

Alkaline Magmatism and Enriched Mantle Reservoirs: Mechanisms, Time, and Depth of Formation

L. N. Kogarko

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

Received May 27, 2005

Abstract—Alkaline magmatism has occurred since 2.5–2.7 Ga and its abundance has continuously increased throughout the Earth's history. Alkaline rocks appeared on the Earth with changes in the geodynamic regime of our planet, i.e., when plume tectonics was supplemented by plate tectonics. Global-scale development of plate tectonics at the Archean–Proterozoic boundary initiated subduction of already significantly oxidized oceanic crust enriched in volatiles and large-scale mantle metasomatism caused the formation of enriched reservoirs as sources of alkaline and carbonatite magmatism. Study of metasomatized mantle material showed the occurrence of traces of primary carbonatite melts, which are strongly enriched in rare elements, according to ion-microprobe analyses. The results obtained allowed us to propose a new two-stage genetic model for Ca-rich carbonatites including (1) metasomatic wehrlitization and carbonatization of mantle material and (2) partial melting of wehrlitized mantle with formation of carbonate-rich melts or three immiscible liquids (at high alkali contents), i.e., silicate, carbonatitic, and sulfide (at high sulfur activity).

DOI: 10.1134/S0016702906010022

INTRODUCTION

The appearance of alkaline magmatism in the Earth's history is related to the initiation of plate tectonics and, as a consequence, of large-scale mantle metasomatism, which led to the formation of enriched mantle reservoirs. Ion-microprobe studies of products of carbonate metasomatism in mantle material from some localities demonstrated that the metasomatizing mantle fluids had very high rare-element concentrations, which are comparable to those in the Lovozero giant deposit and some carbonatites. The results allowed us to propose a new two-stage genetic model for Ca-rich carbonatites and related deposits. According to current data of seismic tomography and heat flow, the metasomatizing fluids enriched in rare elements were probably derived from plumes ascending from anomalous mantle existing in the Earth's interior.

ENRICHED RESERVOIRS IN THE EARTH'S HISTORY

Alkaline igneous rock associations are the most productive for various valuable elements. Modern data on geochemistry, isotopy, and seismic tomography show that alkaline magmas were generated from enriched mantle reservoirs. Giant complex deposits of rare metals (Nb, Ta, Zr, REE, Sr, Ba), radioactive elements, phosphorus, and aluminum are concentrated in alkaline rocks. Almost 100% of world reserves of magmatic Sr and >85% of Nb, Zr, and Ce are related to alkaline igneous rocks and carbonatites. Demand for these elements continuously increases, particularly in industrial coun-

tries; thus, alkaline rocks can be regarded as materials of the future.

The alkaline magmatism is most typical of stable regions (platforms) and is controlled by rift structures and zones with abruptly decreasing thickness of the continental lithosphere. Note, however, that alkaline rocks originate in almost all geodynamic settings, including oceanic ones. Evolution of the magmatic regimes of the Earth is primarily determined by global differentiation of the mantle, as the thickest layer in the Earth's interior.

The postaccretionary history of the Earth comprised multiple episodes of mantle melting resulting in the formation of continental and oceanic crust. During this process, the mantle gradually lost CaO, Al₂O₃, TiO₂, rare lithophile elements and transformed into strongly depleted substrate, which could produce only highly magnesian magmas depleted in rare elements. However, such evolution is not typical in the Earth's history. On the contrary, many data show enrichment of mantle magmas (basalts and picrites) in Ti, LREE, and incompatible elements [1].

Isotopic studies show the existence of mantle reservoirs significantly enriched in rare elements, which could not be possible in the model of continuous global melting of mantle in the postaccretionary Earth evolution. The ideas developed in the last decades suggested active mantle–crust interaction [2] with large-scale exchange of materials and formation of the mantle reservoirs enriched in rare elements. The appearance of alkaline magmatism with extreme concentrations of

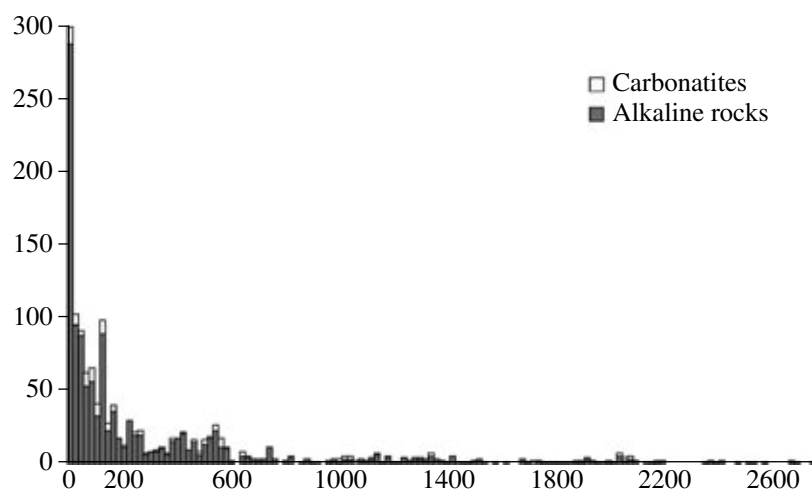


Fig. 1. Distribution of intensity of continental alkaline magmatism with time.

rare elements is undoubtedly related to the generation of such zones in the mantle.

