4

Development of Earth's Hydrosphere

The Earth's hydrosphere and atmosphere evolutionary regimes were crucial in the: (1) determination of the evolution of the Earth's climate; (2) the emergence and development of life on the Earth; and (3) the issue of commercial mineral deposits including the organic hydrocarbon deposits.

Hydrosphere of the Primordial Earth

When the Earth first formed it did not have either a hydrosphere (ocean, rivers, lakes, etc.) or atmosphere (see Figure 1.1). It is suggested that the external, and very mobile geosphere, primarily developed due to the degassing of the Earth's mantle. This degassing did not begin until after the heating of the upper portion of the Earth and the emergence of melted matter nodes within it. There was heating because of the release of energy from the moon-Earth interaction tidal energy and radioactive decay. Tidal energy was released primarily within the Earth's mantle. The first melts of the Earth's mantle material appeared at relatively shallow depths of 200–400 km. Upon the appearance of the first melts, the differentiation of the Earth's matter began, along with the first indications of the tectono-magmatic activity of the primitive Earth, ≈4 BY ago. After that, the matter differentiation of the Earth was fed by a powerful gravitational energy process of high-density melted iron separation from the Earth's matter silicates. The Earth's mantle-degassing substantially depended not only on the mantle temperature, which determined the mantle convection flow intensity, but also on its chemical composition. The key features of this compositional and petrogenic evolution of a convecting mantle chemical composition are illustrated in Figures 4.1 and 4.2.

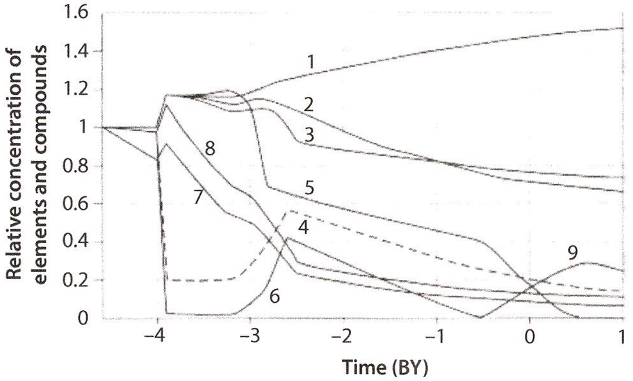

Figure 4.1 Evolution of convecting mantle's chemical composition in relative concentrations (the concentration of a given compound in the primordial Earth's matter is taken as one: *Curve 1* – SiO_2, TiO_2, MgO, CaO, AlO_3; *Curve 2* – H_2O; *Curve 3* – K_2O; *Curve 4* – Ni and other siderophilic and chalcophilic elements and compounds; *Curve 5* – FeO; *Curve 6* – Fe; *Curve 7* – U; *Curve 8* – Th; and *Curve 9* – Fe_3O_4. (After Sorokhtin *et al.*, 2011, figure 4.15, p. 144.)

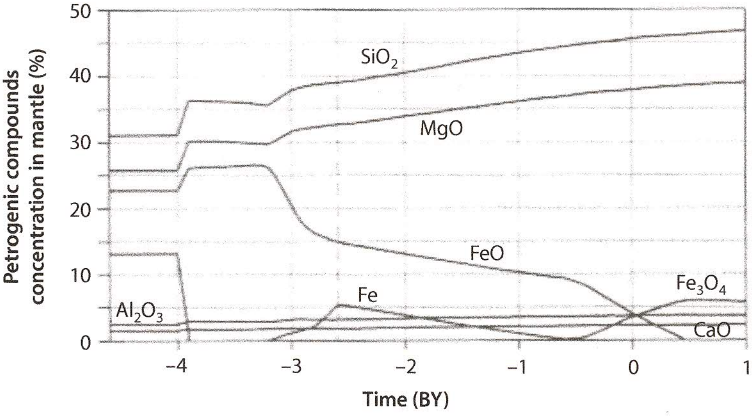

Figure 4.2 Evolution of major petrogenic elements and compounds in the convecting mantle. (After Sorokhtin *et al.*, 2011, figure 4.16, p. 145.)

The emergence of the Earth's lithospheric plate tectonics, especially the development of the Earth's evolution, provides an opportunity for a quantitative description of the ocean-forming processes. Quantitative models of the hydrosphere (global ocean water) and the atmosphere (gas shell) growth are based on the most general concept for the global evolution (Sorokhtin, 1974). This concept of development includes the direct proportionality between the Earth's degassing rates and the lithospheric plate tectonics as to the development of the lithosphere and hydrosphere. The major contribution to the mantle convective mass exchange came from the most powerful energy process, the chemico-density differentiation of the Earth's matter into a high-density iron-oxide core and a residual silicate mantle.

