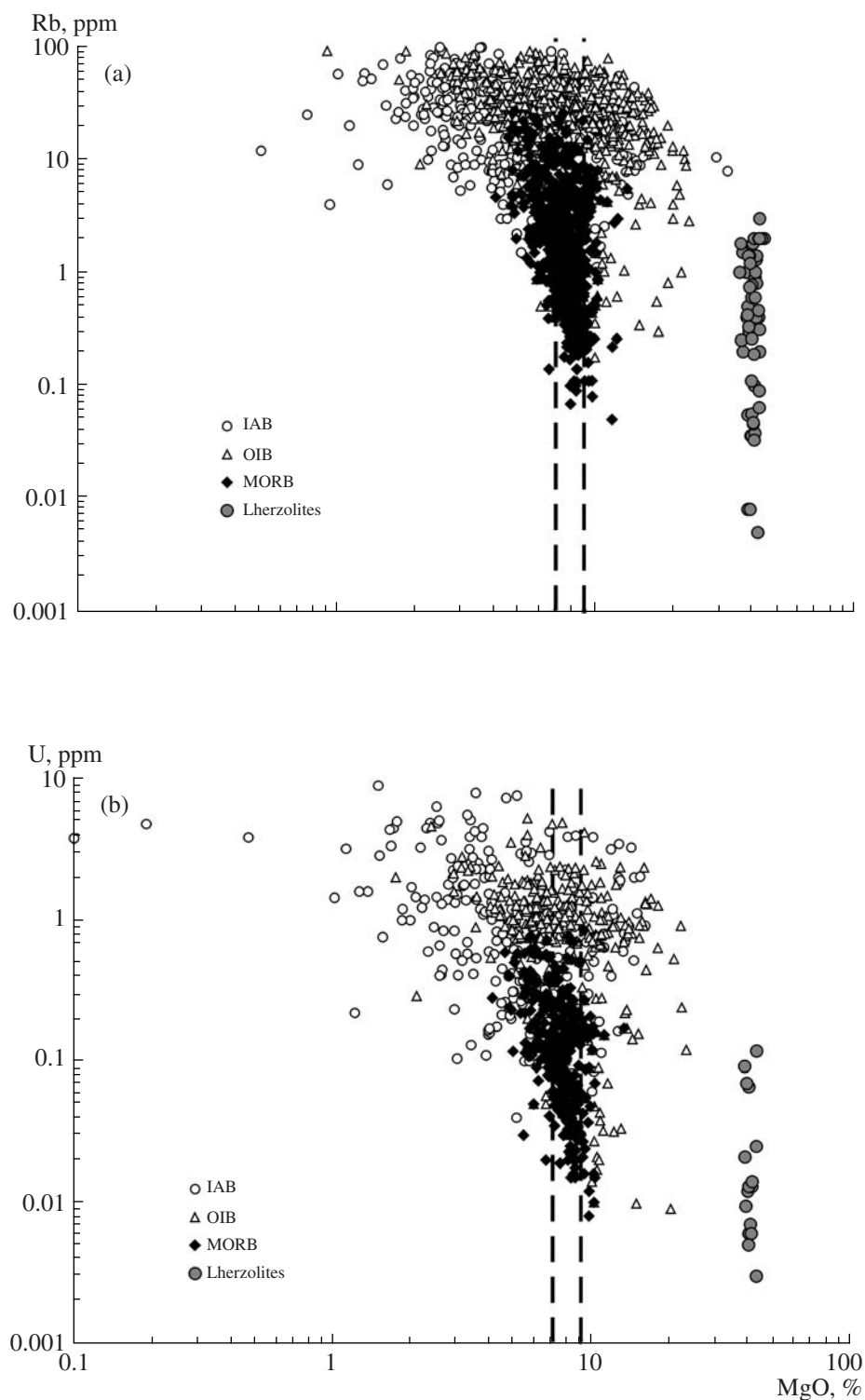
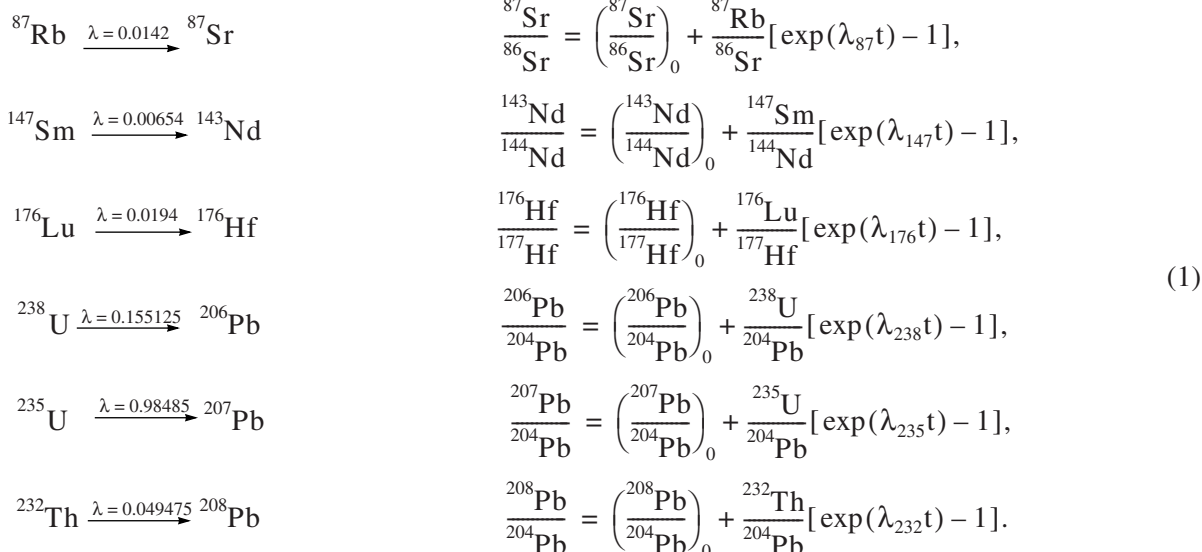


Fig. 5. Variations in the concentrations of rubidium, uranium, and magnesium in oceanic basalts and lherzolites. The tholeiites of mid-ocean ridges with ordinary contents of MgO (7–9 wt %) display considerable variations in trace element contents: two orders of magnitude for uranium and even more for rubidium. Similarly high variations in the contents of trace elements are observed in the lherzolites.

VARIANCES OF ISOTOPE AND ELEMENT RATIOS

Let us try to evaluate if there are reasons to believe that the geochemical heterogeneity of mantle rocks is connected with its isotopic heterogeneity for all the sys-

tems considered here. The following isotope pairs linked by radioactive decay and corresponding equations describing variations in isotope ratios in the mantle will be considered:



(1)

The decay constants (λ) in the left column are given in Gyr^{-1} . All these equations can be written in the general form as

$$\alpha_i = \alpha_0^i + \mu^i[\exp(\lambda^i t) - 1]. \quad (1a)$$

The variance of each isotope ratio at the present moment is the sum of the variance of the initial isotope ratio and the variance of the radiogenic addition:

$$\text{Var}(\alpha_i) = \text{Var}(\alpha_0^i) + \text{Var}(\mu^i[\exp(\lambda^i \langle t \rangle) - 1]). \quad (2)$$

Strictly speaking, this equation is valid for the Gaussian distribution of α and μ , which is not the case, especially for μ (Fig. 8); however, this is not important for our qualitative estimates. In Eq. (2), the unknown variable t was replaced by its average estimate, $\langle t \rangle$, which can be regarded as an average age for all the mantle processes that affected the present-day isotopic variations, i.e., those the memory of which is recorded in isotopic data.

If the variations in all the isotopic systems in the mantle are controlled by radiogenic additions, i.e., the geochemical heterogeneity of the mantle, a correlation must be observed between the variances $\text{Var}(\alpha^i)$ and $\text{Var}(\mu^i[\exp(\lambda^i \langle t \rangle) - 1])$, and the stricter this control is, the stronger is the correlation. The influx of isotopically anomalous material into the mantle, for instance, in subduction zones, increases the contribution of $\text{Var}(\alpha_0^i)$ in Eq. (2) and, consequently, must disturb the correlation between $\text{Var}(\alpha^i)$ and $\text{Var}(\mu^i[\exp(\lambda^i \langle t \rangle) - 1])$.

We cannot perform a direct representative statistical estimate of μ^i in the mantle source rocks of oceanic basalts. However, at high degrees of melting typical of tholeiitic basalts melts are produced with incompatible element ratios very similar to those of the source rock. According to the available experimental data [35], the Sm/Nd ratio of basaltic melt derived by 10–20% partial melting of peridotite ($Ol_{60}Opx_{25}Cpx_{12}Gar_3$) differs from that of the peridotite by only 8–14%, which is comparable with the determination error of many ordinary analyses. Therefore, the available data on the composition of tholeiitic basalts can be used for the approximate estimation of μ^i in their source.