The analysis of literature and our data [3] shows that alkaline magmatism appeared in the Earth's history at about 2.5–2.7 Ga (Fig. 1), and alkaline rocks older than 2.7 Ga are extremely rare. The figure shows continuously increasing activity (abundance and volume) of alkaline magmatism with the Earth's evolution. For example, the total volume of young platonolites in Kenya exceeds 50 000 km³ [4], which is much larger than the volume of alkaline rocks of all other geologic epochs. The increasing scale of alkaline magmatism with time was also noted by Lazarenkov [5]. A similar tendency is characteristic of the evolution of oceanic magmatism. The database for igneous rocks of oceanic islands and seamounts of the Atlantic Ocean, primarily of alkaline composition, helped us to reveal that the intensity of intraplate magmatism significantly grows with time. The appearance of alkaline rocks at the Archean–Proterozoic boundary coincides with several global geologic events, and this boundary became an important benchmark in the Earth's history.

Most researchers believe that the geodynamic regime of our planet changed at this boundary, and plume tectonics was supplemented by plate tectonics [6].

The oxygen atmosphere of the Earth originated particularly at this boundary [7], generally due to hydrogen dissipation to cosmic space and the activity of living organisms. At the earlier stages, the Earth's atmosphere consisted of CH₄, H₂, and CO₂ [8].

At the Archean–Proterozoic boundary, the continental crust extensively grew and stable, cratonic regimes were developed.

The oxygen-bearing atmosphere caused the formation of oxidized marine sediments (jaspilites, carbonates) and the oxidation of paleosoils [7]. Note that the Archean giant sedimentary pitchblende and pyrite deposits of the Witwatersrand type have no analogues

in the later epochs, because the minerals composing their ores are unstable in an oxygen atmosphere [7, 9]. Global development of plate tectonics at the Archean–Proterozoic boundary initiated the subduction of already significantly oxidized oceanic crust with elevated contents of volatiles (generally H₂O and CO₂), which, in turn, resulted in the involvement of these components in mantle cycles. Active mantle–crust interaction increased the concentrations of volatile components in the mantle, which had lost these components during high-temperature accretion at the earlier stages of Earth evolution. Intensive studies of the mantle fluid regime revealed mantle heterogeneity with respect to oxidation–reduction potential. According to recent data [11], oxygen fugacity in the mantle substrate varies within five–six logarithmic units around the quartz–fayalite–magnetite (QFM) buffer system. However, despite the significant redox heterogeneity of the lithospheric and asthenospheric mantle of the Earth, there are some regularities. Most researchers accept the idea that the oldest Archean lithospheric mantle (a diamond source) had low *f*O₂ values. Diamonds are much older than host kimberlites [12–14], >3 Ga in some cases. They contain inclusions of Ni-free metallic iron [15], moissanite, magnesiowuestite [16], and methane [17], which indicates strongly reduced conditions in the old Archean mantle. These data are consistent with data on the V contents in Archean tholeiites [18] and the significant growth of the Ti/V ratio during differentiation caused by fractionation of pyroxenes concentrating reduced trivalent V. Our recent studies revealed the occurrence of Cu-bearing Fe–Ni alloys in the mantle, i.e., the phases composing the Earth's core [19]. Their stability requires very low oxygen fugacities, by three logarithmic units lower than the wuestite–iron buffer [20]. Such conditions probably existed in early geological history at about 4.6 Ga during the core formation. Arculus and Delano [10] experimentally determined the oxidation–reduction regime for mantle xenoliths

using electrochemical cells and demonstrated that low fO_2 values for some rocks and megacrysts in basalts are also close to the wuestite–iron buffer. On the contrary, Bullhaus [21] recently revealed the more oxidized state of most mantle peridotites (from -2 to 0 logarithmic units with respect to QFM), particularly the mantle rocks strongly modified by metasomatic processes (2 and higher logarithmic units relative to QFM). Island-arc andesites and basalts (+3 logarithmic units relative to QFM) closely related to the subduction of oceanic crust and the alkaline rock of oceanic island (+2 logarithmic units relative to QFM) are the most oxidized igneous rocks [21]. Our data demonstrate a significant degree of oxidation of the highly alkaline lavas of Trinidad Island [22] with the oxygen fugacity exceeding fO_2 of the QFM buffer by three orders of magnitude. Study of the oxidation degree of volcanic gases [8] determined fO_2 and CO/CO_2 at 0.01 and 0.03 respectively, which indicates high oxygen fugacities during magma formation in the modern mantle. All these data emphasize the significant heterogeneity of the mantle with respect to redox conditions, verify the existence of relicts of older reduced mantle domains within more oxidized mantle material, and may indicate global processes of mantle oxidation in the Earth's history.