Earlier studies were related to the end of the Earth's formation process ≈4.6 BY ago; however, later models by Monin and Sorokhtin (1984), Sorokhtin and Ushakov (1991 and 2002) were more sophisticated and considered that the primordial Earth after its emergence from the collation of particles was a relatively cold planet. Thus, the degassing would have started, after the preliminary heating of the originally cold Earth, to a temperature where the silicates began to melt in the upper mantle along with the emergence of the first asthenosphere.

The primary mantle degassing is associated with the solubility decline of the volatile components within the silicate melts under lowering temperature and relatively low pressure. As a result, the mantle melts erupted on the surface of the Earth (mostly basalts, and in the Archaean time also komatiite lavas) boiled and released excess volatile elements and compounds into the atmosphere. Some of these volatile components may have been released due to the weathering of the erupted rocks after their sojourn on the surface. However, the main water-degassing mechanism for the Earth was the decline of its solubility under the cooling and crystallization of water-containing olivine basalt melts at low pressure (Figure 4.3).

The rate of the Earth's degassing was in direct proportion with: (1) the erupted mantle rock mass on the surface, per unit of time; (2) their content of volatile elements; and (3) their mobility. For a first approximation, the mantle rock eruption rate may be considered to be proportionate to the Earth's tectonic activity (Figure 4.4). This activity is determined by the rate of its total heat loss, $\dot{Q}_m$, or the derivative over time of the Earth's tectonic parameter, $\dot{z}$:

$$\dot{z}_n = \frac{(\dot{Q}_m - Q_{4.0})}{(Q_{mo} - Q_{4.0})}, \qquad \text{(Eq. 4.1)}$$

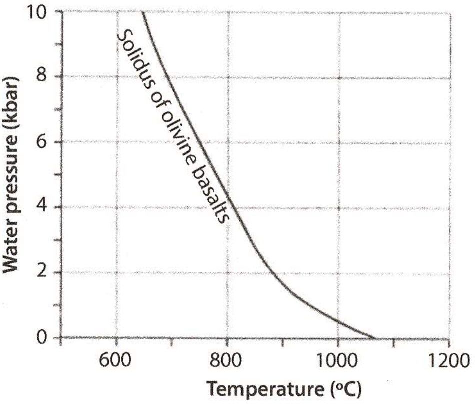

Figure 4.3 Olivine basalt solidus curve versus pressure (content) of water dissolved in the basalt melt. When basalts crystallize, the water dissolved in the basalt melts is released. (After Joly 1929; in: Sorokhtin *et al.*, 2011, p. 422, figure 11.1.)

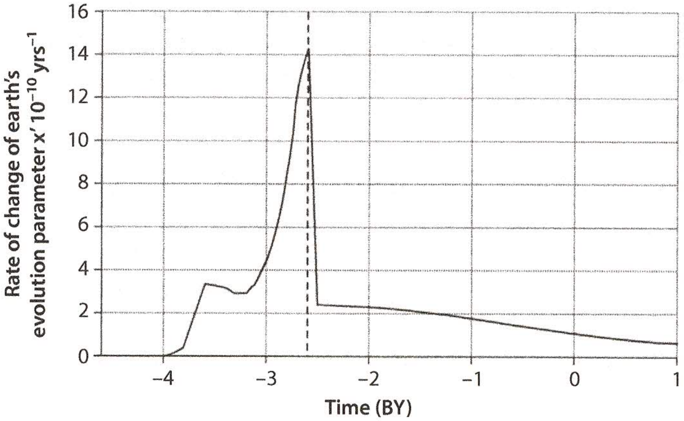

Figure 4.4 Rate of change in the Earth's tectonic parameter $\dot{z}$ determining the rate of the basalt melts surface eruptions and the mantle degassing rate (the dashed line represents core separation time). (After Sorokhtin *et al.*, 2011, Figure 11.2, p. 423.)

