Oxygen Fugacity Regime in the Upper Mantle as a Reflection of the Chemical Differentiation of Planetary Materials

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Abstract—Oxygen fugacity (fO_2) in the Earth's mantle has a bearing on the problems of the chemical differentiation of the Earth's materials and formation of the chemical and phase state of its shells. This paper addresses some problems concerning changes in the redox state of the upper mantle over geologic time and through its depth and the possible influence of fO_2 stratification in the interiors on geochemical processes. Among these problems are the formation of fluids enriched in H_2O, CO_2, CH_4, and H_2; the possible influence of reduced fluid migration from mantle zones with low fO_2 values on reactions in the lithosphere; and the formation of films of silicate liquids with high H_2O and CO_2 contents, which could be responsible for metasomatic transformations in rocks. The formation of a metallic core and accompanying large-scale melting of the silicate part of the Earth are the early mechanisms of the chemical differentiation of the mantle that must have had an effect on the redox state and the composition of volatile components in planetary materials. The molten metallic and silicate phases were prone to gravitational migration, which affected the formation of the metallic core. Volatile components had to be simultaneously formed in the zones of large-scale melting of the early Earth. The composition of these volatiles was largely controlled by the interaction of hydrogen and carbon, the two major gas-forming elements in the mantle, with melt under low fO_2 values. A remarkable feature is that, despite fairly low fO_2 values imposed by the presence of a metallic phase, both reduced (CH_4 and H_2) and oxidized species of hydrogen and carbon (H_2O, OH^- and CO_3^{2-}) are stable in the melt. This peculiarity of carbon and hydrogen dissolution in reduced melts may be crucial for the elucidation of mechanisms for the formation of initial amounts of CO_2 and H_2O connected with incipient melting in the reduced mantle.

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PROBLEM

The behavior of oxygen during the chemical differentiation of planetary materials is closely linked to redox reactions involving iron (Fe^{3+}, Fe^{2+}, and Fe^0), the most abundant element of variable valence on Earth. Another important system of oxygen exchange is C–O–H mantle fluids, which affect both crystalline and molten mantle materials.

The redox state of deep material is quantified by the oxygen fugacity (fO_2) of mineral reactions. Oxygen fugacity in the Earth's mantle affects many geochemical processes related to the chemical differentiation of the Earth and the formation of the chemical and phase state of its shells. The knowledge of fO_2 of mantle rocks is fundamental for hypotheses concerning the early history of the Earth, for the elucidation of specific features of the behavior of siderophile elements and volatile components during metallic core formation [1–3], and the influence of the Earth's core on chemical processes in the mantle [4–6]. There is a significant correlation between the composition of carbon-saturated C–O–H fluids and fO_2, which leads to a suggestion that the bal-

ance of oxygen in the planetary interiors affects the composition of mantle degassing products and the contribution of high-temperature volcanic activity to the emission of CH_4, CO, CO_2, and H_2O in variable proportions into the Earth's early atmosphere [7–14]. In the presence of fluids enriched in CH_4 and H_2, the character of mantle melting and chemical differentiation of magmas is different from that in the presence of H_2O- and CO_2-rich fluids [15–17].

The most important problems are related to the understanding of the evolution of the redox state of planetary materials over geologic time and through the depth of the mantle. Mineral reactions involving ilmenite, spinel, garnet, olivine, pyroxene, carbonate, and elemental carbon with Fe^{2+} and Fe^{3+} redistribution among phases suggest that the present-day lithospheric and asthenospheric layers of the upper mantle are moderately oxidized. The fO_2 values of these layers are above the conditions of equilibrium with a metallic phase. The activity of Fe^{3+} components in upper mantle minerals corresponds to fO_2 values implying the dom-

inance of CO_2 and H_2O in the composition of deep fluids and the stability of carbonate phases.

On the other hand, there are grounds to suggest that the Earth's mantle was reduced during the early stages of its formation, which was controlled by chemical equilibrium with the metallic phase [1, 10, 12, 16–18]. If the average composition of upper mantle olivine is accepted as Fo_{91}, the corresponding fO_2 must be at least five orders of magnitude lower than the fO_2 of the lithospheric and asthenospheric layers of the present-day upper mantle. Under such a redox state of planetary materials, the dominant volatile components must be CH_4 and H_2 in equilibrium with free carbon (graphite or diamond). When and how the upper mantle underwent a considerable increase in fO_2 is still largely unknown. The fO_2 values of upper mantle peridotites from various tectonic structural zones of the Earth suggest that the oxidation process was rather slow, and reducing conditions probably prevailed over at least half of the Earth's history [1, 12, 18]. However, these concepts are still debatable. Canil [19] studied the abundance of V in peridotite xenoliths from the lithosphere and komatiite lavas and argued that the upper mantle reached its modern fO_2 level over a geologically short time period during the early stages of the Earth's formation. However, a critical analysis of geochemical data on the abundance of V in peridotite xenoliths from the lithosphere has led to the conclusion that the behavior of V is strongly influenced by the formation of magmatic cumulates, assimilation of wall-rocks by melts, and metamorphic processes [20, 21]. This casts some doubt on the validity of this element for the estimation of primary fO_2 values in magma formation zones.

It is reasonable to suppose that global variations in fO_2 in geologic time and space with high values in the Earth's upper shells are due to a combination of chemical and physical processes in the planetary interiors. They are related to the chemical differentiation of the Earth in response to the formation of a metallic core; deep degassing; melting; large-scale mass exchange processes in the planetary interiors, such as lithosphere subduction and plume-related ascent of mantle materials; and the effect of pressure on the incorporation of Fe^{2+} and Fe^{3+} into the structure of mantle minerals.

This paper addresses some problems related to changes in the redox state of the upper mantle over geologic time and through its depth and to the possible influence of deep fO_2 stratification on geologic processes. Among these processes are the formation of fluids enriched in H_2O and CO_2 or CH_4 and H_2; the possible influence of the migration of reduced fluids from mantle zones with low fO_2 values on reactions in the lithosphere; and the appearance of silicate melt films with high H_2O and CO_2 contents, which, in our opinion, may be among the reasons for metasomatic transformation in rocks.

The formation of a metallic core and accompanying large-scale melting of the silicate portion of the Earth are early mechanisms of the chemical differentiation of the mantle, which had to influence the redox state and the composition of volatile components of planetary materials. There are many controversies concerning these processes. The understanding of their nature is crucial for the clarification of subsequent paths of the Earth's evolution. The molten metallic and silicate phases were subject to gravitational migration, which affected the formation of the metallic core. Simultaneously, volatile components had to be formed in the zones of large-scale melting of the early Earth. Their composition was largely controlled by the interaction of hydrogen and carbon, the two major gas-forming elements in the mantle, with melts at fairly low fO_2 values. A remarkable feature is that, despite the low fO_2 values imposed by the presence of a metallic phase, both reduced (CH_4 and H_2) and oxidized species of hydrogen and carbon (H_2O, OH^- and CO_3^{2-}) are among the stable components of melts [14]. Such a character of carbon and hydrogen dissolution in reduced melts may be essential for the understanding of mechanisms for the formation of initial amounts of CO_2 and H_2O during incipient melting of the reduced mantle.

When discussing the redox state of the mantle or magmas, fO_2 values of some reference buffer reactions, which also have a geochemical significance, are used for comparison. In terms of oxygen fugacity, the Fe_2SiO_4–Fe_3O_4–SiO_2 (FMQ) buffer equilibrium is closest to the redox state of basaltic magmas near the Earth's surface. The fO_2 values of the Fe–FeO (IW) buffer equilibrium characterize the region of low oxygen fugacity values in the mantle, close to mineral equilibria in the presence of a metallic phase. The FeO–Fe_3O_4 (WM) buffer equilibrium is intermediate between the two extreme buffer reactions, FMQ and IW. The presentation of fO_2 values of deep reactions relative to the fO_2 values of the FMQ or IW buffer equilibria, i.e., $\Delta\log(FMQ) = \log fO_2(FMQ) - \log fO_2(FMQ)$ or $\Delta\log(IW) = \log fO_2(IW) - \log fO_2(IW)$ allows us to discuss the evolution of deep materials and infer their more oxidized or more reduced state relative to FMQ or IW.

