Discussion

HYDROGEN IN THE EARTH'S OUTER CORE, AND ITS ROLE IN THE DEEP EARTH GEODYNAMICS

V. N. Rumyantsev

Geological Institute of RAS, Moscow, Russia

Abstract: The content of hydrogen in the outer core of the Earth is roughly quantified from the dependence of the density of iron (viewed as the main component of the core) on the amount of hydrogen dissolved in the core, with account of the most likely presence of iron hydrogen in the outer core, and the matter's density jumps at the boundaries between the outer liquid core and the internal solid core (that is devoid of hydrogen) and the mantle. Estimations for the outer liquid core show that the hydrogen content varies from 0.67 wt. % at the boundary with the solid inner core to 3.04 wt. % at the boundary with the mantle.

Iron occlusion is viewed as the most likely mechanism for the iron–nickel core to capture such a significant amount of hydrogen. Iron occlusion took place at the stage of the young sun when the metallic core emerged in the cooling protoplanetary cloud containing hydrogen in high amounts, and non-volatile hydrogen was accumulated. Absorption (occlusion) of molecular hydrogen was preceded by dissociation of molecules into atoms and ionization of the atoms, as proved by results of studies focused on $Fe–H_2$ system, and hydrogen dissipation was thus prevented. The core matter was subject to gravitational compression at high pressures that contributed to the forced rapprochement of protons and electrons which interaction resulted by the formation of hydrogen atoms. Highly active hydrogen atoms reacted with metals and produced hydrides of iron and nickel, FeH and NiH. While the metallic core and then the silicate mantle were growing and consolidating, the stability of FeH and NiH was maintained due to pressures that were steadily increasing. Later on, due to the impacts of external forces on the Earth, marginal layers at the mantle–core boundary were detached and displaced, pressures decreased in the system, and iron and nickel hydrides were decomposed to produce molecular hydrogen. Consequences of the hydrides transformation into molecular hydrogen are important in terms of petrology, mineralogy and geodynamics. At high temperatures, molecular hydrogen can be involved in redox reactions with iron silicates and carbonaceous gases (CO and CO_2), and the synthesis of water becomes possible throughout the entire mantle. It is known that water can significantly reduce the temperature of rock melting, which leads to partial melting of the rocks and pluming in the asthenosphere (in the D" layer) at the bottom of the mantle, and causes the hydrolysis of magnesium silicates, which results in the chemically bound state (hydroxyl ions). Highly ductile hydroxyl-containing magnesium silicates can alter rheological properties of the rocks. A combination of rheologically weak areas in the mantle rocks and the external cosmic effects can cause significant impacts on the tectonic activity and facilitate its manifestation throughout the entire mantle.

Key words: heterogeneous accretion of the Earth; protoplanetary cloud; source of hydrogen in the core; synthesis of water in the mantle; plume; hydrous minerals in the mantle; rheological lamination

ВОДОРОД ВО ВНЕШНЕМ ЯДРЕ ЗЕМЛИ И ЕГО РОЛЬ В ГЛУБИННОЙ ГЕОДИНАМИКЕ

В. Н. Румянцев

Геологический институт РАН, Москва, Россия

Аннотация: На основе зависимости плотности железа (основного компонента ядра) от количества растворенного в нем водорода и наиболее вероятного нахождения его во внешнем ядре Земли в форме гидрида железа, а также наличия резких скачков плотности вещества на границах внешнего жидкого ядра с внутренним твердым (лишенным примеси водорода) ядром и с мантией произведена приближенная количественная оценка содержания водорода в названной оболочке. Согласно проведенному расчету, содержание водорода во внешнем жидком ядре меняется от 0.67 мас. % на границе с внутренним твердым ядром до 3.04 мас. % на границе с мантией.

В качестве наиболее вероятного механизма захвата такого значительного количества водорода железоникелевым ядром рассматривается окклюзия, которая происходила непосредственно при формировании металлического ядра в охлаждающемся протопланетном облаке, обогащенном водородом, на стадии молодого Солнца. При этом аккумуляция водорода происходила в нелетучей форме, поскольку окклюзионному поглощению молекулярного водорода, как известно из результатов исследования системы Fe-H$_2$, предшествовала диссоциация молекул на атомы и ионизация последних. Это предотвращало диссипацию водорода. Высокие давления, развивающиеся в уплотняющемся под действием гравитационного сжатия вещества ядре, способствовали принудительному сближению разнозаряженных частиц (протонов и электронов) и их взаимодействию с образованием атомов водорода. Последние, обладая высокой химической активностью, вступали в реакцию с металлами, образуя гидриды железа FeH и никеля NiH. Непрерывное увеличение давления по мере роста и уплотнения металлического ядра, а затем и силикатной мантии способствовало их стабильности. Разложение гидридов железа и никеля с образованием молекулярного водорода оказалось возможным, когда на границе раздела мантия – ядро, вследствие внешних силовых воздействий на Землю стали происходить срывы и смещения граничных слоев, приводящие к снижению давления в системе. Трансформация водорода из гидридной формы в молекулярное состояние имеет важные петрологические, минералогические и геодинамические последствия. Молекулярный водород при высоких температурах принимает участие в окислительно-восстановительных реакциях с железосодержащими силикатами и углеродсодержащими газами (CO, CO$_2$), что определяет возможность синтеза воды во всем объеме мантии. Вода, как известно, существенно снижает температуру плавления пород, приводя к их частичному плавлению (астеносфера, слой D" в основании мантии, в котором зарождаются плюмы), и осуществляет гидролиз силикатов магния, переходя при этом в химически связанное состояние (в виде гидроксил-ионов). Гидроксилсодержащие силикаты магния обладают высокой пластичностью и также изменяют реологические свойства пород. Появление реологически ослабленных участков пород в мантии в сочетании с внешними космическими воздействиями оказывает существенное влияние на тектоническую активность и определяет возможность ее проявления во всем объеме мантии.

Ключевые слова: гетерогенная аккреция Земли; протопланетное облако; источник водорода; синтез воды в мантии; плюм; водосодержащие минералы в мантии; реологическое расслоение

1. INTRODUCTION. STATEMENT OF THE PROBLEM

The Earth core made of solid iron and nickel contains hydrogen in an amount that significantly influences the endogenous life of the planet in a variety of aspects. This problem is among the top and, at the same time, most controversial issues of geochemistry, geophysics, petrology and geotectonics. The problem was stated by V.I. Vernadsky who stated that conditions of the Earth interior are favorable "for the existence of hydrogenous bodies…, including hydrogen solutions in metals" [*Vernadsky*, *1960*, *p. 14*]. Until recently, his ideas have been shared by many researchers, (V.V. Kesarev, V.N. Larin, F.A. Letnikov, A.A. Marakushev, N.P. Semenenko, D. Stevenson, and others). Today the main reason for skepticism about the possibility of the presence of hydrogen in the center of the Earth is a lack of any answer to the question of how to explain this presence, bearing in mind the fact that molecular hydrogen is extremely highly volatile.

