CRYSTAL
CHEMISTRY

Dedicated to the 60th Birthday of M.V. Kovalchuk

Structural Transformations of Minerals in Deep Geospheres: A Review

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Received January 26, 2006

Abstract—The structure and composition of inner geospheres are considered in light of new data on the structural transformations of minerals under high pressure. More than 100 tetrahedral complexes in silicates of the Earth's crust give way to no more than 20 structural types of minerals of this class in the Earth's mantle. The main difference in their structures is associated with the transformation of Si tetrahedra into Si octahedra. New data on the structural transformations of minerals in deep geospheres indicate that the mineralogical diversity of the Earth's crust is substantially richer than that of deep geospheres; however, mantle mineralogy is not as primitive as was supposed even twenty or thirty years ago. The results of recent seismological investigations and quantum-mechanical calculations allow the assumption that there exists a new previously unknown phase transformation under the conditions in the Earth's inner core.

CONTENTS

1. INTRODUCTION

The problem regarding the composition and structure of deep geospheres is one of the most acute problems encountered in geology over the past decades. This is a priority direction in geosciences. In particular, we note that more than 90% of matter in the Universe is under a pressure of more than 1 GPa. Even at present, the newest geophysical data, in combination with the results of theoretical investigations into the structural transformations of minerals, have provided a means for simulating many specific features of the structure and composition of deep geospheres, as well as the processes occurring in them. Analysis of these data favors

the solution of key problems in modern natural science, such as the formation and evolution of the planet, geodynamic conditions of the Earth's crust and the mantle, evaluation of the risk of deep burial of hazardous wastes, Earth's energy resources, and a number of other important problems.

It is well known that many minerals of the Earth's crust crystallize from magmatic melts or accompanying solutions formed in deep geospheres. The formation of minerals in impact zones formed under incidence of cosmic bodies is also associated with high pressures. Moreover, the majority of the solid geosphere contains minerals that lie deep and exist under conditions of strong compression. Evidently, it is these minerals that bear information on the formation and evolution of our planet and, hence, on the Earth's past and future. In this respect, investigation of the structure, properties, and transformation of minerals subjected to high pressures plays a key role in the solution of fundamental problems in the physics and chemistry of the Earth.

In recent years, a large number of studies have been devoted to analysis of the mineralogical diversity of the Earth's mantle [1–7]. The array of experimental and theoretical data increases year by year, which poses the problem as to the their generalization and systematization. Elucidation of this problem is the purpose of the present review.

2. RETROSPECT

High-pressure mineralogy is an interdisciplinary field of modern science and has actively developed over the last seventy years. An English crystallographer, Bernal [8] was the first to suggest that, in the mantle, conventional olivine becomes stable in the form of a polymorphic modification with a spinel structure whose density is 9% higher. This transformation underlay the mineralogical interpretation of the variations observed in the seismic wave velocities at a depth of 400 km, i.e., at the "upper mantle–transition zone" boundary [9]. The conclusion formulated by Bernal was based on the previous inferences by Goldschmidt [10] about the dimorphism of the Mg_2GeO_4 germanate (chemically similar to the olivine) crystallizing in the olivine or spinel structural type. In addition, somewhat more recently, Birch [11, 12] studied the elastic characteristics of the mantle material and concluded that the deep zone located between 300 and 900 km is characterized by a series of phase transformations, one of which is the transformation of the olivine into a modification with a spinel structure.

In subsequent investigations in the field of the high-pressure crystal chemistry and mineralogy of deep geospheres, the period from the early 1950s to the middle 1960s is commonly termed exploratory. Its beginning is associated with 1953, when Coes synthesized a new silica modification (subsequently called coesite) at a pressure of 3 GPa. In 1954, crystals of synthetic diamond were prepared at a pressure of 5 GPa by General Electric researchers. At present, both minerals have been considered indicators of a high-pressure metamorphism, thus implying a relation of rocks containing them to the depth corresponding to the upper mantle.

By developing the ideas put forward by Goldschmidt and Bernal, Ringwood in 1959 described the transformation of the fayalite Fe_2SiO_4 into the polymorphic modification with a spinel structure under a high pressure. More recently, the $(Mg,Fe)_2SiO_4$ modification with a spinel structure was named ringwoodite. In 1961, Stishov (a postgraduate student of the Faculty of Geology of Moscow State University) and Popova (a researcher of the Institute of High-Pressure Physics of the USSR Academy of Sciences) synthesized a new dense silica modification with a rutile structure at a pressure higher than 8 GPa, which was named stishovite [13]. This discovery showed that conventional rocks of the Earth's crust should differ radically in their mineral composition from rocks that form the transition zone between the upper and lower mantles.

The problem of the mineral composition of the Earth's core is substantially more complex than that of the Earth's mantle. Unlike many deep silicates and diamond that are stable under normal conditions, dense iron modifications, which in their density and elastic properties should be similar to the core material, can be studied only directly under high pressures (in situ) or, of late, theoretically on the basis of quantum-mechanical calculations. In 1964, Takahashi and Bassett described the ε modification of iron, which appeared to be stable at pressures higher than 13 GPa. The structure of this modification is represented by the hexagonal closest packing of iron atoms. It has been assumed that this phase is the main component of the Earth's core.