Figure 7 shows the correlation between the standard deviations of α^i and μ^i for all the isotopic ratios in oceanic tholeiites. Standard deviations are used in Fig. 7 instead of variances in order to eliminate the quadratic metric, but this change does not affect the essence and, more importantly, the quality of the dependence. Taking into account that this diagram comprises data for different isotope system, the observed rigorous correlation (correlation coefficient of 0.9997) is amazing. The diagram was constructed for the optimum value $\langle t \rangle = 1.8$ Ga, but within the range from 0.9 to 2.2 Ga, the correlation coefficient does not decrease below 0.999, i.e., the observed correlation is stable with respect to assumptions concerning $\langle t \rangle$. The optimum $\langle t \rangle$ value cannot be connected with a particular geologic event, and it is controlled by the dynamics of mantle mixing and the rate of obliterating the isotopic geochemical heterogeneity. The numerical value of $\langle t \rangle$ is similar to the age

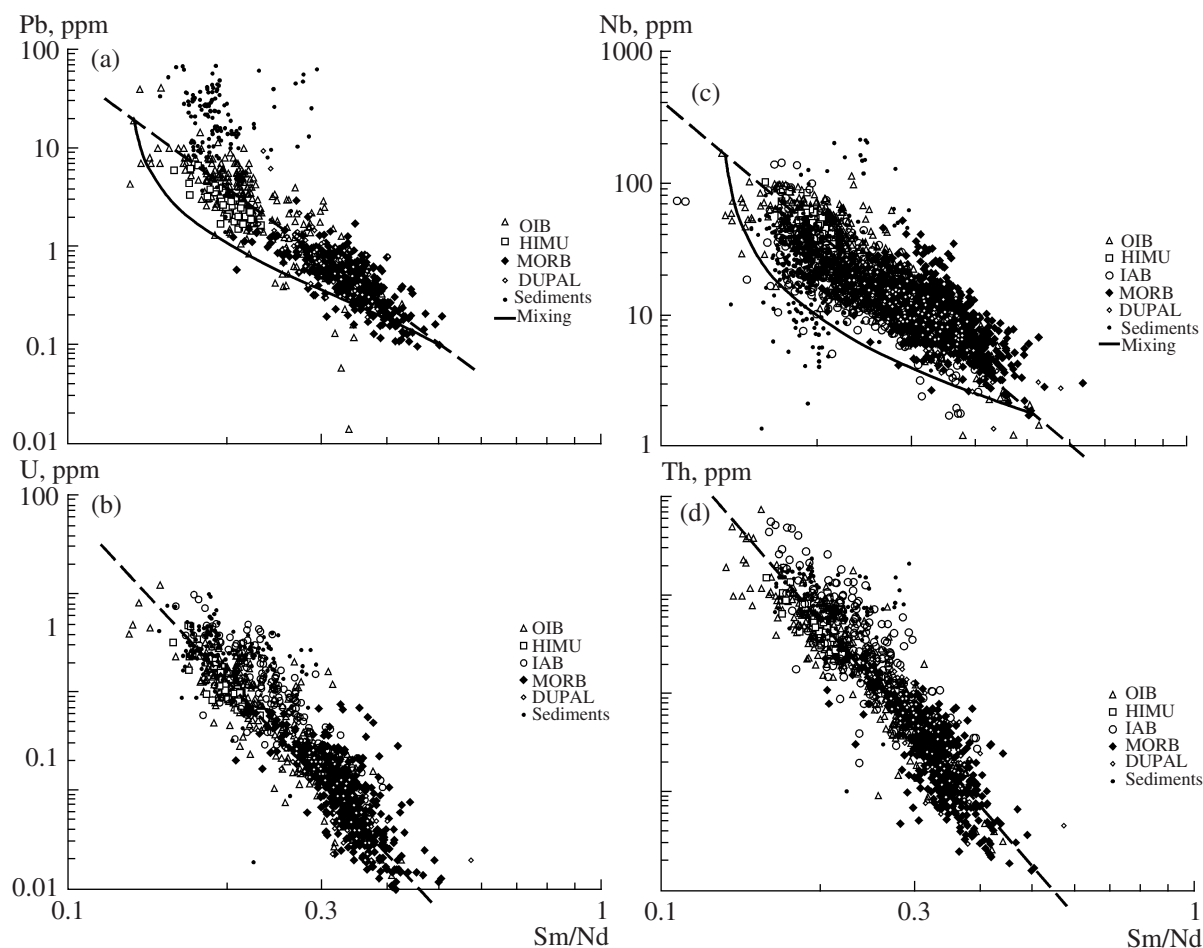


Fig. 6. Variations in the contents of some trace elements as functions of the Sm/Nd ratio in mid-ocean ridge basalts (MORB), intra-plate oceanic basalts (OIB), HIMU basalts, DUPAL basalts from the Indian Ocean and the South Atlantic [21], continental alkali basalts (CAB), and detrital silicate sediments. The direction of the general trend is shown by the dashed line, and the two-component mixing of hypothetical end-member is shown by the solid line.

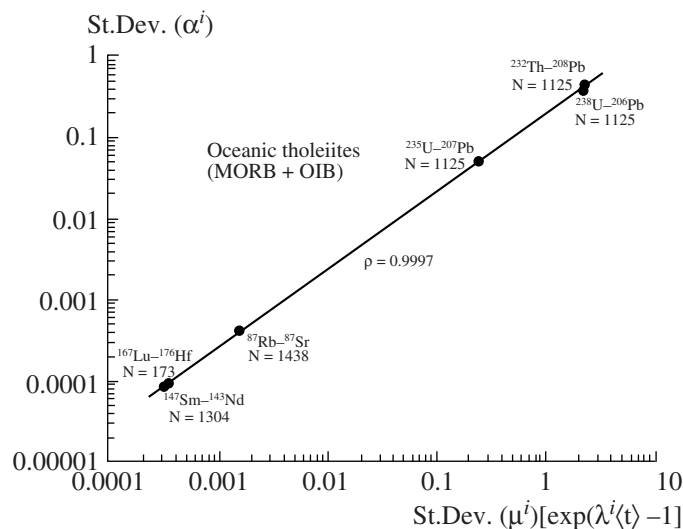


Fig. 7. Correlation between the standard deviations of isotope (radiogenic additions) and element ratios for oceanic tholeiites. The minimum scatter is observed at $\langle t \rangle = 1.8$ Ga, although the quality of the dependency does not change significantly within the range from 0.9 to 2.2 Ga ($\rho \geq 0.999$). The isotopic system and the number of available isotopic measurements which were used for the calculations are indicated near the points. Note the very strong dependency at a range of values of almost four orders of magnitude along either axis.

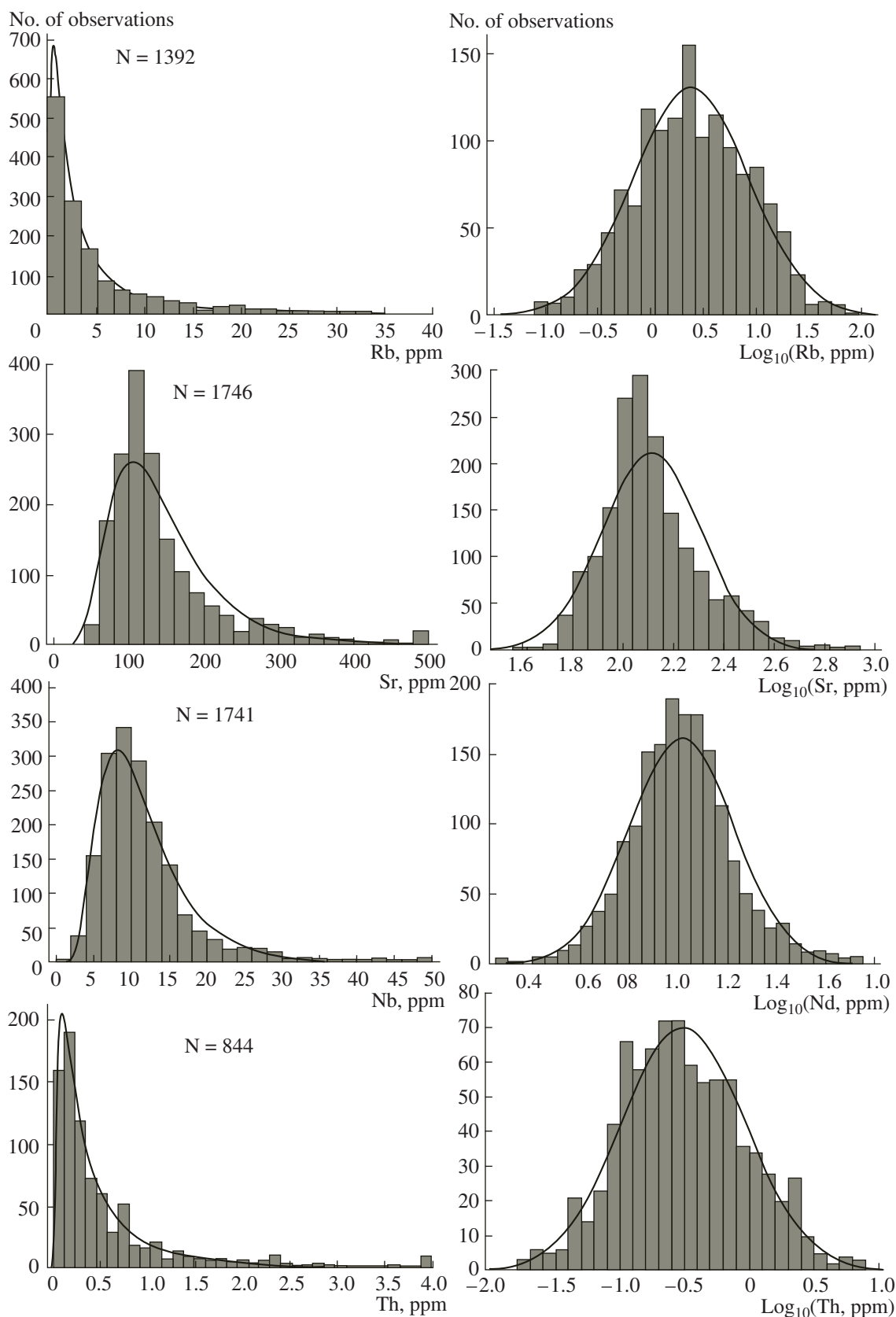


Fig. 8. Histograms of the concentrations of trace elements in MORB illustrating the character of their statistical distributions. For a more general presentation, elements with valencies from +1 to +4 are shown. The solid lines correspond to the theoretical curves of the lognormal (left) and normal (right) distributions.

corresponding to the slope of the trend in the Pb–Pb coordinates (Fig. 2); as will be shown later, this coincidence is not accidental.

The analysis of the diagram in Fig. 7 reveals the following important features and consequences.

(1) Such a strong correlation could hardly be accidental.

(2) It reflects the activity of some global process in the mantle. This process is, of course, represented by particular but geochemically similar events distributed in time.

(3) The correlation between the variances of α^i and μ^i cannot reflect the accumulation of radiogenic isotopes in situ during the postmagmatic history of the rocks, because the data set includes recent and very young basalts. This relation evidently reflects the properties of basalt sources.

(4) The above assumption that the Rb/Sr, Sm/Nd, U/Pb, Th/Pb, and Lu/Hf ratios of tholeiitic basalts correspond to the compositions of their sources is satisfied rather strictly. Otherwise, the correlation observed (Fig. 7) would have been disturbed. Note that such a rigorous correlation was observed for tholeiitic basalts only. When the calculations involved alkaline rocks, whose element ratios do not correspond to the composition of their source, the quality of the dependency was significantly deteriorated. The rocks of the continental crust yielded a low correlation coefficient of 0.57 in the same coordinates.