where $\dot{Q}_m$ is the current value of the heat flow from the mantle, $Q_{4.0} \approx 1.6 \times 10^{37}$ erg is the Earth's heat loss at the start of its tectonic activity 4.0 BY ago and $Q_{mo} \approx 10.77 \times 10^{37}$ erg is today's total heat loss of the Earth's mantle. Then the derivative $\dot{z}$ (Eq. 4.1) and its normalized value

$$\dot{z}_n = \frac{\dot{Q}_m}{\left|\dot{Q}_{mo}\right|},$$

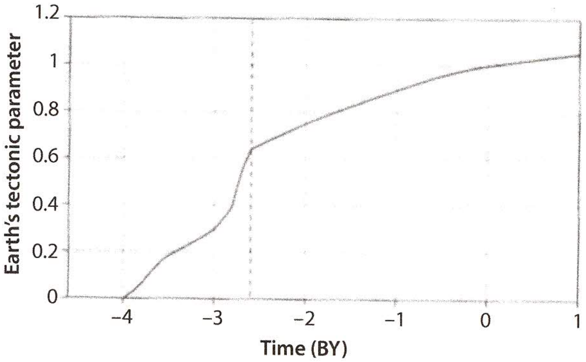

Figure 4.5 Earth tectonic parameter, $\dot{z}$, controlling the mantle magmatic activity products accumulation rate and the mass of the substances degassed from the mantle: the dashed line represents the time core separation ends. (After Sorokhtin *et al.*, 2011, Figure 11.3, p. 423.)

where $\left|\dot{Q}_{mo}\right| = 3.39\times10^{20}$ erg/s is the absolute value of today's Earth deep heat flow. The correlation of the Earth's tectonic parameter change rate versus time is shown in Figure 4.4 and the value of the parameter controlling the magmatic activity is shown in Figure 4.5.

Thus, the mantle degassing rate is in direct proportion with the component content in the mantle m_{i_m}, its mobility factor, χ_i, and the rate of the mantle convective mass exchange $\dot{z}$:

$$\dot{m}_i = -m_{i_m}\chi_i\dot{z} \tag{Eq. 4.2}$$

The mass of an i^{th} degassed volatile component in the mantle and its accumulation in the Earth's external geospheres is determined as:

$$m_i = m_{i_o}(1-e^{-\chi_i z}), \tag{Eq. 4.3}$$

where m_{i_o} is the total mass of the i^{th} volatile component in the mantle and external geospheres. During the Archaean time, the degassing of the mantle mass gradually increased. Thus, it is necessary to consider its increase from $M_{\text{m}} = 0$ to its total amount at the end of Archaean, M_{mS}. The mantle mass was previously estimated in Figure 4.6. It is necessary to use a different equation for the degassing of the water or any other volatile element and compound (such as N_2 and CO_2) in the Archaean time:

$$m_i = m_{i_o}(1-e^{-\chi_i z})\left(\frac{M_m(t)}{M_{m\Sigma}}\right) \tag{Eq. 4.4}$$

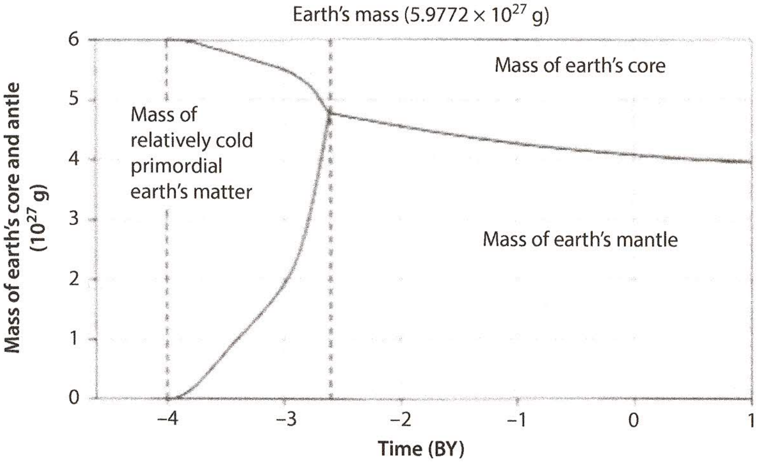

Figure 4.6 Gradual increase of the mantle mass in the Archaean time due to the expansion of the Earth's matter differentiation zone and in its mass in Proterozoic and Phanerozoic due to the core growth. Dashed lines are the times when the core matter separation began about 4 BY ago and when a high-density iron-oxide core separated in the center of Earth about 2.6 BY ago. Since the origin of the Earth 4.6 BY ago and through the very end of Archaean time, the primordial Earth's matter saturated with ore elements was preserved within Earth. (After Sorokhtin *et al.*, 2011, figure 6.6, p. 208.)

where $M_m(t)$ is the mantle mass at the time $4 < t < 2.6$ BY ago. For the Proterozoic and Phanerozoic time, Eq. 4.3 is valid.

To determine the mass of the volatile component m_i, degassed from the mantle (e.g., water), it is necessary to insert in Eqs. 4.3 and 4.4 the initial and boundary conditions for the content of this component (water, nitrogen, and/or carbon dioxide) in the Earth's external geospheres.