An important contribution to studies of this problem was the report published by V.E. Antonov and his colleagues [*Antonov et al.*, *1980*]. They described conditions for the synthesis of iron hydride from elements (P$_{H_2}$=67 kbar, t=250 °C) with the H/Fe atomic ratio of 0.65–0.75, i.e. approximating the stoichiometric value for FeH. Their results were confirmed in subsequent experimental studies conducted by other scientists [*Fukai, 1984; Fukai, Suzuki, 1986; Okuchi, 1997*]. The obtained data suggests that the outer liquid core of the Earth contains considerable quantities of hydrogen mainly in the nonvolatile form, i.e. hydrides of iron (FeH$_x$) which melting point is found to be almost 600 °C below the melting point of pure iron [*Okuchi, 1997*]. It is noteworthy that the studies revealed that the iron density considerably decreases as the content of dissolved hydrogen increases. The idea that hydrogen might be present in the Earth's core in the form of iron hydride becomes more widely recognized by researchers specializing in processes taking place in

the Earth's interior (I.D. Ryabchikov, V.N. Zharkov, N.L. Dobretsov, A.G. Kirdyashkin, Yu.M. Pushcharovsky, D.Yu. Pushcharovsky).

Calculations from the available geochemical and geophysical data confirm the abundance of hydrogen in the Earth's core. According to [*Ryabchikov*, *2003*], the content of hydrogen content in the Earth's core can be estimated from the content of argon and $H/^{36}Ar$ ratio in carbonaceous chondrites, assuming that this ratio remains constant at transition to the core, and it ranges from 0.125 to 0.25 wt. %. This approach seems to yield a somewhat underestimated content of hydrogen since argon does not chemically react with iron and is more prone to migrate into the mantle than hydrogen.

In the studies reported in [*Rumyantsev*, *2010, 2011*], higher values of the hydrogen content in the Earth's core were obtained by calculations from the available geophysical data on density jumps at the boundary between the outer liquid core (containing hydrogen) and the inner solid core (consisting predominantly of iron) [*Kuskov, Khitarov*, *1982*]), with reference to the information from [*Dziewonski, Anderson*, *1981*] that seismological studies detected the core at a depth of 5150 km. According to PREM model [*Dziewonski, Anderson*, *1981*], the matter is subject to a pressure of 3290 kb at the above-mentioned boundary, and its density decreases from 12.76 to 12.17 g/cm^3, i.e. by 0.59 g/cm^3, with the transition from the solid core to the liquid core. According to [*Zharkov*, *1996*], an increase of 0.1 in the proportion of molecular hydrogen reduces the iron density by 0.16 g/cm^3. It follows that the proportion of molecular hydrogen dissolved in the metal in the outer liquid core amount to 0.37 ($FeH_{0.37}$). The weight of the outer core is 1.85 x 10^{27} g [*Bolt*, *1984*]. Based on the assumption that the total content of iron and nickel in the outer core amounts to 90 %, and calculations with reference to the content of iron viewed as the main component of the core, we find that the mass of iron in the outer core is 1.66×10^{27} g. With account of the weight of iron, its atomic weight (55.85) and the proportion of molecular hydrogen dissolved in iron, our estimations show that the hydrogen content in the outer liquid core of the Earth is 1.11×10^{25} g (0.67 wt. %) [*Rumyantsev*, *2010, 2011*]. As known in molecular physics, the weight of one hydrogen atom is 1.67×10^{-24} g, and one gram of hydrogen contains 6.02×10^{23} atoms [*Shchelkin*, *1963*].

In terms of physics and physical chemistry, there are reasons to believe that the most satisfactory explanation of the mechanism of capture of a significant amount of hydrogen by the iron-nickel core of the Earth (as shown below, the hydrogen content is even higher than estimated previously [*Rumyantsev*, *2010, 2011*]) can be provided by the model of the Earth heterogeneous accretion in the cooling protoplanetary cloud. Under this model, the priority of nucleation is

explained by ferromagnetic properties of iron and nickel at temperatures below the Curie point (1043 and 627 K, respectively) [*Voitkevich, Bessonov*, *1986; Harris, Tozer, 1967*].

The abundance of hydrogen in the Earth's core may be a key to understanding the nature of many processes in the Earth interior – at high pressures and temperatures, hydrogen is actively involved in redox reactions with iron silicates (in rocks of the silicate mantle, the content of ferrous iron is about 10 wt. % [*Ringwood*, *1981*]) and carbonaceous gases to form water. Water is known to play a crucial role in geological processes. Its fluxing effect is strong, and even in small quantities (few tenths of a percent by weight), water reduces the melting point of substances by hundreds of degrees, which may lead to partial melting of rocks as well as to changes in rheological properties of the rocks, including a decrease in viscosity and an increase in ductility/plasticity, and rheological inhomogeneities may occur in the mantle, and geodynamic processes in the Earth's interior may be thus significantly impacted.

In view of the above, the major objectives of our paper are to provide a justification for the physical mechanism of capture of a significant amount of hydrogen by the Earth's core at the stage of accretion, and to review mechanisms of water synthesis throughout the entire mantle, taking into account the involvement of hydrogen and the impact of rheologically weak layers on geodynamic processes in the Earth interior (such layers can be formed with the involvement of water).

2. HETEROGENEOUS ACCRETION OF THE EARTH IN THE COOLING PROTOPLANETARY CLOUD, AND CAPTURE OF HYDROGEN BY THE IRON-NICKEL CORE

Has the Earth been formed by the homogeneous accretion of solarnebula matter or by heterogenous accretion in a cooling protoplanetary cloud? This problem has been the subject of hot scientific debates for many years. It was discussed in many publications on geophysics, geochemistry and petrology of the Earth, including those by V.S. Safronov, A.V. Vityazev, G.V. Voitkevich, O.L. Kuskov, S.P. Clark, K.K. Turek'yan, A.E. Ringwood, V.A. Rudnik, E.V. Sobotovich, E.V. Sharkov, O.A. Bogatikov, and others. By now, the debates seem to be over in general, as arguments in favour of the concept of heterogeneous accretion of the Earth are stronger [*Khain, 2003; Yaroshevsky, 2004*].

According to the model of heterogeneous accretion of the Earth, the Earth was formed by condensation of the matter of a protoplanetary cloud. The estimations show that dew-point start temperatures are similar for iron, nickel, and magnesium silicates (+1350… +1470 K) in a cooling protoplanetary cloud (Table 1). Therefore, when considering the reasons for fractiona-

T a b l e   1. **Differentiation of the matter in the protoplanetary cloud during the formation of the Earth [*Rumyantsev*, *2011*]**

Т а б л и ц а   1. **Дифференциация вещества в протопланетном облаке при формировании Земли [*Rumyantsev*, *2011*]**

Mineral phases – products of condensation	Curie (T_C, K) or Neel (T_N, K) temperature [*Frye*, *1985*]	Density, g/cm³ [*Nikolsky*, *1963*; *Betekhtin*, *1956*; *Frye*, *1985*]	Start temperature of mineral phase condensation, K (P=10⁻³ bar)		
			[*Grossman*, *1972*]	[*Larimer*, *1967*]	[*Shapkin, Sidorov*, *1997*]
Metal core					
Fe	1043 (T_C)	7.87	1473	-	1459
Ni	627 (T_C)	8.90	-	1440	-
FeS, troilite	600 (T_N)	4.84	700	680	693
Silicate shell					
Fe_2SiO_4, fayalite	65 (T_N)	4.2	-	-	423
$CaTiO_3$, perovskite	-	4.10	1647	-	1692
Al_2O_3, corund	-	3.97	1758	-	1771
$MgAl_2O_4$, spinel	-	3.55	1513	-	1466
$MgSiO_3$, enstatite	-	3.5	1349	-	1381
$CaMg(Si_2O_6)$, diopside	-	3.3	1450	-	1440
Mg_2SiO_4, forsterite	-	3.22	1444	1420	1431
$Ca(Al_2Si_2O_8)$, anortite	-	2.76	1362	-	1418
$K(AiSi_3O_8)$, microcline	-	2.56	1000	-	1019
$Na(AlSi_3O_8)$, albite	-	2.61	-	-	819

tion of these compounds, following the concepts developed by W.M. Latimer [*1950*], H.C. Urey [*1952*], E. Orowan [*1969*], F. Hoyle [*1972*], A.B. Makalkin [*1980*] and other researchers, a priority should be given to considering different propensity for clumping.