(5) Figure 7 suggests that variations in all the isotopic systems in the mantle cannot be understood without analyzing the geochemical heterogeneity of rocks. These data provide convincing support to the above speculative suggestion on the inevitable generation of an isotopic heterogeneity owing to the existence of a chemical heterogeneity in the mantle.

(6) Perhaps, the most important conclusion that can be drawn directly from Fig. 7 is that all the aforementioned isotope pairs have a common history in the mantle, and it is incorrect to search for a particular mechanism for the formation of anomalies in each particular isotopic system, which was done, for instance, to explain the HIMU anomaly [3].

The diagram of Fig. 7 provides little information about the mechanism of the formation of the chemical heterogeneity. In principle, it could be related both to intramantle differentiation and to the input of chemically anomalous material from an external source, for instance, owing to crustal recycling. However, at the present stage of our study, it was important to establish the prominent role of the chemical heterogeneity of the mantle for the development of its isotopic heterogeneity. A substantiated evaluation of the mechanism of chemical heterogeneity formation in the mantle requires the analysis of its consequences, i.e., to discuss the character of such a heterogeneous distribution of the elements.

CHARACTER OF THE CHEMICAL HETEROGENEITY OF THE MANTLE

The volcanic rocks of mantle origin show distinct multidimensional correlations between trace elements coupled with broad variations in their contents. For instance, MORB magmas, which are produced by high-degree melting of a mantle source, show considerable variations in Pb, Nd, Sr, Nb (more than one and a half orders of magnitude), Rb, U, Th, and Ba (more than two orders of magnitude) (Figs. 3, 6). These variations could in part be related to the stage of formation of igneous rocks; however, as was shown above, they reflect to a large extent the source heterogeneity.

To understand the main mechanism of formation of mantle heterogeneity, it is very important to keep in mind that the relations observed in Figs. 3 and 6 are linear and uniform only in logarithmic coordinates. In contrast, the data points are scattered to form a radiating pattern in linear coordinates. This fact and the model curves depicted in Fig. 6 suggest that the observed arrays are not two-component mixing lines, which rules out, in particular, the suggestion on the recycling-dominated origin of this chemical heterogeneity, i.e., its formation by mixing of crustal and mantle components. Figure 8 shows that the distribution patterns of lithophile trace elements in MORB are unimodal and close to lognormal. The character of correlations and the distribution of trace elements indicate the following:

- the observed variance of each of the lithophile elements considered and multidimensional correlations of their logarithms on the scale of the whole oceanic mantle were formed under the influence of a single geochemical process or a combination of processes, which did not disturb the correlations between the elements and the unimodal distribution of the elements and
- in mathematical terms, the variations observed in the diagrams (Figs. 3, 6, 8) are described by the operations of multiplication and division (this corresponds, for instance, to the equilibrium of trace elements at a phase boundary) rather than the operations of addition and subtraction (mixing-type processes or disequilibrium separation of materials).

Such characteristics of the process provide additional arguments against crustal recycling as the main reason for the observed chemical heterogeneity of the mantle; otherwise, traces of two-component mixing in the mantle should have been observed, even if the components were rather uniformly distributed over the whole mantle section. It is evident that the observed chemical heterogeneity reflects the processes of intramantle differentiation rather than mixing between the most differentiated and depleted materials.

Magmatic and metasomatic processes are the main possible mechanisms of the differentiation of mantle material. The exponential style of variations in the concentrations of incompatible trace elements (Figs. 3, 6)

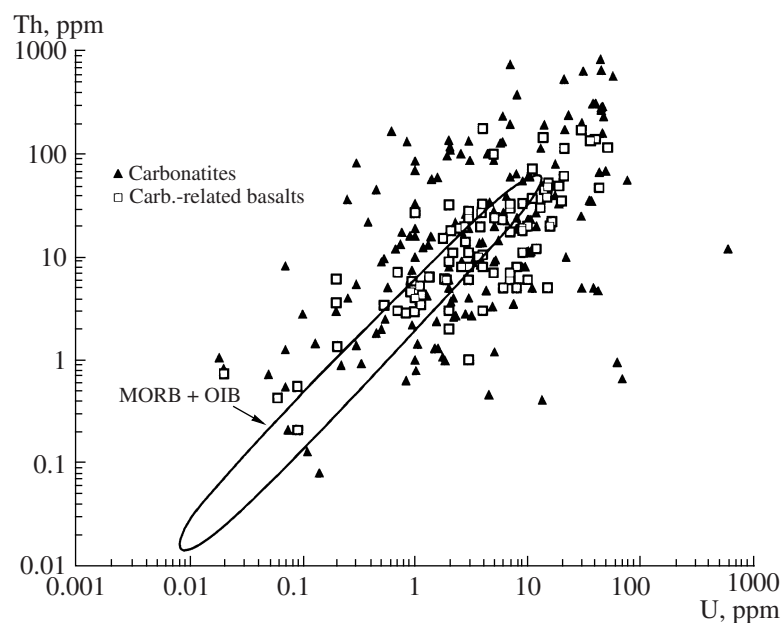


Fig. 9. Contents of thorium and uranium in carbonatites and genetically allied basalts. The contour indicates the compositional field of MORB and OIB (Fig. 3f).

in mantle-derived rocks is in agreement with the magmatic nature of mantle differentiation. However, metasomatism should also be considered as a process capable of changing the composition of mantle materials.

Metasomatic phenomena are often observed in ultrabasic nodules transported to the surface by kimberlites, carbonatites, and alkali basalts. Mantle rocks often show definite mineralogical and geochemical indications of metasomatic transformations. However, there are two complicating factors in the metasomatic model of the formation of broad variations in the concentrations and ratios of the trace elements considered (Figs. 3, 6).

- First, if the compositions of alkali basalts genetically related to carbonatites and phonolites, which were probably formed under the influence of metasomatic processes, are plotted on these diagrams, the data points will be scattered and all the observed relations will be disturbed. This is exemplified by uranium and thorium (Fig. 9) and can be observed for many other elements. In contrast, alkali basalts, including continental ones, not connected with carbonatites fall within the distinct trends previously established in the diagrams of Figs. 3 and 6. Alkali basalts are not distinguished in these diagrams by special symbols, but they can be easily identified by the high contents of trace elements (normally, $\text{Pb} > 2 \text{ ppm}$, $\text{Rb} > 10 \text{ ppm}$, $\text{U} > 1 \text{ ppm}$, and $\text{Nb} > 20 \text{ ppm}$).

- Second, it is known from the experience of investigations of metasomatic rocks in the continental crust and in ore deposits that metasomatism usually produces very contrasting rocks, strongly different from the country rocks with respect to many element ratios. On the contrary, it was concluded above on the basis of the

analysis of Fig. 7 that all the trace elements considered here had a common monotonous mantle history without sharp anomalies in the behavior of particular elements.

Of course, these considerations do not rule out the possible occurrence of mantle metasomatism but significantly limit its role in the global redistribution of elements in the mantle, at least in the source of MORB, OIB, and continental mafic rocks not related to carbonatites and kimberlites. The chemical heterogeneity of mantle-derived rocks is most likely related mainly to magmatic processes occurring within the mantle.

The zone of mantle magmatism is probably restricted to the upper 200–300 km, because at greater depths the temperature does not reach the solidus line. However, even if only this relatively thin mantle zone is affected by magmatic processes, the whole mantle or its significant portion must be differentiated to some extent by now owing to convection. Note that the mantle layer to a depth of 250 km comprises about 10% of the volume of mantle material. The problem of the efficiency of convective mixing of mantle materials will be discussed below.

ISOTOPE ANOMALIES IN THE MANTLE: A SIMPLE MODEL

As can be seen in Fig. 10a, alkali basalts and tholeiites plot within different fields in the Sm/Nd – Rb/Sr coordinates. The average composition of mantle pyrolyte [36] approximately coincides with the center of the field of oceanic tholeiites (point P). Two types of enriched basaltoids are also shown in this diagram:

