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Terrestrial and Chondritic Sm–Nd and Lu–Hf Isotopic Systems: Are They Identical?

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Abstract—This paper presents a critical evaluation of popular concepts on the $^{143}Nd/^{144}Nd$, $^{176}Hf/^{177}Hf$, $^{87}Sr/^{86}Sr$, Sm/Nd, Lu/Hf, and Rb/Sr ratios in the Earth's primitive mantle. We examined the major controversies ensuing from the model of the chondrite uniform reservoir (CHUR) as a proxy for the composition of the primitive mantle (DePaolo and Wasserburg, 1976a). Among them are (1) the high magmatic productivity of the depleted mantle (DM) with no regular isotopic signal from the primitive mantle (PM); (2) the abundance of geochemically enriched rocks, in particular, alkali basalts, with the isotopic characteristics of the DM; (3) the depletion of the source of HIMU basalts in the Nd–Sr–Hf system in contrast to enrichment in the U–Pb system; (4) mass balance calculations for the Sm–Nd isotopic system of the crust and mantle constrain the mass of the DM, which served as a source of the crust, as 1/4–1/5 of the bulk mantle, but these estimates are in conflict with mass balances for the Rb–Sr and U–Pb systems and some other elements; and (5) the neodymium isotopic compositions and Sm/Nd values of high-degree melts from the PM must be similar to those of the source; however, rocks resembling the CHUR in both these parameters have never been reported. These controversies can be resolved only by assuming that the Sm/Nd ratio of the primitive mantle differs from that of the CHUR by 8%. The present-day compositional parameters of the primitive mantle are estimated as

$$\varepsilon_{Nd} = +9,\ ^{143}Nd/^{144}Nd = 0.51310,\ Sm/Nd = 0.350;$$
$$\varepsilon_{Hf} = +13,\ ^{176}Hf/^{177}Hf = 0.28323,\ Lu/Hf = 0.264;\ \text{and}$$
$$\varepsilon_{Sr} = -24,\ ^{87}Sr/^{86}Sr = 0.7028,\ Rb/Sr = 0.020.$$

The uncertainty of the estimated neodymium isotopic parameters can be up to ±1 for ε_{Nd}. The isotopic effects in the Sm–Nd, Lu–Hf, and Rb–Sr systems from the extraction of the Earth's crust from the mantle material is much smaller than the observed isotopic variations in mantle-derived rocks.

INTRODUCTION

Following the pioneering work by DePaolo and Wasserburg (1976a, 1976b), the most popular and almost universally accepted isotopic geochemical models for the structure and evolution of the Earth's mantle (Zindler and Hart, 1986; Allègre and Lewin, 1989; Hofmann, 1997) are based on the assumption that the Sm–Nd system of the Earth's primitive mantle corresponds to the chondritic uniform reservoir (CHUR). It was named uniform, because chondrites of various groups appeared to be fairly homogeneous with respect to Sm/Nd (Jacobsen and Wasserburg, 1980, 1983). The data on chondrites reported by Tatsumoto *et al.* (1981) are accepted as a proxy for the Lu–Hf isotopic system of the primitive mantle.

The Rb–Sr and U–Pb isotopic systems do not show such a correspondence between the compositions of the mantle and chondrites: the chondritic Rb/Sr value is approximately an order of magnitude higher than that of the Earth's mantle, whereas U/Pb is an order of magnitude lower (Wasson and Kallemeyen, 1988). Nonetheless, there is still a general belief that the Sm/Nd and Lu/Hf ratios of the Earth's mantle are identical to those of chondrites.

This assumption cannot be verified through a direct comparison of the compositions of chondrites and terrestrial rocks. The rare lherzolite nodules that could characterize the Earth's primitive mantle (Griffin *et al.*, 1988; Kramm and Wedepohl, 1990; Alibert, 1994; Ionov *et al.*, 1995b) show a considerable scatter in Sm, Nd, Lu, and Hf contents and ratios, which prevents any reliable estimates.

However, a considerable number of analyses have been accumulated to date on the isotopic systematics of neodymium and hafnium in various mantle-derived rocks, which allow the estimation of Sm/Nd and Lu/Hf values not only in their sources but also in the whole mantle participating in petrogenetic processes throughout the Earth history. This paper addresses this problem.

The knowledge of the real composition of the primitive undifferentiated mantle has fundamental significance not only for geochemistry but also for other branches of geosciences and for the understanding of processes occurring in the Earth's interiors. In particular, the determination of the composition of the primitive mantle is mandatory for the investigation of the composition and formation mechanisms of enriched and depleted mantle domains, the nature of isotopic and chemical heterogeneities in the mantle, and the scales of crust–mantle interaction.

CHONDRITE MODEL OF THE EARTH'S MANTLE IN THE Nd–Sr ISOTOPIC SYSTEM

A negative correlation between the neodymium and strontium isotope ratios of mantle rocks (Fig. 1a) was discovered by DePaolo and Wasserburg (1976a, 1976b), who proposed a new model for the evolution of the Earth's mantle. According to this model, the initial primitive mantle corresponded to the CHUR in the Sm–Nd system with the present-day parameters $(\mathrm{Sm/Nd})_{\mathrm{CHUR}} = 0.325$ and $(^{143}\mathrm{Nd}/^{144}\mathrm{Nd})_{\mathrm{CHUR}} = 0.512638$.[1] The relative deviation from the latter value is widely used for the presentation of isotopic measurements:

$$\varepsilon_{\mathrm{Nd}} = 10^4\left[\frac{(^{143}\mathrm{Nd}/^{144}\mathrm{Nd})_{\mathrm{S}}}{(^{143}\mathrm{Nd}/^{144}\mathrm{Nd})_{\mathrm{CHUR}}} - 1\right], \quad (1)$$

where $(^{143}\mathrm{Nd}/^{144}\mathrm{Nd})_{\mathrm{S}}$ is the isotopic ratio of the sample.

The subsequent extraction of the crust with a relatively low Sm/Nd ratio produced the depleted mantle (DM) with higher Sm/Nd. Since radiogenic ^{143}Nd is formed from ^{147}Sm, the isotopic ratio $^{143}\mathrm{Nd}/^{144}\mathrm{Nd}$ increases with time more rapidly in the reservoir with a higher Sm/Nd ratio, i.e., in the depleted mantle.

The negative correlation between $^{143}\mathrm{Nd}/^{144}\mathrm{Nd}$ and $^{87}\mathrm{Sr}/^{86}\mathrm{Sr}$ in various mantle rocks indicates that there is a global negative correlation between Sm/Nd and Rb/Sr in their source (sources). This suggestion is in agreement with geochemical observations: geochemically depleted rocks show relatively high Sm/Nd and low Rb/Sr values.