LOW fO_2 VALUES RECORDED IN MANTLE PERIDOTITES

Oxygen fugacity measurements for mineral reactions in spinel peridotite xenoliths indicate the predominance of rather high fO_2 values in the lithosphere and asthenosphere. They correspond to $\Delta\log fO_2(FMQ)$ from –2 to +1, which implies the dominance of H_2O and CO_2 in the fluid phase and the stability of carbonates in these upper mantle layers (e.g., [18]). These observations served as a basis for the concept that the
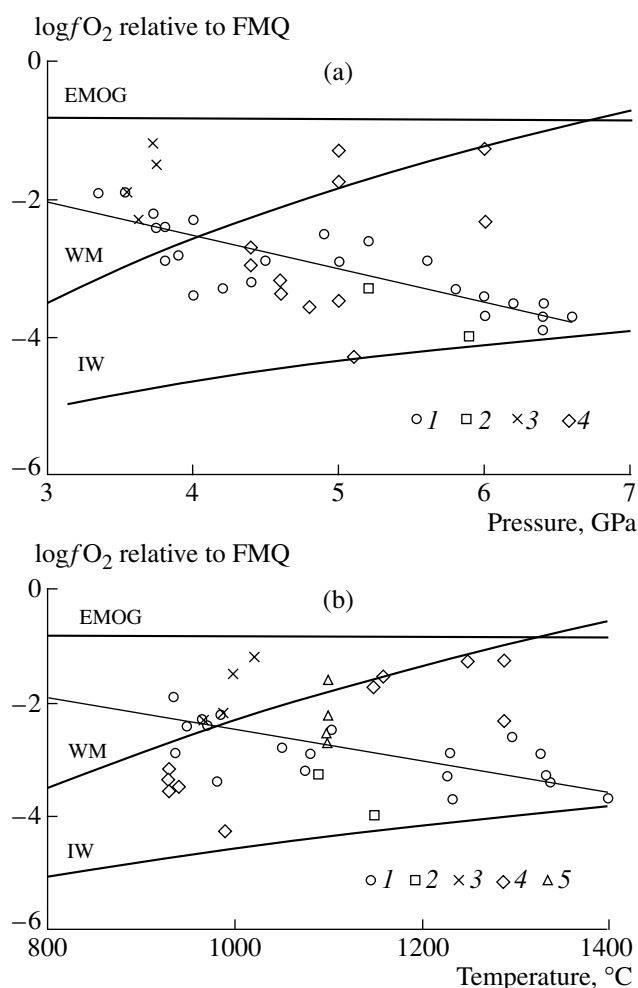
log$f$O$_2$ relative to FMQ

(a)

EMOG

WM

IW

○ 1 □ 2 ×3 ◇4

Pressure, GPa

log$f$O$_2$ relative to FMQ

(b)

EMOG

WM

IW

○ 1 □ 2 ×3 ◇4 △ 5

Temperature, °C

Fig. 1. fO$_2$ values for peridotites and eclogites from the Archean lithosphere on the example of xenoliths from kimberlites of Yakutia [12, 28] and southern Africa [23, 33, 34] relative to the FMQ buffer equilibrium. (a) Dependence of fO$_2$ on the pressure of mineral equilibria. The main tendency is a decrease in fO$_2$. (b) Dependence of fO$_2$ on the temperature of mineral equilibria. Also shown are some standard buffer equilibria (IW, WM, and EMOD). The main tendency is an increase in fO$_2$ with decreasing temperature. (*1*) Peridotite, southern Africa [23]; (*2*) diamondiferous peridotite, southern Africa [34]; (*3*) fO$_2$ increase during growth of garnet of harzburgite xenoliths under conditions of metasomatic transformations, southern Africa [23]; (*4*) diamondiferous chrome-pyrope peridotite, Yakutia [12, 28]; and (*5*) diamondiferous kyanite eclogite, Yakutia [35].
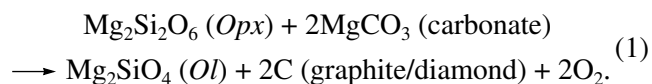
prevailing fO$_2$ values in the mantle correspond to the FMQ buffer equilibrium. However, geochemical studies of the past years demonstrated the existence of upper mantle zones with low fO$_2$ values approaching the IW buffer equilibrium [12, 18, 21–23]. They may reflect the former reduced state of the mantle or result from the influence of deep mantle layers, which must occur under low-fO$_2$ conditions as a result of Fe^{2+} and Fe^{3+} partitioning between mantle phases at pressures higher than 10 GPa [11, 24, 25].

Low fO$_2$ values were obtained for some samples of abyssal spinel and garnet peridotites from orogenic lherzolite massifs, where Δlog$f$O$_2$(FMQ) varies from –2.5 to –3.0 [22, 26]. Some garnet peridotites from the Archean lithosphere showed very low fO$_2$ values, with Δlog$f$O$_2$(FMQ) from –3 to –5 [12, 18, 21, 23, 27, 28]. Low fO$_2$ values are characteristic of weakly depleted spinel lherzolite xenoliths without any evidence for metasomatic transformations [12, 29]. These data are described below in more detail by the example of some diamondiferous eclogites and peridotites of Archean age, magmatic complexes of the Archean crust, and fertile peridotite xenoliths from the lithospheric and asthenospheric layers of the upper mantle beneath the Central Asian and Tien Shan regions.

Peridotites and Eclogites of the Archean Lithosphere

Garnet xenoliths are of special interest for the present discussion because they are derivatives of the Archean lithosphere and provide a record of processes accompanying the chemical differentiation of the mantle during the early stages of its evolution [30, 31]. The depletion and, correspondingly, differentiation of the mantle lithosphere beneath the Siberian craton took place about 3.2 Ga ago [32]. The same Archean age of depletion (3.2 Ga) was obtained for garnet peridotite xenoliths from southern African kimberlites. Diamondiferous eclogite xenoliths from the kimberlites of the Udachnaya pipe are products of the differentiation of lithospheric mantle. This differentiation occurred 2.7–3.0 Ga ago, but its nature has been a subject of debate [31]. Eclogites are regarded as products of the recycling of the oceanic crust. On the other hand, geochemical data do not rule out the formation of eclogites through the melting of ancient mantle reservoirs.

The estimation of the redox state of peridotite and eclogite xenoliths from kimberlites and mineral inclusions in diamonds from the Siberian craton and southern Africa suggested considerable variations in fO$_2$ during their formation [12, 23, 27, 28] (Fig. 1). The fO$_2$ values of xenoliths from the ancient lithosphere fall mainly between the WM and IW buffer equilibria within the stability field of graphite and diamond. The upper boundary of this field in the peridotite (harzburgite) system is the EMOG/EMOD reaction [36]

$$Mg_2Si_2O_6 \ (Opx) + 2MgCO_3 \ (carbonate)$$
$$\longrightarrow Mg_2SiO_4 \ (Ol) + 2C \ (graphite/diamond) + 2O_2. \quad (1)$$

A conspicuous feature of the redox state of peridotite xenoliths is the rather low fO$_2$ values under extremely high pressures (Fig. 1). The Δlog(FMQ) values at 6–7 GPa are about –4.5, which is close to fO$_2$(IW). The very low fO$_2$ values in the rocks of the Archean lithosphere are supported by the presence of a primary iron phase, wüstite, and magnetite in some Yakutian diamonds [37]. Mineral inclusions in dia-

monds with low fO_2 values were also reported from other regions worldwide. For instance, an investigation of mineral inclusions in diamonds from Tanzania corresponding to the $Fe–FeO–Fe_2O_3$ system suggested that the fO_2 values in the zones of diamond formation in the mantle were lower or close to $fO_2(IW)$ [38]. Low fO_2 values were obtained for inclusions in Colorado diamond on the basis of $Fe^{3+}/\Sigma Fe$ determination in pyroxenes and garnets [39].

The data shown in Fig. 1 indicate an increase in fO_2 with decreasing pressure along the 43 mW/m² geotherm, which can be described to a fist approximation by the following expression:

$$\Delta \log(FMQ) = -0.31P \text{ (GPa)} - 1.55; \quad \sigma^2 = 0.52. \quad (2)$$

The influence of fluid on mineral equilibria in peridotites was revealed by the determination of Fe^{3+} content in the central and marginal parts of zoned garnets from metasomatized harzburgite xenoliths [23]. These data showed that the growth of these crystals during metasomatic events was accompanied by a significant increase in fO_2 by two logarithmic units (Fig. 1).

Low V contents in garnet peridotite xenoliths from the Archean lithosphere were interpreted by Canil [19] as an indication of high fO_2 values approaching FMQ. However, this is in conflict with fO_2 determinations based on mineral equilibria [12, 21, 23, 27] (Fig. 1). Lee *et al.* [20] analyzed the data of Canil [19] and supposed that the low V contents that were used for the estimation of fO_2 could have been produced by the addition of pyroxene due to melt–peridotite reaction during melt ascent or by the processes of cumulate formation; i.e., the low concentrations of V are probably not indicative of partial melting under high fO_2 values. Lee *et al.* [20] concluded that low fO_2 values are more consistent with diamond stability. It should also be kept in mind that mantle peridotites are metamorphic rocks, which underwent a prolonged and complex geochemical history, and the behavior of V cannot be understood within the model of single-stage melting and melt extraction.