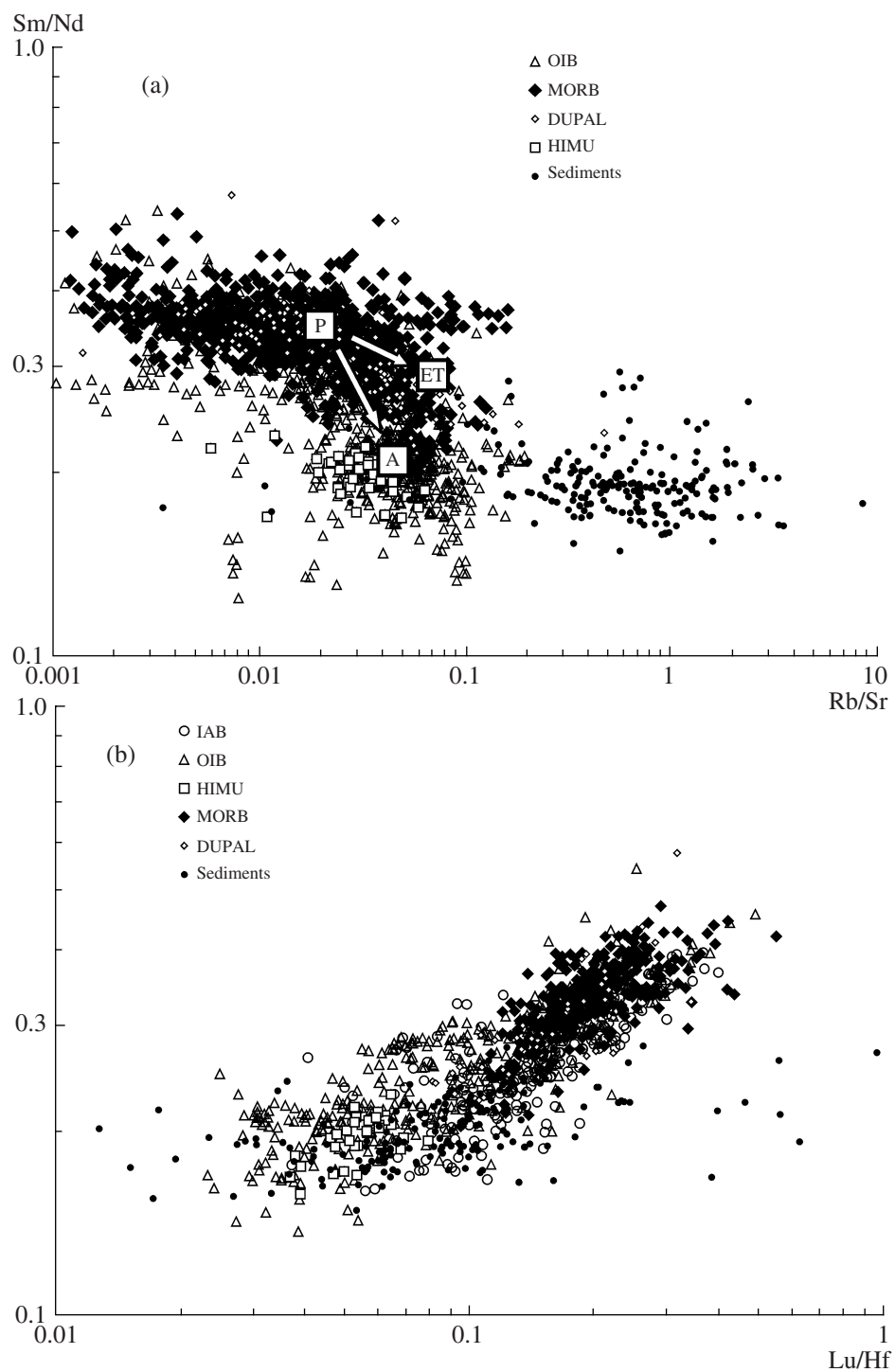


Fig. 10. Correlations between trace element ratios in mid-ocean ridge basalts (MORB), intraplate oceanic basalts (OIB), HIMU basalts, DUPAL basalts from the Indian Ocean and the South Atlantic [21], continental alkali basalts (CAB), and detrital silicate sediments. The negative correlation between Sm/Nd and Rb/Sr in the oceanic basalts is in agreement with the negative correlation between $^{143}\text{Nd}/^{144}\text{Nd}$ and $^{87}\text{Sr}/^{86}\text{Sr}$ (Fig. 1a), and the positive correlation between Sm/Nd and Lu/Hf in the oceanic basalts is in agreement with the positive correlation between $^{143}\text{Nd}/^{144}\text{Nd}$ and $^{176}\text{Hf}/^{177}\text{Hf}$ (Fig. 1b).

enriched tholeiites (point ET) and alkali basalts (point A). It is important that these two characteristic points are located within a common essentially continuous set of the compositions of mantle-derived igneous rocks, which implies that none of the chemical elements considered in our analysis departs from the other elements. Let us assume that the melts of both types were generated in the mantle but did not escape, partially or completely, and crystallized to form rocks, i.e., enriched domains of the ET and A types were formed in the mantle. Since they differ from the average composition of the ambient mantle rocks with respect to the Rb/Sr and Sm/Nd ratios, the strontium and neodymium isotope ratios of these geochemically anomalous rocks will evolve anomalously with time, which is shown by arrows in Fig. 1a. The dashed and solid lines correspond to type A and ET anomalies, respectively. Ticks on the arrows indicate the time in billion years necessary for the development of respective changes in strontium and neodymium isotopic compositions.

A comparison of Figs. 1a and 10a suggests that long-lived geochemical anomalies related to with alkaline magmatism could be responsible for the isotopic anomalies of the EM-I type, and geochemical anomalies in the mantle generated by enriched tholeiitic melts could be sources of isotopic anomalies of the EM-II type. The analysis of published isotopic data shows that EM-I anomalies are more frequently found in the alkaline rocks of oceans and continents, carbonatites, kimberlites, and genetically allied alkali-rich rocks. The isotopic anomalies of the EM-II type are more common in continental plateau basalts, which are dominated by tholeiitic series rocks. Of course, this difference is not rigorous, and the boundary between the EM-I and EM-II anomalies in Fig. 1a is also not rigorous; however, the tendency of inheritance of the geochemical style of mantle magmatism is clearly manifested.

Thus, the isotopic anomalies of the EM-I and EM-II types can be adequately explained by past magmatic intrusive processes occurring in the mantle.

Although this model is seemingly very obvious, it ignores some important factors; primarily, it is static and assumes that, once appearing, an anomaly will exist forever. Such a situation is unlikely to occur in the convecting mantle.

AGE OF CHEMICAL ANOMALIES IN THE MANTLE

Very important conclusions can be drawn from the observed positive correlation between $^{143}\text{Nd}/^{144}\text{Nd}$ and Sm/Nd for MORB and other mantle-derived volcanics (Fig. 4a). The analysis of this diagram suggests that, contrary to the widespread belief [37], the formation of geochemical anomalies in the mantle is a prolonged process that lasted hundreds of millions of years. Geochemically enriched rocks with low Sm/Nd values and high neodymium isotope ratios, similar to those of

N-MORB, were never found on Earth. The area designated by a question mark in Fig. 4a is empty, although there are a number of points to the right and below it (i.e., having the same Nd isotope signatures and the same Sm/Nd ratios, respectively). This implies that the formation of a geochemical anomaly in the mantle was long enough for the isotopic ratios to change owing to radioactive decay. The minimum model age of such geochemical anomalies for MORB is 100–150 Ma. The model age of some young oceanic basalts is up to 1 Ga [38–42], and that of continental basalts may be as high as 2 Ga [43–53] and even older [54].

At first glance, the Rb–Sr data are chaotically distributed in the $^{87}\text{Sr}/^{86}\text{Sr}$ –Rb/Sr diagram (Fig. 4b). This could be expected because of a greater difference between the chemical properties of rubidium and strontium as compared with those of samarium and neodymium. Nonetheless, this diagram exhibits the same relationships that were observed in the Sm–Nd system. As can be seen in Fig. 4b, there are no points in the right lower corner. The area designated by a question mark is empty although there are a number of points to the left (i.e., with the same strontium isotope compositions) and above this area (i.e., with the same Rb/Sr ratios). Similar to the Sm–Nd system, this means that the formation of geochemically enriched compositions in the mantle lasted for a considerable time. Similar conclusions can be drawn from the analysis of the U–Pb and Lu–Hf isotopic systems.

Figures 4a and 4b, as well as similar diagrams for the U–Pb and Lu–Hf systems (not shown), indicate a relationship between the chemical characteristics of rocks, in particular, their Sm/Nd and Rb/Sr ratios, and the isotopic compositions of the elements. This lends additional support to the suggestion that the incompatible element ratios of mafic volcanics (especially tholeiites) characterize to some extent the composition of their mantle source.

The above considerations place constraints on the mechanism of formation of geochemical heterogeneities in the mantle. It is evident that geochemically enriched rocks are derived in most cases from long-lived enriched sources. These enriched sources were probably developed gradually, step-by-step, and with long hiatuses; therefore, the whole process of their evolution appears to be rather slow and comparable with the decay rates of long-lived parent isotopes. This is the only reasonable way to explain why chemically enriched rocks with high Rb/Sr and low Sm/Nd ratios do not show the lowest strontium isotope ratios and the highest neodymium isotope ratios.

This mechanism can be related to intrusive processes within the mantle under asthenospheric conditions favorable for the formation and movement of silicate melts. As was shown in the previous section, a previously formed enriched material may again be affected by partial melting and mix with the enclosing undifferentiated rocks. This scenario is viable, because the

enrichment of lithophile components makes the rock less refractory. Such events may occur repeatedly, until a sequential melting event will eventually result in the transportation of the formed melt portion from the mantle to the crust.

At deeper levels, the formation of silicate melts is inhibited, and differentiation processes in the plastic convecting mantle may resemble the development of metamorphic layering. Such a differentiation could hardly result in a relative movement of enriched and depleted compositions over considerable distances; rather, it sets the stage for the subsequent magmatic mobilization of geochemically enriched rocks. In general, it should be admitted that this research field is still insufficiently developed for the clear understanding of at least the main features of mantle differentiation at great depths.

The points of mid-ocean ridge basalts plot in Fig. 4a along a line with a slope corresponding to about 0.15 Ga. This trend can hardly be directly interpreted as a mantle isochron corresponding to a particular independent event of such an age. This is primarily suggested by the fact that the same rocks form a trend corresponding to about 1.7 Ga in the Pb–Pb isotope coordinates (Fig. 2). The order of magnitude discrepancy between the “ages” obtained for the Pb–Pb and Sm–Nd systems is compelling evidence that the observed isotopic heterogeneity is not related either to any real event of the global differentiation of mantle material or to the hypothetical influx of an ancient crustal component into the mantle. In both cases, an agreement should have been expected between the Pb–Pb and Sm–Nd model ages of the observed geochemical anomalies.

The question why the mid-ocean ridge basalts yield different age trends in the Pb–Pb (Fig. 2) and Sm–Nd (Fig. 4a) systems is very important for chemical geodynamics. This phenomenon is directly connected with the characteristics of the two isotopic systems and global mixing of mantle materials.

MANTLE CONVECTION AND ISOTOPIC SYSTEMS

The fact that neither Figs. 2 and 4 nor other diagrams of the isochron type for mantle rocks display trends approaching the geochron is very important for the understanding of the degree of chemical mobility of mantle materials. In terms of ordinary geochronology, this implies that the mantle is in general rejuvenated in all the isotopic systems. There are no regions in the mantle, both on global and any local scales, which could have been regarded as geochemically closed relative to each other and isolated since the time of Earth formation. Otherwise, it had to be admitted that such reservoirs of primordial mantle are either dead as sources of matter or have not yet been found, which seems to be improbable given the current knowledge of

mantle rocks. Therefore, the entire mantle is entrained into the convective material exchange.

The gently sloping trend of MORB in the $^{143}\text{Nd}/^{144}\text{Nd}$ –Sm/Nd coordinates (Fig. 4a) clearly reflects the geochemical role of convection in the mantle: if there was no convection, we would have observed a trend with a slope corresponding to an age of about 4.5 Ga, which is the case, for instance, for lunar basalts. Convection partially homogenizes the isotopic ratios of neodymium and other elements and, consequently, results in a significant isotopic rejuvenation of the mantle on the whole. On the other hand, Fig. 4a shows that there are regions with ancient model ages beneath ocean islands and, especially, beneath continents. These regions have been unaffected by global mixing for a considerable period of time or are affected with a considerable time delay compared with the main volume of the suboceanic mantle.