Mantle oxidation might be generally caused by iron disproportionation into the Earth's core [23]. According to Galimov [23], about 95% of the iron core was formed over about 100 m.y. of the earliest evolution of the Earth. Further growth of the core by consumption of FeO from the mantle resulted in oxygen generation over the next 100–500 m.y. of the Earth's history in the amount sufficient for mantle oxidation to QFM buffer values. Some researchers believe and our calculations verify their ideas that subduction accompanied by influx of oxidized H_2O-CO_2 fluid into mantle cycles could also increase oxygen fugacity in mantle fluids. This process is distinctly pronounced in zones of global mantle metasomatism. A significant increase of volatile influx into the mantle due to the activation of subduction at the beginning of the Proterozoic stimulated large-scale mantle metasomatism, because the oxidized fluid phase ($H_2O + CO_2$) is capable of transporting great amounts of silicate material [24]. According to [25] and our calculations, annual addition of H_2O and CO_2 into mantle due to the subduction of oceanic crust with hydrous minerals and carbonates is 10^{14} g mol/y and 6×10^{12} g mol/y, respectively. Note that carbonatites containing 20% C compose no more than 6–27% in alkaline igneous associations. Relation of carbonatites with the oceanic crust recycling is verified by the wide scatter of δC_{13} values for carbonatite complexes worldwide [26]. Thus, changes in the geodynamic regime of the Earth and the strong activation of the mantle–crust interaction led to the global metasomatic migration of material and the formation of zones enriched in rare elements in the mantle substrate, a source of alkaline magmas. Coincidence of these events could not be accidental and prob-

ably indicates a basic relation of these processes. Alkaline igneous rocks appeared at the end of Archean as a result of the above events and were not abundant during the whole Proterozoic, at least until the end of the Vendian (Fig. 1). Some small peak occurred only at the end of the Middle Proterozoic, between 1300 and 1000 Ma. Instead, the activity of alkaline magmatism continuously increased from 600 Ma, with peaks at about 550, 400, and 250 Ma, and particularly strongly from 200–180 Ma, reaching the maximum at about 40 Ma in the Eocene. A similar increase in the abundance of alkaline rocks is also typical of individual continents, i.e., North and South America, Eastern Europe, Siberia, and Africa. The role of kimberlites, lamproites, and carbonatites also strongly increased since the end of the Ordovician with a maximum in the Late Cretaceous and Early Paleogene. It should be mentioned, however, that the primary distribution could be disturbed because of the significant consumption of old alkaline rocks of oceanic islands and seamounts in subduction zones. It primarily concerns the Mesozoic igneous rocks of the eastern Pacific Ocean. Thus, continental alkaline massifs are probably best preserved. If the subducted rocks could be taken into account, the temporal distribution of alkaline rocks would be less contrasting, but would not principally change. Hence, this distinctly heterogeneous distribution with a strong increase of alkaline rock abundance in the Phanerozoic requires some specific interpretation. Most alkaline rock massifs were emplaced in intraplate environments due to mantle plume activity. Only some of them are located at spreading axes above hot spots, e.g., the Azores archipelago in the Atlantic Ocean. According to seismic tomography data, there is a close relationship between descending slabs of the subducted oceanic lithosphere and nearby ascending mantle plume jets at the deep mantle level near the mantle–core boundary. As a result, even the volcanics emplaced within the lithospheric plates show isotopic and geochemical signatures of recycled crustal material, which was revealed, for example, for Hawaiian volcanoes [27]. One more suggestion should also be considered. It is possible that periods of the whole-mantle convection and two-layer convection (separately for the lower and upper mantles) alternated in the Earth's history. The two-layer convection dominated during epochs of assembly of supercontinents (Pangeas), while the whole-mantle convection operated during the supercontinental epochs and breakup initiation. The alkaline rocks appeared with the formation of the first (sufficiently well documented) Pangea-0 supercontinent. According to Ringwood's ideas [28], the slabs subducted during periods of two-layer convection could be retained at the upper and lower mantle boundary, where they could be entrapped by plumes. There is a dependence between mantle viscosity and convection structure, and probability of the whole-mantle convection increases with increasing viscosity caused by gradual cooling of the Earth. The whole-mantle convection is probably operating now,

while the two-layer convection was typical of the Late Archean, and plumes were initiated at the base of the transitional zone between the lower and upper mantles at depths of about 660–670 km. Significant changes in deep geodynamics are suggested at the end of the Neoproterozoic. They corresponded to the initiation of the Rodinia breakup (early Late Riphean) and may have been expressed in dominant whole-mantle convection. The latter may have further developed later, at 400–250 and, particularly, 200–180 Ma, during the epoch of the initiation of Wegener's Pangea breakup. According to seismic tomography data, many slabs of the subducted oceanic lithosphere (eastern Pacific periphery, Mongolia–Okhotsk and South Anui paleo-oceans [29]) began to reach at that time the D" layer at the mantle base and to stimulate plume ascent from this depth. Thus, the fluid-rich material from the mantle base (1000–1200 km), rather than from the lower/upper mantle boundary (670 km), could ascend to the surface.

The demonstrated increase in the activity and abundance of alkaline magmatism in the Earth's history may have been caused by the gradual involvement of progressively deeper mantle horizons into the whole-mantle convection and advection (plumes), progressively increasing material exchange between the Earth's surface and crust and its deeper interior due to recycling, and progressively increasing filtration of metasomatizing fluid flows through the mantle.