Subsequent rapid progress in experimental techniques favored high-pressure investigations of quite different physical and chemical properties of a large number of minerals. The obtained results, in combination with seismological data, led to the revision of the traditional model of the Earth structure and formulation of many new problems, such as the problem regarding the change in the composition at the boundary between the lower and upper mantles or the problem of the temperature inside the core (see, for example, [1]). The development of the scientific concepts in this field allowed a number of assumptions to be made concerning materials that form deep geospheres of other planets. It has been assumed that the role of upper and lower mantles in the interior of giant planets can be played by dense gas shells (composed of compressed hydrogen and helium gases in Saturn and Jupiter) or ice shells (containing H_2O, NH_3 and CH_4 in Uranus and Neptune). It has turned out that, at high pressures, noble gases are not necessarily inert and can form a number of compounds, such as $He(N_2)_{11}$, $NeHe_2$, and $Ar(H_2)_2$. It is remarkable that, at high pressures (>30 GPa), argon and xenon appear to be in a crystalline state at higher temperatures than iron, whose melting temperature is lower than those of these elements. This implies that, at high pressures, iron can play the role of a volatile element, whereas argon and xenon can serve as "refractory" materials. Iron and potassium incompatible in general positions in structures of minerals in the Earth's crust can form alloys under high pressures.

These and other data indicate that minerals of the Earth's crust and deep geospheres differ substantially in their properties and structures. Note that, during analysis of new results obtained in high-pressure mineralogy, it is necessary to take into account one important circumstance. The majority of inferences associated with the solution of this extremely complex problem are made on the basis of unique experiments that can be performed by researchers of a small number of leading laboratories. F. Birch (one of the founders of the modern mineralogy of deep geospheres) [12] emphasized that an uninformed reader should understand the ambiguity of the inferences made in these cases. With some irony, he offered examples of terminological equivalents that are characteristic of publications concerned with complex high-pressure experiments and their interpretation at the level of standards applied to conventional investigations. In particular, Birch wrote that what is considered a "possible inference" in conventional publications is treated as an "unquestionable inference" in papers with results of high-pressure investigations.
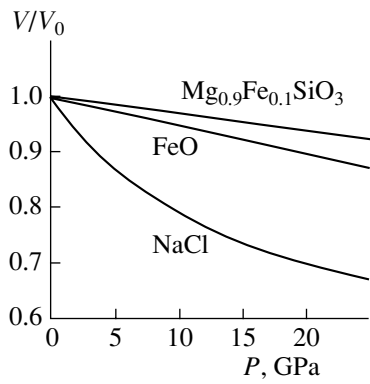
Fig. 1. Typical compressibility curves for crystals (Mao et al., 1969, 1991).

Fig. 2. Change in the volume proportions of the minerals with an increase in the pressure (depth) [19]. Designations: *TZ*—transition zone, *CMB*—core–mantle boundary, Cpx + Opx—clinopyroxenes and orthopyroxenes, *HS*—high-spin states of iron atoms, and *LS*—low-spin states of iron atoms.

Similarly, the adjective "specific" will be used instead of the adverb "ambiguously," and the expression "a mixture of all elements" in the Earth's core will be replaced with "pure iron."

The experiments performed in the past decades revealed that chemically different minerals are characterized by different compressibilities. The quantitative evaluation of the compressibilities requires the use of the so-called equations of states $P = f(V, T)$, which relate the pressure, volume, and temperature. In particular, the equation of state for an ideal gas has the form $P = RT/V$, where P, V, and T are the pressure, volume, and temperature of the gas, respectively; and R is the gas constant equal to 8.314 J/(mol K) (the difference between the heat capacities at constant pressure and constant temperature).

For liquids and solids, it is common practice to separate the temperature and pressure effects; that is,

$$P(V, T) = P_{300 K}(V) + P_{thermal}(V, T),$$

where $P_{300 K}(V)$ is the dependence of the pressure on the volume at room temperature and $P_{thermal}$ is the pressure associated with the thermal expansion. In this case, the dependence of the volume on the temperature is described by the equation

$$V = V_0[1 + \alpha(T - T_0)],$$

where the thermal expansion coefficient α is a function of the temperature: $\alpha = \alpha_0 + \alpha_1 T + \ldots$.

At relatively low pressures (lower than 1 GPa), the compressibility $\beta = \Delta V/V\Delta P$ and its reciprocal referred to as the bulk modulus $K = 1/\beta$ are virtually constant and the equation of state can be written in the form $V = V_0(1 - P/K)$. Figure 1 shows the relative changes in the volume of the (Mg,Fe)SiO$_3$ mineral with the perovskite structure, wustite, and halite with an increase in the pressure. It can be seen from Fig. 1 that the compressib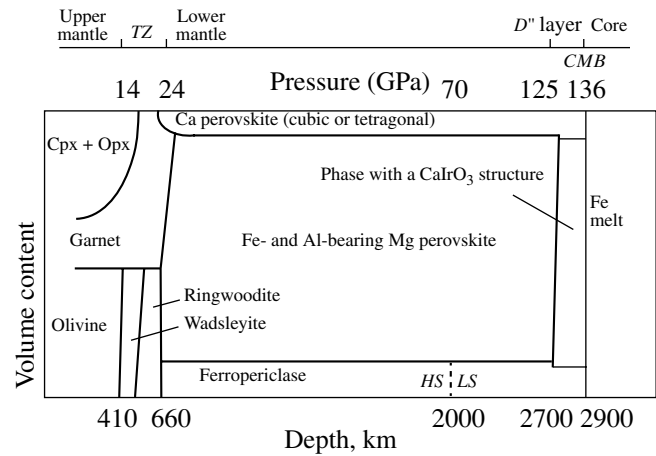ility of the halite is higher than those of the oxides due to the weaker interatomic bonds in the halite structure. A more general theory of the equations of state for solids has been developed in detail, but it is based on more complex approaches [14–16].