In terms of physics, the intensity of convective mixing in the mantle can be qualitatively estimated from the following considerations. The extrapolation of the average linear velocity of lithospheric plate movement (5 cm/yr) over the entire history of the Earth yields the distance which could be traveled by a given point within 4.5 Gyr as more than 2×10^5 km. If the intensity of convection and, correspondingly, the rate of material transport is controlled by radiogenic heat, which was more intensely released in the past, this distance will be greater than 5×10^5 km, i.e., two orders of magnitude greater than the present-day mantle thickness. The trajectory of any particular point can be arbitrarily complex. This is suggested most clearly by two observations: (1) the absence of agreement between the zones of spreading and subduction both in the total length and in the geographic distribution and (2) complicated and irregular patterns observed in seismic tomography images with a dispersion and gradual obliteration with depth of high-density zones extending from island arcs at the Earth's surface to the deep mantle along the direction of subduction [55]. These facts indicate a relatively intense movement and mechanical mixing of mantle materials over distances greater than the thickness of suboceanic lithospheric plates.

On a smaller scale, when an individual block of mantle rocks should be considered as a solid, the mixing of materials is controlled by other processes. The isotopic homogenization of material may accompany various magmatic phenomena (melting, melt transportation, magma crystallization, etc.), but these processes are rather local. An efficient mechanism for the complete isotopic homogenization on the scale larger than the size of an individual magmatic body is unknown and hardly possible [56].

The mobilization of trace components and the accompanying effect of isotopic homogenization can be significantly intensified by the phase transitions that occur when a convective flow intersects the major geophysical boundaries in the mantle. For instance, the pla-

gioclase–spinel, spinel–garnet, and olivine–perovskite transitions at the boundary of the upper and lower mantle or the process of iron release from silicates at the mantle–core boundary [57] promote extensive (if not complete) recrystallization. The influence of these phase transformations on the migration of elements and the resulting isotopic homogenization of the mantle material is still not fully understood. It can only be supposed that the consequences of fundamental transformations of minerals in deep zones and rock recrystallization may be comparable with the effects of metamorphic or magmatic processes in relatively shallow environments.

It should be kept in mind that the magmatic processes discussed here and the probable recrystallization at phase boundaries exert a homogenizing influence on the isotopic composition of elements in mantle rocks but can produce the opposite effect on their chemical composition, i.e., differentiation (for instance, with respect to the Sm/Nd, Rb/Sr, U/Pb, and Lu/Hf ratios) rather than homogenization.

ISOTOPIC ANOMALIES IN THE MANTLE: A STATISTICAL MODEL

The above considerations suggest that the following two important tendencies in the evolution of mantle isotopic systems should be taken into account:

(1) the tendency toward increasing chemical heterogeneity of the mantle owing to the differentiation of its rocks, and

(2) the tendency toward isotopic homogenization owing to the mixing of mantle materials on various scales.

Both of these processes affect the entire mantle, at least those parts that serve as sources of igneous rocks accessible to observation. It is evident that simple reservoir models with a finite number of homogeneous constituents are not appropriate for the simulation of these processes in isotopic systems. Therefore, we propose a statistical model of the isotope geochemical evolution of the heterogeneous mantle, whose essential features are given in Table 1.

Table 1. Description of the statistical model of mantle source evolution

Model event	Comments
The initially homogeneous mantle with primary isotopic compositions of all elements is divided into a number of small identical domains	The number of model domains was chosen to obtain a robust result within a reasonable computation time. At a small number (less than 3×10^2), the results of repeated calculations may be significantly different. The result is stable at 10^3 – 10^6 domains in the system. The diagrams of Figs. 11 and 12 show 10^4 points.
The time scale is divided into a number of equal steps, Δt	The number of model steps, S , was taken to be 100 after testing various values. The results are reproducible already at $S > 30$. This parameter controls the frequency of mixing events between domains and, consequently, affects the general efficiency of the model homogenization process.
In every step and in every domain, the Rb/Sr, Sm/Nd, Lu/Hf, U/Pb, and Th/Pb ratios are changed randomly in accordance with the prescribed distributions of all of the elements (Fig. 8)	The value of variance increment at each step, D , was chosen to provide by the end of the process the observed present-day statistical distributions and multidimension correlations of U/Pb, Th/Pb, Sm/Nd, Rb/Sr, and Lu/Hf in MORB (Fig. 11). The variances of all cross ratios (e.g., Hf/Nd, Pb/Sr, and U/Rb) were also controlled in order to attain the maximum agreement between the model sets and natural observations with respect to all of these parameters.
The isotopic composition of Sr, Pb, Nd, and Hf changed at every step and in every domain in accordance with the law of radioactive decay	This process leads to increasing isotopic heterogeneity in the model chemically heterogeneous source.
At every step, the isotopic ratios of Sr, Pb, Nd, and Hf were pairwise equilibrated in some randomly selected domains	The complete element and isotope homogenization of two domains is modeled. The modeling of the mixing process involved a random sample of domains (F) that took part in the interaction during a sequential step. The pair domain was selected at a random distance (L). The parameter L was taken to be normally distributed with a mathematical expectation of 0 and a standard deviation 10–30 times lower than the total number of domains.

Table 2. Initial parameters of isotopic systems used in the statistical model

Isotope system	α_0^i	μ^i
^{87}Rb – ^{87}Sr	0.69897	0.0579
^{147}Sm – ^{143}Nd	0.506766	0.2116
^{176}Lu – ^{177}Hf	0.279813	0.0374
^{238}U – ^{206}Pb	9.307	8.54
^{235}U – ^{207}Pb	10.294	0.0619
^{232}Th – ^{208}Pb	29.476	32.12

In order to construct the model, it can be accepted that, to a good approximation, the variances of the logarithms of Rb, Sr, Sm, Nd, Lu, Hf, Pb, U, and Th contents and ratios, as well as the correlation coefficients of these values in MORB, correspond to those of their mantle source. The logarithms of element concentrations were used to bring all of the values to a normal distribution (Fig. 8) and facilitate the comparison of variances and correlation coefficients between model and real data. The correlation matrix constructed for this purpose included 170 parameters. In order to simulate the geochemical variance of the mantle source, a multidimensional random number generator was created with a correlation of elements with respect to all of the revealed parameters.

The model was implemented in the C programming language. All random parameters were modeled using a random number generator programmed to produce random values uniformly distributed in the (0, 1) interval. A transition from the uniform distribution to Gaussian and lognormal distributions was carried out using well-known algorithms [58].

The isotopic ratios of the mantle at 4.5 Ga that were used for modeling were taken in accordance with the conclusions of [16] and are shown in Table 2. They correspond to the present-day values $\epsilon_{\text{Nd}} = +9$, $\epsilon_{\text{Hf}} = +13$, and $^{87}\text{Sr}/^{86}\text{Sr} = 0.7028$ for the primitive mantle.

The model parameters S, D, F, and L (Table 1) are interrelated and can vary within wide ranges, which results in similar distributions of the isotope ratios of the elements. For instance, an increase in the number of steps (S) in the model results in a decrease in the final variance of all isotopic ratios but is compensated by a proportional decrease in the size of the sample of domains participating in isotopic exchange (F) or a decrease in the relative variance added at every step D. The parameters D and F can vary considerably in parallel without any significant effect on the result. This indicates that the model is in general robust.

Figure 12 illustrates the influence of the intensity of mixing in the source on the ultimate distribution of lead and neodymium isotopes. At $F = 0.2$, when 40% of

domains take part in the pairwise equilibration of isotopic ratios at every step, the model distributions of lead and neodymium isotopic compositions are similar to those observed in MORB (Figs. 12a, 12b). More vigorous mixing ($F = 0.5$) leads to an isotopically almost homogeneous composition of the model source (Figs. 12c, 12d). The same result is attained by an increase in the number of steps in the model. When the interactions between domains are suppressed ($F = 0.01$), the variance of isotopic ratios increases manyfold, and the points extend along the geochrons in both of the isotopic systems (Figs. 12e, 12f), which could be expected at the absence of mixing in the mantle.

Two competing processes operate in the statistical model: an increase in geochemical heterogeneity and obliteration of chemical and isotopic heterogeneities by mixing processes. The isotopic heterogeneity is generated by the chemical heterogeneity and radioactive decay, and, consequently, its generation is not an independent process. Figure 12 clearly shows that both the processes exert a significant influence on the final distribution of isotopic variations in the mantle source. If any of the processes, an increase in heterogeneity or its obliteration, dominated over the other, the observed patterns would have been similar to those shown in Figs. 12c and 12d or 12e and 12f.

The most intriguing result of the statistical model is that in the $^{207}\text{Pb}/^{204}\text{Pb}$ – $^{206}\text{Pb}/^{204}\text{Pb}$ coordinates (Fig. 12b), the points form a cloud extending along a line with a slope corresponding to ~ 1.7 Ga, which is similar to what is observed in oceanic volcanics. In the $^{143}\text{Nd}/^{144}\text{Nd}$ – $^{147}\text{Sm}/^{144}\text{Nd}$ – $^{143}\text{Nd}/^{144}\text{Nd}$ – $^{147}\text{Sm}/^{144}\text{Nd}$ coordinates (Fig. 12a), the model points form a shallower trend, which is also in agreement with the natural MORB data. The apparent discrepancy between the “ages” of trends in the $^{207}\text{Pb}/^{204}\text{Pb}$ – $^{206}\text{Pb}/^{204}\text{Pb}$ and $^{143}\text{Nd}/^{144}\text{Nd}$ – $^{147}\text{Sm}/^{144}\text{Nd}$ diagrams is related to the well-known characteristic features of the disturbance of these isotope systems. If a rock is affected by secondary isotopic rehomogenization, the slope of isochron in the $^{143}\text{Nd}/^{144}\text{Nd}$ – $^{147}\text{Sm}/^{144}\text{Nd}$ or $^{87}\text{Sr}/^{86}\text{Sr}$ – $^{87}\text{Rb}/^{86}\text{Sr}$ coordinates decreases, whereas in the $^{207}\text{Pb}/^{204}\text{Pb}$ – $^{206}\text{Pb}/^{204}\text{Pb}$ coordinates, the points are shifted toward the center of mass of the diagram, but the slope of the isochron may remain unchanged (of course, until the process will lead to the complete isotopic homogeneity). Although the physical analogy between the disturbance of the isochron of a particular geologic body and the behavior of isotopic systems in the mantle during its convective mixing is rather imperfect, changes in the slope of trends in the isotopic coordinates are governed in both cases by identical relations. During the partial homogenization of material, a steeper (older) slope is retained in the $^{207}\text{Pb}/^{204}\text{Pb}$ – $^{206}\text{Pb}/^{204}\text{Pb}$ coordinates, which include isotopes of a single element, compared with the coordinates involving the ratios of isotopes of different elements (e.g., $^{147}\text{Sm}/^{144}\text{Nd}$ and $^{87}\text{Rb}/^{86}\text{Sr}$). Approximately the same $\langle t \rangle$ value was obtained in Fig. 7, which compared the variances of isotope and element ratios in