According to [*Harris, Tozer, 1967*; *Voitkevich, 1979*; *Voitkevich, Bessonov, 1986*], due to the fact that metal particles (Fe, Ni) composing the inner core have higher ductility than magnesium silicates, and Fe and Ni have ferromagnetic properties at temperatures below the Curie temperature (1043 and 627 °K, respectively), fractionation of metal and silicate particles can take place in a cooling protoplanetary cloud after their condensation with the early formation of a metal core. G.V. Voitkevich notes that at temperatures below 1000 K, "heterogeneous accumulation seems quite inevitable" [*Voitkevich*, *1979, p. 120*].

Thus, the sequence of accumulation of substances is logically determined by physical properties of such substances – strongly ferromagnetic substances are the first, then weakly ferromagnetic ones, including troilite (FeS) (Neel temperature = 600 K; almost all meteorites contain some amounts of troilite) and cohenite (Fe, Ni)₃C (Curie temperature = 483 K; cohenite is found in iron meteorites), and, finally, silicates and other non-magnetic compounds that precipitate due to gravitational attraction to massive metal condensations that formed earlier [*Voitkevich, Bessonov, 1986*]. The above-mentioned authors believe that this sequence of accumulation of metal and silicate particles generally determines the zonal structure of the Earth. It should be noted that according to the concept developed in

[*Rudnik, Sobotovich, 1984*], the interior structure of the Earth comprises shells that formed at the stage when the Earth was growing.

It seems promising to use the approach assuming that the differentiation of the Earth matter occurs mainly at the stage of its formation with account of physical properties of mineral facies. This approach is supported by the tabulated data (Table 1), including magnetic properties, densities of mineral facies, start temperatures of condensation in the protoplanetary cloud, and gives grounds for the following general conclusions:

1. The Earth core is composed mainly by the densiest mineral facies (Fe, Ni) that have magnetic properties at certain temperatures. Such properties (but not the dew-point temperatures that are similar for metal and silicate particles) are the major factor predetermining the early and rapid formation of the metallic core as clumping of iron and nickel particles was fast. Given the highest Curie temperature of iron, the inner solid core consisting mainly of iron is the first to take shape. This conclusion about the composition of the inner core can be drawn from results of theoretical and experimental seismological data published in [*Kuskov, Khitarov, 1982*]. However, an explanation has not been provided as the ferromagnetic properties of iron at temperatures below 770 °C were not taken into account.

In many studies, iron meteorites are regarded as analogues of the iron-nickel core of the Earth [*Vinogradov, 1975*; *Voitkevich, 1979*; *Rudnik, Sobotovich, 1984*; *Yaroshevsky, 2004*], and meteorite compositions sug-

gest that other minerals may be contained in the metal core in small amounts. Such minerals may have magnetic properties at lower temperatures than those for iron: schreibersite $(Fe,Ni)_3P$ (Curie temperature = = 413 °C), cohenite $(Fe,Ni)_3C$ (Curie temperature = = 210 °C), troilite FeS (Neel temperature = 327 °C), and carlsbergite CrN (Neel temperature = 0 °C). In iron meteorites, only the content of troilite can reach significant values (up to 4.7 wt. %) [*Florensky et al., 1981*].

Troilite is present in all types of meteorites (except ureilites), and its contents differ [*Florensky et al., 1981*]. It can thus be regarded as an 'omnipresent' mineral. Higher rates of electrical conductivity of rocks may be related to significant concentrations of troilite in deep zones of the Earth interior. As noted in [*Kuskov, Khitarov*, *1982*], the presence of troilite in the Earth core can only be explained under the hypothesis of heterogeneous accretion of the matter in the protoplanetary cloud after significant cooling (below 327 °C).

2. The metallic core and the silicate shell of the Earth differ significantly in chemical composition, density, propensity of constituent compounds for clumping, and redox conditions of their formation. The core is sharply segregated from the silicate shell – physical characteristics of its components strongly differ from those of the shell (magnetic properties of iron and nickel are manifested at temperatures below 770 °C, and the densities are higher than those of silicate particles), and it was formed in the reductive setting (lack of oxygen-yielding compounds). The pattern of mineral deposits in the silicate shell correlates with their densities and the sequence of condensation. The same conclusion was stated by A.D. Shcheglov and I.N. Govorov [*Shcheglov, Govorov*, *1986*].

3. In view of the above features and the earlier formation of the metal core in comparison with the silicate shell in the protoplanetary cloud, differentiation of the matter by gravity can be regarded as a fundamental feature of natural systems which was manifested already at the early stages of the Earth formation. Another reasonable assumption is that accretion of condensed particles, which took place simultaneously with differentiation of the matter by gravity, proceeded much faster in the dispersed protoplanetary cloud than in the Earth as it can be fulfilled much easier by the system of gravitational stability. This case follows the principle of minimum energy dissipation [*Moiseev*, *1990*]: "When nature permits the existence of several processes that can reach the same goal, the process requiring the minimum energy consumption takes place" (cited in [*Letnikov, 2007, p. 11*]).

4. Stratification of the silicate shell of the Earth, which took place at the stage of formation in the cooling protoplanetary cloud, goes on in the already formed solid planetary body. In the course of the Earth solidification, pressures were increased, solid phase transformations took place, and denser mineral phases were formed. At a depth of about 410 km, olivine α-$(Mg, Fe)_2SiO_4$ was structurally transformed into a denser phase, wadsleyite β-$(Mg, Fe)_2SiO_4$. At depth of about 520 km, wadsleyite was trans formed into γ-modification, $(Mg, Fe)_2SiO_4$ with the spinel structure [*Pushcharovsky Yu.M., Pushcharovsky D.Yu.*, *2010*].

Thus, an explanation for the formation mechanism of the iron–nickel core can be provided by the model of heterogeneous accretion of the Earth in the cooling protoplanetary cloud, with account of ferromagnetic properties of iron and nickel at temperatures below the Curie point, while the hypothesis of homogeneous accretion of the Earth fails to solve this problem [*Kuskov, Khitarov*, *1982*].

The heterogeneous accretion model of the Earth provides a justification for the early and rapid formation of the iron-nickel core in agreement with modern ideas concerning the early evolution of the Solar system [*Dorofeeva, Makalkin, 2004; Kuskov et al., 2009*] which are based on results of astronomical studies of young stars considered similar to the young Sun.