The generalization of the results obtained with the use of high-pressure X-ray chambers have made it possible to formulate a number of high-pressure high-temperature crystal chemical principles that expand scientific concepts regarding the state of matter in deep geospheres (Urusov and Pushcharovsky, 1984, 1986). In addition to these concepts, new crystal chemical data obtained in the past years allow one to relate structural transformations of minerals to seismological models [17, 18] (Figs. 2, 3) that characterize a change in the seismic wave velocities, density, and pressure in deep geospheres. In the present work, the transformations of minerals are considered within the traditional model of the Earth's mantle structure, even though there is an alternative model recently proposed by one of the authors of this review (Yu.M. Pushcharovsky and D.Yu. Pushcharovsky, 1999). The key idea of the alternative model—the recognition of the middle mantle that lies at depths between 840 and 1700 km and is separated from the upper and lower mantles by boundary zones 170 and 500 km thick, respectively—has steadily gained favor.

3. THE UPPER MANTLE (24–410 km)

According to the chemical and mineralogical compositions, the models of the upper mantle composition are termed the pyrolite model (the main minerals are olivine, pyroxenes, and garnet in a ratio of 4 : 2 : 1); the piclogite model (the main minerals are pyroxene and garnet, the olivine accounts only for 40%); and the eclogite model that, apart from the pyroxene–garnet assemblage characteristic of eclogites, involves a num-
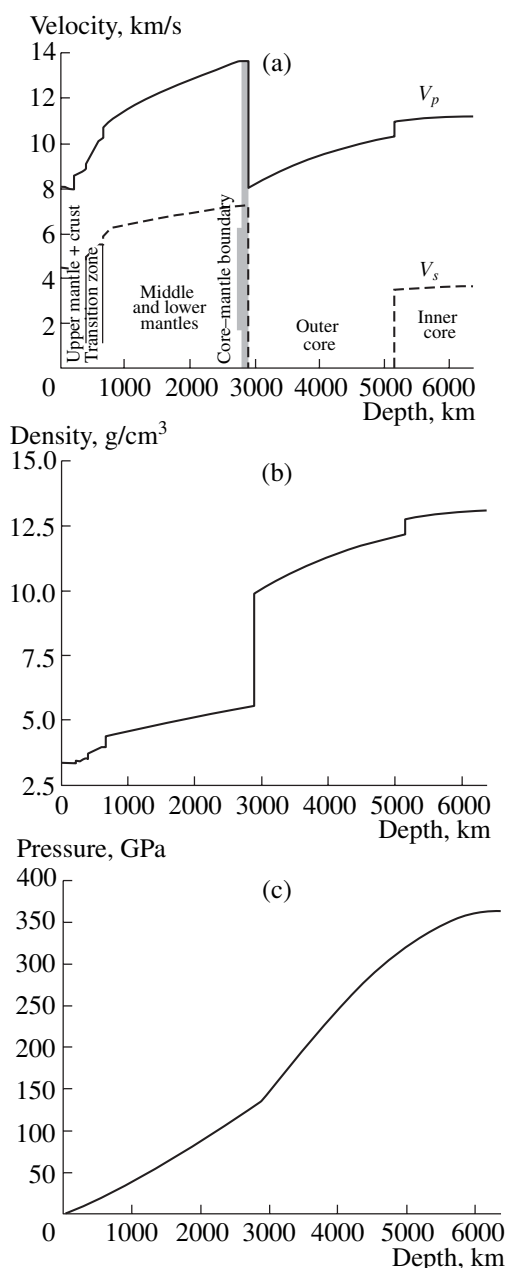
Fig. 3. Profiles of (a) the longitudinal (V_p) and transverse (V_s) seismic wave velocities, (b) the density, and (c) the pressure in the Earth's interior according to the Preliminary Reference Earth Model [17].

ber of rarer minerals, including Al-bearing kyanite Al_2SiO_5 (up to 10 wt %).

The locations of many seismic discontinuities revealed to date in deep geospheres correlate with the depths of structural transformations of mantle minerals (Fig. 2). Note that not all the boundaries determined from the seismic data are global, even though they can be associated with the transformations of minerals. For example, the first seismic discontinuity observed at a depth of ~220 km (the so-called Lehmann discontinuity) corresponds to the transformation of the mono-

clinic structures of pyroxenes into the orthorhombic structures [20]. One more local seismic discontinuity recorded at a relatively small depth of ~300 km is attributed to the formation of the stishovite in eclogite rocks [21]. In this case, the stishovite can be formed as a result of the transformation of the coesite or through the transformation of clinopyroxenes according to the reaction $2(Mg,Fe)SiO_3 = (Mg,Fe)_2SiO_4$ (wadsleyite) + SiO_2 (stishovite). This reaction proceeds at a pressure of 15 GPa and a temperature of 1600–1700 K, i.e., under the conditions corresponding to a depth of ~450 km. However, at lower temperatures, the reaction can occur at lower pressures corresponding to depths of the order of 300 km.

4. THE MANTLE TRANSITION ZONE
(410–670 km)

The global boundary at a depth of 410 km is associated with the olivine–wadsleyite structural transformation. The boundary at a depth of 520 km is attributed to the subsequent transformation of the wadsleyite into the spinel-like ringwoodite. The role of the wadsleyite, as one of the most important mantle component, was originally noted by Ringwood and Major in 1970, even though this mineral at that time was not found in nature and only its synthetic analogue β-$(Mg,Fe)_2SiO_4$ was known [22]. These researchers proposed to name a future mineral with the above composition as wadsleyite after Australian chemist Wadsley for his work in the field of the structural crystallography of minerals and inorganic compounds.