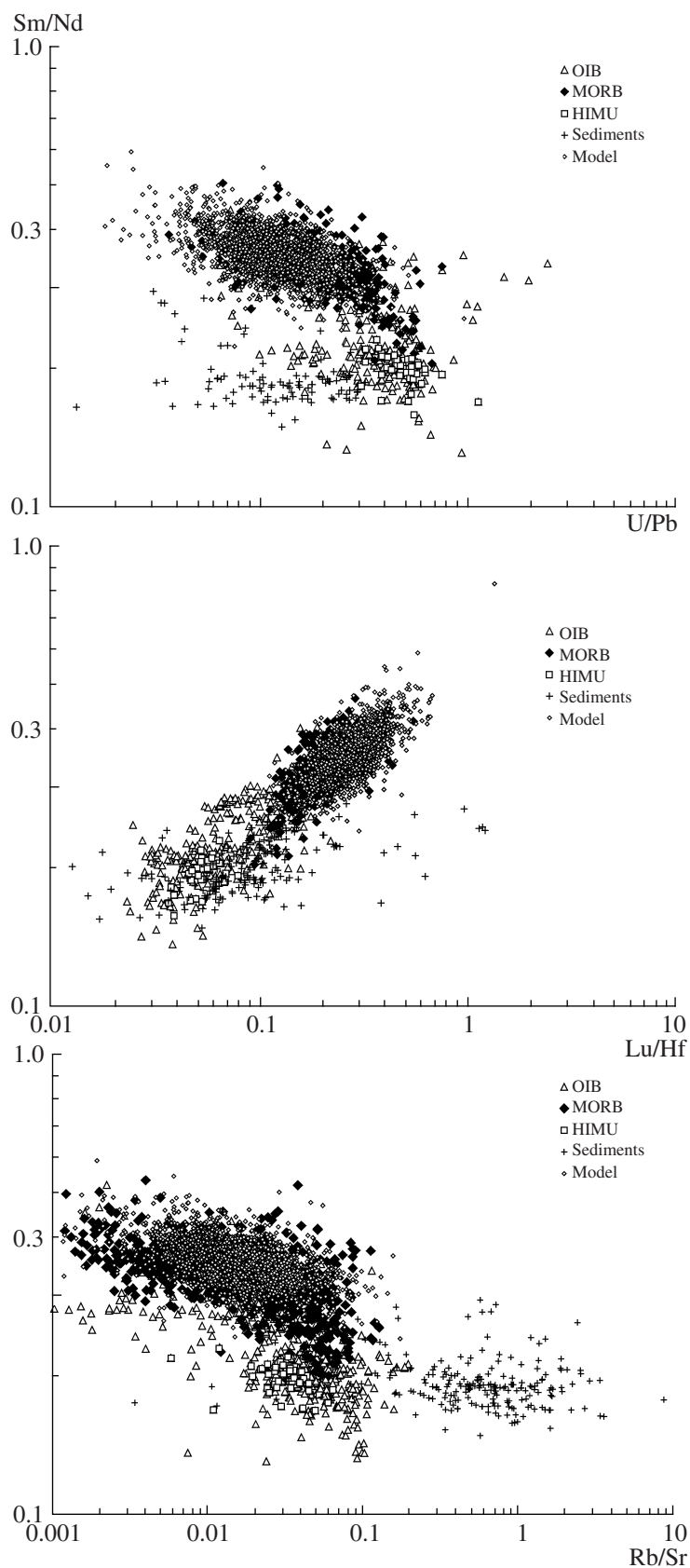


Fig. 11. Diagram illustrating the agreement between the final compositions of domains in the statistical model and the real compositions of MORB. The values of S, D, L, and F were adjusted in such a way as to attain an agreement between the variances of element ratios in the source and in MORB.

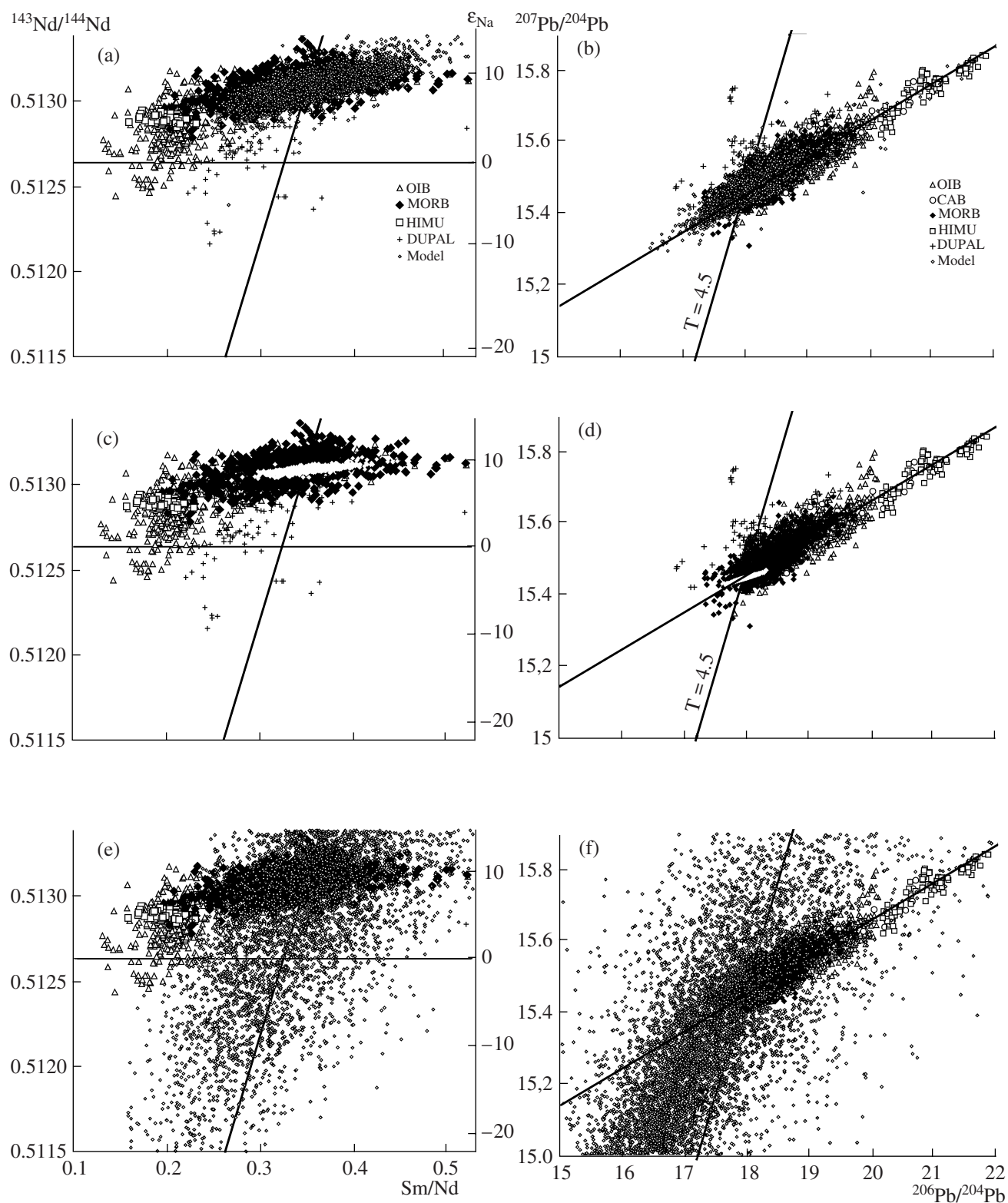


Fig. 12. Diagram illustrating the agreement between the model distributions of neodymium and lead isotope ratios and the real data for MORB. The diagram shows the results of three variants of calculations differing in the fraction of domains participating in pairwise mixing at every step (F): (a) and (b) $F = 0.2$, (c) and (d) $F = 0.5$, and (e) and (f) $F = 0.01$.