Orthogneisses of the Archean Lithosphere

The Archean age of the lithosphere of the Siberian craton is similar to the age of crustal rocks from the Aldan and Anabar regions [40]. This allows us to suppose their simultaneous stabilization. Electrochemical measurements of the intrinsic oxygen fugacity of 3.5-Ga-old zircons from the oldest tonalites (orthogneisses) of the Omolon massif (Siberia) [41] yielded fO_2 values between $fO_2(IW)$ and $fO_2(WM)$ at temperatures of 800–1000°C and $\Delta \log(FMQ)$ between –3.5 and –5.0 (Fig. 2). The zircons that were used for the determination of age and fO_2 bear geochemical indications for comagmatic relationships with the tonalite magmas, and their oxygen isotope composition sug-
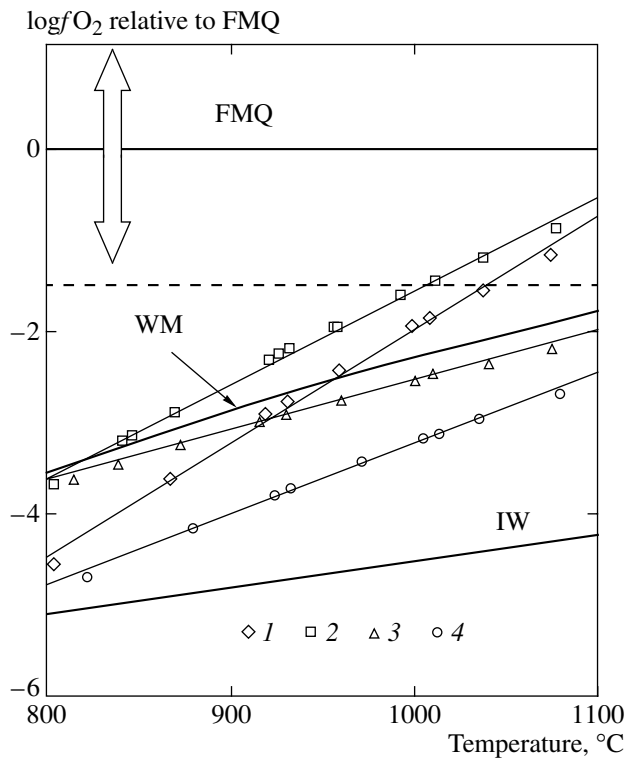

Fig. 2. fO_2 values for some orthogneisses and igneous complexes from the Archean crust exemplified by the electrochemical measurements of ancient zircons [41]. The arrow shows the field of fO_2 values in the upper mantle peridotites showing geochemical indications of metasomatic transformations and depletion with respect to basaltic components. Also shown are standard buffer equilibria (IW and WM). (*1*) Zircon from the gabbro of the Orekhovo–Pavlograd zone of the Ukrainian shield, 2.65 Ga; (*2*) zircon from the abyssal charnokites of the Baltic shield, 2.4 Ga; (*3*) zircon from the granitoids of granite–greenstone assemblages of the Middle Dnepr area, 3.25 Ga; and (*4*) zircon from the orthogneisses (tonalites) of the Omolon massif, Siberia, 3.5 Ga.

gests that they have not been affected by fluids since tonalite formation [41]. According to these data, the tonalite magmas of the Omolon massif were derived under redox conditions comparable to those of the oldest peridotite xenoliths from the Archean lithosphere beneath the Siberian craton.

Zircon crystals used for fO_2 measurement from other magmatic complexes of the Precambrian crust are also characterized by fO_2 values much lower than $fO_2(FMQ)$. The fO_2 values of 3.25-Ga-old zircons from the granite–greenstone assemblage of the Middle Dnepr region are close to $fO_2(WM–0.5)$ with $\Delta \log(FMQ)$ between –3 and –4 (Fig. 2). On the other hand, the fO_2 values of 2.65-Ga-old zircon from the gabbro of the Orekhovo–Pavlograd zone of the Ukrainian shield showed higher values at 800–1000°C between –1.5 and –3.5.
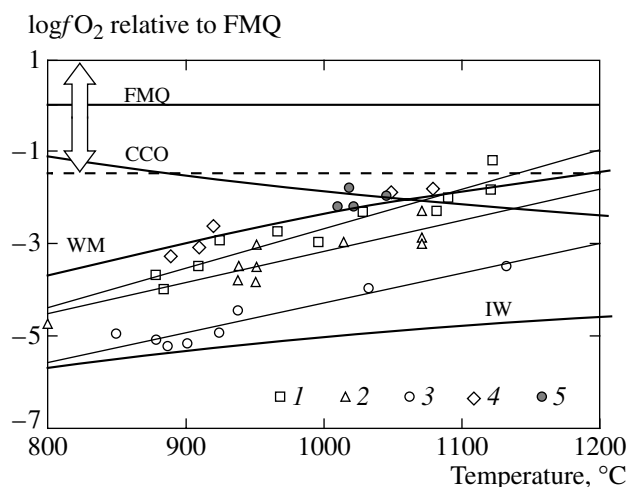
log$f$O$_2$ relative to FMQ

Fig. 3. fO$_2$ values for weakly depleted spinel and garnet peridotites from noncratonic volcanic provinces by the example of xenoliths from the alkali basalts of Baikal [47, 48], Mongolia [29, 46], and the Tien Shan [49] relative to the FMQ buffer equilibrium. All the data are reduced to the same pressure of 1.5 GPa. The arrow indicates the fO$_2$ field of the upper mantle peridotites showing geochemical indications of metasomatic alterations and depletion in basaltic components. Also shown are some standard buffer equilibria (IW, WM, and CCO). (*1*) Spinel lherzolite, Baikal [47]; (*2*) garnet and garnet–spinel lherzolites, Mongolia [46]; (*3*) spinel lherzolite, Tien Shan [49]; (*4*) spinel lherzolite, Mongolia [29]; (*5*) garnet peridotite, Vitim [48].
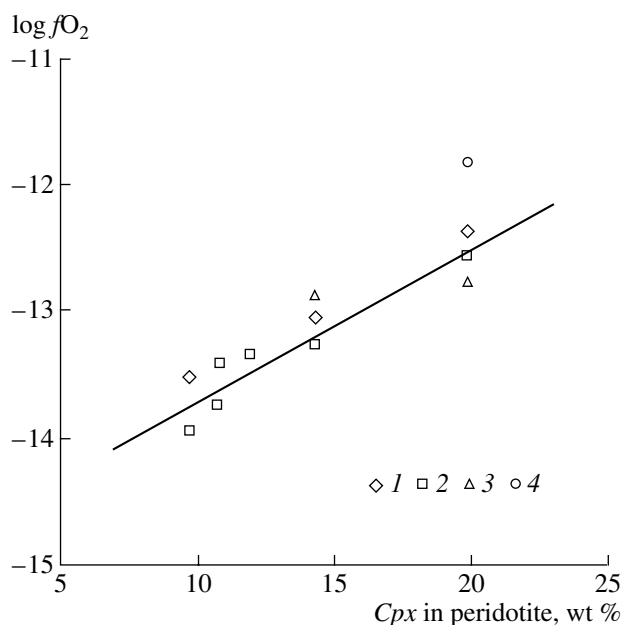

Fig. 4. Intrinsic oxygen fugacity for individual minerals from "dry" spinel lherzolite xenoliths (Mongolia) as a function of clinopyroxene content at 1.5 GPa and 960–1010°C [12]. The fO$_2$ values were determined using oxygen electrochemical cells. The correlation between the fO$_2$ of minerals and the composition of spinel lherzolites (abundance of clinopyroxene) indicates a decrease in fO$_2$ with extraction of basaltic components. (*1*) Orthopyroxene; (*2*) olivine; (*3*) clinopyroxene; and (*4*) spinel.

*Weakly Depleted Peridotite Xenoliths
from Noncratonic Volcanic Provinces*

Spinel and garnet peridotite xenoliths from noncratonic volcanic provinces represent a younger lithospheric mantle compared with peridotite xenoliths from the ancient cratonic lithosphere [42]. The fO$_2$ values of mineral equilibria in these peridotites may provide insights into the evolution of the redox state of the lithosphere in geologic time. In this context, of particular interest are spinel and garnet lherzolites carried to the Earth's surface by alkali basalt magmas in the rift zones of Mongolia and Baikal, especially those that show "dryness," a low degree of basaltic component depletion, and no evidence for metasomatic transformations [43–45].