Among the major scientific conclusions providing important insights for understanding the planet formation mechanism [*Dorofeeva, Makalkin*, *2004; Kuskov et al., 2009*], the following are outstanding:

(1) Planets formed out of a disk of gas and dust surrounding the Sun which took shape simultaneously with the Sun;

(2) The whole range of events, from the formation of the Solar system to the formation of giant planets in the protoplanetary disk, took place within ~10 million years. In terms of time, this period coincides with the duration of T Tauri phase that is characterized by a more intensive stellar wind consisting of (mostly) hydrogen molecules and helium (98 wt. %);

(3) According to estimations in [*Dorofeeva, Makalkin*, *2004*], the disk around the Sun was formed within ~10^5 years, and it took approximately 90 thousand years to reach maximum temperatures in the disk, at which the major rock-forming components, i.e. iron and magnesium silicates involved in the formation of the terrestrial planets, were still in the evaporated state. After the disc of gas and dust was cooled to temperatures below ~2000 K ("margin of the complete evaporation zone" [*Shapkin, Sidorov*, *1997, p. 1196*]), the protoplanetary material began to condensate.

Early, at the stage of the young Sun, the iron-nickel core of the Earth was formed, condensed particles of iron and nickel were in direct contact with hydrogen (being the main component of the protoplanetary cloud) which lead to occlusive absorption of hydrogen [*Galaktionova*, *1967*], and the Earth did not have its own magnetic field to ensure its protection from the ingress of plasma brought by the stellar wind containing molecular hydrogen and helium and ionized parti-

cles (protons H+ and electrons). In view of the above, it becomes possible to better understand how hydrogen in significant amounts was captured by the growing metal core of the Earth.

According to [*Galaktionova, 1967*], bulk occlusion of hydrogen by iron becomes significant at temperatures of 400–500 °C and intensifies with increasing temperatures. It is noteworthy that absorption of molecular hydrogen is preceded by dissociation of molecules into atoms and ionization of the latter to form extremely fine particles, protons (radius of 1×10^{-5} Å) and electrons. The metal structure of iron and nickel, due to the presence of large cavities, allows these highly mobile particles to move freely and get absorbed in the entire volume of the iron–nickel core.

Experiments described in [*Galaktionova, 1967*] show that bulk occlusion of hydrogen is considerably influenced by both the temperature increase and the longer exposure of iron in the hydrogen atmosphere. In the experiment lasting 55 days under normal conditions (25 °C, 1 bar), the occluded hydrogen amount increased approximately 200 times in comparison with that in the short-term experiments. Given this trend and the lack of kinetic limitations to the long-term (millions of years) formation of the iron-nickel core, it can be assumed that the metal core of the Earth occluded an enormous amount of hydrogen in the proton form during its formation in the cooling protoplanetary cloud, and the occluded amount cannot be estimated precisely. Dissipation was prevented by hydrogen accumulated in the metal core in the non-volatile form. The proton form of hydrogen in the emerging iron-nickel core of the Earth prevented losses of hydrogen in case of collisions with planetesimals which were accompanied by short-term temperature rises.

Consolidation of the core due to gravitational compression of the matter was accompanied by high pressures that contributed to the forced rapprochement of protons and electrons and facilitated their interaction to form hydrogen atoms. Highly chemically active hydrogen atoms [*Nekrasov, 1962*] reacted with metals to form hydrides of iron and nickel (FeH and NiH). The critical role of pressure in the formation of iron hydride is confirmed by experiments [*Antonov et al., 1980*; *Fukai, Suzuki, 1986*; *Okuchi, 1997*] and thermodynamic calculations of the solubility of hydrogen in iron at temperatures ranging from 25 to 1000 °C and pressures from 1 to 100 kbar [*Fukai, 1984; Fukai, Sugimoto, 1983*]. It is established that at high pressures (above ~70 kbar) and temperatures above 250 °C, the solubility does not depend on temperature. The pressure was continuously increasing with the growth and consolidation of the metallic core and the silicate mantle and provided for the natural system to become more isolated, and iron and nickel hydrides became more stable.

The core structure was loose at the early stages, ex-

cluding rapid consolidation accompanied by heat emission due to gravitational contraction. Radioactive elements were lacking in the emerging metal core or present in very low contents, and iron and nickel hydrides were absent. Therefore, heating and melting of the outer parts of the core took place slowly and might have lasted for hundreds of millions of years, as suggested by traces of remnant magnetization in the ancient rocks of the Earth's crust.

As mentioned above, the molecular proportion of hydrogen dissolved in the metal in the outer liquid core at its margin with the solid inner core (not containing iron hydride) amounted to 0.37 ($FeH_{0.37}$). The geophysical studies give evidence that the density of matter within the outer liquid core is not constant – it decreases towards the silicate mantle (which may be associated with a higher content of hydrogen in iron hydride). At the depth of 2891 km, it is minimal, 9.90 g/cm³. At the specified depth, the mantle density is 5.57 g/cm³ [*Dziewonski, Anderson, 1981*]. The above-described calculation procedure can be applied to estimate the composition of iron hydride in the outer core at the boundary with the mantle. In this case, the density of matter calculated from the boundary with the solid inner core (density of 12.76 g/cm³) differs by 2.86 g/cm³ [*Dziewonski, Anderson, 1981*]. Given that an increase in the proportion of molecular hydrogen in iron by 0.1 leads to a decrease in the density of iron by 0.16 g/cm³, it is estimated that at the boundary of the silicate mantle, iron hydride is enriched in hydrogen (3.04 wt. %) and present as $FeH_{1.79}$. This indicates that the material of the outer core of the Earth is significantly differentiated by its chemical composition.

3. THE ASTHENOSPHERIC D" LAYER, AND ITS ROLE FOR PLUMING IN THE LOWER MANTLE.

The D" ('softened') layer is located at the base of the mantle at the boundary with the outer liquid core. In [*Zharkov, 1983*], it is viewed as "a potential source of tectonic movements". The possible causes are the proximity of the melting point; the presence of the cosmic 'slag' in the silicate matter (the slag was captured by the lower mantle strata "as melt-outs during the formation of the Earth's core" and contribute to its partial melting); stress relaxation (sliding) along boundaries of the gains at high temperatures [*Zharkov, 1983, p. 92–93*].

In [*Melikhov, Lygin, 2008*], the maximum density drop is noted at the boundary between the mantle and the metal core, as compared to that at the boundaries with other shells (according [*Dziewonski, Anderson, 1981*], it amounts to 4.3 g/cm³). This surface is characterized by the lowest cohesion between the geosphere layers and the highest possibility of lateral stripping and displacement of the marginal layers. When the

earth is subject to impacts of external forces, "advance shifting by inertia would take place in the less dense silicate mantle" [*Melikhov, Lygin, 2008, p. 14*].

In view of the high content of hydrogen in the outer liquid core of the Earth, it is reasonable to have more certainty when speaking about the reasons for lowering of the viscosity of the mantle base and linking this processes with the production of water in the given zone with the involvement of molecular hydrogen that resulted from the decay of iron and nickel hydrides and is supplied from the outer liquid core of the Earth.

According to results of the seismological studies conducted in the D" layer (a 10 to 40 km-thick layer directly neighbouring the core), the velocity of longitudinal waves, V_p is decreased by 5–10 to 30 % and thus significantly differs from that of the overlying mantle [*Garnero*, *2004*; *Mori, Helmberger, 1995*; *Williams, Garnero*, *1996*]. With account of the available experimental data [*Khitarov et al., 1983*], we can state that the degree of melting of silicate rocks in this area of ultra-low velocities is high, and it is close to complete meltdown on some sites. It is established that when basalt is melting in the presence of water in the system, and the water content is gradually increasing (within a few percent by weight), the velocity of longitudinal waves is gradually reduced, and the decrease may reach almost 10 % against that in "dry" conditions. In case of complete melting of the rocks, velocity V_p drops by 30–45 % [*Khitarov et al.,1983*].