Probably, the only difficulty with this model was that the chondritic Rb/Sr and $^{87}\mathrm{Sr}/^{86}\mathrm{Sr}$ ratios are much higher than those of mantle rocks. Because of this, the same pristine mantle source was referred to as the uniform reservoir (UR) in the Rb–Sr system, and its strontium isotope composition was defined by the intersection of the inverse correlation trend of neodymium and strontium isotopic ratios with the CHUR line or $\varepsilon_{\mathrm{Nd}} = 0$ (Fig. 1a). The calculated value $(^{87}\mathrm{Sr}/^{86}\mathrm{Sr})_{\mathrm{UR}} = 0.7045$ can be used to calculate the $(\mathrm{Rb/Sr})_{\mathrm{UR}}$ ratio. Assuming that the age of the Earth is $T = 4.56$ Ga and the initial strontium isotope ratio is $(^{87}\mathrm{Sr}/^{86}\mathrm{Sr})_{\mathrm{BABI}} = 0.69897$ (Papanastassiou and Wasserburg, 1969), we obtain

$$(^{87}\mathrm{Rb}/^{86}\mathrm{Sr})_{\mathrm{UR}} = [(^{87}\mathrm{Sr}/^{86}\mathrm{Sr})_{\mathrm{UR}} - (^{87}\mathrm{Sr}/^{86}\mathrm{Sr})_{\mathrm{BABI}}]/[\exp(\lambda_{87}T) - 1]. \quad (2)$$

This yields $(\mathrm{Rb/Sr})_{\mathrm{UR}} = 0.029$.

Similar to $\varepsilon_{\mathrm{Nd}}$ (Eq. 1), the $\varepsilon_{\mathrm{Sr}}$ value is calculated for any current strontium isotopic ratio relative to $(^{87}\mathrm{Sr}/^{86}\mathrm{Sr})_{\mathrm{UR}} = 0.7045$.

Figure 1a presents the available data for mid-ocean ridge basalts (MORB) (Cohen *et al.*, 1980; Cohen and O'Nions, 1982; O'Nions *et al.*, 1977; Zindler *et al.*, 1984; Macdougall and Lugmair, 1986; Graham *et al.*, 1988; Klein *et al.*, 1988; Hegner and Tatsumoto, 1987; Dosso *et al.*, 1991; Hickeyvargas, 1991; Mertz *et al.*, 1991; Mühe *et al.*, 1993, 1997; Bach *et al.*, 1994, 1996; Cousens *et al.*, 1995; Mahoney *et al.*, 1995; Staudigel *et al.*, 1995; Niu *et al.*, 1996; Salters, 1996; Rehkamper and Hofmann, 1997; Schiano *et al.*, 1997; Salters and White, 1998; Smith *et al.*, 1998; Schilling *et al.*, 1999; Bourdon and Hemond, 2001; Chauvel and Blichert-Toft, 2001; Woodhead *et al.*, 2001), oceanic intraplate and ocean island basalts (OIB) (Hofmann *et al.*, 1984; Roden *et al.*, 1984; Wright and White, 1987; Roden *et al.*, 1988; Nakamura and Tatsumoto, 1988; Gautier *et al.*, 1990; Chen *et al.*, 1991; Tatsumoto and Nakamura, 1991; Halliday *et al.*, 1992, 1995; Desonie *et al.*, 1993; Weis *et al.*, 1993; Hemond *et al.*, 1994; Nohara *et al.*, 1994; Esperanca and Crisci, 1995; Rocholl *et al.*, 1995; Mahoney *et al.*, 1996; Spath *et al.*, 1996; Woodhead, 1996; Chauvel *et al.*, 1997; Turner *et al.*, 1997; Volker *et al.*, 1997; Widom *et al.*, 1997; Dodson *et al.*, 1998; Deniel, 1998; Elburg and Foden, 1999; Kurz and Geist, 1999; Janney *et al.*, 2000), continental basalts (Hawkesworth *et al.*, 1979; Chauvel and Jahn, 1984; Worner *et al.*, 1986; Musselwhite *et al.*, 1989; Kramm and Wedepohl, 1990; Chazot and Bertrand, 1993; Ionov *et al.*, 1995a; O'Brien *et al.*, 1995; Hart *et al.*, 1997; Marzoli *et al.*, 1999), and silicate terrigenous deposits and sedimentary rocks (Taylor *et al.*, 1983; Briqueu *et al.*, 1986; Goldstein and Jacobsen, 1987, 1988; Nelson and DePaolo, 1988; Asmerom and Jacobsen, 1993; McDermott *et al.*, 1993; Bosch *et al.*, 1994; Cousens *et al.*, 1994; German *et al.*, 1995; Allègre *et al.*, 1996; Dupré *et al.*, 1996; Ling *et al.*, 1997; Gallet *et al.*, 1998; Pettke *et al.*, 2000). As can be seen in Fig. 1a, the mantle array has become somewhat more blurred compared with that presented by DePaolo and Wasserburg (1976a), but its general patterns have not changed. The upper left quadrant in Fig. 1a with low strontium isotopic ratios and high neodymium isotopic ratios corresponds to the DM reservoir. The lower right quadrant comprises enriched sources, and the formation of the enriched mantle is usually explained by the subduction and partial entrainment of crustal materials into the mantle (Zindler and Hart, 1986; Allègre and Lewin, 1989; Hofmann, 1997).

The chondritic composition of the primitive mantle was also accepted for the Lu–Hf isotope system (Tatsumoto *et al.*, 1981), with the present-day values Lu/Hf =

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[1] All neodymium isotope ratios are normalized in this paper to $^{146}\mathrm{Nd}/^{144}\mathrm{Nd} = 0.7219$.