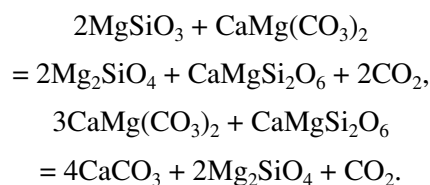
GLOBAL MANTLE METASOMATISM AND GENESIS OF ENRICHED MANTLE RESERVOIRS

Large-scale interstitial pellicular melting by the mechanism suggested by Ringwood [28] may have occurred as a geochemical consequence of the global degassing of the subducted material and the release of oxidized fluids (H₂O and CO₂). We imply that the melts enriched in H₂O and CO₂, generated at low-melting degree and capable of transporting great amounts of incompatible rare elements and alkalis, presented the main metasomatizing agent in the mantle. Experimental data show [30] that aqueous fluid can contain at high pressure a few tens of percent of alkali-rich silicates.

It was demonstrated earlier (e.g., [31]) that metasomatic processes play a highly important role in the generation of alkaline magmas. Strong enrichment of alkaline magmas in rare lithophile elements and depletion with respect to radiogenic isotopes can be accounted for only by the metasomatic influx of rare lithophile elements into zones of alkaline magma generation. This idea can be verified, for example, by our isotopic data [32] on the worlds largest alkaline complexes on the Kola Peninsula (Khibina and Lovozero massifs) accompanied by giant rare-metal deposits. These data show strong depletion of the initial mantle source of alkaline magmas with respect to rare elements. In the $\epsilon_{Nd}-\epsilon_{Sr}$ diagram, the rocks and ores of the Khibina and

Lovozero massifs fall within the field of depleted compositions [31, 32]. This paradox can only be explained by the very rapid addition of metasomatizing material strongly enriched in incompatible rare elements to the melted mantle domain when there was not enough time for the accumulation of radiogenic isotopes (⁸⁷Sr and ¹⁴³Nd), and the Sr and Nd isotopic ratios still corresponded to the initial depleted compositions. Recent detailed studies of mantle material from various regions [33, 34] and our data [3, 37] demonstrated the significant role of metasomatism in the geochemical history of the mantle. Crystallization of amphiboles, phlogopite, apatite, primary carbonates, minerals of the lindsleyite–mathiasite series, and other minerals concentrating rare elements is related to metasomatic reactions in mantle substrate, most likely, to low-degree melts. As was shown experimentally by Fransis [35], partial melting of strongly amphibolized metasomatized mantle can generate alkaline melts. High-alkali glasses in metasomatized mantle xenoliths were also described by Edgar [36]. When studying strongly metasomatized and carbonatized nodules from volcanics of the Montana Clara Islands (Canary Islands) and Fernando de Noronha (Brazil), we found glasses (in association with primary carbonates) corresponding in composition to phonolites and trachites oversaturated in alkalis. Thus, alkaline magmas could have been generated during the partial melting of metasomatized mantle.

Recently, we actively studied the processes of mantle carbonate metasomatism in various regions. In the oceanic mantle of some Atlantic islands [3, 37], we revealed primary carbonates developed metasomatically by the following reactions:



Metasomatic clinopyroxenes and olivines are products of these reactions. Using a CAMECA ion microprobe, we determined concentrations of metasomatic pyroxenes in oceanic and continental carbonatized mantle (Canary Islands, Fernando de Noronha, and East Antarctica). With the partition coefficients of rare elements in pyroxene–carbonate melt equilibria [38, 39], we calculated the concentrations of rare and rare earth elements in the metasomatizing mantle carbonate melts. Note that the average composition of the Lovozero massif accompanied by giant rare metal deposits fall within the interval of concentrations calculated for metasomatizing mantle fluids (Fig. 2). These data are consistent with the compositions of carbonate melts in the metasomatized mantle of some other regions [39]. All melts are enriched to a various degree in LREE and incompatible elements. This REE distribution (with LREE enrichment) indicates that metasomatic melt-fluids were generated in crystal melt equilibria, because

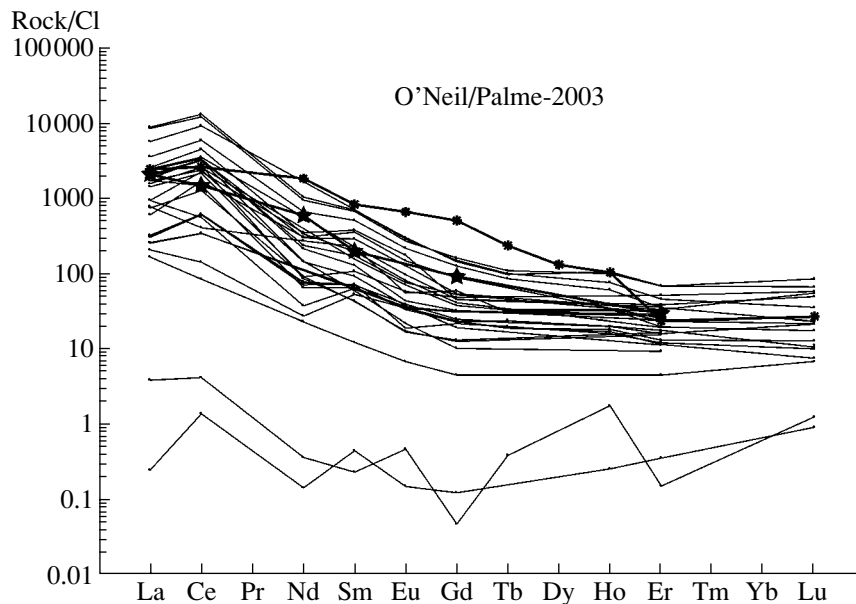


Fig. 2. Spidergram for the mantle metasomatizing melt-fluids (calculated by ion microprobe analyses of metasomatic clinopyroxenes of mantle rocks from Fernando de Noronha Island, East Antarctica, and Canary archipelago). Stars—average composition of rocks of the Lovozero alkaline massif, asterisks—average composition of carbonatites.