Formation of the Hydrosphere

The Earth's matter differentiation mechanisms were drastically different from today's in the Archaean and post-Archaean time. Thus, it is to be expected that the mobility factors χ_i of the volatile components (or at least some of them) were significantly different.

During the Archaean time, the silicate matter of the convecting mantle, together with its volatile components, went through a layer of melted iron (see Figure 4.7). The oxides, with their lower heat of formation, rather than the oxide of bivalent iron (63.64 kcal/mol) must have dissociated and released their oxygen for the oxidation of iron to the bivalent oxide. The water (both vapor or fluid) molecule heat of formation is 57.8 kcal/mol.

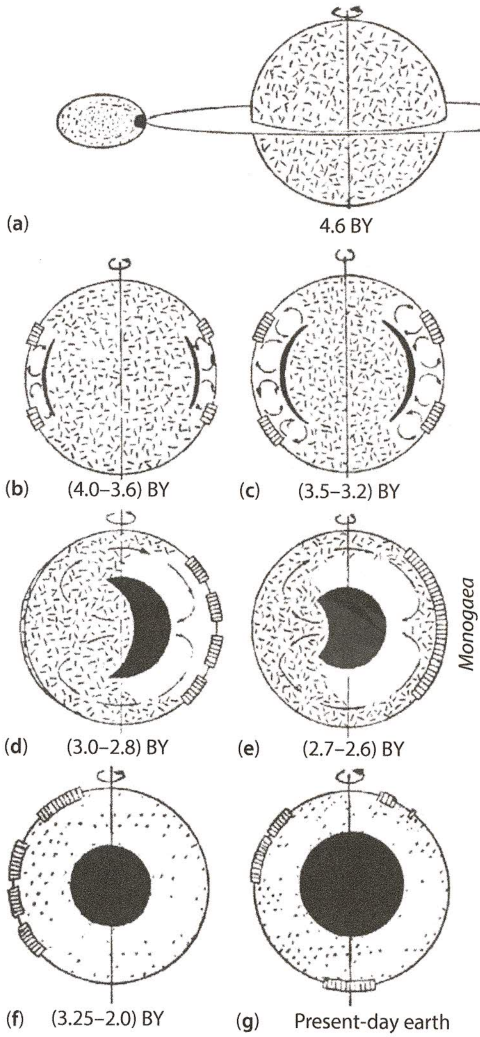

Figure 4.7 Earth structure evolution: (A) the young Earth and moon formation; (B–F) consecutive stages of the Earth's core separation and formation; (G) present-day Earth. The dashes represent the primordial matter; solid black is iron and its oxides melts; white is the Archaean depleted mantle impoverished in iron, its oxides, and siderophilic elements; the dots are the current-type mantle; and the boxes are continental massifs. (After Sorokhtin *et al.*, 2011, figure 4.1, p. 117.)

Therefore, the water must have dissociated on the metallic iron melts in the Earth's matter differentiation zones:

$$Fe + H_2O \rightarrow FeO + H_2 + 5.84\ \text{kcal/mol.} \qquad \text{(Eq. 4.5)}$$

The carbon dioxide heat of formation is 94.05 kcal/mol. Thus, carbon dioxide could have crossed through this zonal differentiation layer without difficulty. In the Archaean time, the water mobility factor in the degassing Eqs. 4.2 and 4.3 was significantly lower than that in the post-Archaean time, whereas the carbon dioxide mobility factor could remain constant during the entire time of its degassing from the mantle. It is noteworthy that together with the water, many other oxides with low formation heat dissociated in Archaean time on the iron melts. They were reduced to free elements.

The water mobility factors in Archaean time and thereafter significantly differed. Thus, to estimate the mantle degassing it is necessary to put together two degassing equations, Eq. 4.3 and 4.4, with different mobility factors. Then combine them by the degassing process continuity condition at the Archaean-Proterozoic time boundary. In this case, these two equations include three variables: two water mobility factors and the original water mass ($m_{H_2O_0}$) in the Earth's matter.

To solve the problem quantitatively, it is necessary to determine and insert into the equations three independent boundary conditions.