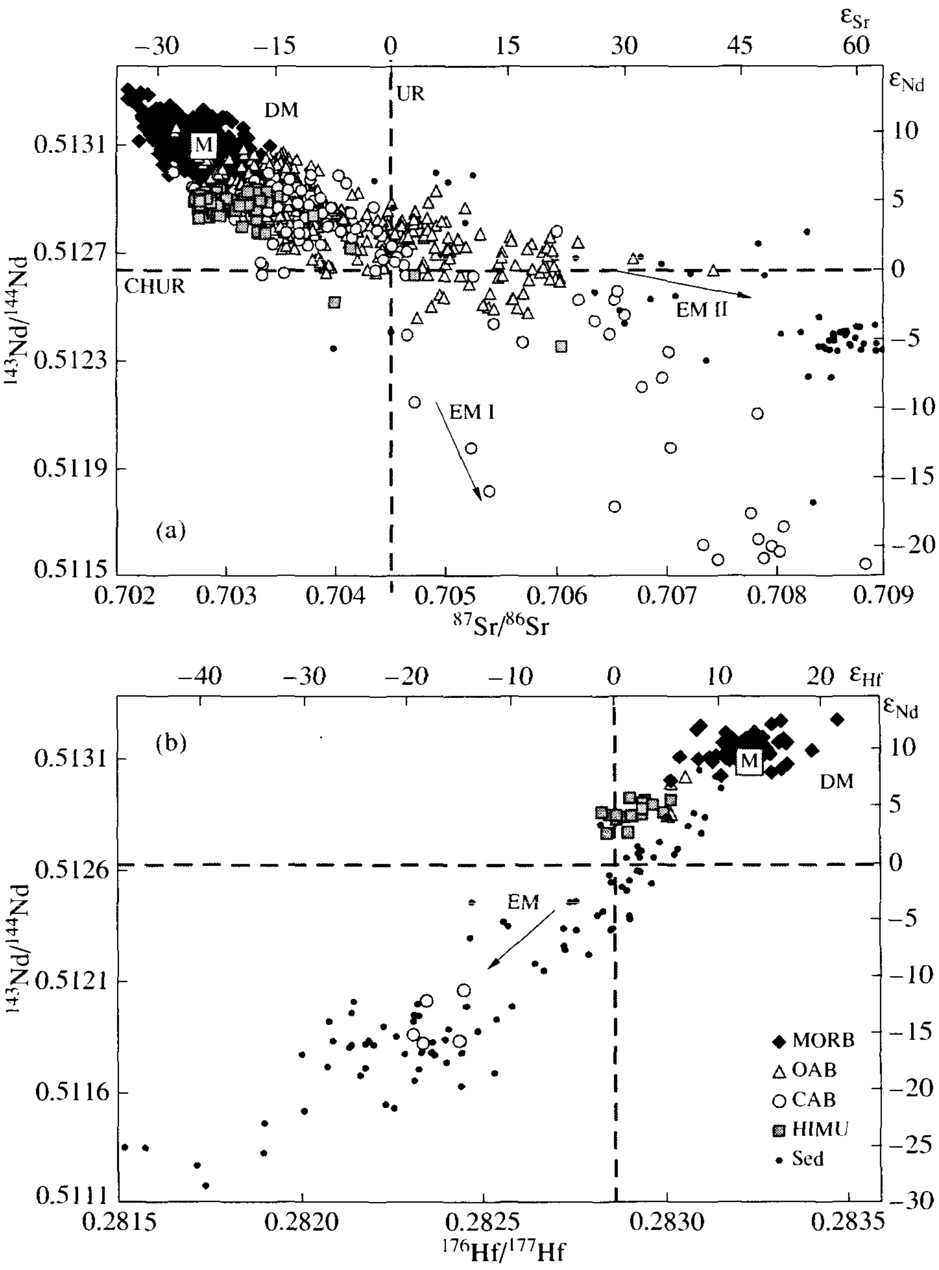

Fig. 1. Neodymium, strontium, and hafnium isotopic ratios in mid-ocean ridge basalts (MORB), oceanic alkali basalts (OAB), continental alkali basalts (CAB), basalts from high-U/Pb sources (HIMU), and various sedimentary rocks (Sed).

0.235 and $^{176}Hf/^{177}Hf = 0.28286$. This reference isotopic ratio is used for the calculation of ε_{Hf}. Although fewer data are available for hafnium isotopic compositions compared with neodymium and strontium, Fig. 1b displays a distinct positive correlation between the neodymium and hafnium isotopic ratios in various terrestrial rocks (Salters and Hart, 1991; Salters, 1996; Salters and White, 1998; Godfrey *et al.*, 1997; Schiano *et al.*, 1997; Nowell *et al.*, 1998; Vervoort *et al.*, 1999; Chauvel and Blichert-Toft, 2001; David *et al.*, 2001; Woodhead *et al.*, 2001), which is indicative of a positive correlation between Sm/Nd and Lu/Hf in the sources of these rocks.

In both diagrams (Figs. 1a, 1b), the isotopic compositions of the supposed primitive mantle ($\varepsilon_{Nd} = 0$, $\varepsilon_{Hf} = 0$, and $\varepsilon_{Sr} = 0$) (Tatsumoto *et al.*, 1981; Jacobsen and Wasserburg, 1980, 1983) fall within the mantle arrays. This circumstance has sustained over the past three decades the apparent correctness of the choice of these values for the origin of the isotopic coordinate system. However, as will be shown below, there are grounds to reanalyze, using the growing data base, the feasibility of the model created by DePaolo and Wasserburg (1976a, 1976b) and their talented followers.

CONTRADICTIONS IN THE CHONDRITIC MODEL

Although the hypothesis of the chondritic Sm–Nd isotopic composition of the primitive mantle (DePaolo and Wasserburg, 1976a, 1976b) has significant advantages for modeling exercises, it was never rigorously proved. In contrary, all the available information on the composition of extraterrestrial matter suggests its heterogeneity, both chemical and isotopic. The most convincing evidence for the heterogeneity of extraterrestrial matter was obtained by the investigation of the oxygen isotope systematics of chondrites and achondrites (Clayton and Mayeda, 1996, 1999). The accumulation of isotopic data for the terrestrial mantle-derived rocks also reveals new contradictions in the chondritic model. Let us consider the most important among them.

Productivity of Depleted and Undepleted Mantle

The depleted mantle with $\varepsilon_{Nd} > 0$ and $\varepsilon_{Hf} > 0$ appears to be the most productive melt source on Earth. This fact is rather peculiar, because it would be reasonable to expect that previous melting episodes have removed the least refractory mobile component from this mantle reservoir, and, if other conditions are the same, depleted sources must be less productive than undepleted ones.

In contrast, the primitive mantle with $\varepsilon_{Nd} = 0$, $\varepsilon_{Hf} = 0$, and $\varepsilon_{Sr} = 0$ do not systematically manifest itself as any rocks with a homogeneous isotopic composition. If the primitive mantle does exist and its fraction in the bulk mantle mass is between 1/2 and 3/4, as was estimated by various authors (Zindler and Hart, 1986; Allègre and Lewin, 1989; Hofmann, 1997), it would be reasonable to expect widespread occurrence of rocks with corresponding isotopic signatures. A stable cluster would have been observed in the isotopic coordinates formed by the rocks derived from the undepleted mantle. However, this is not the case. The geological community has tacitly recognized this fact by using the model age parameter T_{DM}^{Nd} (DePaolo, 1981) instead of T_{CHUR}^{Nd}, which was initially proposed by DePaolo and Wasserburg (1976a, 1976b).

Sources of Alkali Basalts

The majority of continental and oceanic alkali basalts are enriched in incompatible elements but appear to be derived from a depleted mantle source (Fig. 1). This contradiction is traditionally explained by the metasomatism of their mantle source immediately before the melting event (Menzies and Murthy, 1979). It is conceivable that metasomatism played a role in the formation of alkaline basaltoids, but it is not clear why lithophile trace elements are efficiently accumulated in the depleted mantle, whereas the primitive mantle remains untouched.

Isotopic Systematics of HIMU Basalts

Major contradictions in the geochemical models based on the chondritic composition of the Earth are related to the origin of HIMU basalts. These basalts were reported from both oceanic and continental settings, including several islands of French Polynesia archipelagoes in the Pacific (Woodhead, 1996; Chauvel *et al.*, 1992, 1997; Salters and White, 1998; Eiler *et al.*, 1997; Hauri and Hart, 1993; Nakamura and Tatsumoto, 1988; Schiano *et al.*, 2001), an island chain in the Atlantic stretching from St. Helena to the coast of Cameroon and extending into the continent (Graham *et al.*, 1992; Reisberg *et al.*, 1993; Ballentine *et al.*, 1997; Salters and White, 1998), the Comores Archipelago (Spath *et al.*, 1996; Reisberg *et al.*, 1993), the East African rift system (Simonetti and Bell, 1995), and the Hobbs Coast in the Pacific margin of Antarctica (Hart *et al.*, 1997). These rocks are invariably rift-related alkali basalts in continental settings, and the oceanic island chains with the HIMU signatures are mostly interpreted as hot spot tracks.