The spinel and garnet lherzolites of Mongolia [12, 29, 46] and Baikal [12, 47, 48] show fO$_2$ values within Δlog(FMQ) between –2 and –4 at temperatures of 900–1100°C and a pressure of 1.5 GPa (Fig. 3). The fO$_2$ values of the spinel and garnet lherzolites of Baikal are close to fO$_2$(WM) and show the linear relationship

$$\Delta\log(\text{FMQ}) = 0.0085t(°C) - 11.19; \quad \sigma^2 = 0.89. \quad (3)$$

The fO$_2$ values of the spinel lherzolites of Mongolia are about one logarithmic unit below fO$_2$(WM) and can be approximated by the linear equation

$$\Delta\log(\text{FMQ}) = 0.0067t(°C) - 9.92; \quad \sigma^2 = 0.81. \quad (4)$$

Unique lithospheric xenoliths of spinel and garnet peridotite with low fO$_2$ values were found in pipes and dikes of Mesozoic alkaline basaltoids in the Southern and Central Tien Shan (Fig. 3). These xenoliths characterize the composition of the upper mantle in the areas of Hercynian orogenic zones with a very thick crust and lithosphere [50]. According to geochemical observations, a specific feature of transformations in the deep materials of the Tien Shan is the low oxidation state of rocks inherited from Precambrian time. This is reflected in the high fraction of Fe^{2+}; wide occurrence of graphite, native metals (Fe, Ni, Pt, and Ir), and moissanite; and the presence of diamond [50]. The measured fO$_2$ values for representative mantle samples from the Southern and Central Tien Shan are in agreement with these observations [49]. At temperatures of 900–1100°C and a pressure of 1.5 GPa, they fall between the WM and IW buffer equilibria in the T–fO$_2$ plane at Δlog(FMQ) values between –3 and –5 and show the linear relationship

$$\Delta\log(\text{FMQ}) = 0.0064t(°C) - 10.716; \quad \sigma^2 = 0.90. \quad (5)$$

Melting is one of the large-scale phase transformations in the Earth's mantle that are expected to affect fO$_2$ values. They are controlled by Fe^{2+} and Fe^{3+} partitioning between magmatic liquid and residual crystals.
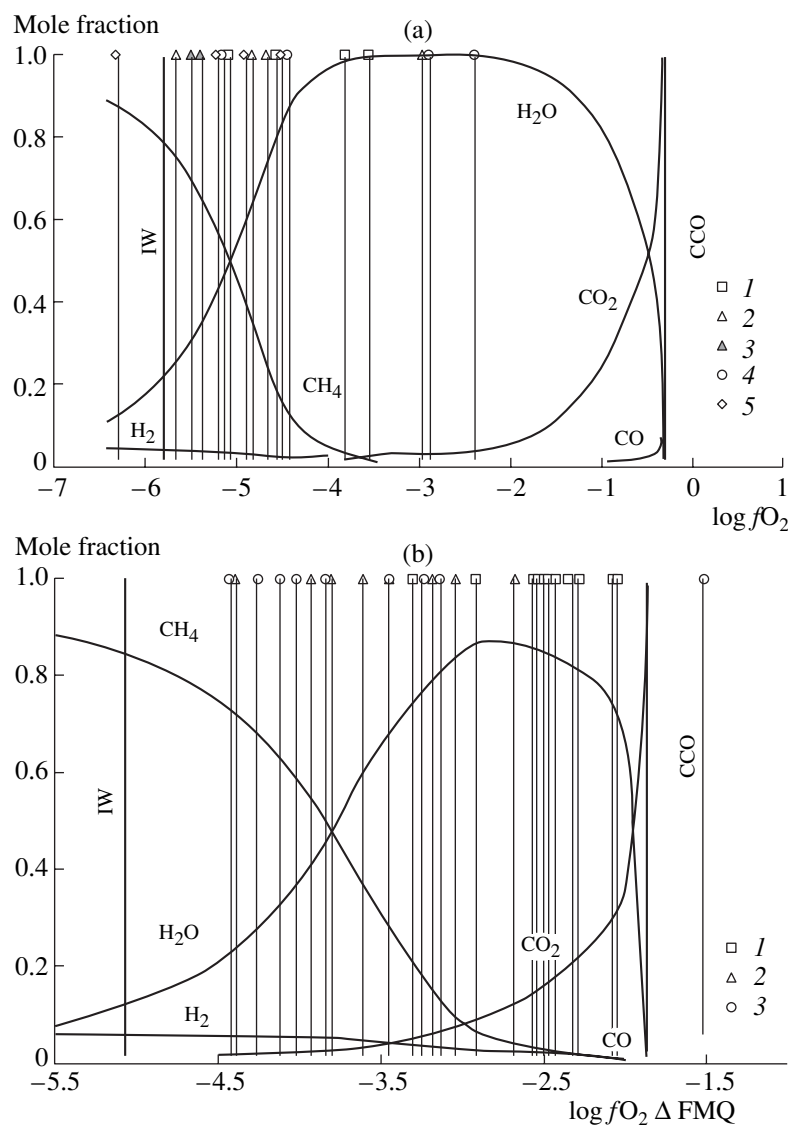
Fig. 5. Composition of the carbon-saturated fluid phase in equilibrium with (a) diamondiferous peridotites and eclogites of the Archean lithosphere at 5 GPa and 1100°C and (b) fertile spinel and garnet peridotites from the lithosphere of the rift zones of Mongolia and Baikal at 1.5 GPa and 1000°C. The fO_2 values of individual samples are shown by vertical lines. (a) (*1*) Diamondiferous kyanite eclogite, Yakutia [35]; (*2*) diamondiferous chrome-pyrope peridotite, Yakutia [52]; (*3*) diamond [53]; (*4*) diamondiferous chrome-garnet peridotites, inclusions in diamond, Australia, Yakutia, and southern Africa [54]; and (*5*) sulfide inclusion in diamond, Yakutia [55]. (b) (*1*) Spinel and garnet peridotites, Mongolia [12, 29, 46]; (*2*) spinel and garnet peridotites, Tien Shan; and (*3*) spinel and garnet peridotites, Baikal [12, 47].

In this equilibrium Fe^{3+} behaves as a moderately incompatible element and is accumulated in the melt. This provides higher fO_2 values in melts compared with those of their sources (e.g., [51]).

On the other hand, partial melting in the presence of free carbon may be accompanied by a decrease in fO_2 owing to a decrease in Fe^{3+} concentration in the melt [12, 22, 52] through the reaction

$$C \text{ (mantle)} + Fe_2O_3 \text{ (melt)} = CO_2 \text{ (melt)} + FeO \text{ (melt)}. \qquad (6)$$
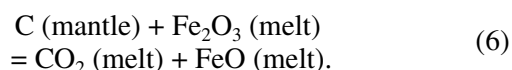
The extent of fO_2 decrease is controlled by the amount of free carbon and its solubility in the melt.

This effect is recorded in the spinel and garnet lherzolites of Mongolia, whose redox state corresponds to the stability field of free carbon. Microscopic inclusions of graphite crystals, 2–3 μm in size, were detected in olivine and pyroxene by micro-Raman spectroscopy [17]. These rocks display an fO_2 decrease with decreasing abundance of clinopyroxene [12], i.e., with progressive melting and extraction of the basaltic component (Fig. 4).

*Composition of C–O–H Fluids in Upper Mantle Zones
with Low fO₂ Values*

The redox state of diamondiferous peridotites falls within the stability field of free carbon and is consistent with considerable variations in CO_2, H_2O, and CH_4 contents in the equilibrium fluid phase (Fig. 5a). The lowest fO_2 values correspond to fluids with high fractions of CH_4 (90–97 mol %), and the highest fO_2 conditions give CO_2–H_2O-rich fluids. Thus, samples from the ancient lithosphere recorded conditions of a dramatic change in the composition of C–O–H fluids, from predominantly methane through water–methane to CO_2-rich fluids after the attainment of the water maximum and transition into the field of existence of carbonate phases.

A similar compositional stratification of C–O–H fluids was also established for peridotite xenoliths from the Baikal rift zone and the Tien Shan (Fig. 5b). The redox state of the least depleted spinel lherzolites of Baikal and Mongolia also corresponds to the stability of free carbon (graphite). The composition of C–O–H fluids may vary from H_2O–CH_4 to H_2O–CO_2 with a high fraction of CO_2 after passing the maximum water content (Fig. 5b). On the other hand, a number of researchers showed that highly depleted upper mantle spinel peridotites with indications of metasomatic alterations show fO_2 values beyond the T–P–fO_2 stability field of free carbon. Thus, there is probably a boundary of carbon occurrence in the upper mantle related to the evolution of deep materials.