1. ***The first boundary condition*** can be the total mass of water in the present-day ocean and the continental crust. Our estimates are based on publications by Ronov and Yaroshevsky (1978) and amended by Sorokhtin *et al.* (2011), whose observations suggest the following assumptions for which the mass of water in the hydrosphere may be assumed: (1) The ocean currently contains 1.42×10^{24} g of water (in the continental crust together with the continental waters and icebergs of 0.446×10^{24} g. (2) The oceanic crust contains approximately 0.358×10^{24} g of irreducible water. (3) Altogether, the Earth's external geospheres (the hydrosphere) contain 2.23×10^{24} g of water. This amount of water was degassed from the Earth's depths over its geological life, that is, over the last 4.5 BY. Strictly speaking, this is not exactly accurate because a significant part of the water that reached the surface in Proterozoic and Phanerozoic time was constantly returned into the mantle through the plate subduction zones. Some portion of it dissociated in hydration of the oceanic crust rocks and in the upper atmosphere (affected by the solar radiation). The authors assume that not the absolute mass, but only its effective value is equal to the difference between the masses of the degassed and the

subducted water. In this situation, all calculations are valid and only the effective value of the mobility factors X will be somewhat lower than their actual values.

2. ***A second boundary condition*** is the total water mass on Earth, $(m_{H_2O})_0$. The first step is to determine to calculate its mass in the present-day mantle. The water concentration in the mantle is a fundamental problem considered by petrologists. It has not been conclusively resolved. The reason is that upon reaching the Earth's surface, practically all the mantle water immediately (during the rise and discharging onto the surface) is intensely contaminated by the surface water. Even the most depth-associated xenoliths, e.g., such as garnet peridotites or eclogites from the kimberlite blow pipes, turn out to be just fragments of the oceanic crust sucked-in to great depths underneath the continents through the former subduction zones (Sorokhtin, 1985; Sorokhtin *et al.*, 1996, 2004). Nevertheless, fresh basalts of the oceanic islands, despite a possibility that they capture some marine water, which filter through the stratovolcanoes, usually contain very little water, no greater than 0.3% OH (Joder and Tilly, 1962).

   This and other theoretical considerations lead most modern petrologists dealing with the origin of mantle rocks to believe that the mantle water content is exceptionally low: Ringwood (1981) assumed the mantle water content at 0.1% and Pugin and Khitarov (1978) believed in a lower value of 0.025 to 0.1%. Sorokhtin and Ushakov (1991, 2002) estimated values no greater than 0.05 to 0.06%. After a review of all estimates, one can conclude that the mantle is exceptionally dry. The total water content in today's mantle is $\approx 2.007 \times 10^{24}$ g and the total water mass on Earth, $(m_{H_2O})_0 \approx 4.23 \times 10^{24}$ g.

3. ***A third boundary condition*** for the calculations could be the hydrosphere's water mass at an intermediate point in time (if it is possible). Using additional geological data, it is a solvable problem. As the ocean gradually increased in volume, there should have been a moment in its evolution when the oceanic water covered the mid-oceanic ridge crests with their associated rift zones. After that, hydration of the oceanic crust rocks must have been rapidly increasing and so must have been the release of the ore element from the rift zones to the ocean.

Therefore, the geochemistry of oceanic deposits must have drastically changed after the described event as they now include abundant ore elements brought out from the mantle.

The most characteristic such element and the clear indicator of the sought-for boundary (the moment of the oceanic crust saturation with water) is iron. Metallic (free) iron was still available in the Precambrian mantle in noticeable amounts (see Figure 4.2). Rising together with the hot mantle matter into the rift zones, it reacted with the marine water (devoid of oxygen) rich in carbon dioxide forming bicarbonates of iron:

$$Fe + H_2O + 2CO_2 \rightarrow Fe(HCO_3)_2 \qquad \text{(Eq. 4.6)}$$

After the ocean covered the mid-oceanic ridge crests, the dissolved $Fe(HCO_3)_2$ began spreading all over the ocean. In the shallow water, the bivalent iron helped by bacteria (especially cyanobacteria) was oxidized to the trivalent form and precipitated forming thick iron ore deposits:

$$2Fe(HCO_3)_2 + O \rightarrow Fe_2O_3 + 2H_2O + 4CO_2 \qquad \text{(Eq. 4.7)}$$

Because of the iron release from the oceanic rift zones, at least two unique massive iron ore formation epochs are identified in the World Ocean history. The first was at the end Archaean time (the Kivatin-type iron ore formations) 3 BY ago. The second was at the end of the Early Proterozoic time, nearly 2.2 BY ago, known as the Krivoy Rog-type ores. This second iron accumulation stage is most identifiable in the Earth's geological record.