The wadsleyite and ringwoodite are treated as the main accumulators of water in the transition zone (410–460 km), whose volume exceeds that of the World ocean [23]. In this case, even an insignificant water content (0.1 wt %) in the transition zone is equivalent to a water shell 1 km thick that covers the Earth's surface. From the crystal chemical standpoint, this specific feature of the composition of the formally anhydrous wadsleyite and ringwoodite is determined by the replacement of a number of O^{2-} anions with OH^- hydroxyl groups in their structures. In the wadsleyite structure, a prerequisite for this replacement is the presence of the O atom that does not participate in the formation of SiO_4 tetrahedra and is coordinated only by five Mg atoms (Fig. 4) [24]. As a result, the bond valence sum at this anion is equal to 1.67. This result can be explained by the random filling of the corresponding position with OH groups (up to 33%) and O^{2-} anions (no less than 67%) in combination with a distortion of cation coordination polyhedra.

A very complex concentric shell termed the mantle transition zone is located at depths from 410 to 670 km and predominantly contains phases with the garnet-, wadsleyite-, and spinel-type structures and, probably, $(Mg,Al)(Si,Al)$ solid solutions with a structure of the ilmenite (akimotoite $MgSiO_3$) type. This assemblage of

minerals below the global boundary at a depth of 670 is replaced with perovskite-like phases (which occupy approximately 80% of the volume of the lower mantle) and Mg wustite (20%) with the NaCl-type structure. As secondary minerals, this region can also involve high-pressure silica phases, such as the rutile-like stishovite and its orthorhombically distorted analogue with a $CaCl_2$ structure, seifertite with the α-PbO_2-type structure, potassium aluminosilicate $KAlSi_3O_8$ with a hollandite structure, and the $MgAl_2O_4$ and $NaAlSiO_4$ polymorphs with structures of calcium ferrite $CaFe_2O_4$ and calcium titanite $CaTi_2O_4$.

5. THE LOWER MANTLE

The aforementioned boundaries at depths of 410, 520, and 670 km are treated as global by the majority of researchers. According to the seismological data, there are other (less pronounced) boundaries, for example, at depths of 900, 1200–1300, and 2700 km, as well as local or intermediate boundaries at depths of 1700, 1900–2000, ~2850 km, and others. The nature of many boundaries remains unknown to date, even though these boundaries in many cases correspond to the structural transformations of minerals. A number of recently revealed transformations are given below.

670–850 km: $(Ca_{0.5}Mg_{0.5})Al_2Si_2O_8$ (anorthite-type structure) $\longrightarrow$ hollandite-type structure [25];

850–900 km: $Mg_3Al_2Si_3O_{12}$ pyrope $\longrightarrow$ $(Mg,Fe)SiO_3$ (perovskite),

$Mg_3Al_2Si_3O_{12}$ pyrope $\longrightarrow$ Al_2O_3 (corundum) + $(Mg,Fe)SiO_3$ (ilmenite),

$MgAl_2O_4$ (spinel-type structure) $\longrightarrow$ $MgAl_2O_4$ ($CaFe_2O_4$-type structure) [26];

~1200 km: $MgAl_2O_4$ (spinel-type structure) $\longrightarrow$ $MgAl_2O_4$ ($CaTi_2O_4$-type structure) [27];

~1500 km: SiO_2 stishovite $\longrightarrow$ SiO_2 ($CaCl_2$-type structure) [28, 36],

FeO (metallization of interatomic bonds) [29];

~2300 km: SiO_2 ($CaCl_2$-type structure) $\longrightarrow$ seifertite [30, 36];

~2700 km: $MgSiO_3$ (perovskite-type structure) $\longrightarrow$ $MgSiO_3$ ($CaIrO_3$-type structure);

~2850 km: $MgSiO_3$ ($CaIrO_3$-type structure) $\longrightarrow$ $MgSiO_3$ (perovskite-type structure).

Let us consider only the newest data. At pressures corresponding to a depth of 1200 km, the phase with the $MgAl_2O_4$ spinel composition crystallizes in a structure of the Ca titanate type. Until recently, the jump with an increase in the seismic velocity at a depth of 1200 km was associated with the structural transformation of the stishovite [13] into the phase with a structure of the $CaCl_2$ type, which is an orthorhombically distorted structural analogue of the rutile [28]. The SiO_2 post-stishovite modification ($CaCl_2$ analogue) is stable at
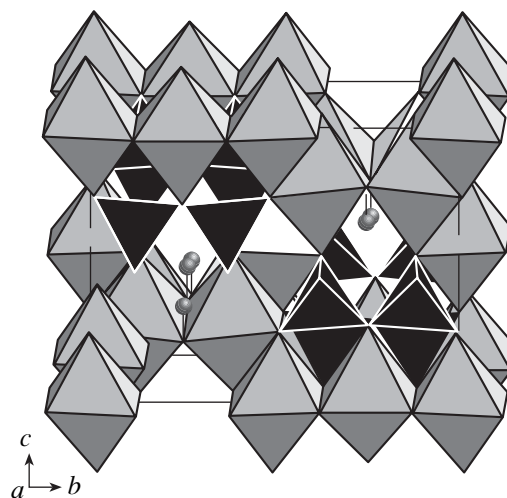

Fig. 4. Wadsleyite structure along the [100] direction. Gray spheres are the protons bonded to the O(2) atoms located at the joint of five (Mg,Fe) octahedra.

pressures higher than ~50 GPa. At room temperature, this pressure corresponds to a depth of ~1200 km; however, in combination with an increase in the temperature in the mantle, conditions arising at the given pressure are equivalent to those at depths of ~1500 km.