DEPTH STRATIFICATION OF fO_2 IN THE UPPER MANTLE

It had long been believed that the mantle is characterized by fO_2 values close to FMQ through its whole depth. The cratonic lithospheric peridotites showing very low fO_2 values were regarded as representatives of those mantle zones that preserved to some extent fO_2 values typical of the early stages of the formation of the Earth's reduced mantle [12, 18, 56]. However, recent experimental and theoretical studies suggested that the system of main phase transformations in the upper mantle, transition zone, and lower mantle must be characterized by a decrease in fO_2 owing to the effect of pressure on solid-state reactions involving Fe^{2+} disproportionation to $Fe^0 + Fe^{3+}$ [11, 25, 57, 58]. It is expected that this effect defines the main trend in redox state variations in the mantle with depth. These concepts are supported by the pressure dependency of fO_2 established for the mineral equilibria of garnet peridotite xenoliths from the ancient lithosphere. The general tendency is a decrease in fO_2 with increasing pressure, which results in the attainment of fO_2 values below the IW buffer equilibrium at $P \approx 7$ GPa, i.e., at depths of about 200 km. A similar fO_2 decrease with increasing pressure was established for garnet peridotite xenoliths

from the Archean lithosphere by Woodland and Koch [21], who explained this phenomenon by the character of Fe^{3+} incorporation in the structure of high-pressure minerals.

The control of fO_2 in the mantle has been discussed over more than two decades (e.g., [1, 12, 18, 59]). If the mantle, as supposed, is a closed system and there is no oxygen exchange with external sources, its fO_2 is controlled by the bulk composition under given temperatures and pressures. The degree of fO_2 preservation during fluid infiltration or other oxygen fluxes reflects the buffer capacity of various equilibria depending on the concentration of oxide components.

Wood *et al.* [59] supposed that fO_2 must decline with depth within the garnet-peridotite facies. This conclusion was based on a high negative ΔV value for the reaction involving Fe^{3+} in garnet, assuming that this reaction is the major control on fO_2. This concept has subsequently been developed by Ballhaus [60] and McCammon and Kopylova [61], who also inferred an fO_2 decrease with increasing pressure. Variations in fO_2 in the spinel–garnet-peridotite facies must be different from those in the garnet peridotite facies because of the different ΔV values of redox reactions. The volume change for the spinel–garnet reaction

$$Fe_3^{2+}Fe_2^{3+} + Si_3O_{12} + Fe_3O_4 \ (sp) + 2FeSiO_3 \ (opx) \\ = 5Fe_2SiO_4 \ (ol) + O_2 \tag{7}$$
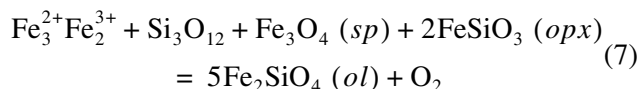
is –17.8 cm³, which is much lower than the value of −26.4 cm³ for the garnet peridotite reaction

$$2Fe_3^{2+}Fe_2^{3+}Si_3O_{12} \ (gr) \\ = 4Fe_2SiO_4 \ (ol) + 2FeSiO_3 \ (opx) + O_2. \tag{8}$$
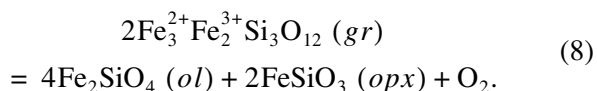
Consequently, a more pronounced fO_2 decrease with depth should be expected within the garnet facies. This is supported by the results of McCammon and Kopylova [61], who demonstrated that the slope of the linear dependency $\Delta\log fO_2(FMQ)$–P is 0.09–0.11 $\log fO_2$ per 1 kbar for garnet peridotites compared with 0.04 $\log fO_2$ per 1 kbar for spinel–garnet peridotites. Thus, the fO_2 of the cratonic upper mantle depends on its chemical composition and mineral boundaries. This corresponds to the model when fO_2 values are controlled under closed-system conditions or under conditions when percolating fluids exert no significant influence on the fO_2 of solid-phase reactions owing to their small masses.

According to the estimates by Ballhaus and Frost [11], the decrease of fO_2 is sufficient for the attainment of conditions for the stability of metallic phase and CH_4-rich fluids at pressures of about 10 GPa (depths of about 300 km) [60]. These inferences are supported to some extent by the extrapolation of the fO_2–P dependency for garnet peridotites from the Archean lithosphere into the high-pressure region. Such an extrapola-

tion was performed by us and Woodland and Koch [21] and showed that Fe saturation conditions can be achieved in the system at depths of about 400 km.

Experimental and theoretical studies of the redox states of the transition zone and lower mantle suggest that these zones of the Earth must occur under low fO_2 values owing to the incorporation of Fe^{3+} into the structure of high-pressure phases. These concepts are important for the understanding of the effect of fluid migration from the lower mantle on geochemical processes in the upper levels of the Earth.

The supposed mineral assemblage of the transition zone is wadsleyite + majorite garnet (410–520 km) and silicate spinel + majorite garnet (520–660 km). The incorporation of Fe^{3+} + into the wadsleyite structure depresses Fe^{3+} + activity and decreases fO_2 until the attainment of conditions for the metallic phase saturation of the system.

$(Mg, Fe)SiO_3$ perovskite and $(Mg, Fe)O$ magnesio-wüstite are the main phases of the lower mantle. According to experiments [57], considerable amounts of Fe^{+3} can be accommodated in the structure of Al-bearing perovskite, which causes an fO_2 decrease in the system. It is supposed that the fO_2 value of the lower mantle also corresponds to the conditions of saturation in metallic phase, providing of course, that perovskite contains significant amounts of Fe^{3+}.

Thus, the investigations of the pressure effect on Fe^{2+} disproportionation to $Fe^0 + Fe^{3+}$ in solid-state reactions in the lower upper mantle, transition zone, and lower mantle provide compelling evidence to suggest lower fO_2 values compared with those inferred from the analysis of spinel-peridotite xenoliths from the lithospheric and asthenospheric layers of the upper mantle. Consequently, volatile flows from the deep planetary levels into the upper mantle levels, if they exist, must have a reduced character.

In addition to phase transformations due to pressure increase with depth, the stratification of the redox state of the mantle, its lithospheric and asthenospheric levels, must be affected by global mass exchange processes. They have a complex character and their geochemical consequences are still not fully understood. The most important of them are related to mantle–core interaction, formation of hot plumes in the mantle, and subduction of the lithosphere into the mantle.

Within the concept of the multistage evolution of the Earth's metallic core, its interaction with the silicate mantle material may be responsible for the generation of high fO_2 values in the upper planetary shells [6]. It is supposed that after the formation of the major portion of the core (about 95%), during the earliest 100 Ma of the Earth's evolution, the core continued to grow but

already at the expense of mantle FeO disproportionation through the reaction

$$3Fe^{2+}O \text{ (mantle)} \Rightarrow Fe^0 \text{ (core)} + Fe_2^{3+}O_3. \qquad (9)$$
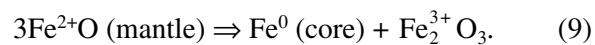
The second stage lasted over the following 150–300 Ma and produced an increase in the chemical potential of oxygen in the upper levels of the mantle up to fO_2 values near FMQ during phase transformations in an ascending mantle plume.

Since the pioneering study of Arculus and Delano [1], the processes of lithosphere subduction have been regarded as one of the main mechanisms of fO_2 increase in the upper mantle [62, 63]. Within these concepts, an increase in fO_2 in mantle materials is a consequence of H_2O, CO_2, and Fe^{3+} fluxes, which accompany the descent of oxidized lithospheric slabs. Based on the abundances of Fe^{3+} and Fe^{2+} in mid-ocean ridge basalts, ocean island basalts, gabbros, and ophiolite complexes and mass balance calculations, Lecuyer and Richard [64] concluded that the recycling flux of Fe^{3+} into the mantle was 4×10^3 kg/s over 2 Ga. The deep CO_2 and H_2O fluxes were estimated as 10^{10}–10^{11} and 10^{11}–10^{12} kg/s, respectively [10, 65]. According to these estimates, H_2O is the most important oxidizing agent in the mantle next to Fe^{3+}, whereas the role of CO_2 is less significant. These fluxes are sufficient to explain the present-day $Fe^{3+}/\Sigma Fe$ ratio of the mantle.

The mechanisms of O and Fe^{3+} accumulation in the mantle related to the descent of lithospheric slabs remain obscure. According to experimental data, Fe^{3+} can be gradually accumulated in the mantle owing to the incorporation into the structures of garnet [59] and perovskite [57, 66]. McCammon [57] showed that aluminum-bearing perovskite can accommodate considerable amounts of Fe^{3+} and be in equilibrium with metallic iron. If there is no interaction between the subducted material and the metallic core, Fe^{3+} must be gradually accumulated in the deep mantle layers. The hypothesis of a secular increase in the $Fe^{3+}/\Sigma Fe$ ratio of the mantle is actively debated. It was supposed that the subcratonic mantle has probably been progressively oxidized since the Early Archean [12, 18, 67]. However, Canil [19, 68] recently proposed a hypothesis of a relatively constant fO_2 value in the upper mantle over geologic time. This hypothesis is based on the character of V partitioning among silicate liquid, olivine, pyroxene, and spinel, which suggested that Archean komatiitic magmas were formed under fO_2 conditions typical of modern mid-ocean ridge basalt magmas.