Similar to other alkali basalts, HIMU rocks are enriched in many lithophile elements, including U, Pb, Rb, Sr, and light rare earth elements. They were distinguished to a separate groups because of their high lead isotopic ratios, especially $^{206}Pb/^{204}Pb$, which are indicative of a high U/Pb ratio in their source, i.e., high $\mu = {}^{238}U/^{204}Pb$. Thus, their sources are distinctly enriched in the U–Pb isotopic system. As can be seen in Fig. 2, their μ value may be as high as 22, whereas the average mantle parameter is almost three times lower, about 8 (Zartman and Doe, 1981; Zartman and Haines, 1988).

This phenomenon is usually explained by the preferential removal of lead by island-arc magmas from descending oceanic plates in subduction zones (Hofmann, 1997; Rehkamper and Hofmann, 1997), which can produce local mantle domains with elevated U/Pb ratios. The strongest argument for this hypothesis proposed by Hofmann *et al.* (1986), Rehkamper and Hofmann (1997), and Miller *et al.* (1994) is the low Ce/Pb ratios of island-arc basalts compared with other oceanic rocks. Figure 3a presents the data from the above-cited studies and other sources (Edwards *et al.*, 1991; Gribble *et al.*, 1996; Thirwall *et al.*, 1996; Hoogewerff *et al.*, 1997; Kepezhinskas *et al.*, 1997; Stracke and Hegner, 1998; Shinjo, 1999; Turner and Foden, 2001) to illustrate that the Ce/Pb ratio of island-arc basalts is indeed systematically lower than that of MORB and continental and oceanic alkali basalts, including HIMU rocks. However, it is also evident from Fig. 3b that the generation of island-arc basalts cannot lead to an increase in the U/Pb ratio of the mantle, because their μ values are close to eight, i.e., similar to the average mantle composition. It is obvious that the extraction of any amount of island-arc melts from rocks with the same U/Pb ratio cannot significantly change this parameter.

As can be seen in Fig. 3b, the U/Pb ratio of MORB and continental and oceanic alkali basalts increases

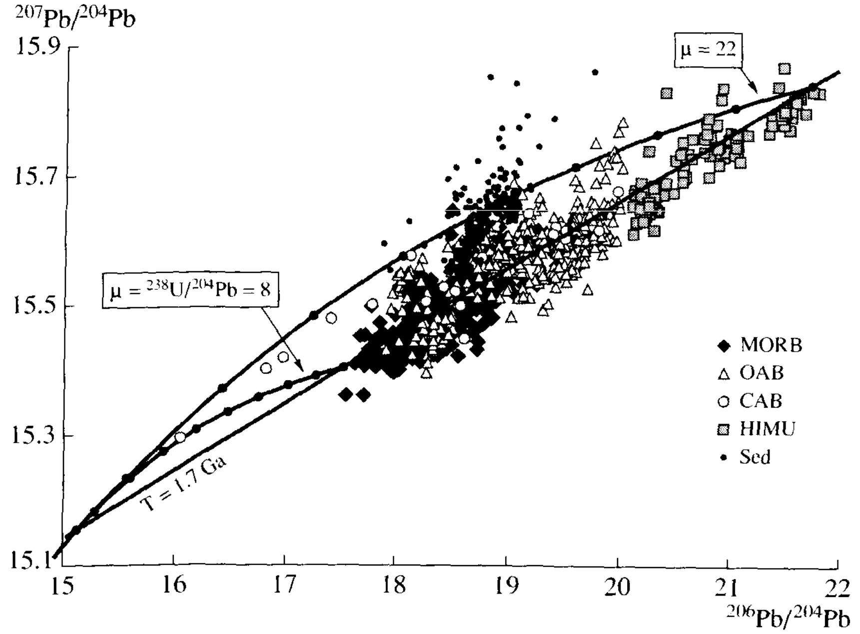

Fig. 2. Lead isotopic ratios in the same rocks that are shown in Fig. 1. HIMU basalts are distinguished arbitrarily by the boundary $^{206}Pb/^{204}Pb > 20$.

with increasing concentrations of uranium and lead, i.e., with increasing degree of lithophile element enrichment. In particular, according to the data presented in Fig. 3b, the average $^{238}U/^{204}Pb$ ratio of HIMU basalts is 34 ($n = 69$), which is in agreement with the high μ composition of their source (Fig. 2). The enrichment of the sources of HIMU basalts in the U–Pb system is in conflict with their Sr–Nd isotopic systematics (Fig. 1a), which is suggestive of their derivation from a depleted source ($\varepsilon_{Nd} = +5.1 \pm 0.9$ and $\varepsilon_{Sr} = -22 \pm 6$).

This is another major contradiction of modern isotopic geodynamics.

Imbalance of the Crust–Upper Mantle System

Mass balance calculations for the Sm–Nd isotopic systems of the crust and mantle constrain the mass fraction of the depleted mantle as 1/4–1/5 of the bulk mantle (Zindler and Hart, 1986; Allègre and Lewin, 1989; Hofmann, 1997). Only in such a case, the change in the Sm/Nd ratio of the mantle due to crust extraction could provide the difference of 8–12 between the observed ε_{Nd} values of the DM and CHUR.

In order to illustrate this point, Fig. 4 shows the results of numerical simulation of continental crust extraction from the mantle. The input data for these calculations are given in the table. The rate of crust growth was taken to vary with time (Fig. 4a) in accordance with the inferences by Taylor and McLennan (1985). When the primordial mantle with Sm/Nd = 0.325 produces crustal material with Sm/Nd = 0.219 (table), the Sm/Nd ratio of the residual depleted material increases to a variable degree depending on the amount of the extracted crustal component. Therefore, the present-day $^{143}Nd/^{144}Nd$ ratio of the DM depends on its volume, i.e., on whether the crust was extracted from the bulk mantle or its small part.