The area of the oceans in Proterozoic is the global area minus the continental area. The continental crust thickness has had minor change with respect to time; therefore, the area of the continents can be considered as proportional to their mass. The mass evolution of continents is presented in Figure 4.8. The area of the oceans 2.2 BY ago was $\approx 3.48 \times 10^{18}$ cm^2. The average ocean depths at that time was ≈ 930 m. Thus, the World Ocean water mass 2.2 BY ago was $\approx 0.325 \times 10^{24}$ g (Figure 4.9). Knowing the bound water mass in the crust 2.2 BY ago, it is possible to calculate, using a reconstruction (Sorokhtin and Ushakov, 2002) of the development of the oceanic crust structure (Figure 4.10) and the continental crust mass at that time (see Figures 4.8). It may be estimated that by the end of Archaean time, the average irreducible water concentration in the continental crust rose to 0.6%. Today it is 2%. Thus, 2.2 BY ago the continental crust contained $\approx 0.109 \times 10^{24}$ g of water. Assuming the average density of the pelagic deposits at ≈ 2.2 g/cm^3 with 20% water, the hydrated basalts and gabbros (density ≈ 2.9 g/cm^3) containing $\approx 2.5\%$, and the serpentinites (density

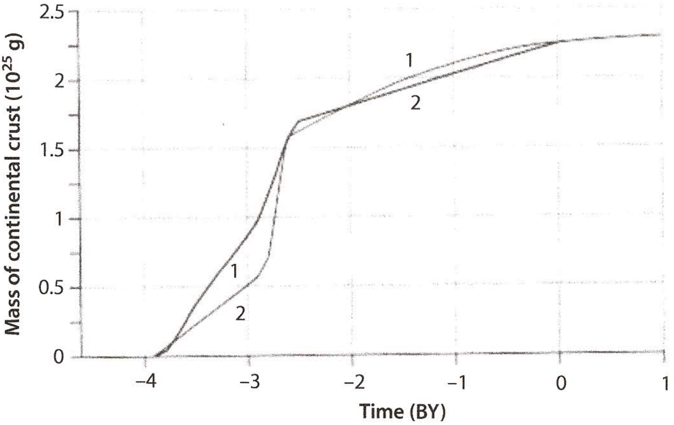

Figure 4.8 Continental crust mass growth: (1) authors' version and (2) Taylor and McLennan (1985) curve. (After Sorokhtin *et al.*, 2011, figure 7.7, p. 250.)

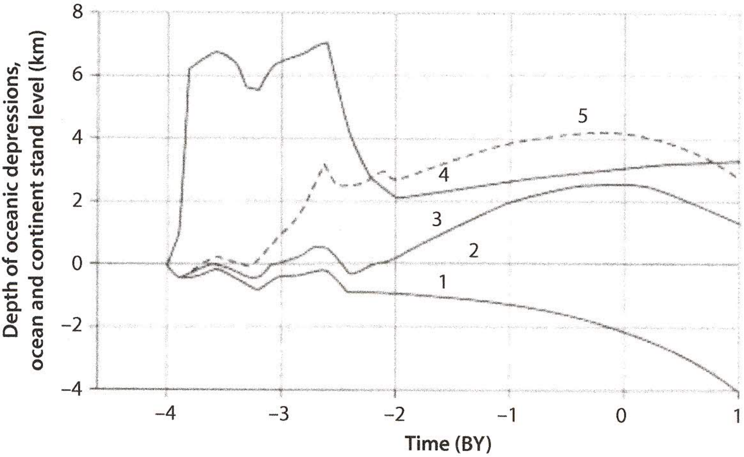

Figure 4.9 Evolution in the positions of the oceanic and continental surfaces compared with the average mid-oceanic ridge crests stand level: *Curve 1* – average depth of the oceanic depressions; *Curve 2* – mid-oceanic ridge crests stand level; *Curve 3* – world-ocean surface level; *Curve 4* – average continent stand level (relative to mid-oceanic ridge crests stand level); and *Curve 5* – ocean surface position in the case of no water dissociation on iron melts in the Archaean time under the reaction: $Fe + H_2O = FeO + H_2 + 5.84$ kcal/mol. (After Sorokhtin *et al.*, 2011, figure 11.6, p. 428.)