The experiments show that hydrogen, unlike water, does not have any fluxing effect [*Sokol, Fedorov, 1991*]. Therefore, the formation of ultralow velocity zones in the D" layer seems to be associated with the formation of water in this layer. Water synthesis may be possible at the boundary between the core and the mantle as a result of the interaction of hydrogen with iron silicates, as revealed by experiments reported in [*Persikov, Apelbaum*, *1985*; *Sokol, Fedorov*, *1991*]. The experiments were conducted at high pressures (0.25–0.30 to 30–55 kbar) and temperatures (1350 to 1550 °C). According to [*Sokol, Fedorov, 1991*], hydrogen interacted with fayalite (Fe_2SiO_4) under the specified conditions, and ferrosilite ($FeSiO_3$) and coesite (SiO_2), as well as water and metallic iron were found among the products:

$$2Fe_2SiO_4 + 3H_2 \rightarrow FeSiO_3 + 3Fe + SiO_2 + 3H_2O. \qquad (1)$$
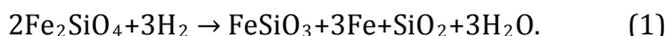
Considering the mechanism of interactions between ferrosilite and hydrogen at higher temperatures and pressures (no such experiments has been reported yet), we need to bear in mind that any possibility for the formation of silicon oxide in the lower mantle is excluded [*Pushcharovsky, Oganov*, 2006] and may use the following equation:

$$FeSiO_3 + 3H_2 \rightarrow Fe + Si + 3H_2O. \qquad (2)$$

Partial oxidation of iron in the presence of water may yield wustite as follows:

$$Fe + H_2O \rightarrow FeO + H_2. \qquad (3)$$

It is of interest that the assumed composition of the D" layer is similar to that of enstatite chondrites that are distinguished by the highest degree of reduction [*Florensky et al., 1981*]. In enstatite chondrites, iron is present mainly in the metallic form. Such chondrites contains FeO (1.70 wt. %) and Si (silicon) as a component of perryite (Ni, Fe)$_2$Si and kamacite (α-Fe, Ni) (up to 1.6 wt. %) [*Frye*, *1985*; *Florensry et al.*, *1981*].

The partially molten layer of refractory silicate rocks, which is detected at the very bottom of the mantle in the absence of any local source of heating (due to small variations of temperatures in the outer core because of its high thermal conductivity [*Dobretsov et al.*, *2006*; *Kirdyashkin et al.*, *2004*]), is an important argument in favour of the assumption proposed by N.L. Dobretsov and A.G. Kirdyashkin that the lower mantle plumes originating in layer D" cannot be of the purely thermal nature [*Dobretsov, Kirdyashkin*, *2000*]. A chemical additive is needed to lower the melting point of silicate rocks and provide for pluming. The best candidate is water resulting from the interaction of hydrogen and the iron-containing silicate material (the fluxing effect of water is strong). Plumes in the lower mantle, which formed with the involvement of the chemical additive, are termed 'thermochemical plumes' [*Dobretsov, Kirdyashkin*, *2000*]. Such plumes favour the migration of volatile components and should be viewed as fluid conductors, i.e. the main channels of the removal of the volatile components from the core and the mantle. According to [*Kirdyashkin A.A., Kirdyashkin A.G.*, *2013, p. 718*], "the thermochemical plumes are the most important regulators of heat exchange in the mantle. Besides, with account of the major role of the cellular free convection in the heat removal from the outer core to the surface mantle, plumes in the mantle can put a significantly effect on the mantle structure. When the entire volume of the mantle is involved in remelting and recrystallization due to pluming, ...the mantle becomes chemically non-uniform and subject to layering by density and viscosity. In its turn, layering of the mantle by density and viscosity leads to the layered mantle convection". With reference to this thermophysical model, it seems reasonable to review the ideas that the lower mantle of the Earth has never been completely melted [*Levin et al., 1972; Ringwood, 1981; Fedorin*, *1991*]. According to [*Kirdyashkin et al., 2000*], free-convection currents occur periodically in the Earth mantle, and the period ranges from 200 to 600 Ma.

Transformations of hydrogen from hydrides into the molecular form at the core–mantle interface can be ex-

plained on the basis of specific geodynamic features of the interface itself, including its high propensity to detachment and displacement of the marginal layers due to impacts of external forces on the Earth [*Melikhov, Lygin*, *2008*] which cause the pressures in the system to decrease. Besides, a specific feature of transition metal hydrides – the possibility of their steady state only at high pressures – also needs to be taken into account. Decomposition of iron hydride to form molecular hydrogen and a metal can be represented as follows:

$$FeH \rightarrow Fe+H. \tag{4}$$

Hydrogen atoms are recombined to form molecular hydrogen [*Archakov*, *1985*]:

$$2H \rightarrow H_2+435 \text{ kJ/mol}. \tag{5}$$

The reaction described in [*Buallo*, *1985*] is accompanied by heat emission in a considerable amount. It has been noted in many publications that during upward and lateral migration, molecular hydrogen acts as a heat transfer agent and plays an important role in the tectonic and magmatic activity of the Earth. The particles of metal iron and nickel sink into the liquid core and make the internal solid core to grow, and crystallization is accompanied by heat emission.

4. SYNTHESIS OF WATER IN THE MANTLE WITH THE INVOLVEMENT OF MOLECULAR HYDROGEN, AND THE ROLE OF WATER IN THE FORMATION OF INHOMOGENEITIES IN THE EARTH INTERIOR
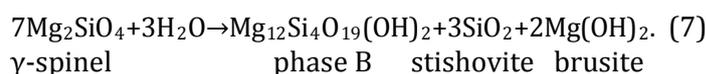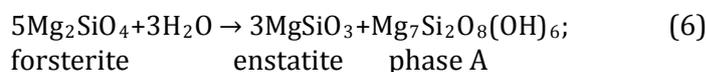
Seismic tomography studies of the Earth interior structure give evidence that seismic heterogeneities are most abundant in the mantle, from the mantle–core interface [*Dziewonski, Woodhouse, 1987; Su et al., 1994; Bijwaard et al., 1998*]. The records show different values concerning rheological properties (viscosity and ductility) of the mantle rocks [*Pushcharovsky, 2001*] and may be viewed as an important, albeit indirect evidence of the variability in different parts of the mantle [*Karakin et al., 2003*] . The rheological inhomogeneities facilitate lateral stripping or tectonic flow of the matter which result in tectonic piling-up – parts characterized by higher values of density, velocity and viscosity are located in other areas than (rear) parts with lower values of velocity and viscosity [*Pushcharovsky, 1995, 2001*].

The seismic tomography results show that asthenolayers and asthenolenses are numerous throughout the entire mantle and represent slip zones of denser and more viscous layers of the mantle [*Pushcharovsky, 2001*]. In view of this fact, Yu.M. Pushcharovsky be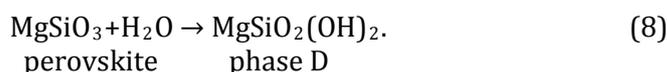lieves that the notion of 'tectonosphere' should be extended to include the entire mantle of the Earth [*Pushcharovsky, 2001; Pushcharovsky Yu.M., Pushcharovsky D.Yu., 2010*].