As can be seen in Fig. 4a, if the crust were extracted from the bulk mantle, the resulting shift in ε_{Nd} would be no higher than 1.5. If half of the mantle were involved, the effect would be 3 in ε_{Nd}. If 25% of the CHUR-like mantle served as a source of the Earth's crust, the average present-day ε_{Nd} value of the depleted mantle must differ from that of the primitive mantle by 7.2. This estimate approaches the common isotopic parameters of MORB, although it is still somewhat too low (Fig. 4a). Since the mass fraction of

Input data for the numerical simulation of crust extraction from the Earth's mantle

Element (ppm), ratio	Primitive mantle (McDonough and Sun, 1995)	Continental crust (Taylor and McLennan, 1985)
Sm	0.406	3.5
Nd	1.25	16
Sm/Nd	0.325	0.219
Rb	0.6	32
Sr	21	260
Rb/Sr	0.029	0.12
Lu	0.0675	0.30
Hf	0.287	3.0
Lu/Hf	0.235	0.10

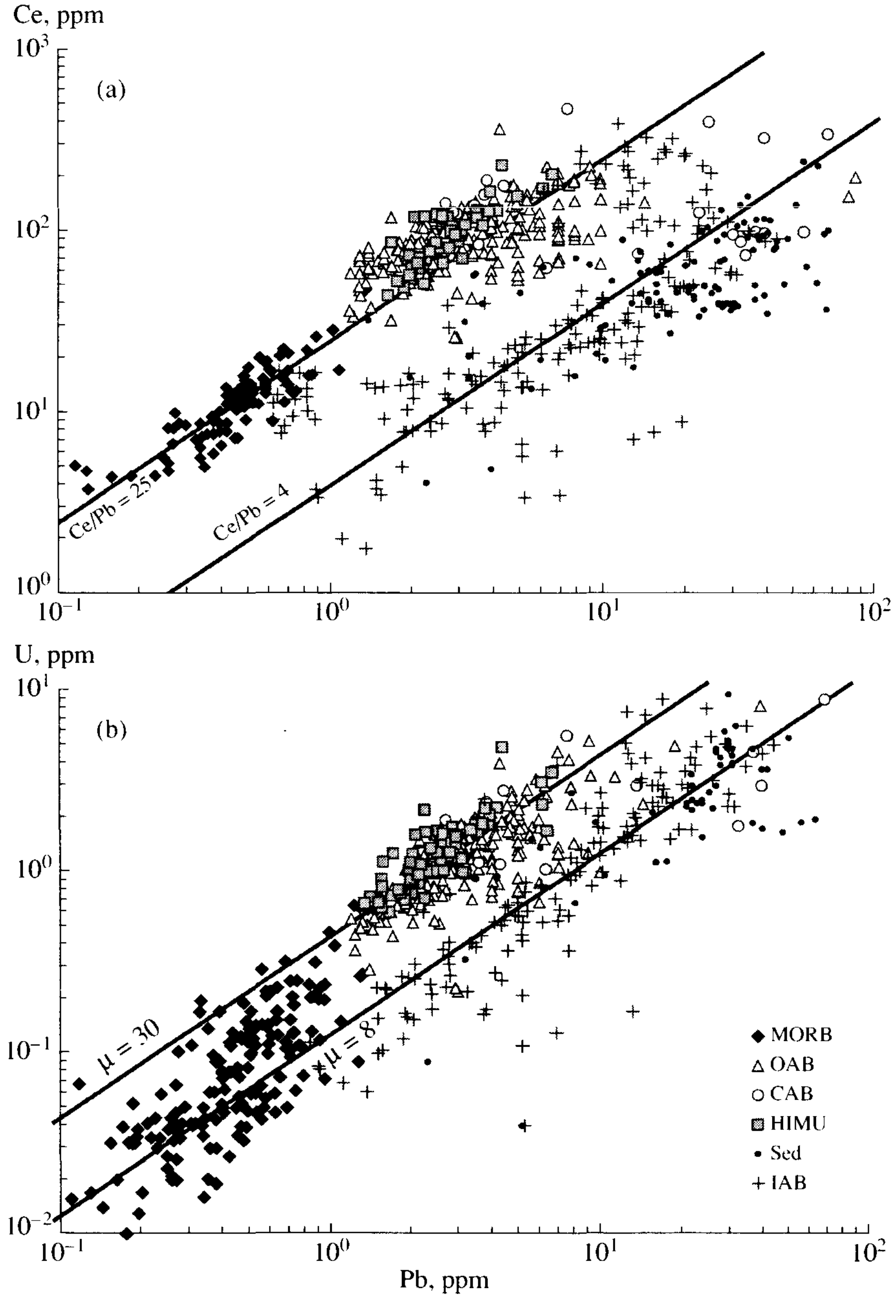

Fig. 3. Variations in the concentrations of cerium, lead, and uranium in the same rocks that are shown in Fig. 1 and in island-arc basalts.

the upper mantle (to the 660 km seismic discontinuity) is 27% of the bulk mantle, this coincidence intrigued many researchers and allowed them to correlate the geophysical upper mantle with the geochemical depleted mantle, which is now universally accepted.

Strictly speaking, in order to provide the observed value ε_{Nd} = 9–10 in the model DM, its mass fraction must be 20–21% of the bulk mantle. However, the Sm–Nd balance between the crust, primitive mantle, and depleted mantle is not consistent with other isotopic systems, for instance, the Rb–Sr system. Figure 4b shows that in the case of crust formation from one-fourth of the mantle, there is not enough rubidium even at its complete extraction. This imbalance problem has long been recognized (Taylor and McLennan, 1985) and concerns not only rubidium—there are not enough lead and uranium in the upper mantle to produce the continental crust. In order to balance the concentrations of Rb, Pb, U, and some other elements between the crust, primitive mantle, and depleted mantle, it is necessary to suppose that the whole mantle was involved in the formation of the crust rather that its upper part only.

Sm–Nd Isotopic Systematics of Basic Rocks

The chemical properties of samarium and neodymium are very similar. Because of this, the combined partition coefficients of Sm and Nd during partial melting of peridotites differ probably by no more than 10–20% (Shimizu, 1980). This means that, at low degrees of partial melting, the Sm/Nd ratio of the melt can differ from that of the source by no more than 10–20% (Gast, 1968). At higher degrees of melting of about several tens of percent, which probably corresponds to the formation conditions of tholeiitic and ultrabasic melts, the liquids are only slightly different from the source rocks with respect to the Sm/Nd ratio. Therefore, present-day melts derived by high degrees of melting of the primitive mantle must be similar in composition to the CHUR reservoir, i.e., Sm/Nd $\approx$ 0.325 and ^{143}Nd/^{144}Nd = 0.512638 ($\varepsilon_{Nd} \approx 0$).

Differentiation processes complicate these relationships.

The general behavior of the Sm–Nd isotope system during partial melting is shown in Fig. 5. Line *1* corresponds to the results of differentiation of the primary source *P* to enriched (*E*) and depleted (*D*) compositions at a certain time in the past. The accumulation of ^{143}Nd shifted these rocks to the present-day state shown by line *2*. All the points corresponding to enriched and depleted rocks (*E* and *D*) plot along a single line (isochron), which passes through the point of the initial primitive source (*P*). The recent process of *P* differentiation is shown by line *3*. Any mixture of enriched and depleted rocks of the same age must lie in these coordinates on the line passing through *P* (Langmuir *et al.*, 1978).

The higher the degree of melting in the primitive source, the closer lie points *E* and *D* to point *P*. The model of the chondritic primitive mantle composition implies that many tholeiitic basalts of ocean islands (plume or hot-spot basalts), which contain a considerable contribution from the lower undepleted mantle (Zindler and Hart, 1986; Allègre and Lewin, 1989; Hofmann, 1997), must plot near the CHUR composition in Fig. 5.