≈ 3 g/cm^3) up to 11%, 2.2 BY ago the oceanic crust contained $\approx 0.385 \times 10^{24}$ g of water. Thus, the total water mass in the hydrosphere was:

$$(0.325 \times 10^{24}) + (0.385 \times 10^{24}) + (0.109 \times 10^{24}) \approx 0.819 \times 10^{24}\text{ g.} \quad \text{(Eq. 4.8)}$$

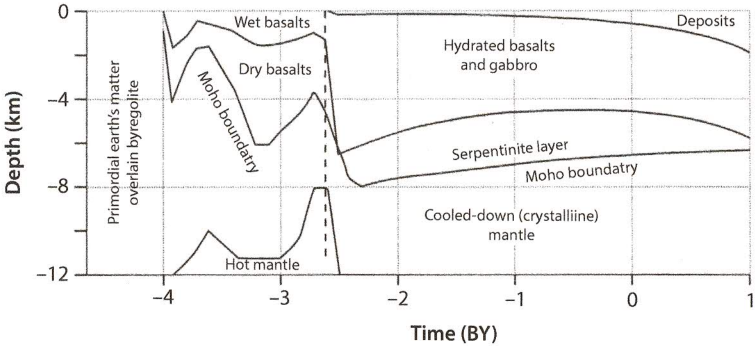

Figure 4.10 Generalized model of the oceanic crust evolution. (After Sorokhtin *et al.*, 2011, figure 7.1, p. 243.)

Constructing a system of Eqs. 4.3 and 4.4 separately for the Archaean and the post-Archaean time, one can substitute into them today's water masses in the Earth, in its hydrosphere, and in the Early Proterozoic hydrosphere ≈2.2 BY ago. These equations have different water mobility factors. Thus, they need to be merged into a common system through the condition of degassing continuity at the Archaean-Proterozoic time boundary. After that the correlation of the mantle degassed-water versus time can be determined. The water mobility factor in the Archaean time turns out to be $\chi_1 = 0.123$ and in the Proterozoic and Phanerozoic it was almost 12 times greater, $\chi_2 = 1.45$.

The water accumulation in the Earth's hydrosphere is illustrated in Figure 4.11. This figure demonstrates that the water accumulation regime in the external geospheres changed substantially near the Archaean-Proterozoic time boundary. The change was especially drastic for the water accumulation in the oceanic crust, which caused the formation of the serpentinite layer of the oceanic crust at the beginning of Proterozoic. This layer is the most capacious reservoir of the irreducible water on Earth.

After determining the total water mass in the Earth and the water mobility factors for the Archaean and post-Archaean time, using Eq. 4.3 one can determine the water accumulation rate in the Earth's hydrosphere. The water-from-mantle to hydrosphere degassing rate is shown in Figure 4.12. This graph indicates that the maximum water degassing rate occurred 2.5 BY ago, which is early in Proterozoic time. At the same time, maximum tectonic activity had occurred during the Archaean. This apparent discrepancy was caused by the fact that in the Archaean time, most of the

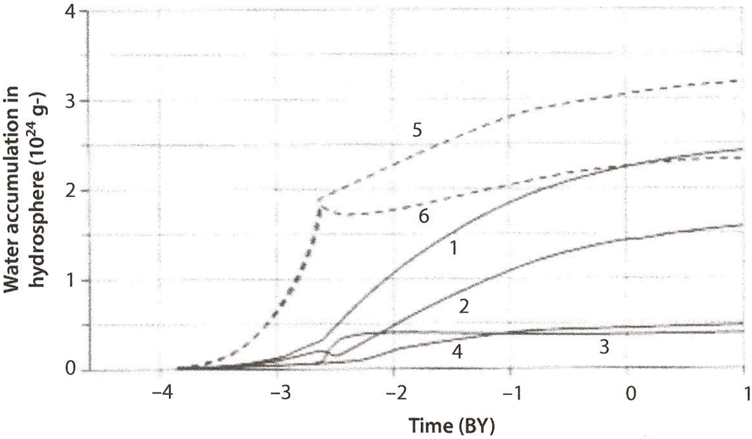

Figure 4.11 Water accumulation in the Earth's hydrosphere: *Curve 1* – total mass of water degassed from the mantle; *Curve 2* – oceanic water mass; *Curves 3 & 4* – water mass bonded in the oceanic and continental crust; and *Curves 5 & 6* – water mass degassed form the mantle and the oceanic water mass under a hypothetical scenario of no water dissociation in the Earth's matter differentiation zones in the Archaean time according to the reaction Eq. 4.5. (After Sorokhtin *et al.*, 2011, figure 11.4, p. 427.)