the LREE partition coefficients in most mantle rock-forming minerals, particularly in garnets, are notably lower than the HREE partition coefficients. Most calculated compositions of metasomatic melt-fluids show minima of HFSE (Ti, Zr, Nb) (Fig. 2). This is consistent with experimental data [38] on the low solubility of these elements in high-temperature carbonatite liquids. However, HFSE maxima (Ti, Zr) were revealed in some cases (Fig. 2), which could indicate alkaline carbonate-silicate compositions of metasomatizing agent, because HFSE solubility strongly increases in highly alkaline silicate melts [39]. Despite some differences in the compositions of metasomatizing melts, all of them are enriched in incompatible rare elements and LREE. Universal enrichment of mantle fluids in rare elements is a basic geochemical feature of the Earth's mantle.

The ascending mantle plumes induce low-degree melting of the surrounding mantle (particularly at the base of the plumes), which produces carbonate melts enriched in rare elements and volatile components. These melts have very low viscosities, rapidly penetrate to upper horizons, and metasomatically replace mantle peridotites (stage 1). Further ascent of the diapir causes the partial melting of metasomatized mantle and the generation of alkaline and carbonatite magmas (stage 2). The proposed model of the formation of enriched reservoirs is generally consistent with the geochemistry of metasomatizing melt-fluids, but requires very low melting degrees of mantle material. If the mantle source of giant rare-metal deposits of the Kola Peninsula was strongly depleted in rare elements [32], the mass of the depleted material producing metasomatizing fluids should be huge. It is more logical to suggest that the plume itself, significantly enriched in rare elements as

compared even to primitive mantle, was the source of rare elements for the giant alkaline intrusions. Let us consider these problems in the next section.

DEPTH OF FORMATION OF ENRICHED MANTLE RESERVOIRS

According to modern concepts, two global reservoirs, upper and lower, can be distinguished in the Earth's mantle. However, recent data of seismic tomography [40] indicate the occurrence of new structural heterogeneity in the lower mantle below about 1000 km until D" layer at 2300 km. P-wave velocities significantly decrease in this interval [40]. These data suggest the existence of three dynamic regimes in the Earth's mantle. The above heterogeneity continues over about two thirds of the transitional lower mantle-core layer (Fig. 3) and comprises 20–30% of the whole Earth's mantle. The heterogeneity is related to elevated viscosity and density of the material at the base of the lower mantle. The size and shape of this region (megaplume) may indicate the chemical heterogeneity of the lower mantle. If this seismic heterogeneity had thermal origin, it could not exist for a long time because of tremendous heat flux from the core. Density in the anomalous zone probably increases due to the decomposition of silicates and the formation of high-density oxides (magnesiowuestite, stishovite) at pressures >650 kbar. Crystallization of magnesiowuestite enriched in Fe is another mechanism of the formation of heavy mantle material. The suggestion of the existence of an anomalous layer in the lower mantle is consistent with modeling of the thermal regime of the Earth. The heat flux of the whole Earth is estimated at 44 TW; the heat flux of the crust is