It was demonstrated that, at a higher pressure of ~100 GPa, this SiO_2 modification transforms into the phase with an α-PbO_2 structure [30]. This phase, called seifertite, has been found in meteorites. Reasoning from the results of investigations of similar compounds and theoretical simulation of the structure of silica modifications, Prewitt [31] recently assumed that silicon oxide SiO_2 with a pyrite structure can be synthesized in the immediate future, even though the formation of this phase according to the theoretical estimates requires extremely high pressures (~210 GPa). Actually, in 2005, Kuwayama et al. [32] synthesized this phase and refined its structure by the Rietveld method at a pressure above 200 GPa. The stability field of the phase under consideration is beyond the range of the physicochemical parameters characteristic of the Earth's mantle. At present, there are no grounds to believe that silica can occur in the Earth's core. However, this phase can be considered a probable mineral in rocky cores of giant planets, where the pressures can be as high as a few thousand GPa.

The structure of the silicon oxide SiO_2 under the conditions corresponding to the lower mantle is of interest not only due to the possible formation at large depths but also due to the possible effect on the hypothetical reaction of decomposition of the $MgSiO_3$ perovskite into the MgO periclase and SiO_2 silica. However, according to the recent experimental [33, 34] and

theoretical [35] data, the given reaction cannot proceed under the mantle conditions.

It should be noted that, in [36], the authors cast serious doubt on the presence of stishovite, its orthorhombic analogue with a $CaCl_2$ structure, and other high-pressure silicon oxide forms in the mantle. According to the results of the theoretical simulation of the phase diagram of the SiO_2 oxide at pressures and temperatures possible at large depths and petrological investigations of ultrabasic rocks of the peridotite, harzburgite, and pyrolite compositions at high pressures, the inference has been made that the content of free SiO_2 in the mantle is very insignificant. This oxide can occur in considerable amounts only in specific mantle regions close to subduction zones of basalt blocks. In the majority of the mantle, the ratio $MgO/SiO_2 > 1$ holds true and the SiO_2 oxide enters into the reaction with the MgO oxide to form the mineral $MgSiO_3$ with a perovskite structure. Therefore, the presence of the silica is excluded in the lower mantle, unlike the upper mantle, where, as was noted above, stishovite can be formed.

Under high pressures, minerals can undergo quite different transformations. Knittle and Jeanloz [29] demonstrated that the FeO wustite can metallize at a pressure of ~70 GPa. It seems likely that this process is accompanied by the transformation of the wustite from a halite-like structure to a nickeline-like structure [37]. In deep zones of the lower mantle, high pressures can lead to a change in the electronic structure of atoms of particular elements, their deformation, and disturbance of the sphericity. For example, Badro et al. [38] found the transition of Fe atoms from a high-spin state to a low-spin state in the $(Mg_{0.83}Fe_{0.17})O$ ferropericlase at pressures of ~60–70 GPa corresponding to depths of ~1600 km. In the same zone of the lower mantle at a pressure of ~90 GPa (~2100 km), the Al_2O_3 oxide with a corundum structure can transform into the phase with an orthorhombic structure of the Rh_2O_3 (II) type with a decrease in the molar volume by 4% [39]. The specific feature of this transformation under pressure, like the transformation of the SiO_2 oxide into a structure of the pyrite type [36], is the disappearance of the closest anion packing and the formation of phases that contain no closest atomic packings and are characterized by a disturbance of the sphericity of ions and their strong distortion. However, the presence of the Al_2O_3 oxide as an individual phase in the Earth's mantle is highly improbable and the inclusion of the above transformation is important from the crystallographic rather than from the geophysical standpoint.

In recent years, there have appeared data on a change in the electronic structure of iron atoms in perovskite-like phases of the $(Mg_{0.9}Fe_{0.1})SiO_3$ composition. In this case, the content of iron in the low-spin state increases from pressures of ~70 GPa (~1850 km) and reaches a maximum at 120 GPa (~2700 km), i.e., in the vicinity of the D'' layer [40]. This two-step transition of iron atoms from the high-spin state to the low-spin state in perovskite-like phases (unlike the ferropericlase) can be explained by the filling of both cation positions with iron atoms in the $MgSiO_3$ phase. Since the symmetry and crystal field forces (as well as the cation–anion distances) in both positions are different, the spin transitions in cations occupying these positions are also different. It was experimentally established [41] that the Fe^{3+} valence state (rather than the Fe^{2+} valence state, as was believed earlier) of Fe impurities in the $MgSiO_3$ phase with a perovskite structure is dominant. Furthermore, since Fe^{2+} ions continuously transfer from the upper mantle and transition zone, the formation of the $MgSiO_3$ perovskite-like phase in the lower mantle should be accompanied by the reaction

$$3Fe^{2+} \text{ (perovskite)} \longrightarrow 2Fe^{3+} \text{ (perovskite)} + Fe^0 \text{ (metal)},$$
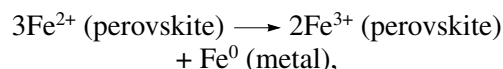
which was experimentally confirmed by Frost et al. [41]. Recent calculations (Zhang and Oganov, *Earth and Planetary Science Letter*, in press) also confirmed this reaction and showed that Fe^{3+} cations in the perovskite structure (as well as in the postperovskite structure in which Fe^{3+} ions are also dominant) tend to occupy the nearest Mg and Si positions. According to these calculations, the reaction described in [41] is attended by a strong exothermic effect and can increase the temperature of the entire mantle by 100 K.

The recently revealed structural transformations of the most important carbonates, which apparently represent the main carbon minerals in the mantle, occur at pressures corresponding to the middle mantle. It is known that the magnesite, calcite, and dolomite are the most abundant carbonates in the Earth's crust. Fiquet et al. [42] demonstrated that the magnesite is stable to a pressure of at least 80 GPa, which corresponds to depths of ~1900 km.