The same reasoning can be applied to the Lu–Hf system.

Figure 6a shows the observed isotopic compositions of oceanic basalts and sediments in the same coordinates. The data for oceanic basalts form a distinct trend, which goes surprisingly far from the point of the model primitive mantle composition according to DePaolo and Wasserburg. None of the 1158 points from our database on oceanic basalts plots near the CHUR. This conclusion remains true if all 2788 points corresponding to basic and ultrabasic terrestrial rocks are plotted in Fig. 6a.

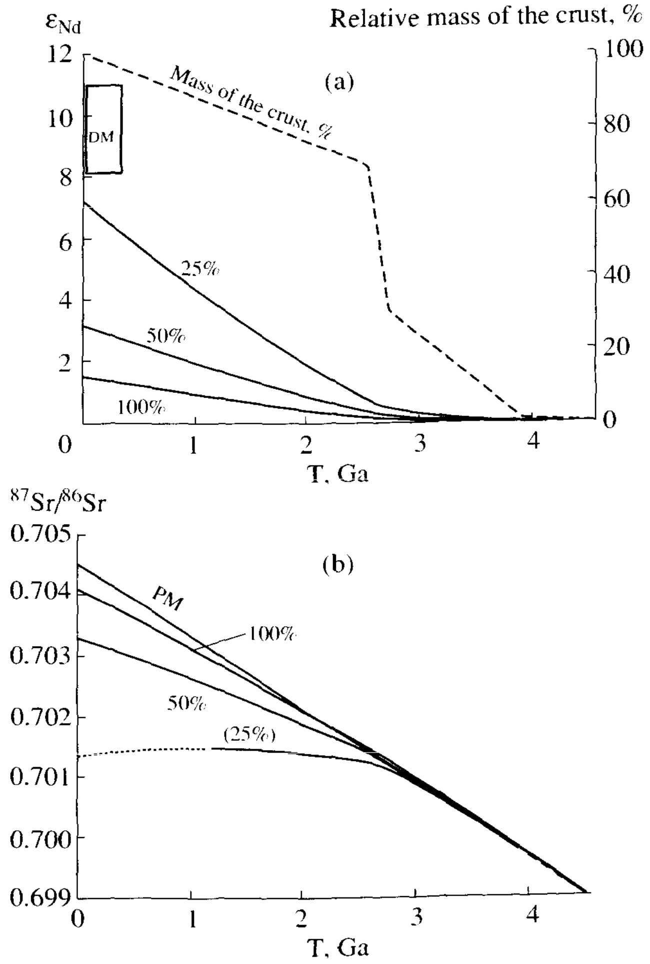

Fig. 4. Examples of the numerical simulation of changes in the (a) neodymium and (b) strontium isotopic compositions of the depleted mantle in response to the extraction of the continental crust. The dashed line shows the growth trend of the crustal mass. Also shown is the DM field corresponding to mid-ocean ridge basalts. Three variants of calculations are given: extraction from the bulk mantle volume (curve labeled 100%), half of the mantle (50%), and one-fourth of the mantle (25%). In the latter variant, there is not enough rubidium for crust formation, and the model curve 25% is truncated at about 1.1 Ga.

The same relationships are observed in the Lu–Hf system (Fig. 6b). The only significant difference between Figs. 6a and 6b is in the number of points: there are much fewer hafnium isotopic data compared with neodymium. Nonetheless, Fig. 6b also shows a distinct trend formed by oceanic basalts, and this trend is far from the point of the average chondrite composition (CHUR in Fig. 6b).

The data shown in Fig. 6 may imply that (1) all the known mantle-derived igneous rocks come from the depleted mantle, whereas the primitive mantle is absolutely inert as a magma source, or (2) the Sm/Nd and Lu/Hf ratios of the primitive mantle are not identical to those of the CHUR.

According to currently accepted models of mantle structure (Zindler and Hart, 1986; Allègre and Lewin, 1989; Hofmann, 1997), most igneous rocks are derived from its depleted part, but neither of these models pos-

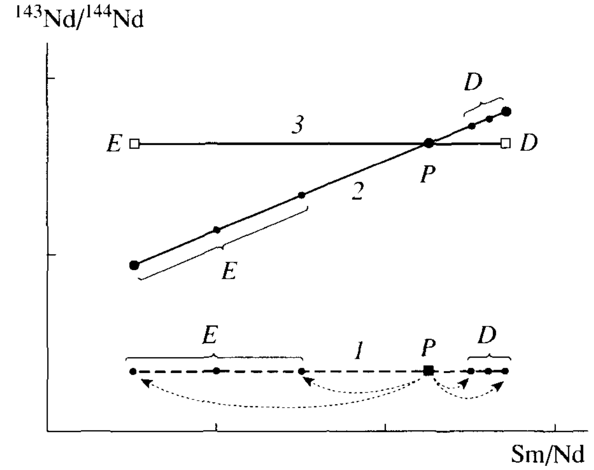

Fig. 5. Relationships between the primitive (*P*) source and enriched (*E*) and depleted (*D*) rocks derived from it. Line *1* shows the model of formation of enriched rocks *E* (with low Sm/Nd) and complementary depleted rocks *D* from source *P* by variable degree of melting at some time moment in the past. All the isotopic ratios change with time owing to the decay of ^{147}Sm to ^{143}Nd, and these rocks are represented now by line *2*. It would be more correct to plot $^{147}Sm/^{144}Nd$ along the x axis, but this ratio differs from Sm/Nd by an almost constant value of 0.6046. Any mixtures of *E* and *D* also form lines passing through point *P*. Line *3* simulates a present-day differentiation process of in source *P*. Note that both the straight lines pass through point *P*, and the higher the degree of melting, the smaller is the distance between points *E* and *D* and *P*.

tulates complete isolation of the lower and upper mantle. But such a conclusion follows from Fig. 6, if the chondritic composition of the primitive mantle is accepted. A suggestion on the absence of mass exchange between the lower and upper mantle leads to insurmountable physical contradictions (Morgan, 1998). It is known that convective heat transfer is much more efficient than conductive heat transfer. Therefore, if convective heat transfer occurred separately in the lower and upper mantle without mass transfer across their boundary, heat would have accumulated and temperature would have increased in this zone. The inevitable melting of rocks would have resulted in mechanical movement, i.e., would have destroyed this thermal barrier in the mantle. Seismic tomography (Yung and Nataf, 1988; Rubie and van der Hilst, 2001) also suggests significant involvement of the lower mantle in geodynamic processes expressed on the surface.

Thus, the data presented in Fig. 6 indicate that there are probably no sources in the mantle with the CHUR compositional characteristics.

Sm/Nd AND Lu/Hf RATIOS OF THE PRIMITIVE MANTLE

Contradictions related to the assumption on the strictly chondritic Sm/Nd and Lu/Hf values in the Earth's primary mantle were discussed in the previous section. They motivated our efforts to make more adequate estimates of these ratios and corresponding Nd and Hf isotopic compositions. This problem can be solved using the data shown in Fig. 6.