In the seismic tomography studies, a complex mosaic pattern of seismic discontinuities was revealed in both horizontal and vertical profiles (asthenolayers and asthenolenses). A satisfactorily explanation of such a pattern can be proposed if we assume a possibility of a selective reaction between molecular hydrogen (supplied from the boundary between the mantle and the outer core of the Earth) and iron-containing silicates of the mantle, which results in the production of water, as specified above in (1) and (2).

At higher pressures and temperatures, water is a highly chemically active agent [*Gavrish, Galinker, 1967; Tödheide, 1982; Rumyantsev, 1988, 2005*]. Once formed, water initiates hydrolytic breakup of magnesium silicates, that dominate in the mantle, and becomes chemically bound in the newly-formed minerals in the form of hydroxyl ions. Hydroxyl-containing magnesium silicates are less dense than their anhydrous analogues (Table 2), and their presence (as well as areas with low viscosity) can be revealed by seismological studies as low-velocity anomalies or rheologically weak zones [*Rumyantsev, 2011*]. The experiments reported in [*Liu, 1987; Frost, Fei, 1998*] show that hydroxyl-containing minerals can be produced in conditions with a wide temperature range (525 to 1400 °C) and pressures (~40 to 260–280 kbar):

$$5Mg_2SiO_4+3H_2O \rightarrow 3MgSiO_3+Mg_7Si_2O_8(OH)_6; \tag{6}$$
forsterite   enstatite   phase A

$$7Mg_2SiO_4+3H_2O \rightarrow Mg_{12}Si_4O_{19}(OH)_2+3SiO_2+2Mg(OH)_2. \tag{7}$$
γ-spinel   phase B   stishovite   brusite

In experiments described in [*Frost, Fei, 1998*], forsterite and water (20.5 wt. %) were used as source agents, and phase D was recorded at the highest pressure. In almost all that experiments that lasted maximum for three hours, melting was observed, and phases A, B, ß-Mg_2SiO_4, γ-Mg_2SiO_4, and $MgSiO_3$ (perovskite) were present (depending on temperature and pressure) among the solid products, in addition to phase D. Pressure-temperature conditions for stability of phase D were not studied in much detail. According to [*Frost, Fei, 1998*], phase D may occur in the lower mantle. Given the presence of magnesia perovskite phase in the lower mantle [*Pushcharovsky Yu.M., Pushcharovsky D.Yu., 2010; Gasparik, 1993*] and potential synthesis of water by oxidation of hydrogen in the flows ascending throughout the entire lower mantle, the reaction for phase D is as follows:

$$MgSiO_3+H_2O \rightarrow MgSiO_2(OH)_2. \tag{8}$$
   perovskite   phase D

T a b l e   2. **Comparison of anhydrous and hydrous magnesium silicates by density**

Т а б л и ц а   2. **Сравнительные данные по плотности безводных и водосодержащих силикатов магния**

Mineral phases		ρ phase density, g/cm^3	$\Delta\rho$	ρ decrease, %
Anhydrous	Forsterite Mg_2SiO_4	3.214	0.714	22.2
Hydroxyl-containing	Serpentine $Mg_3Si_2O_5(OH)_4$	2.50		
Anhydrous	Forsterite Mg_2SiO_4 and potential vadsleite ß-Mg_2SiO_4	3.214 (3.467)	0.264 (0.517)	8.21 (16.1)
Hydroxyl-containing	Phase A $Mg_7Si_2O_8(OH)_6$	2.95		
Anhydrous	Ringwoodite γ-Mg_2SiO_4	3.549	0.179	5.04
Hydroxyl-containing	Phase B $Mg_{12}Si_4O_{19}(OH)_2$	3.37		
Anhydrous	Perovskite $MgSiO_3$	4.083	0.583	14.3
Hydroxyl-containing	Phase D $MgSiO_2(OH)_2$	3.5		

N o t e. Sources of the data on density of magnesium silicates: *Liu* [*1987*]; *Tyburczy et al.* [*1991*]; *Frost* and *Fei* [*1998*].

П р и м е ч а н и е. Данные по плотности силикатов магния взяты из работ: *Liu* [*1987*]; *Tyburczy et al.* [*1991*]; *Frost and Fei* [*1998*].

Table 2 shows densities of high-pressure anhydrous magnesium silicates and hydroxyl-containing mineral phases that result from hydrolysis. In all the cases, the density of both the anhydrous and hydroxyl-containing mineral phases increases with depth, which provides for gravitational stability of the natural system. The so-called phase 10Å is present among the high-pressure mineral phases; it contains water not only in the hydroxyl form, but also in the molecular form, $Mg_3Si_4O_{10}(OH)_2 \cdot H_2O$. This phase was yielded by the reaction between talc and water at 500 °C and 60 kbar in the experiment described in [*Chinnery et al.*, *1999*]:

$$Mg_3Si_4O_{10}(OH)_2 + 2H_2O \rightarrow Mg_3Si_4O_{10}(OH)_2 \cdot H_2O. \quad (9)$$
$$\text{talc} \qquad\qquad\qquad \text{phase 10Å}$$

In the above-mentioned experiment, the pressure corresponds to that at a depth of 185 km, i.e. the upper mantle conditions. The laboratory results are in complete agreement with the field observation data – nanoinclusions of high-pressure phase $Mg_3Si_4O_{10}(OH)_2 \cdot nH_2O$ were recently found in the single-crystal grains of olivine and xenoliths of country rocks sampled from Udachnaya kimberlite pipe [*Khisina, Virt, 2008*].

It is known that the density of the matter has a significant impact on velocities of propagation of longitudinal elastic waves [*Vakhromeev et al.*, *1997*]. Typically, velocity V_p is significantly reduced with decreasing density. According to the data from [*Zharkov, 1983; Moskaleva, 1974; Kern, Shenk, 1985*], velocity V_p in hydroxyl-containing minerals, such as talc, mica, and serpentine, is considerably lower than that in anhydrous magnesium silicates. This group includes high-pressure hydroxyl-containing magnesium silicates that should be recorded in seismological studies as low-velocity anomalies (similar to sites with lower viscosity).

Results of seismic tomography studies of the Earth interior structure [*Bijwaard et al., 1998; Dziewonski, Anderson, 1981*] give evidence that velocity V_p deviates insignificantly (0.5–1.5 % in the lower mantle, and 2–4 % in the upper mantle) from the standard values (model PREM) for the solid mantle, and thus there are no grounds to link causes of such deviations to partial melting of the mantle material. It is most likely that low-velocity anomalies may result from the formation of hydroxyl-containing mineral phases (which density is lower than that of anhydrous analogues) on migration routes of hydrogen in the silicate mantle, which trace the sites containing ferrous iron. According to estimations in [*Ringwood, 1981*] and other publications, the water content in the upper mantle is about 0.1 wt. %. This estimated value may be approximated to the entire mantle as water-containing minerals are present in both the lower mantle and the upper. Given the mass of the mantle (4.0×10^{24} kg, according to [*Bolt, 1984*]), the water content in the mantle may amount to 4×10^{21} kg, and it would be equivalent to over three times the amount of water in the oceans (1.4×10^{21} kg [*Bolt, 1984*]). Therefore, the mantle should be viewed as a huge 'flow-through' renewable water resource that is maintained by the oxidation of hydrogen supplied from the Earth's outer core and constantly supplies water to the hydrosphere.