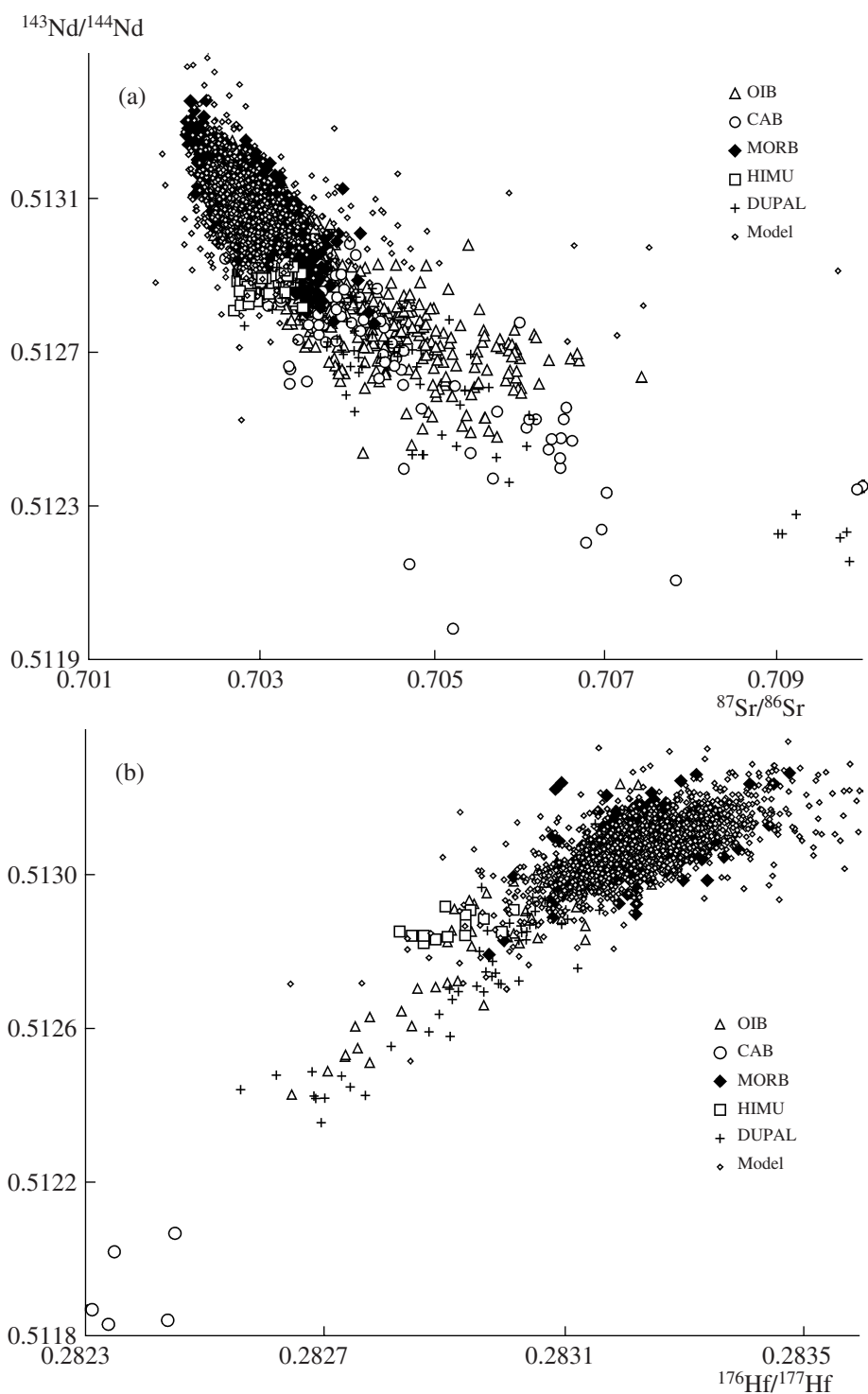


Fig. 13. Diagram illustrating the agreement between the model distributions of neodymium, strontium, and hafnium isotope ratios and the real data for MORB.

mantle rocks. This supports the interpretation of this value as an average age of all mantle processes that have affected the modern isotopic compositions of Sr, Nd, Hf, and Pb.

The $^{143}\text{Nd}/^{144}\text{Nd}$ – $^{87}\text{Sr}/^{86}\text{Sr}$ (Fig. 13a) and $^{143}\text{Nd}/^{144}\text{Nd}$ – $^{176}\text{Hf}/^{177}\text{Hf}$ (Fig. 13b) diagrams also display satisfactory agreement between the model points and the real isotopic compositions of MORB.

In the $^{207}\text{Pb}/^{204}\text{Pb}$ – $^{206}\text{Pb}/^{204}\text{Pb}$ coordinates (Fig. 12b), the model points form a trend with a slope of about 1.7 Ga, and the most radiogenic moull leads are definitely shifted toward the field of typical HIMU compositions. This sheds light on the possible nature of the HIMU isotope anomaly. Perhaps, the most radiogenic lead was formed in those rare areas of the mantle that acquired a high U/Pb ratio owing to intramantle differentiation and escaped homogenization with the enclosing rocks. The scarcity of such rocks on Earth is in agreement with the small fraction of corresponding points in the results of statistical modeling.

The parameters of the statistical model discussed above (i.e., S, D, F, and L) are rather difficult to use for quantitative estimates of the rate of mantle mixing or the intensity of the differentiation of its material. However, at a qualitative level, the model shows that there is a distinct statistical correspondence between the chemical heterogeneity of mantle-derived igneous rocks and variations in the Sr, Nd, Pb, and Hf isotope ratios in them. In particular, intramantle processes alone provide a consistent explanation for the negative correlation of neodymium and strontium isotopic compositions; the correlation of $^{206}\text{Pb}/^{204}\text{Pb}$ and $^{207}\text{Pb}/^{204}\text{Pb}$; the nature of the EM-I, EM-II, and HIMU components; etc.

CONCLUSIONS

Geochemically enriched oceanic volcanics with high Rb/Sr and low Sm/Nd ratios usually show enriched isotopic signatures (high $^{87}\text{Sr}/^{86}\text{Sr}$ and low $^{143}\text{Nd}/^{144}\text{Nd}$) (Fig. 4). This provides compelling evidence for the prolonged formation and existence of geochemically enriched and depleted rocks in the mantle. The suggestion on the rapid metasomatic enrichment of the source directly before melting [37] appeared from the analysis of a limited amount of data on enriched and nonenriched rocks and the hypothesis that the Sm–Nd isotopic characteristics of the primitive mantle are identical to those of CHUR, which resulted in that the majority of mantle sources were classified as depleted. The rejection of this concept allowed us to resolve many controversies in mantle geochemistry [16].

There is a strong statistical relationship between the variances of Sr, Nd, Hf, and Pb isotopic ratios and the variances of the element ratios Rb/Sr, Sm/Nd, Lu/Hf, U/Pb, and Th/Pb in oceanic tholeiites (correlation coefficient of 0.9997), which indicates a highly probable genetic link between these parameters in the mantle and a common mantle history of these elements.

The concept that the mantle is a chemically and isotopically homogeneous reservoir, whose homogeneity is disturbed only by the input of anomalous material from the outside, primarily from the crust, is not consistent with the available geochemical data. The chemical heterogeneity of the mantle is most likely caused by

magmatic processes within it: partial melting of rocks, movement of melts, and formation of intrusive bodies. Isotopic evidence indicates that these processes have repeatedly affected all mantle rocks, at least those that served as sources of observable igneous rocks, which resulted in that age trends approaching the age of the Earth were never observed in any isotopic system.

The simulation reported in this paper showed that there is a statistical agreement between the character of isotopic and chemical heterogeneity in the mantle. The HIMU, EM-I, and EM-II isotopic anomalies were produced by two concurrent processes: the magmatic differentiation of mantle material and its not very efficient mixing.

For the isotopic systems of lithophile elements considered here, the chemical heterogeneity of the mantle is the main reason for its isotopic heterogeneity. The geochemical role of other factors is evidently relatively small.

ACKNOWLEDGMENTS

This study was financially supported by Program no. 6 of the Earth Science Division of the Russian Academy of Sciences and the Russian Foundation for Basic Research, project no. 05-05-64699.

REFERENCES

1. D. J. DePaolo and G. J. Wasserburg, "Inferences about Magma Sources and Mantle Structure from Variations of $^{143}\text{Nd}/^{144}\text{Nd}$," *Geophys. Res. Lett.*, **3**, 743–746 (1976).
2. A. Zindler and S. Hart, "Chemical Geodynamics," *Annu. Rev. Earth Planet. Sci.* **14**, 493–571 (1986).
3. A. W. Hofmann, "Mantle Geochemistry: The Message from Oceanic Volcanism," *Nature*, **385**, 219–229 (1997).
4. G. J. Wasserburg and D. J. DePaolo, "Models of Earth Structure Inferred from Neodymium and Strontium Isotopic Abundances," *Proc. Natl. Acad. Sci. USA*, **76**, 3594–3598 (1979).
5. S. B. Jacobsen and G. J. Wasserburg, "A Two-Reservoir Recycling Model for Mantle–Crust Evolution," *Proc. Nat. Acad. Sci. U.S.A.* **77**, 6298–6302 (1980).
6. S. B. Jacobsen and G. J. Wasserburg, "Transport Models for Crust and Mantle Evolution," *Tectonophysics* **75**, 163–179 (1981).
7. R. E. Zartman and B. R. Doe, "Plumbotectonics—The Model," *Tectonophysics* **75**, 135–162 (1981).
8. R. E. Zartman and S. M. Haines, "The Plumbotectonic Model for Pb Isotopic Systematics among Major Terrestrial Reservoirs—A Case for Bi-Directional Transport," *Geochim. Cosmochim. Acta* **52**, 135–162 (1988).
9. S. B. Jacobsen, "Isotopic and Chemical Constraints on Mantle–Crust Evolution," *Geochim. Cosmochim. Acta* **52**, 1327–1339 (1988).
10. C. J. Allegre and E. Lewin, "Chemical Structure and History of the Earth: Evidence from Global Non-Linear Inversion of Isotopic Data in a 3-Box Model," *Earth Planet. Sci. Lett.* **96**, 61–88 (1989).