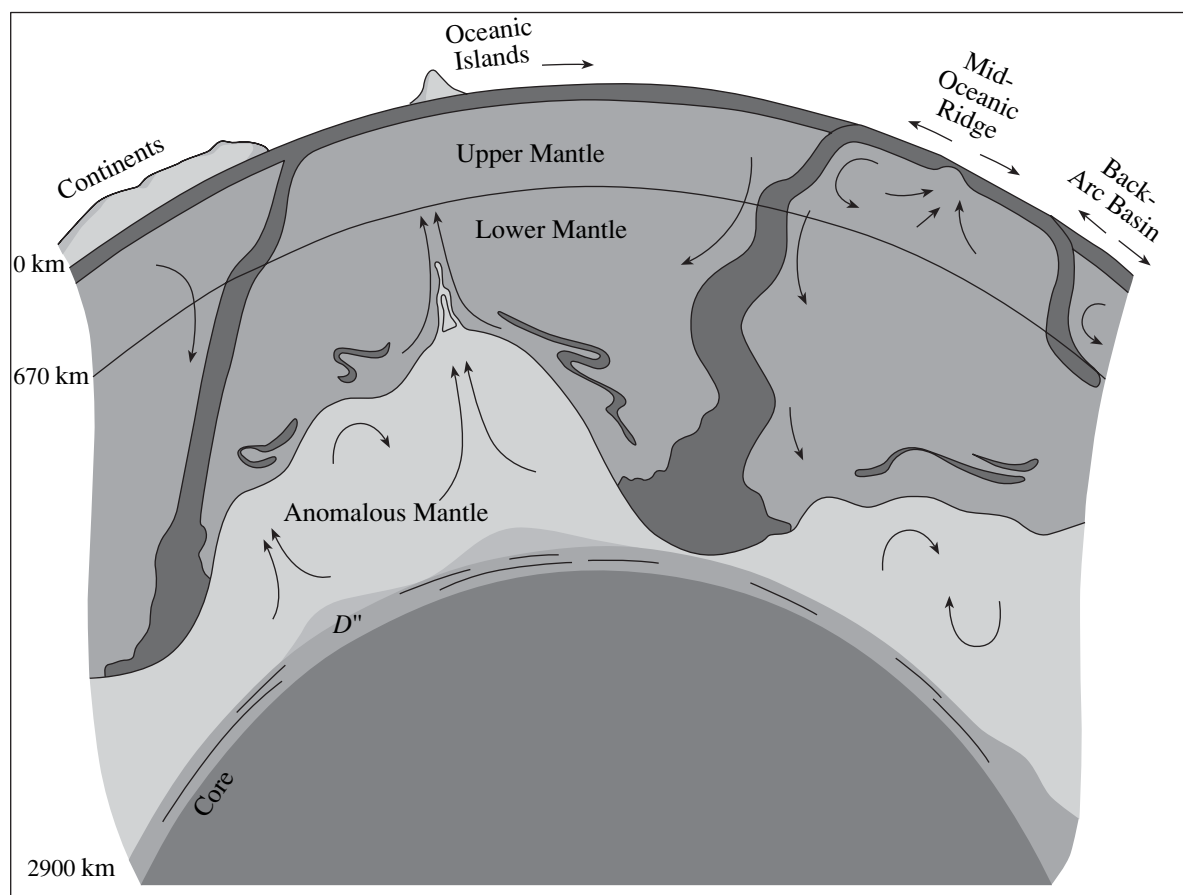


Fig. 3. Structural scheme of the Earth's upper and lower mantle (after [40]).

6 TW due to high concentrations of radioactive elements [40], and the remaining 38 TW should be supplied by the mantle and core. Even if the whole Earth was chondritic in composition, its heat flux would be only 31 TW [41]. It is established now that 25–90% of mantle substrate (MORB sources) is depleted in rare and radioactive elements, and, thus, heat flux of the Earth should be lower than 31 TW [41], but it is actually much higher (44 TW). Hence it follows that a layer producing huge heat amount corresponding to U concentration of 25.6 ppm should exist in the mantle [41].

The origin of this zone enriched in rare and radioactive elements in the mantle is not clear. A proposed model suggests the long-term development of a reservoir isolated since the early stages of the Earth's evolution and originating either during the evolution of the global magmatic ocean or by the recycling of Archean crust enriched in mafic components and incompatible rare elements. Elevated contents of radioactive elements should cause active heat generation and very high temperatures in the D'' zone. Under the effect of heat flow from the core, hot and dense material of the lower mantle could rise and produce superplumes, e.g., African or East Pacific. We also considered the possi-

bility of magma generation for the Kola alkaline igneous province from an anomalous zone in the lower mantle. According to [42], the total volume of alkaline rocks of the Khibina and Lovozero massifs is about 11 000 km³. Using the average contents of rare elements in these rocks (e.g., Zr and Th), we can estimate the volume of the primitive or depleted mantle as sources of these rocks. According to our isotopic studies [31, 32], the giant alkaline intrusions of the Kola Peninsula were generated from a mantle source depleted in rare elements. The further calculation showed that the volume of mantle material for the formation of the Khibina and Lovozero massifs should be about 3.7×10^6 km³ for primitive mantle and 3.8×10^7 km³ for depleted mantle. These volumes are not realistic and are comparable or even exceed the volumes of the largest mantle plumes. For example, the volume of the Siberian superplume is about 7×10^6 km³ [43]. Moreover, there is no geological evidence of the relation of the Kola alkaline province with any large plume. Thus, our calculations may indicate a much more enriched source of alkaline magmas for the Kola alkaline province. They could be derived from an anomalous layer of the lower mantle. General regularities in fractionation of rare and radio-

active elements in mantle reservoirs allow us to estimate the distribution of incompatible elements in the anomalous layer. As was mentioned above, U content in the anomalous zone is 25.6 ppm [40]. If all incompatible elements are proportionally fractionated in mantle processes, their contents should be (like the U content) by about two orders of magnitude higher than in the primitive mantle. These estimates are semiquantitative. However, such concentrations at 15% melting degree of anomalous lower mantle domains (this melting degree is normally accepted for superplumes producing flood basalts) and the addition of 5–30% of metasomatizing fluid could provide for the generation of alkaline magmas with concentrations of rare elements close to their average concentrations in the ultrabasic alkaline magmas parental for the ultrabasic alkaline rock associations in Polar Siberia and the Kola Peninsula. The calculations suggested Nb contents of 0.7 ppm in the primitive mantle, 70 ppm in the anomalous mantle, 490 ppm (calculated value) in a metasomatizing melt, and 131 ppm in parental magma [42] and assumed 5% melting degree of a metasomatically modified substrate. At these Nb concentrations, the calculated contribution of metasomatic material is 1.3%. At lower melting degree of 1%, the amount of the metasomatizing melt-fluid will be very low (about 0.013%). Our studies, together with literature data [44] demonstrate that the concentrations of metasomatic minerals (amphibole, mica, apatite, etc.) in the mantle are low (a few fractions of percent). Metasomatic processes in the mantle frequently do not cause the formation of specific minerals. The addition of rare elements by metasomatizing melts can be low and only increases their concentrations in rock-forming minerals.