The ideas that the redox state of the Earth's mantle was invariant in geologic time despite the subduction of lithospheric plates are based on the buffering of oxygen penetrating into the Earth's interiors. Lecuyer and Richard [64] suggested that this could be related to reactions with the Earth's metallic core. If descending lithospheric slabs or their derivatives reach the Earth's

core, their interaction may play the role of a redox buffer for the Earth's mantle through the reaction

$$Fe^0 \text{ (core)} + 2Fe^{3+} \text{ (lithospheric material)} = 3Fe^{2+} \text{ (mantle).} \quad (10)$$
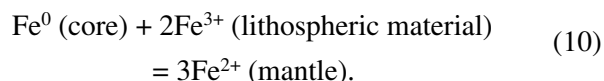
According to this hypothesis, a constant redox state has been maintained in the mantle owing to reaction (10) over the major part of the Earth's history.

Another possible buffering process is the interaction between Fe^{3+} and metallic drops that could be conserved in the mantle owing to incomplete separation from the silicate matrix during core differentiation [64]. This process is in line with the inferences of Ballhaus [18] on the saturation of the deep mantle, starting from the transition zone, with respect to metallic phase.

Geochemical data indicate a connection between an increase in fO_2 and metasomatic transformation in the deep lithosphere [18, 29, 69]. The majority of peridotite xenoliths with high fO_2 values, i.e., $\Delta \log fO_2(\text{FMQ})$ between −2 and +1, show indications of metasomatic alteration [18]. Furthermore, there is geochemical evidence for the confinement of the appearance of metasomatic phenomena in the mantle to a certain moment of its evolution related to the development of alkaline magmatism on Earth [69]. Among the supposed reasons for this phenomenon is a change in the geodynamics of planetary materials [69], because the onset of plate tectonics corresponds to the time of the earliest metasomatic events (2.5–2.7 Ga).

REDOX MELTING UNDER CONDITIONS OF fO_2 STRATIFICATION WITH DEPTH AND MIGRATION OF REDUCED FLUIDS

The stratification of fO_2 in the upper mantle and the possible migration of reduced C–O–H fluids into the lithospheric and asthenospheric zones with high fO_2 values provide favorable conditions for melting, which is controlled by the significant fO_2 dependence of the contents of H_2O, CO_2, CH_4, and H_2 in C–O–H fluids in the stability field of free carbon (graphite or diamond). A notable feature is the existence of a maximum in H_2O content (90–96 mol %) under certain fO_2 values (Fig. 6). Under fO_2 values below the water maximum point, the dominant component of C–O–H fluid is CH_4, the fraction of which increases with decreasing fO_2, i.e., with increasing depth. Under fO_2 values above the water maximum point, the dominant component of C–O–H fluid is CO_2. These variations in the composition of C–O–H fluid in the carbon-bearing mantle provide conditions for its local melting (redox melting) [16, 17]. It must be confined to the maximum H_2O content in the fluid owing to a significant depres-

sion of the melting temperature of peridotite with increasing H_2O activity (Fig. 6).

The melting can be corroborated by the migration of CH_4-rich fluids from the deep reduced parts of the upper mantle [70] and their reactions with relatively more oxidized lithospheric layers. This process results in an increase in H_2O concentration on the front of CH_4 interaction with lithospheric rocks, which can be described by the following general reaction:

$$CH_4 \text{ (fluid)} + O_2 \text{ (lithospheric rocks)} \longrightarrow 2H_2O \text{ (fluid)} + C \text{ (graphite, diamond).} \quad (11)$$
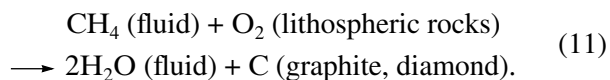
Reaction (11) is accompanied by sequential changes in fluid composition along the carbon saturation surface with increasing fO_2 and H_2O content. This must cause a dramatic depression of mantle solidus temperature and provide favorable conditions for melting without significant changes in T and P.

A characteristic feature of redox melting is carbon crystallization (graphite or diamond) from the C–O–H fluid phase under strongly variable fO_2 conditions. Within these concepts, the isotopic systematics of diamonds can be crucial for the elucidation of mass exchange conditions in the upper mantle stratified with respect to redox conditions [71].

It is not yet clear if upper mantle melting occurs under conditions of redox state stratification. However, the character of fO_2 stratification with depth suggests that redox melting in the mantle is a petrologically viable mechanism for the partial melting of the lower upper mantle. It was conjectured that kimberlite and alkaline magmas could be related to this type of melting [15]. It is possible that the redox mechanism cannot cause high-degree melting of peridotites. Owing to the low contents of volatile components in the mantle [5], this mechanism produces only intergranular liquid films with high H_2O and CO_2 contents. In such a case, the migration of this liquid could be responsible for metasomatic transformations at depths above the occurrence of reduced fluids. In other words, this melting mechanism is observed only as metasomatic transformations of rocks affected by melts with high contents of volatiles migrating in thin films.

There is also geochemical evidence for the confinement of metasomatic phenomena in the mantle to a certain moment of its evolution related to the development of alkaline magmatism and, probably, an fO_2 increase in the upper mantle [69]. One possible reason for this phenomenon is a change in the geodynamics of planetary materials, because the appearance of metasomatism corresponds to the time of the onset of plate tectonics (2.5–2.7 Ga). The increase of fO_2 concomitant with the appearance of metasomatic phenomena can be explained by a change in the regime of core–mantle interaction. In terms of the redox melting hypothesis, a
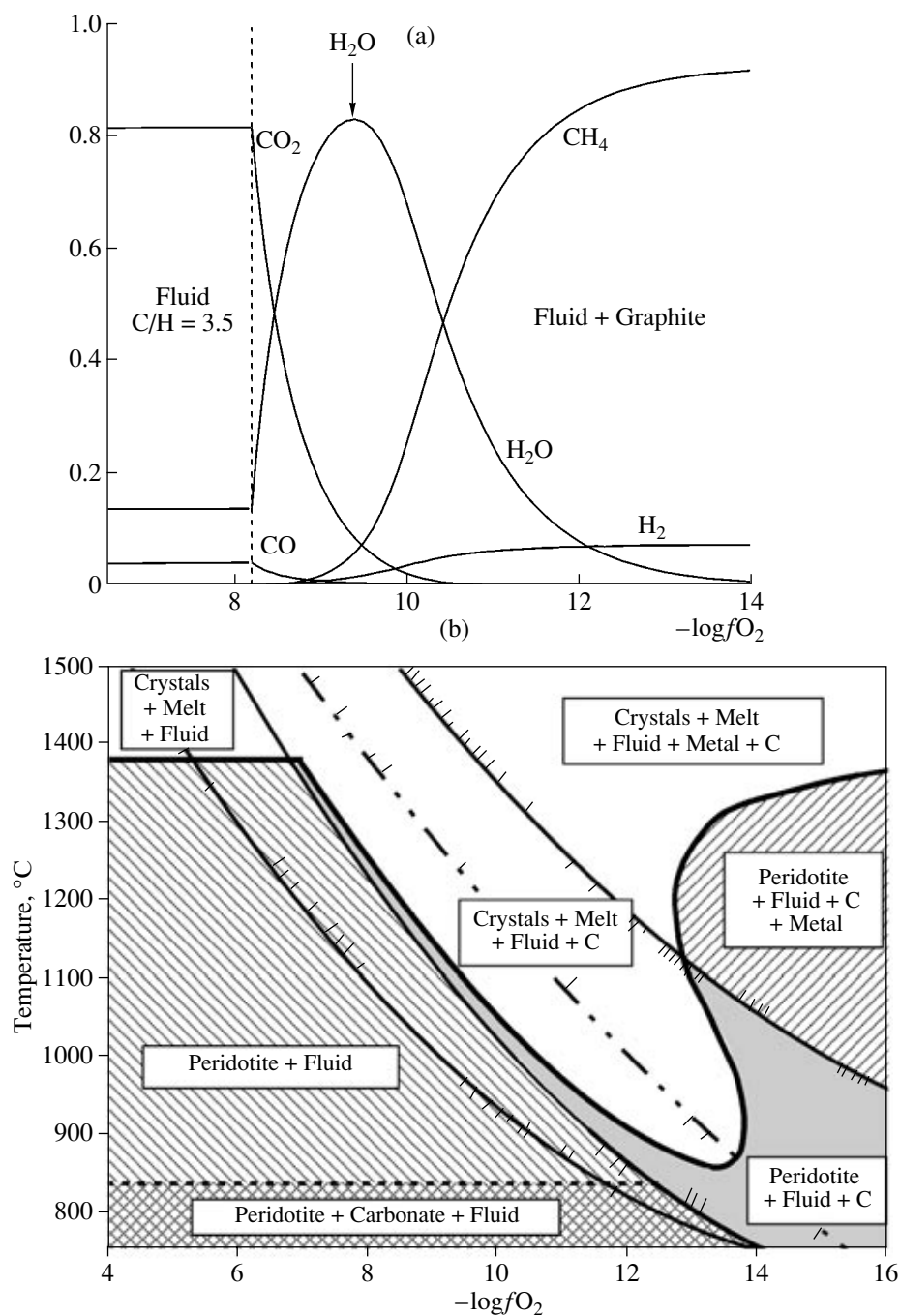
Fig. 6. Redox melting caused by the oxidation of C–O–H fluids during their migration from mantle zones with low fO_2 values. (a) Composition of C–O–H fluids saturated with carbon as a function of fO_2 at 2 GPa and 1200°C. The existence of the maximum H_2O content in the C–O–H system provides favorable conditions for peridotite melting at certain fO_2 values. (b) Melting temperature of peridotite as a function of H_2O activity in the carbon-saturated C–O–H fluid. The minimum melting temperature corresponds to the maximum concentration of H_2O in C–O–H fluid.

new geodynamic environment could promote the propagation of a fluid front with a high fraction of CH_4 and encourage interaction with oxidized lithospheric layers thereby providing favorable conditions for the formation of silicate melt films with high H_2O and CO_2 contents. These events could be among the reasons for the activation of metasomatic processes.