11. J. D. Kramers and I. N. Tolstikhin, "Two Terrestrial Lead-Isotope Paradoxes, Forward Transport Modeling, Core Formation and the History of the Continental Crust," *Chem. Geol.* **139**, 74–110 (1997).
12. I. N. Tolstikhin and A. W. Hofmann, "Primitive Crust on the Top of Metal Magma Ocean," *Phys. Earth Planet. Inter.* **148**, 109–130 (2005).
13. A. Meibom and D. L. Anderson, "The Statistical Upper Mantle Assemblage," *Earth Planet. Sci. Lett.* **217**, 129–139 (2003).
14. J. B. Kellogg, *Toward an Understanding of Chemical and Isotopic Heterogeneity in the Earth's Mantle* (Harvard Univ., Harvard, 2004).
15. S. R. Hart, "Heterogeneous Mantle Domains: Signatures, Genesis and Mixing Chronologies," *Earth Planet. Sci. Lett.* **90**, 273–296 (1988).
16. Yu. A. Kostitsyn, "Terrestrial and Chondritic Sm–Nd and Lu–Hf Isotopic Systems: Are They Identical?," *Petrologiya* **12**, 451–466 (2004) [*Petrology* **12**, 397–411 (2004)].
17. D. J. DePaolo and G. J. Wasserburg, "Nd Isotopic Variations and Petrogenetic Models," *Geophys. Res. Lett.* **3**, 249–252 (1976).
18. B. L. Weaver, "The Origin of Ocean Island Basalt End-Member Compositions—Trace-Element and Isotopic Constraints," *Earth Planet. Sci. Lett.* **104**, 381–397 (1991).
19. C. Chauvel, S. L. Goldstein, and A. W. Hofmann, "Hydration and Dehydration of Oceanic-Crust Controls Pb Evolution in the Mantle," *Chem. Geol.* **126**, 65–75 (1995).
20. M. Rehkamper and A. W. Hofmann, "Recycled Ocean Crust and Sediment in Indian-Ocean MORB," *Earth Planet. Sci. Lett.* **147**, 93–106 (1997).
21. S. R. Hart, "A Large-Scale Isotope Anomaly in the Southern Hemisphere Mantle," *Nature* **309**, 753–757 (1984).
22. B. Dupre and C. J. Allegre, "Pb–Sr Isotope Variation in Indian Ocean Basalts and Mixing Phenomena," *Nature* **303**, 142–146 (1983).
23. D. M. Miller, S. L. Goldstein, and C. H. Langmuir, "Cerium/Lead and Lead-Isotope Ratios in Arc Magmas and the Enrichment of Lead in the Continents," *Nature* **368**, 514–520 (1994).
24. C. Edwards, M. Menzies, and M. Thirlwall, "Evidence from Muriah, Indonesia, for the Interplay of Supra-Subduction Zone and Intraplate Processes in the Genesis of Potassic Alkaline Magmas," *J. Petrol.* **32**, 555–592 (1991).
25. M. F. Thirlwall, A. M. Graham, R. J. Arculus, et al., "Resolution of the Effects of Crustal Assimilation, Sediment Subduction, and Fluid Transport in Island-Arc Magmas: Pb–Sr–Nd–O Isotope Geochemistry of Grenada, Lesser Antilles," *Geochim. Cosmochim. Acta* **60**, 4785–4810 (1996).
26. R. F. Gribble, R. J. Stern, S. H. Bloomer, et al., "MORB Mantle and Subduction Components Interact to Generate Basalts in the Southern Mariana Trough Back-Arc Basin," *Geochim. Cosmochim. Acta* **60**, 2153–2166 (1996).
27. J. A. Hoogewerff, M. J. Vanbergen, P. Z. Vroon, et al., "U-Series, Sr–Nd–Pb Isotope and Trace-Element Systematics across an Active Island Arc–Continent Collision Zone—Implications for Element Transfer at the Slab–Wedge Interface," *Geochim. Cosmochim. Acta* **61**, 1057–1072 (1997).
28. R. Shinjo, "Geochemistry of High Mg Andesites and the Tectonic Evolution of the Okinawa Trough–Ryukyu Arc System," *Chem. Geol.* **157**, 69–88 (1999).
29. A. Stracke and E. Hegner, "Rifting-Related Volcanism in an Oceanic Post-Collisional Setting: the Tabar–Lihir–Tanga–Feni (TLTF) Island Chain, Papua New Guinea," *Lithos* **45**, 545–560 (1998).
30. J. D. Woodhead, J. M. Hergt, J. P. Davidson, et al., "Hafnium Isotope Evidence for 'Conservative' Element Mobility during Subduction Zone Processes," *Earth Planet. Sci. Lett.* **192**, 331–346 (2001).
31. J. S. Stacey and J. D. Kramers, "Approximation of Terrestrial Lead Isotope Evolution by a Two-Stage Model," *Earth Planet. Sci. Lett.* **26**, 207–221 (1975).
32. I. D. Ryabchikov, *Thermodynamic Analysis of the Behavior of Minor Elements during Crystallization of Silicate Melts* (Nauka, Moscow, 1965) [in Russian].
33. P. W. Gast, "Trace Element Fractionation and the Origin of Tholeiitic and Alkaline Magma Types," *Geochim. Cosmochim. Acta* **32**, 1057–1086 (1968).
34. G. M. Yaxley and D. H. Green, "Reactions between Eclogite and Peridotite—Mantle Refertilization by Subduction of Oceanic Crust," *Schweiz. Mineral. Petrogr. Mitt.* **78**, 243–255 (1998).
35. T. H. Green, "Experimental Studies of Trace-Element Partitioning Applicable to Igneous Petrogenesis—Sedona 16 Years Later," *Chem. Geol.* **117**, 1–36 (1994).
36. W. F. McDonough and S. S. Sun, "The Composition of the Earth," *Chem. Geol.* **120**, 223–253 (1995).
37. M. Menzies and V. R. Murthy, "Nd and Sr Isotope Geochemistry of Hydrous Mantle Nodules and Their Host Alkali Basalts: Implications for Local Heterogeneities in Metasomatically-Veined Mantle," *Earth Planet. Sci. Lett.* **46**, 323–334 (1979).
38. Q. C. Cheng, J. D. Macdougall, and P. Zhu, "Isotopic Constraints on the Easter Seamount Chain Source," *Contrib. Mineral. Petrol.* **135**, 225–233 (1999).
39. C. Deniel, "Geochemical and Isotopic (Sr, Nd, Pb) Evidence for Plume–Lithosphere Interactions in the Genesis of Grande-Comore Magmas (Indian Ocean)," *Chem. Geol.* **144**, 281–303 (1998).
40. I. Gautier, D. Weis, J. P. Mennessier, et al., "Petrology and Geochemistry of the Kerguelen Archipelago Basalts (South Indian Ocean): Evolution of the Mantle Sources from Ridge to Intraplate Position," *Earth Planet. Sci. Lett.* **100**, 59–76 (1990).
41. S. H. Richardson, A. J. Erlank, A. R. Duncan, et al., "Correlated Nd, Sr and Pb Isotope Variation in Walvis Ridge Basalts and Implications for the Evolution of Their Mantle Source," *Earth Planet. Sci. Lett.* **59**, 327–342 (1982).
42. M. Tatsumoto and Y. Nakamura, "Dupal Anomaly in the Sea of Japan: Pb, Nd, and Sr Isotopic Variations at the Eastern Eurasian Continental Margin," *Geochim. Cosmochim. Acta* **55**, 3697–3708 (1991).
43. A. Dodson, D. J. DePaolo, and B. M. Kennedy, "Helium Isotopes in Lithospheric Mantle: Evidence from Tertiary

- Basalts of the Western USA," *Geochim. Cosmochim. Acta* **62**, 3775–3787 (1998).
44. R. W. Carlson, S. Esperanca, and D. P. Svisero, "Chemical and Os Isotopic Study of Cretaceous Potassic Rocks from Southern Brazil," *Contrib. Mineral. Petrol.* **125**, 393–405 (1996).
 45. F. Garland, S. Turner, and C. Hawkesworth, "Shifts in the Source of the Parana Basalts through Time," *Lithos* **37**, 223–243 (1996).
 46. W. Hildreth, A. N. Halliday, and R. L. Christiansen, "Isotopic and Chemical Evidence Concerning the Genesis and Contamination of Basaltic and Rhyolitic Magma beneath the Yellowstone Plateau Volcanic Field," *J. Petrol.* **32**, 63–138 (1991).
 47. M. F. Horan, R. J. Walker, V. A. Fedorenko, et al., "Osmium and Neodymium Isotopic Constraints on the Temporal and Spatial Evolution of Siberian Flood-Basalt Sources," *Geochim. Cosmochim. Acta* **59**, 5159–5168 (1995).
 48. P. C. Lightfoot, C. J. Hawkesworth, J. Hergt, et al., "Remobilization of the Continental Lithosphere by a Mantle Plume: Major-Element, Trace-Element, and Sr-Isotope, Nd-Isotope, and Pb-Isotope Evidence from Picritic and Tholeiitic Lavas of the Norilsk District, Siberian Trap, Russia," *Contrib. Mineral. Petrol.* **114**, 171–188 (1993).
 49. P. C. Lightfoot, C. J. Hawkesworth, K. Olshefsky, et al., "Geochemistry of Tertiary Tholeiites and Picrites from Qeqertarsuaq (Disko Island) and Nuussuaq, West Greenland with Implications for the Mineral Potential of Comagmatic Intrusions," *Contrib. Mineral. Petrol.* **128**, 139–163 (1997).
 50. J. Mahoney, J. D. Macdougall, G. W. Lugmair, et al., "Origin of the Deccan Trap Flows at Mahabaleshwar Inferred from Nd and Sr Isotopic and Chemical Evidence," *Earth Planet. Sci. Lett.* **60**, 47–60 (1982).
 51. H. E. O'Brien, A. J. Irving, S. Mccallum, et al., "Strontium, Neodymium, and Lead Isotopic Evidence for the Interaction of Postsubduction Asthenospheric Potassic Mafic Magmas of the Highwood Mountains, Montana, USA, with Ancient Wyoming Craton Lithospheric Mantle," *Geochim. Cosmochim. Acta* **59**, 4539–4556 (1995).
 52. D. W. Peate and C. J. Hawkesworth, "Lithospheric to Asthenospheric Transition in Low-Ti Flood Basalts from Southern Parana, Brazil," *Chem. Geol.* **127**, 1–24 (1996).
 53. S. S. Schmidberger and E. Hegner, "Geochemistry and Isotope Systematics of Calc-Alkaline Volcanic Rocks from the Saar–Nahe Basin (SW Germany): Implications for Late Variscan Orogenic Development," *Contrib. Mineral. Petrol.* **135**, 373–385 (1999).
 54. R. Vollmer, P. Orgen, J. G. Schilling, et al., "Nd and Sr Isotopes in Ultrapotassic Volcanic Rocks from the Leucite Hills, Wyoming," *Contrib. Mineral. Petrol.* **87**, 359–368 (1984).
 55. D. C. Rubie and R. D. van der Hilst, "Processes and Consequences of Deep Subduction: Introduction," *Phys. Earth Planet. Inter.* **127**, 1–7 (2001).
 56. A. W. Hofmann and S. R. Hart, "An Assessment of Local and Regional Isotopic Equilibrium in the Mantle," *Earth Planet. Sci. Lett.* **38**, 44–62 (1978).
 57. E. M. Galimov, "Redox Evolution of the Earth Caused by a Multi-Stage Formation of Its Core," *Earth Planet. Sci. Lett.* **233**, 263–276 (2005).
 58. N. Hastings and B. Peacock, *Statistical Distributions*, (Butterworth, London, 1975; Statistika, Moscow, 1980).