The calcite transforms into the aragonite in the upper mantle. Moreover, the dolomite decomposes into the magnesite and aragonite also in the upper mantle. Until recently, the specific features of the behavior of these minerals at depths larger than 1000 km remained unknown in many respects. Isshiki et al. [43] found the phase transition of the magnesite at pressures exceeding 110 GPa; however, the experimental data were insufficient for determining the structure of the new phase of the $MgCO_3$ compound. More recently, Ono et al. [44] revealed that the aragonite at pressures higher than ~40 GPa transforms into a new phase, whose structure could not be determined either experimentally or with the use of conventional methods for the theoretical simulation. Recently, Oganov and Glass proposed a new simulation method that provides a way of predicting crystal structures at any specified pressure on the basis only of the chemical composition. This approach was used successfully to determine the structure of the $CaCO_3$ postaragonite phase [45]. The struc-
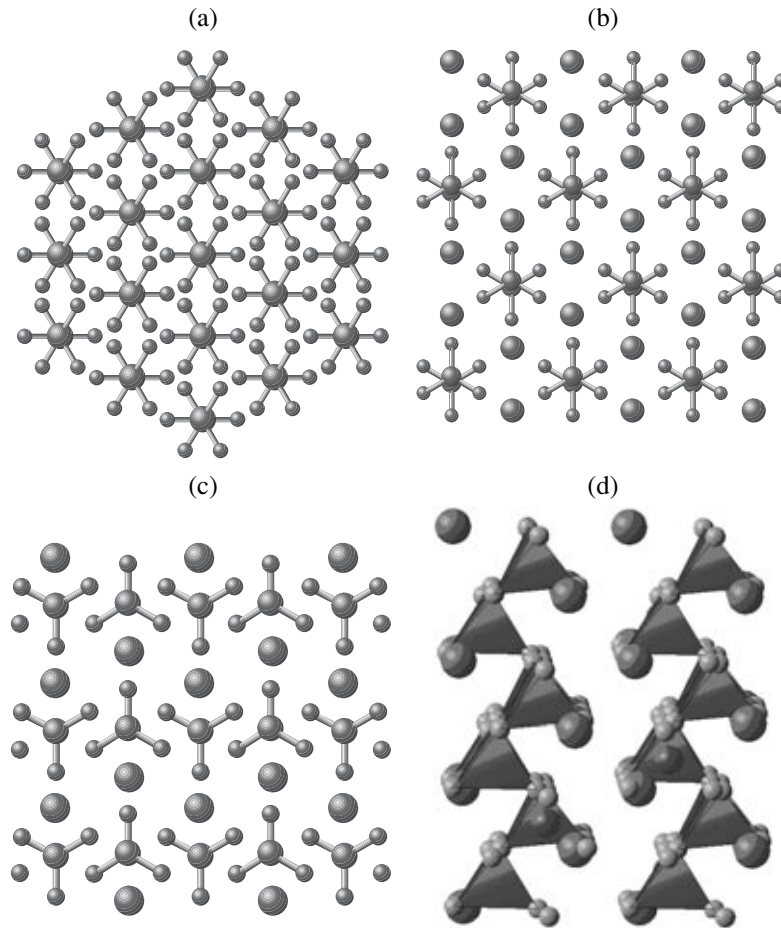
(a)   (b)

(c)   (d)

Fig. 5. Structures of the (a) calcite, (b) aragonite, (c) postaragonite phases stable at pressures higher than 42 GPa and (d) the $CaCO_3$ pyroxene-like phase formed at pressures higher than 137 GPa [45]. Large spheres are the calcium atoms, intermediate spheres are the carbon atoms, and small spheres are the oxygen atoms.

ture belongs to a new structural type and allows one to explain all the experimentally measured characteristics of this phase (the X-ray powder diffraction pattern, the compressibility, and the stability field). The structures of the calcite, aragonite, and new postaragonite phase are compared in Figs. 5a–5c. Note that the coordination number of Ca atoms increases from 9 for the aragonite to 12 for the postaragonite phase. According to the calculations, the postaragonite phase at 137 GPa should transform into a new modification with a structure that is similar to pyroxene structures (Fig. 5d) characterized by the space group $C222_1$, the formation of chains from CO_4 tetrahedra, and a rather large coordination number of Ca atoms (equal to 10). A similar structure is also possible for the high-pressure $MgCO_3$ phase, even though other variants of the atomic arrangement for the magnesium carbonate at these pressures cannot be ruled out.

Therefore, quite different transformations can occur in the mantle. The results of investigations into the structural transformations of minerals in deep geospheres suggest that the lower mantle is not so homoge-

neous as was believed earlier. In general, we can make the inference that mineralogical diversity of the Earth's crust is substantially richer as compared to deep geospheres. However, the new data demonstrate that mantle mineralogy is not so primitive as was supposed even twenty or thirty years ago. Modern experimental methods permit one to simulate mineral transformations that proceed at depths corresponding to the core–mantle boundary and even in the core itself. Admittedly, the number of questions is larger than the number of answers. The modern concepts associated with this problem are the subject matter of the next sections.