Therefore, the evolution of alkaline magmatism in the Earth's history was determined by the intensity of mantle metasomatism causing the formation of enriched mantle reservoirs as sources of alkaline magmas. The global development of metasomatism in the mantle was related to the subduction of oceanic crust initiated at the Archean–Proterozoic boundary. The genesis of alkaline and carbonatitic magmas and related giant rare-metal deposits may have been caused by mantle metasomatism induced by the partial melting of the anomalous substrate in the lower mantle. Such anomalous zones are revealed in recent studies using seismic tomography [40, 41].

ACKNOWLEDGMENTS

This study was supported by the Russian Foundation for Basic Research (project no. 05-05-64144).

REFERENCES

1. J. H. Campbell and R. W. Griffiths, "The Changing Nature of the Mantle Hotspots through Time: Implications for the Chemical Evolution of the Mantle," *J. Geol.* **99**, 497–523 (1990).
2. A. W. Hofmann, "Mantle Geochemistry: The Message from Oceanic Volcanism," *Nature* **385**, 219–229 (1997).
3. L. N. Kogarko, I. Henderson, and A. H. Pacheco, "Primary Ca-rich Carbonatite Magma and Carbonate–Silicate–Sulfide Liquid Immiscibility in the Upper Mantle," *Contrib. Mineral. Petrol.* **121**, 267–275 (1995).
4. N. A. Logachev, *Volcanic and Sedimentary Rock Associations in Rifts of Eastern Africa* (Nauka, Moscow, 1977) [in Russian].
5. V. G. Lazarenkov, *Analysis of Associations of Continental and Oceanic Alkaline Rocks* (Nedra, Leningrad, 1988) [in Russian].
6. V. E. Khain, *Top Problems of Modern Geology* (Nauka, Moscow, 1994) [in Russian].
7. H. Holland, *The Chemical Evolution of the Atmosphere and Ocean* (Princeton Univ. Press, Princeton, 1984).
8. P. E. Cloud, "Atmospheric and Hydrospheric Evolution on the Primitive Earth," *J. Geol.* **100**, 729–736 (1992).
9. J. C. Walker, *Evolution of the Atmosphere* (Macmillan Publ., New York, 1977).
10. R. J. Arculus and J. W. Delano, "Implications for the Primitive Atmosphere of the Oxidation State of Earth's Upper Mantle," *Nature* **288**, 72–74 (1980).
11. S. Haggerty and S. Tompkin, "Redox State of Earth's Upper Mantle from Kimberlitic Ilmenites," *Nature* **303**, 295–300 (1983).
12. S. H. Richardson, "Latter-Day Origin for Diamonds of Eclogitic Paragenesis," *Nature* **322**, 623–626 (1986).
13. S. D. Kramers, "Lead, Uranium, Strontium, Potassium, and Rubidium in Inclusion-bearing Diamonds and Mantle-derived Xenoliths from Southern Africa," *Earth Planet. Sci. Lett.* **42**, 58–70 (1979).
14. M. Ozima, S. Zashu, and O. Nitoh, "Primitive Helium in Diamonds," *Geochim. Cosmochim. Acta* **47**, 2217–2224 (1983).
15. N. V. Sobolev, E. S. Efimova, and L. M. Pospelova, "Diamondiferous Peridotite Xenoliths in Kimberlites and the Problem of Diamond Nature," *Geol. Geofiz.*, No. 12, 25–29 (1981).
16. H. Meyer, "Inclusions in Diamonds," in *Mantle Xenoliths*, Ed. by P. H. Nixon (Wiley, Chichester, 1987), pp. 501–522.
17. A. A. Giardini and C. E. Melton, "The Nature of Cloud-like Inclusions in Two Arkansas Diamonds," *Am. Mineral.* **60**, 931–933 (1975).
18. J. W. Shervais, "Ti–V Plots and the Petrogenesis of Modern and Ophiolitic Lavas," *Earth Planet. Sci. Lett.* **59**, 101–118 (1982).
19. I. D. Ryabchikov, L. N. Kogarko, T. Ntaflos, and G. Kurat, "Native Metals in Mantle Xenoliths," *Dokl. Akad. Nauk* **338** (1), 95–98 (1994).
20. H. S. C. O'Neil, "The Origin of the Moon and the Early History of the Earth: A Chemical Model," *Geochim. Cosmochim. Acta* **55** (2), 1159–1172 (1991).
21. C. Bullhaus, "Redox States of Lithospheric and Asthenospheric Upper Mantle," *Contrib. Mineral. Petrol.* **114**, 331–348 (1993).
22. L. N. Kogarko and I. D. Ryabchikov, "Redox Equilibria in Alkaline Lavas from Trindade Island, Brazil," *Int. Geol. Rev.* **36**, 473–483 (1991).