High plasticity is another important feature of the hydroxyl-containing magnesium silicates, which is di-

rectly related to the rheology of the mantle layering. In the layered structure of the silicates, perfect cleavage occurs parallel to the silicate sheet [*Frye*, *1985*]. Obviously, this feature is typical of high-pressure hydroxyl-containing magnesium silicates. It is reasonable to believe that the minerals formed in the mantle play an active role in the process of its rheological stratification, and the rheological heterogeneity of the geological environment (as noted in many publications) fosters tectonic deformations that seem to be mainly caused by impacts of external cosmic factors. Such impacts of various geological processes have been discussed over the past two decades by many researchers (A.A. Barenbaum, Yu.V. Barkin, V.M. Golubev, V.R. Melikhov, E.E. Milanovsky, Yu.M. Pushcharovsky, V.E. Khain, N.A. Yasamanov, and others).

The (dominantly) subhorizontal inhomogenities in the Earth interior [*Pushcharovsky*, *1995*] (and the corresponding subhorizontal rheologically weak zones that may result from the layer-by-layer 'spreading' of molecular hydrogen) are another evidence in support to the above-mentioned assumption that the mineral matter of the mantle was stratified by density mainly at the stage of the Earth accretion when sedimentary differentiation took place. At the stage of the geological development of the Earth, the system has continued to seek the gravitational stability by processes in the interior wherein the pressure was increasing and the matter was transformed into the denser mineral phases.

5. THE ROLE OF WATER-HYDROGEN FLUIDS IN SERPENTINIZATION OF ULTRABASITES IN THE EARTH INTERIOR AND TECTONIC ACTIVITY AT THE BOUNDARY BETWEEN THE CONTINENTAL CRUST AND THE MANTLE

Many researchers consider the Mohorovicic seismic discontinuity, or the Moho, as the rheologically weak and tectonically active zone – it is the global interface whereat plastic flow and detachment take place and the crust slips against the upper mantle [*Leonov, Perfiliev, 1999; Pavlenkova, 1996*; *and others*]. V.R. Melikhov and I.V. Lygin point out that the solid crust of the Earth is the second (after the boundary between the mantle and the outer liquid core), "spherical layer in terms of differential properties, which is prone to inertial motion to get stratified from the underlying mantle and to tectonic slip, horizontal displacement, thrusting…" [*Melikhov, Lygin*, *2008, p. 19*]. The Moho is traced almost continuously underneath the continents and oceans as a major geophysical boundary of the lithosphere. At the Moho, abrupt changes in P-wave and S-wave velocities (V_p and V_s, respectively) and density changes are indicative of a change in the chemical composition of rocks. Deep seismic sounding records at

the Moho show that velocity V_p increases from 6.8–7.2 to 7.8–8.2 km/sec [*Pavlenkova*, *1996*], which correlates with a significant change in the density of the matter. According to [*Dziewonski, Anderson*, *1981*], the density at the Moho increases by 16.6 %, from 2.90 g/cm³ at the crust bottom to 3.38 g/cm³ in the top layers of the lithospheric mantle, and velocity V_p increases by 19.1 % (from 6.8 to 8.1 km/sec). In view of relatively high absolute values of the longitudinal wave velocities at the base of the continental crust in combination with relatively low temperatures, there are no grounds to assume partial melting of the crustal material and any corresponding significant decrease in its viscosity. It can thus be suggested that tectonic flow processes develop due to the presence of a solid underlying layer, which is most favorable for the displacement of the overlying layers and plastic flow processes.

The above-mentioned values of density and velocity V_p of the rocks in the crust bottom (with account of the assumed high ductility of the rocks) were referred to by many researchers [*Moskaleva*, *1974; Peive, 1981; Rezanov et al., 1984*] who suggest that tectonic flow processes, that are widely manifested at the Moho, are related to the presence of water-containing serpentinized ultramafic rocks at the Moho as the plasticity of such rocks is higher than that of non-serpentinized rocks. This assumption is supported by data obtained by seismic surveys of the deep structure of both the continental and oceanic crust – high longitudinal wave velocities (6.7–6.6 km/sec and above) are recorded in the rocks that occur commonly at the bottom of both the continental and oceanic crust, and such velocities are higher than those typical of gabbroic rocks [*Kosminskaya, Davydova, 1978*].

According to [*Buallo*, *1985*], peridotites can be easily serpentinized even in case of an insignificant (about 1 %) water content in the system, which follows directly from the specific chemical composition [*Rumyantsev*, *2005*] of magnesium silicates (olivine and pyroxene). These major minerals of ultrabasic rocks are salts of weak silicic acid and weak alkali that are highly prone to hydrolytic degradation even at normal temperatures. Results of theoretical studies [*Nekrasov*, *1962*] and experiments [*Gavrish, Galinker*, *1967*; *Rumyantsev*, *1988; Rumyantsev, 2005; Tödheide*, *1982; and others*] show that hydrolysis is considerably intensified with increasing temperatures. At a temperature of 350 °C and above, the hydrolytic impact of water is sufficient enough to cause the break-up of sodium chloride. At 500 °C and 2 kbar, the hydrolysis constant for the salt increases by nine orders in comparison with that in normal conditions [*Tödheide*, *1982*].

Serpentinization of ultrabasic rocks is an important factor influencing the rock density. According to [*Moskaleva*, *1974*], serpentinization of harzburgites to 13–15 % causes the density to decrease from about

3.2 g/cm^3 in the unaltered state to 2.9 g/cm^3, and the velocity of longitudinal waves is reduced from about 8.1 to 6.8 km/sec and decease further with the increasing degree of serpentinization. These data are in good agreement with the above-mentioned values of velocity V$_p$ and the rock density values recorded at the Moho.

The deep seismic sounding surveys give evidence that serpentinization of ultrabasic rocks takes place in the continental crust at depths of 15–35 km. Meteoric water cannot reach such depths [*Pinneker*, *1985*], so there is a need to discover a potential mechanism supplying water that is involved in serpentinization.

Hydrogen as a source of water required for serpentinization of ultrabasic rocks in the Earth interior (and this is a key point for hydrolysis) must be of the juvenile origin – this idea is supported by the following: hydrogen is abundant in the Earth's core; mobility of hydrogen is anomalously high; isotopically light ('cosmic') hydrogen was discovered in the composition of serpentinized ultrabasic rocks sampled from Kempirsay (South Urals, Russia) [*Ukhanov et al.*, *1987*] and early serpentinites of the ophiolite complexes [*Yurkova*, *1991*]; isotope characteristics differ significantly for hydrogen in serpentinites formed under the influence of ocean water (such serpentinites have a triple or quadruple content of deuterium) and hydrogen in early deep serpentinites [*Yurkova*, *1991, 2002*]. Isotopic light hydrogen was detected on various sites of the globe, and such cases are described in [*Ukhanov et al.*, *1987*]. The isotopically light composition of molecular hydrogen confirms its anomalously high penetration capacities and gives grounds to suggest that molecular hydrogen originates from the Earth interior.

It is most probable that water for hydrolysis and serpentinization of ultrabasic rocks at depth is produced by the reaction between carbon monoxide and hydrogen as described by Fischer–Tropsch mechanism:

$$CO + 3H_2 \rightarrow CH_4 + H_2O. \tag{10}$$

R.M. Yurkova [*1991*] was the first to propose this assumption based on the abundance of tiny ferrous nickel inclusions (2–5 microns) in ultrabasic rocks and the role of ferrous nickel as a catalyst which substantially reduces the temperature of water synthesis in reaction (10), and taking into account the assumption that hydrogen from the depth can be supplied into to the deep zone of early serpentinization, as suggested by the fluid inclusions in serpentines containing H$_2$, as well as CH$_4$ and CO. In this reaction, in the absence of any catalysts, water is produced at quite high temperatures, above 620 °C [*Storch et al.*, *1954*]. Studies of hydrogenation of carbon monoxide as well as carbon dioxide show that water can be yielded at a temperature from 250 to 400 °C after catalysts (disperse Ni, Fe, Co) are added to the system.