6. MINERAL COMPOSITION AT THE CORE–MANTLE BOUNDARY (D″ LAYER)

In the early 1940s, Australian seismologist Bullen proposed the scheme for the Earth's structure consisting of zones and separated the D' zone (984–2700 km) inside the lower mantle and the D'' layer (2700–2900 km) at the core–mantle boundary. At present, this
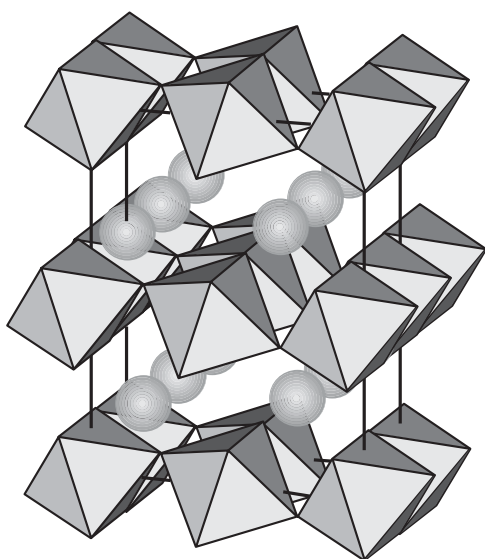
Fig. 6. Structure of the $MgSiO_3$ postperovskite modification. Magnesium atoms are located between layers formed by the silicon octahedra [33].

scheme has been substantially changed and only the D'' layer has been widely used in the literature. The main feature of the D'' layer lies in a decrease in the seismic velocity gradients as compared to those in the overlying mantle region.

The core–mantle boundary is treated as the most pronounced manifestation of the differences between the material properties in the Earth's interior. Analysis of the experimental data demonstrates that, beginning with this depth (beginning with temperatures of 3000 K and pressures of 25–70 GPa), the iron melt and the $(Mg,Fe)SiO_3$ phase with a perovskite structure interact to form stishovite and an iron alloy containing silicon and oxygen. According to Badro et al. [38], the FeSi compound, in addition to all the minerals inherent in the middle and lower mantles, can occur at the core–mantle boundary.

The most unexpected recent finding revealed from quantum-mechanical calculations and direct experiments is the transformation of the $MgSiO_3$ perovskite phase into the phase with a structure of the $CaIrO_3$ type at pressures of 125–127 GPa and temperatures of 2500–3000 K corresponding to depths of 2700–2740 km, i.e., to the upper boundary of the D'' layer (Fig. 6) [33]. The density of this phase, which is frequently termed the postperovskite phase, is 1.2% higher than that of the perovskite phase. Note that the $MgSiO_3$ phase with a $CaIrO_3$-type structure is the main mineral of the D'' layer covering the depth range 2700–2890 km. The same inferences were independently and almost simultaneously made by Murakami et al. [34] on the basis of the performed experiments. It should be noted that the idea of the possibility of crystallizing minerals that have the above structure and are charac-

teristic of the core–mantle boundary was put forward in [46] on the basis of the experiments on compression of the Fe_2O_3 compound. At a pressure of 30 GPa, α-Fe_2O_3 (hematite) transforms into the perovskite-like modification, which with a further compression to pressures higher than 50 GPa acquires the aforementioned postperovskite structure [33, 47].

In [48], it was demonstrated that the perovskite and postperovskite modifications of the $MgSiO_3$ compound are the extreme terms of the polytypic series of structures (Fig. 7). The intermediate structures of this series are metastable at $T = 0$ K. However, since their enthalpies are only slightly higher than those of the perovskite and postperovskite, they can be stabilized by impurities and temperature effects. This circumstance enables us to assume that the phases with these structures can occur as secondary minerals in the lower mantle and the D'' layer. Moreover, the given structures correspond to distortions of the atomic packing in the main motifs of the perovskite and postperovskite and, according to [48], are formed under plastic deformations. These data, in combination with the predicted elastic constants of the postperovskite, made it possible to interpret the observed unusual character and a pronounced anisotropy of the D'' layer.

The Al_2O_3 oxide with a $CaIrO_3$ structure stable at pressures above 130 GPa is the final product of the corundum transformation [49]. As was noted above, the corundum at a pressure of 90 GPa crystallizes in a structure of the Rh_2O_3 (II) type, in which, unlike many high-pressure phases, the closest packing of oxygen atoms is absent. According to the geophysical data, the deep zones of the lower mantle are characterized by a very high electrical conductivity, whose origin is not quite clear under the assumption that $(Mg,Fe)SiO_3$, $(Mg,Fe)O$, and $CaSiO_3$ are the main minerals of these zones. However, the previously established sharp increase in the electrical conductivity of the Al_2O_3 oxide at a pressure of 130 GPa and a temperature of 1500 K, in combination with the transformation of this phase under similar conditions into a $CaIrO_3$-type structure, permits us to assume that a high electrical conductivity should be observed for the $MgSiO_3$ postperovskite modification and, hence, be responsible for the electrical conductivity of the entire zone containing this phase.

An important potential component of the lower mantle is the Fe_xO wustite, whose composition corresponds to a stoichiometric coefficient $x < 0.98$. This implies that the wustite structure involves both Fe^{2+} and Fe^{3+} ions. According to the experimental data obtained by Boehler (1996), the melting temperature of the wustite at the boundary between the lower mantle and the D'' layer is estimated at ~5000 K. This is considerably higher than the anticipated temperatures (~4000–4300 K) at these depths (the mean adiabatic temperature of the mantle is approximately equal to 2700 K, and the tem-

perature at the bottom of the lower mantle can be higher by approximately 1400 K). Consequently, the wustite can be retained in the solid form at this depth. The concept of the phase boundary between the solid lower mantle and the liquid outer core requires a more flexible approach and does not mean that there is a sharp boundary between them.

7. MINERAL AND CHEMICAL COMPOSITIONS OF THE CORE

The inner core 1225 km in radius exists in a solid state and has a high density of 12.5 g/cm³. The outer core exists in a liquid state and has a density of 11 g/cm³. The jumps in the longitudinal wave velocity and the density are observed at the core–mantle boundary. In the mantle, the density decreases to 5.5 g/cm³. The D″ layer is in direct contact with the outer core, which has a substantial (especially, thermal) effect on the D″ layer because the temperature in the core is considerably higher than the mantle temperature. At some locations, mantle plumes, i.e., great upward flows of a hot material from the Earth's mantle into the crust, originate at the D″ layer.