Assuming that the pristine isotopic compositions of neodymium and hafnium in the solar system were largely homogeneous, the point of the primitive mantle must be sought on the geochron in both the isotopic systems (line T = 4.56 Ga in Fig. 6). On the other hand, when we discussed Fig. 5, it was inferred that the primitive mantle lies most likely on the trend formed by oceanic basalts in Fig. 6. Thus, the target point is situated at the intersection of the geochron and the mantle array in Fig. 6, and the most probable point is denoted as *M* and has the following parameters:

$\varepsilon_{Nd} = +9$, $^{143}Nd/^{144}Nd = 0.51310$, Sm/Nd = 0.350;
and $\varepsilon_{Hf} = +13$, $^{176}Hf/^{177}Hf = 0.28323$, Lu/Hf = 0.264.

A realistic uncertainty estimate of ±1 in ε_{Nd} and ε_{Hf} corresponds to uncertainties of ±0.8% in the Sm/Nd and Lu/Hf ratios.

The negative correlation between the neodymium and strontium isotopic ratios allows us to determine the Rb–Sr parameters of the primitive mantle (point *M* in Fig. 1a): $\varepsilon_{Sr} = -24$ and $^{87}Sr/^{86}Sr = 0.7028$. Using Eq. (2) we obtain $(Rb/Sr)_{PM} = 0.020$ for the primitive mantle.

The Sm/Nd ratio is strongly correlated with other lanthanide proportions. In particular, the obtained Sm/Nd value for the primitive mantle can be used to estimate its La/Lu ratio and construct the chondrite-normalized spectrum of rare earth elements. Figure 7a shows covariations of Sm/Nd and $(La/Lu)_n$ for oceanic basalts. As expected, the CHUR point with the parameters Sm/Nd = 0.325 and $(La/Lu)_n = 1.0$ plots on the correlation line. The value Sm/Nd = 0.350 determined above for the primitive mantle allows us to obtain from this diagram $(La/Lu)_n = 0.7$. Using the estimated proportions of the four rare earth elements, the combined spectrum can be constructed (Fig. 7b).

The primitive mantle composition estimated in this paper in the Sm–Nd, Lu–Hf, and Rb–Sr isotopic systems resolves all the contradictions of isotopic geodynamics highlighted in the previous section. There is no need to answer the question, why the primitive mantle is magmatically dead; we can determine which rocks are most similar to it with respect to Nd, Hf, and Sr isotopic parameters using Figs. 1 and 6.

We come now to a sound conclusion that the sources of alkaline and HIMU basalts are variably enriched in incompatible elements and have elevated La/Lu (low Sm/Nd) ratios in comparison with the primitive mantle. There remains the possibility that the sources of these rocks underwent metasomatic alteration but this is not strictly required for almost all alkali basalts.

If our hypothesis is correct, changes in the Sm/Nd, Lu/Hf, and Rb/Sr ratios in the depleted mantle caused by crust extraction throughout the Earth history have

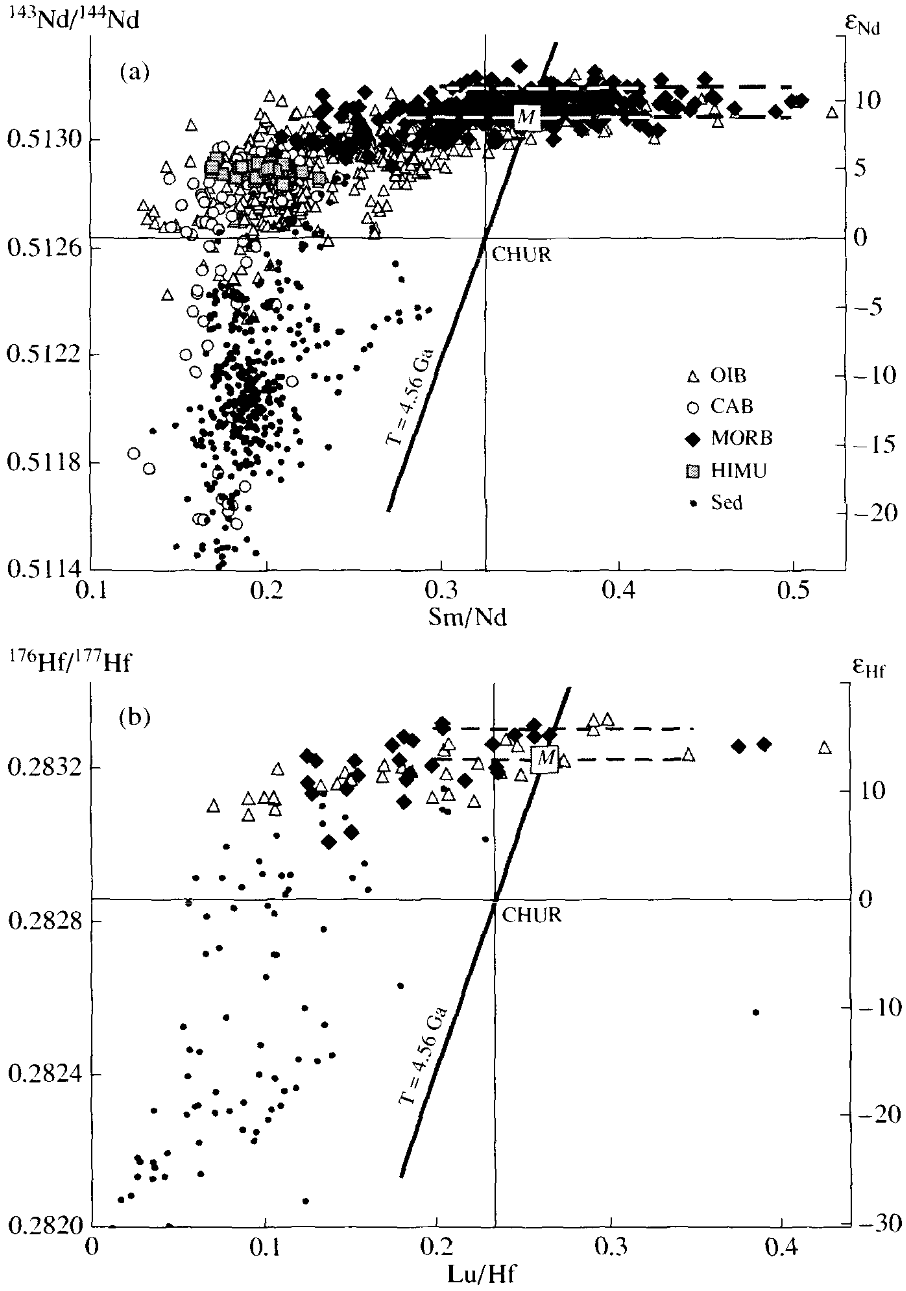

Fig. 6. Correlation of neodymium isotopic composition with (a) Sm/Nd ratio and (b) hafnium isotopic composition and Lu/Hf ratio for mid-ocean ridge basalts (MORB), intraplate oceanic basalts (OIB), continental alkali basalts (CAB), HIMU basalts, and terrigenous sedimentary rocks (Sed). The bold solid line corresponds to the geochron (4.56 Ga) passing through the CHUR point. Other symbols and sources of data are given in the text.

made only a minor contribution to the Nd, Hf, and Sr isotopic variations in modern mantle rocks in comparison with their observed isotopic heterogeneity. In the light of the results presented above, the reasons for the isotopic variations in mantle-derived rocks deserve a more comprehensive analysis and a special publication. Only some general points are mentioned here.