MAGMATIC TRANSFER OF HYDROGEN AND CARBON COMPOUNDS FROM THE DEEP ZONES OF REDUCED PLANETARY MATERIALS

The transfer of volatile components from deep zones to the planetary surface is primarily controlled by the solubility of volatiles in magmas and the redox state of their mantle source. The theories of the formation of
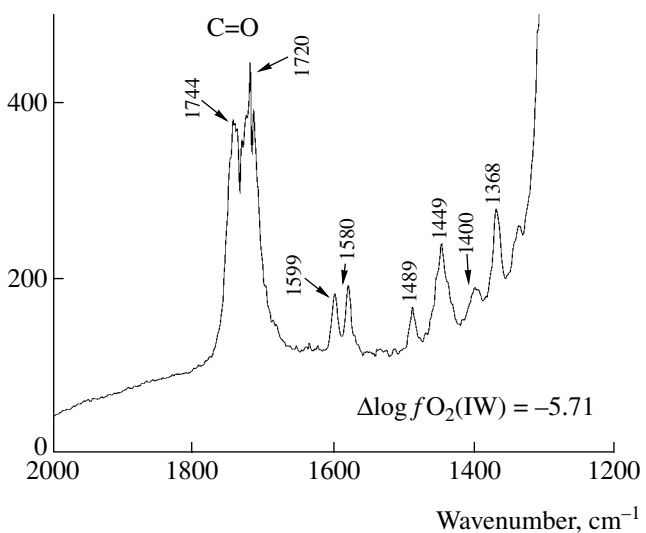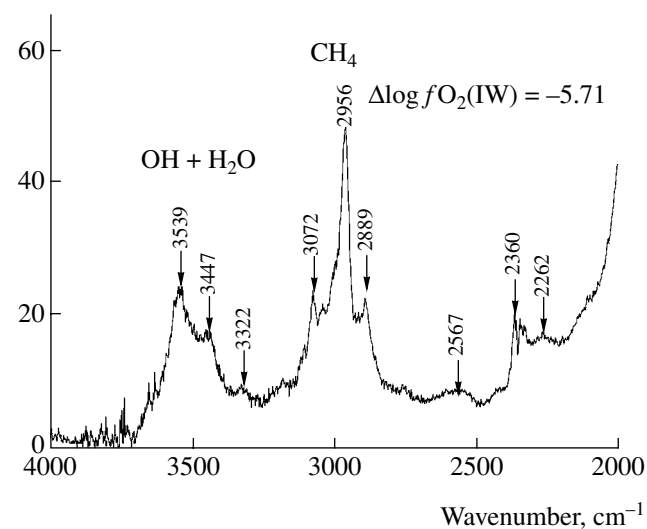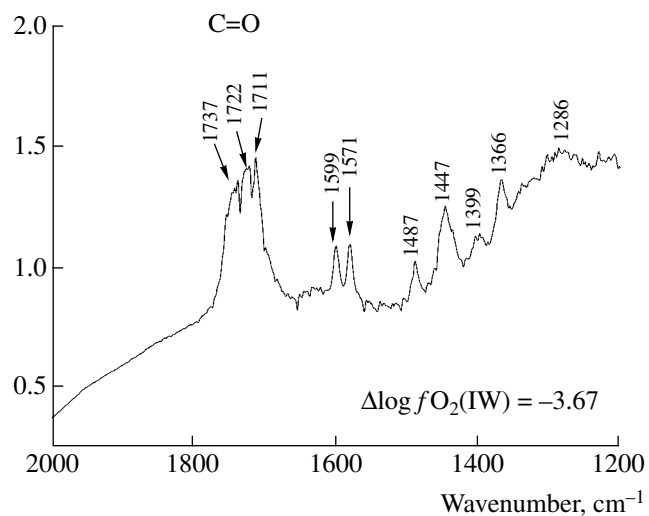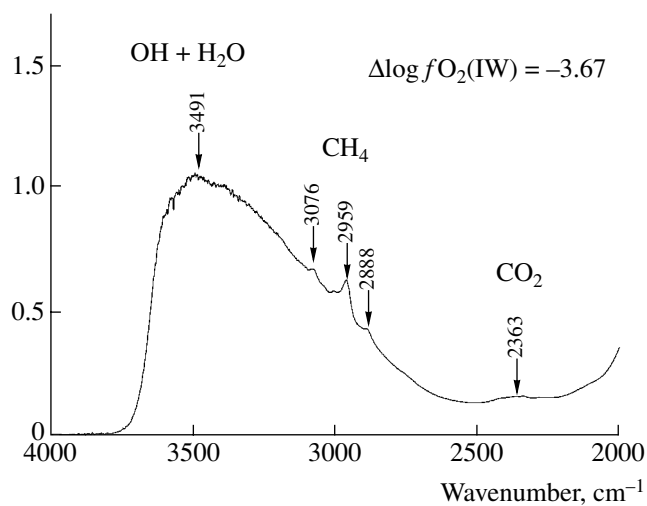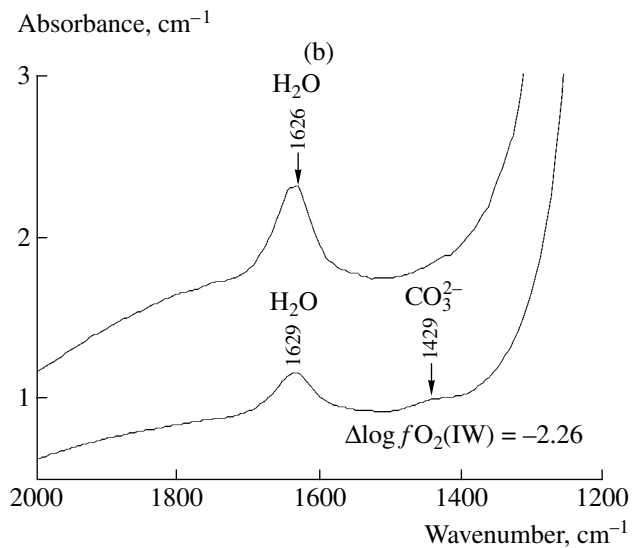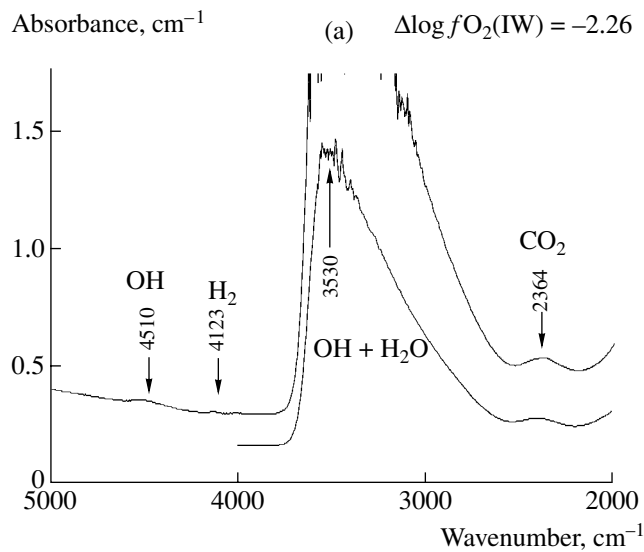
the Earth connect the composition of gases extracted by primary planetary magmas with large-scale melting in the pristine mantle, which occurred in the presence of a metallic phase [3, 72]. The molten metallic and silicate phases were subjected to gravitational migration, which affected the formation of the planetary metallic core. Simultaneously, volatile components had to be generated in the zones of large-scale melting of the early Earth. This process was controlled by the interaction of H, C, and their compounds with silicate and metallic melts and is still not adequately understood.