23. E. M. Galimov, "Redox Evolution of the Earth Caused by a Multistage Formation of Its Core," *Earth Planet. Sci. Lett.* **233**, 263–276 (2005).
24. D. H. Green, T. J. Falloon, and W. R. Taylor, "Mantle-derived Magmas: Roles of Variable Source Peridotite and Variable C–H–O Fluid Comparisons," in *Magmatic Processes: Physicochemical Principles*, Ed. by B. Mysen, *Geochem. Soc. Spec. Publ.*, No. 1, 158–172 (1987).
25. J. F. Kasting, D. H. Egger, and S. P. Raeburn, "Mantle Redox Evolution and the Oxidation State of the Archean Atmosphere," *J. Geol.* **101** (2), 245–257 (1993).
26. K. Bell, *Carbonatite Genesis and Evolution* (Unwin Hyman, London, 1989).
27. H. Bunge and S. Grand, *Nature* **405**, 337–340 (2000).
28. A. E. Ringwood, "Slab–Mantle Interactions: 3. Petrogenesis of Intraplate Magmas and Structure of the Upper Mantle," *Chem. Geol.* **82**, 187–207 (1990).
29. P. Kearey and F. J. Vine, *Global Tectonics* (Blackwell, Boston, 1996).
30. R. F. Wendland and W. S. Harrison, "Rare Earth Partitioning between Immiscible Carbonate and Silicate Liquids and CO Vapor: Results and Implication for the Formation of Light Rare Earth-enriched Rocks," *Contrib. Mineral. Petrol.* **69**, 409–419 (1979).
31. L. N. Kogarko, "Problems in Studies of the Origin of Giant Rare Metal Deposits in the Kola Peninsula," in *Russian Arctic Zone: Geological History, Metallogeny, and Geoecology* (St. Petersburg, 2002), pp. 773–788 [in Russian].
32. L. N. Kogarko, U. Kramm, and B. Grauert, "New Data on the Age and Origin of Alkaline Rocks of the Lovozero Pluton: Constraints from Rubidium and Strontium Isotopic Geochemistry," *Dokl. Akad. Nauk SSSR* **260** (4), 1000–1005 (1981).
33. J. K. Meen, J. C. Ayers, and E. J. Fregeau, "A Model of Mantle Metasomatism by Carbonated Alkaline Melts: Trace-element and Isotopic Compositions of Mantle Source Regions of Carbonatite and Other Continental Igneous Rocks," (Unwin Hyman, London, 1989), pp. 464–500.
34. L. N. Kogarko, "The Upper Mantle Heterogeneity and the Magmatism of Oceanic Islands," in *Oceanic Magmatism* (Nauka, Moscow, 1986), pp. 73–80 [in Russian].
35. D. Fransis, "Some Implications of Xenolith Glasses for the Mantle Sources of Alkaline Mafic Magmas," *Contrib. Mineral. Petrol.* **108**, 175–180 (1991).
36. A. D. Edgar, F. E. Lloyd, D. M. Forsyth, and R. L. Barnett, "Origin of Glass in Upper Mantle Xenoliths from the Quaternary Volcanics of Gees, West Eifel, Germany," *Contrib. Mineral. Petrol.* **103**, 277–286 (1989).
37. L. N. Kogarko, G. Kurat, and T. Ntaflos, "Carbonate Metasomatism of the Oceanic Mantle beneath Fernando de Noronha Island, Brazil," *Contrib. Mineral. Petrol.* **140**, 577–587 (2001).
38. G. Rivalenti, M. Mazzucchelli, V. Girardi, *et al.*, "Composition and Processes of the Mantle Lithosphere in Northeastern Brazil and Fernando de Noronha: Evidence from Mantle Xenoliths," *Contrib. Mineral. Petrol.* **138**, 308–325 (2000).
39. J. Adam and T. Green, "Experimentally Determined Partition Coefficients for Minor and Trace Elements in Peridotite Minerals and Carbonatitic Melt, and Their Relevance to Natural Carbonatites," *Eur. J. Mineral.* **13**, 815–827 (2001).
40. R. D. van der Hilst and H. Karason, "Compositional Heterogeneity in the Bottom 1000 Kilometers of Earth's Mantle: Toward a Hybrid Convection Model," *Science* **283**, 1885–1888 (1999).
41. L. H. Kellogg, B. H. Hager, and R. D. van der Hilst, "Compositional Stratification of the Deep Mantle," *Science* **283**, 1881–1884 (1999).
42. A. A. Arzamastsev, F. Bea, V. N. Glaznev, *et al.*, "The Kola Alkaline Province in Paleozoic: The Composition of Parental Magmas and the Magma Generation Conditions," *Russ. Zh. Nauk o Zemle* **3** (1), 1–35 (2001).
43. E. E. Milanovsky, "Rift Zones of the Geologic Past and Their Associated Formations: Report 2," *Int. Geol. Rev.* **18**, 619–639 (1976).
44. M. A. Menzies and C. J. Hawkesworth, *Mantle Metasomatism* (Academic, London, 1987).