In agreement with the previous suggestions (Zindler and Hart, 1986; Allègre and Lewin, 1989; Hofmann, 1997; DePaolo and Wasserburg, 1976a, 1976b), depleted mantle sources are characterized by higher neodymium and hafnium isotopic ratios and lower strontium isotopic ratios compared with the primitive mantle composition. They are plotted in Fig. 1a above and to the left of point *M*, and in Figs. 1b and 6, above and to the right of it. However, in contrast to the CHUR model, the range of isotopic variations in the depleted mantle is rather narrow. The horizontal dashed lines in Fig. 6 are the limits of the calculated variations in the neodymium and hafnium isotopic ratios of the mantle

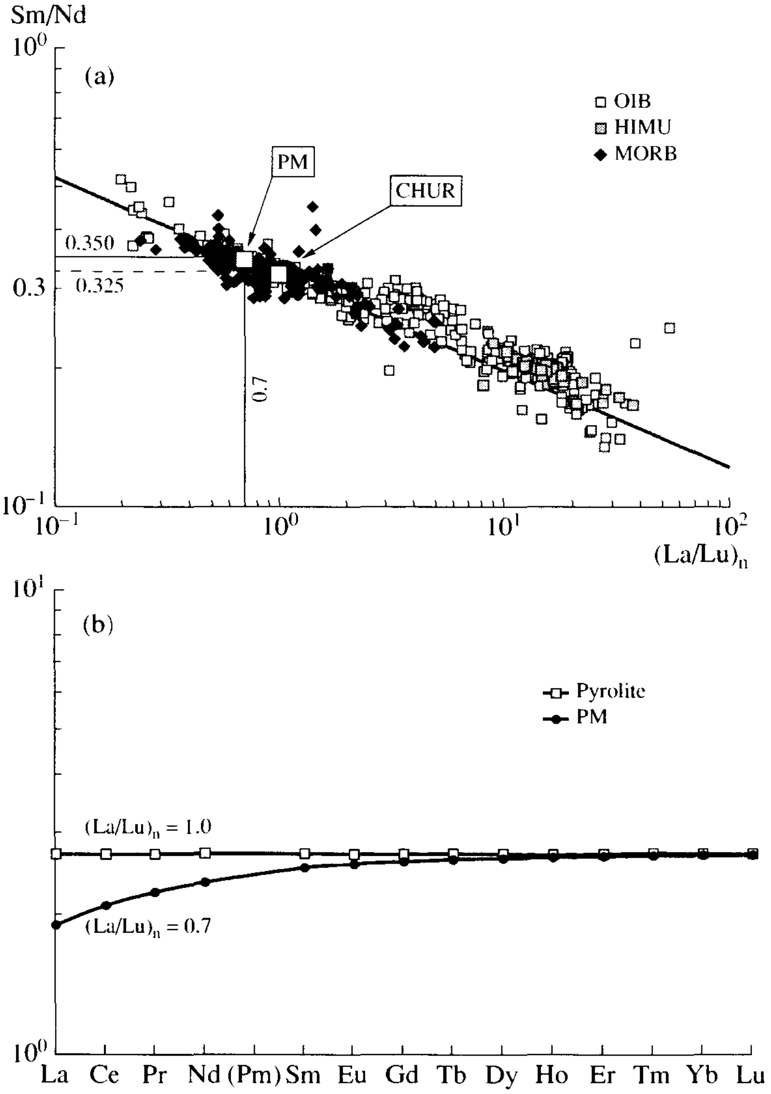

Fig. 7. Generalized diagram illustrating the procedure of determination of the chondrite-normalized REE spectrum of the primitive mantle. (a) Correlation between the Sm/Nd ratio and the chondrite-normalized La/Lu ratio in mid-ocean ridge basalts (MORB), intraplate oceanic basalts (OIB), and HIMU basalts. The observed correlation establishes a link between La/Lu and Sm/Nd values. (b) Chondrite-normalized spectrum of the primitive mantle (PM) compared with the pyrolite composition (McDonough and Sun, 1995).

related to crust extraction from the whole mantle. Theoretically, the variably depleted sources must occur between these two lines. If the observed scatter of neodymium isotopic ratios were much smaller than this range, it could be concluded that the Earth's crust was rather uniformly extracted from the mantle material or the depleted mantle were effectively homogenized. The scatter in the isotopic compositions of the rocks with Sm/Nd values similar to that of point *M* (Fig. 6a) indicates that this is not the case. Possible variations in the degree of mantle depletion during the formation of the crust could give rise to significant isotopic variability. This is probably reflected in the trends displayed in Fig. 6, because they are apparently somewhat wider than calculated ranges of 2 units in ε_{Nd} and 3 units in ε_{Hf}. Some mantle rocks are slightly depleted, while others are stronger depleted; in general, the scatter of points suggests that the mantle is variably depleted, or, in other words, the depleted mantle does not make up the whole mantle.

CONCLUSIONS

There are no mantle-derived rocks similar to the CHUR with respect to both the Sm/Nd and $^{143}Nd/^{144}Nd$ ratios, which is probably indicative of the absence of such material on Earth.

The hypothesis of the chondritic Sm/Nd and Lu/Hf ratios for the Earth's primitive mantle (DePaolo and Wasserburg, 1976a, 1976b; Jacobsen and Wasserburg, 1980, 1983; Tatsumoto *et al.*, 1981) leads to a number of contradictions, which have not been resolved during the past three decades of extensive isotopic investigations. These contradictions can be eliminated by assuming a small difference between the compositions of the primitive mantle and chondrites: by 8% for the Sm/Nd ratio and 12% for Lu/Hf. The supposed present-day composition of the primitive mantle in the Sm–Nd, Lu–Hf, and Rb–Sr isotopic systems is the following:

$\varepsilon_{Nd} = +9$ $^{143}Nd/^{144}Nd = 0.51310$ $Sm/Nd = 0.350$ $^{147}Sm/^{144}Nd = 0.2116$

$\varepsilon_{Hf} = +13$ $^{176}Hf/^{177}Hf = 0.28323$ $Lu/Hf = 0.264$ $^{176}Lu/^{177}Hf = 0.0375$

$\varepsilon_{Sr} = -24$ $^{87}Sr/^{86}Sr = 0.7028$ $Rb/Sr = 0.020$ $^{87}Rb/^{86}Sr = 0.0572$

The uncertainty in the isotopic composition of neodymium can be up to ±1 in ε_{Nd}.

The isotopic effect in the Sm–Nd, Lu–Hf, and Rb–Sr systems from the extraction of the Earth's crust from the mantle material is much smaller than the observed isotopic variations in mantle-derived rocks.

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