Experiments on the interaction of CH_4, H_2, and elemental carbon with silicate melts revealed an important feature of redox reactions in silicate liquids that can explain the formation of volatile components during early melting processes. Despite the low fO_2 values, both reduced (CH_4, H_2, and Si–C) and oxidized species of hydrogen and carbon (H_2O, OH^-, and CO_3^{2-}) are stable in the melts [14, 16]. Experimental studies [14, 70] demonstrated a significant correlation between the proportions of reduced and oxidized carbon species in the primary melts and the fO_2 values of the reduced mantle (Figs. 7a, 7b). When $\Delta\log fO_2(IW)$ values range from –2 to –3, which corresponds to the equilibrium of Fe with upper mantle olivine, oxidized H species (OH and H_2O) are predominant in melts equilibrated with Fe metal. If the chemical differentiation of the early mantle occurred under lower fO_2 values, for instance at $\Delta\log fO_2(IW)$ between –3 and –5 corresponding to the enstatite-chondrite model of mantle formation [73], the primary melts probably contained both oxidized H species (OH groups) and compounds with C–H bonds (CH_4 and other molecules). These volatile H and C compounds associate with the formation of a liquid Fe phase enriched in Si (1–12% Si) (Fig. 7).

Thus, the fO_2 regime of the formation of the magma ocean is of fundamental importance for the estimation of the composition of gases extracted from reduced planetary materials and delivered to the surface by high-temperature volcanic activity. Melting of a reduced carbon-bearing mantle at $\Delta\log fO_2(IW)$ values between –2 and –3 produces magmas containing more oxidized carbon and hydrogen species than in the mantle source. Therefore, the transition of the reduced mantle into a molten state is a possible mechanism for the

formation of H_2O and CO_2 in the geologic past and their primary input to the planetary surface. This feature of H and C interaction with silicate melts may be crucial for the determination of mechanisms for the transformation of reduced H and C species of the early mantle [73] into the major present-day species (OH^-, H_2O, and CO_3^{2-}). Under $\Delta\log fO_2(IW)$ between –3 and –5, high-temperature volcanic gases must be enriched in CH_4 and H_2.

It is suggested that the proportions of oxidized and reduced H and C species in the early atmosphere were closely connected to the character of global chemical differentiation during the formation of the metallic core, which could be a multistage process [6]. These concepts postulate that the first stage of core growth took place under reduced conditions imposed by the pristine terrestrial materials and was accompanied by the emission of CH_4, H_2, and CO into the atmosphere. The second stage of core growth was related to reaction (9) and resulted in oxidation of the upper portions of the mantle and enrichment of the primordial atmosphere in CO_2 and N_2. Experimental studies on the interaction of C and H with melts under pressures corresponding to depths of about 150 km suggest that the significant predominance of CH_4 in high-temperature volcanic gases requires melting in the presence of metallic iron at $\Delta\log fO_2(IW)$ values between –3 and –5. The supposed increase in fO_2 during the second stage of core formation must result in the formation of oxidized C and H species in the melt (OH^- and CO_3^{2-}). Correspondingly, it is reasonable to expect a change in the composition of high-temperature volcanic gases, which will contain H_2O in addition to CH_4, although the evolving mantle will remain in a reduced state, at fO_2 values below the IW buffer equilibrium.

Considering the role of early mantle melting in the evolution of redox state, the dynamics of magmatic liquids must be accounted for. The occurrence of considerable melt volumes in the Earth's gravitational field inevitably results in convective instability and extensive radial mass transfer, which must affect the behavior of volatile components and their stratification in the silicate liquid [74]. It is supposed that under conditions of vigorous convection and mass exchange, hydrogen dissipation and melt degassing in the near-surface zones

Fig. 7. Influence of fO_2 on the speciation of H and C in silicate melts of the system iron-bearing melt + molten metallic phase Fe (0.1–7.0% Si) + C (graphite) + H_2 at 4 GPa, 1550–1600°C, and $\log fO_2(IW) = -2.26$, $\log fO_2(IW) = -3.67$, and $\log fO_2(IW) = -5.71$. In order to determine the mechanisms of H and C dissolution, quenched reduced melts were investigated by IR spectroscopy. (a) IR spectra of C–H-bearing glasses within the region 5000–2000 cm^{-1} under various experimental fO_2 values. (b) IR spectra of the same samples of C–H-bearing glasses within the region 2000–1000 cm^{-1}. The results of these investigations highlight one notable feature of the interaction of H and C with reduced silicate melt: a dramatic change in the mechanism of their dissolution at decreasing fO_2. During melting at $\Delta\log fO_2(IW) = -2.26$, the predominant hydrogen species in the melt is the OH^- group, whereas melting at $\Delta\log fO_2(IW) = -5.71$ produces liquids with most hydrogen occurring in C–H bonds (CH_4). At $fO_2(IW) = -5.71$ cm^{-1}, there is a large narrow absorption peak typical of the C=O bond.

will result in an increase in fO_2 and burning of graphite in the magma ocean with a concomitant increase in the fraction of oxidized H and C species [74]. Owing to these processes, the composition of magmatic gases arriving at the planetary surface will change. The general tendency is a change from reduced degassing products (CO, CH_4, and H_2) to oxidized species (CO_2 and H_2O).

Within these concepts, the evolution and degassing of the magma ocean, its differentiation and crystallization must produce primary layering in the mantle with respect to redox state and relatively oxidized layers in the upper mantle compared with the deeper zones not affected by melting.

CONCLUSIONS

The chemical differentiation of the Earth is closely connected to the transfer of oxygen within the planetary interiors under the influence of metallic core formation, deep degassing, melting, subduction processes, etc. These processes are directly reflected in the evolution of the redox state of deep-seated materials, which is quantitatively characterized by fO_2 values in various mineral reactions. In terms of chemistry, the fO_2 value of mantle rocks is a fundamental parameter for any hypothesis concerning the early history of the Earth, the composition of the primordial atmosphere, and the composition of gases delivered by magmas to the Earth's surface. As to the solution of the problems of fO_2 regime in the upper mantle and its lithospheric and asthenospheric levels, our investigations lead to the following conclusions.

(1) There are many lines of evidence that relatively high fO_2 values dominate in the lithosphere and asthenosphere. They correspond to $\Delta\log fO_2$(FMQ) between -2 and $+1$, which provides the prevalence of H_2O and CO_2 in the fluid phase and stability of carbonates in these layers of the upper mantle. On the other hand, recent studies have demonstrated that there are zones with rather low fO_2 values ($\Delta\log fO_2$(FMQ) between -3 and -5) in the lithosphere of cratonic and noncratonic mantle areas, which is indicative of a significant depth stratification of the redox state of the upper mantle.

(2) Lithospheric peridotites with very low fO_2 values can be regarded as samples from those mantle zones that retained to some extent the fO_2 values typical of the early stages of formation of the Earth's mantle. However, more plausible reasons for the low fO_2 values are probably the effect of pressure on solid-phase transformations with the participation of Fe^{2+} and Fe^{3+} and Fe^{2+} disproportionation to $Fe^0 + Fe^{3+} +$ in mineral reactions in the upper and lower mantle.

(3) The areas of carbon-bearing lithosphere with low fO_2 values ($\Delta\log fO_2$(FMQ) between -3 and -4.5) correspond to the conditions of dramatic changes in the composition of C–O–H fluids: from predominantly methane to water–methane and CO_2-rich fluids.

(4) Migration of fluids in the fO_2-stratified mantle provides conditions for melting (redox melting), which is controlled by the maximum H_2O content in carbon-saturated fluids under certain fO_2 values. It is suggested that the limited amounts of volatile components in the mantle result in the formation of intergranular melt films with high contents of volatiles, the migration of which may be among the reasons for metasomatic transformations above the depth of occurrence of reduced fluids.

(5) The theories of the formation of the Earth suggest that the composition of gases extracted by primary planetary magmas is related to large-scale melting of the early mantle, which occurred in the presence of a metallic phase. Experiments on the interaction of H and C with silicate melts under low fO_2 conditions within the stability field of Fe–Si metallic phase revealed an important feature of redox reactions in silicate liquids. Despite the low fO_2 values, the melt contains both reduced (CH_4, H_2, and Si–C) and oxidized (H_2O, OH^-, and CO_3^{2-}) species of hydrogen and carbon. In this context, a transition of the reduced mantle into a molten state is a plausible mechanism for the formation of H_2O and CO_2 in the geologic past and their primary input to the planetary surface. This feature of the interaction of H and C with silicate melts may be crucial for the understanding of the mechanisms of the transformation of reduced C and H species that occurred in the early mantle to the currently predominant oxidized forms (OH^-, H_2O, and CO_3^{2-}).

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