The synthesis of hydrocarbon mixtures containing gases CO, CO$_2$ и H$_2$ has been the subject of recent comprehensive studies [*Ione et al.*, *2007*], and various natural catalysts have been tested. At temperatures ranging from 300 to 400 °C, high catalytic activity is typical of iron-containing minerals and chromite, which are present in serpentinized ultrabasic rocks. The fact that such rocks also contain accessory minerals of native iron, ferrous nickel and cobalt suggests strongly reducing conditions of serpentinization [*Marakushev, 1975; Shteinberg, Chashchukhin, 1977*]. Therefore, the formation of water in such conditions according to reaction (10) is quite realistic. In a more oxidizing environment, when carbon dioxide is present in the composition of fluids, water is yielded as follows [*Marakushev*, *1975*; and others]:

$$CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O. \tag{11}$$

In this case, the formation of methane can be considered as a factor favorable for the occurrence of hydrocarbon deposits.

The process of serpentinization, given the presence of brucite in the reaction products, is as follows [*Shteinberg, Chashchukhin*, *1977*]:

$$2Mg_2SiO_4 + 3H_2O \rightarrow Mg_3Si_2O_5(OH)_4 + Mg(OH)_2 \tag{12}$$
forsterite   serpentinite   brucite
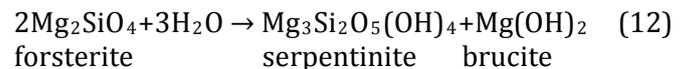
Reaction (12) takes place with a significant increase in the rock volume (22.8 cm^3/mol) [*Marakushev*, *1975*]. The pressure and geodynamic activity of serpentinized ultrabasic rocks is ensured by this specific feature, as well as by the decompression of ultrabasic rocks due to serpentinization (leading to the gravitational instability of the system), high ductility of serpentinites, and excessive pressures (exceeding the lithostatic load) of endogenous reduced fluids with dominating hydrogen compositions in the serpentinization zone [*Marakushev*, *1975; Yurkova, 2002*]. The geodynamic activity is manifested by diapirs penetrating into the lower and middle layers of the continental crust as a result of 'cold' penetration from the mantle lithosphere [*Knipper, 1969; Moskaleva, 1974; Peive, 1981; Karus, Sarkisov, 1986; Yurkova, 2002*]. A possibility for the ingress of serpentinized diapirs from a depth of about 40–50 km can be suggested from the data obtained in experiments reported in [*Slutsky et al.*, *1984*] – serpentine (antigorite) is stable until the temperature reaches 630 °C and the pressure amounts to 24 kbar, and serpentine in the group of deveylite is stable until the pressure reaches 35 kb. The rheological stratification of the mantle material at higher temperatures seems to be possible in case of the presence of talc Mg$_3$Si$_4$O$_{10}$(OH)$_2$. In the experiments conducted by the above-mentioned researchers, talc remained stable at

temperatures up to 760–815 °C at pressures up to 10–35 kb. Similar to other hydroxyl-containing minerals, talc is classified as a silicate that has perfect cleavage [*Frye*, *1985*], and it is highly plasticity.

6. MAIN RESULTS

1. According to the available experimental data, there is a high probability that hydrogen in the outer liquid core of the Earth is contained in the hydride form. The estimations show that at the boundary with the mantle, the hydrogen content amounts to 3.04 wt. %, and hydrogen is present in the form of iron hydride $FeH_{1.79}$.

2. The abundance of hydrogen in the metal core at the very early stage of accretion of the Earth has become possible as hydrogen was captured in the non-volatile (proton) form from the protoplanetary cloud. Later on, while the Earth was growing, hydrides of iron and nickel (which are also non-volatile) were formed under the impacts of high pressures associated with the gravitational contraction and increasing lithostatic loading.

3. Hydrogen is transformed from the hydride to molecular form at the boundary between the core and the mantle. Causes for such transformation can be explained by a specific geodynamic feature of the boundary – its high propensity to detachment and displacement of the marginal layers under the impacts of external forces on the Earth, which reduces the pressure in the system. Besides, a specific property of transition metal hydrides – such hydrides are stable only at high pressures – should be taken into account. Iron hydride decomposes to form to form molecular hydrogen and the metal, and this reaction is accompanied by heat emission in considerable amounts. Molecular hydrogen is involved in upward and lateral migration flows as a heat transfer fluid that plays an important role in the tectonic and magmatic activity of the Earth.

4. The transition of hydrogen from the non-volatile hydride form to the molecular form has important petrological, mineralogical and geodynamic consequences. At high temperatures (above 1350 °C), molecular hydrogen is involved in redox reactions to form water.

Water is chemically active at high temperatures. Firstly, its fluxing action is strong – even small amounts of water, such as tenths of a percent by weight, can reduce melting temperatures of substances by hundreds of degrees, and this leads to a decrease in viscosity and partial melting of rocks, which is observed at the base of the D″ layer (this fact is referred to by researchers who support the concept that plumes originated at the D″ layer) and in the asthenosphere, which are the major inhomogeneities in the Earth mantle. Secondly, when water is produced under high temperatures and pressures, it is immediately involved in hydrolytic reduction of magnesium silicates, the main component of the mantle matter. Water becomes chemically in the composition of secondary minerals in the form of hydroxyl ions. Hydroxyl-containing magnesium silicates are less dense but more ductile than the anhydrous analogues, and this properties contribute to the occurrence of rheologically weakened zones. In such environment, conditions are favourable for the development of tectonic movements, tectonic deformation, and lateral detachments, and the main causes seem to be related to the external cosmic impacts.

Due to the presence of molecular hydrogen in the mantle and the temperature sufficient for its reaction with the iron-containing silicates, amounts of water can be formed throughout the entire mantle and, consequently, inhomogeneities can occur at depth throughout the whole volume of this shell of the Earth. Interaction between hydrogen and carbon-containing gases, CO and CO_2 is another potential mechanism of water synthesis in the upper mantle and in the lower crust, i.e. at the depths inaccessible for the penetration of meteoric water. Water-containing serpentinized ultrabasic rocks have higher ductility, and this is the reason why processes of tectonic flow of the matter are common at the Moho.

5. It is assumed that the (dominating) sublateral inhomogeneities in the mantle interior resulted from stratification of the mineral matter by density in the course of its sedimentary differentiation in the cooling protoplanetary cloud.

6. This study supports the heterogeneous accretion model that provides insight for developing solutions for a number of challenging issues in studies of the origin and the interior structure of the Earth which core was 'cold' at the final stages of its formation.

7. ACKNOWLEDGEMENTS

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Rumyantsev, Valerian N., Candidate of Chemistry, Senior Researcher
Geological institute of RAS
7 Pyzhevsky Lane, Moscow 119017, Russia
✉ e-mail: ya.valerrum@yandex.ru

Румянцев Валериан Николаевич, канд. хим. наук, с.н.с.
Геологический институт РАН
119017, Москва, Пыжевский пер., 7, Россия
✉ e-mail: ya.valerrum@yandex.ru