The inner core is surrounded by the liquid outer core 3480–3490 km in radius. The density of the outer core is approximately 10% lower than the density of molten iron. This allows one to make the inference that the composition of the outer core involves a number of light elements (Si, S, O, C, H). The boundary between the outer and inner cores is sharp. The velocity jump is as large as 0.78 km/s. It is believed that the inner core consists of an iron–nickel alloy and contains a considerably smaller amount of light elements. The nickel content is estimated at 5–15 wt %. As is known, Fe–Ni alloys with a nickel content of up to 25 at % under room conditions have a structure with an I cell. At higher nickel contents, alloys have structures with an F cell. According to experimental data, the $Fe_{0.8}Ni_{0.2}$ alloy with an I cell at room temperature under compression transforms into a structure with the hexagonal closest packing of metal atoms. This structure is formed at a pressure of 7–14 GPa and retained up to 260 GPa. The density of the formed phase is equal to 14.35 g/cm³ and close to the density of the ε-Fe phase (14.08 g/cm³), which also has the hexagonal closest packing and, as was noted above, dominates in the Earth's core.

In [50], the quantum-mechanical calculations were used to determine the differentiated composition of the Earth's core: 8.5 mol % Si + S and 0.2 mol % O in the inner core and 10 mol % Si + S and 8 mol % O in the outer core (the Si and S contents were not separated in these calculations). The temperature at the boundary between the inner and outer cores was estimated at 5600 K. Recent seismological observations indicate that, inside the inner core, there is a seismic boundary that can be explained by the transformation of the iron structure. At present, it has been assumed that the most
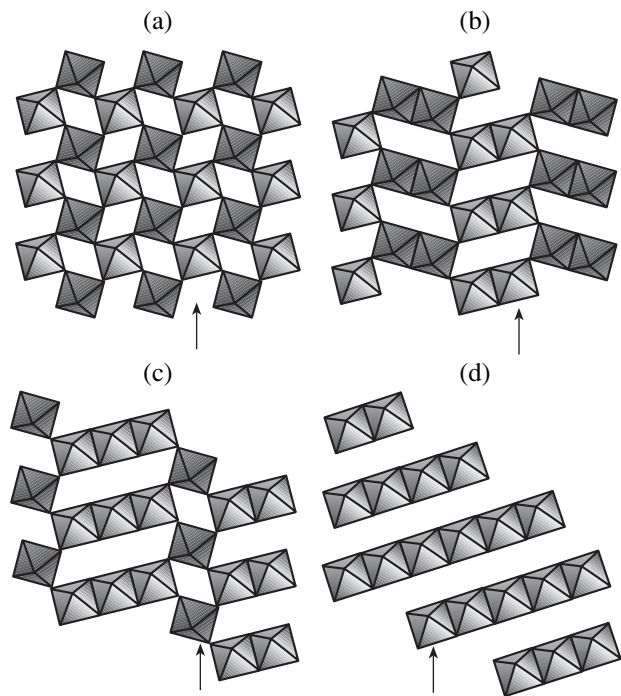

Fig. 7. Polytypes of the $MgSiO_3$ compound [48]: (a) perovskite, (b) a new type of structure consisting of 2×2 octahedral units, (c) a new type of structure consisting of 3×1 octahedral units, and (d) postperovskite. Only octahedral motifs are represented. Magnesium atoms are not shown. Arrows indicate the most probable displacements under plastic deformations.

stable form of pure iron under conditions of the Earth's core should be a modification based on the hexagonal closest packing of Fe atoms. However, the modification with a body-centered cell turns out to be more stable for iron containing Si and S impurities at temperatures close to the melting temperature [51, 52]. In the inner core, the presence of stoichiometric phases in the Fe–S and Fe–Si systems (for example, the Fe_3S phase) cannot be ruled out.

The presence of hydrogen in the core has been debated for a long time owing to the low solubility of hydrogen in iron at atmospheric pressure. However, the experimental results [J.V. Badding, H.K. Mao, and R.J. Hemley (1992)] demonstrated that the iron hydride FeH can be formed at high temperatures and pressures and appears to be stable at pressures higher than 62 GPa, which corresponds to a depth of ~1600 km. In this respect, the hydrogen in the form of the iron hydride can be contained in large amounts in the core.

8. CONCLUSIONS

Over many decades, considerable progress in geosciences has been achieved, to a large extent, owing to the advances made in physics and chemistry. In some sense, high-pressure mineralogy redresses the "injustice" and gives a deeper insight into the scientific

knowledge in many allied fields. However, investigation into the physical and chemical properties of minerals at high pressures plays the key role in the understanding of the most important features of the composition and structure of deep geospheres. It should be noted that, in the last decade, extremely valuable data have been obtained in the study of such a complex problem as the mineral composition and transformations of minerals in deep geospheres of our planet. This holds true for both the mantle and the core. New results and the performed geochemical and crystal chemical analyses primarily indicate a mineralogical variability along the Earth radius, i.e., along the vertical. However, there is a horizontal variability because geospheres are inhomogeneous in the lateral direction [3]. This aspect of the problem, as before, calls for further investigation. In conclusion, it should be emphasized that, every year, the mineralogical knowledge of deep geospheres is extended and the list of possible minerals is constantly complemented. A consistent concept of the Earth's interior is beginning to emerge. In this respect, mineralogy plays a central role in the interpretation of seismological (sometimes, very paradoxical) observations. It is hoped that results of new investigations will favor the fundamental solution of this interdisciplinary scientific problem.

ACKNOWLEDGMENTS

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Translated by O. Borovik-Romanova