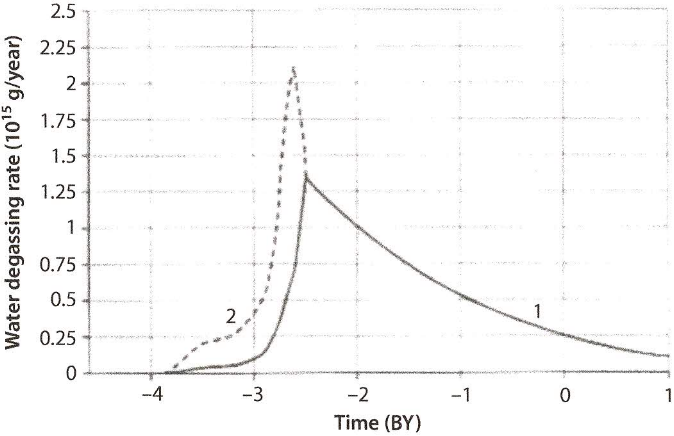

Figure 4.12 Mantle-to-hydrosphere water degassing rate: *Curve 1* – accounting for water dissociation in the Earth's matter differentiation zones in the Archaean time and *Curve 2* – not accounting for such dissociation. (After Sorokhtin *et al.*, 2011, figure 11.5, p. 427.)

degassed water was still within the mantle, dissociated over the iron melts in the Earth's matter differentiation zones as follows:

$$H_2O + Fe \rightarrow FeO + H_2. \qquad \text{(Eq. 4.9)}$$

The heavy hydrogen isotope is mostly associated with iron, whereas the light hydrogen isotope was found in the degassed water. In the Proterozoic time and even more so in Phanerozoic time, there was no water dissociation in the mantle. According to Eq. 4.2, water (without any losses) entered the Earth's hydrosphere. Currently the yearly rate of water degassed from the mantle is $\approx 2.6 \times 10^{14}$ g/year or 0.26 km^3/year.

The average depth of oceanic depressions may be estimated from the Earth's tectonic activity (see Figure 4.13) and from the average oceanic plate longevity (see Figure 4.14). Determination of the average depth of

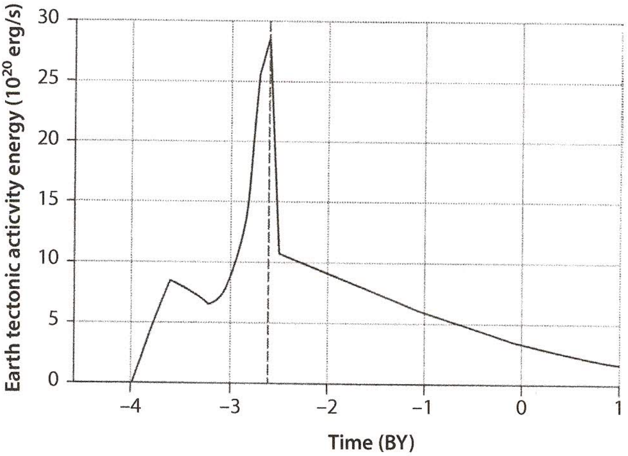

Figure 4.13 Energy expression of the Earth's tectonic activity (vertical dashed line denotes the core formation time). (After Sorokhtin *et al.*, 2011, figure 5.17, p. 187.)

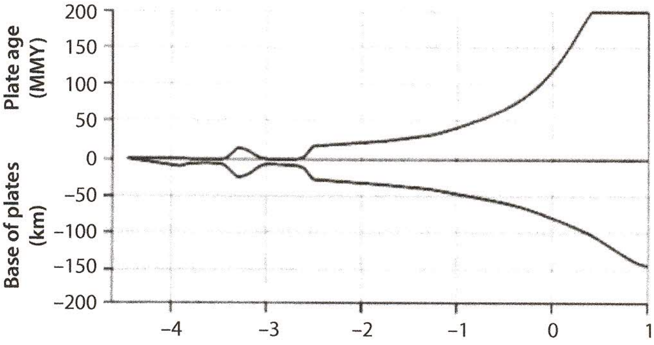

Figure 4.14 Evolution of oceanic lithospheric plates and their average thickness. (After Sorokhtin *et al.*, 2011, figure 7.3, p. 245.)

the oceanic depressions and their areas can be estimated, keeping in mind that the oceans in the Early Archaean time were positioned only in the low latitudes. It is now possible from the determined mass of water mass in the ocean to obtain the ocean surface elevation relative to the average standing level of the mid-oceanic ridge crests. The results are displayed in Figure 4.9.

Figure 4.9 establishes that the oceanic depression depths, relative to the average standing level of the mid-oceanic ridge crests, in the Early Archaean time were small: 80 to 200 m. There wasn't a large quantity of water in the oceans during this period. During the Early and Middle Archaean time, there were still no real oceans on the Earth. What existed were numerous isolated shallow-water marine-type basins. During this period, the level of these seas rose over the mid-oceanic ridge crests and the Earth's primordial matter areas, but especially the lithospheric plate pileup zones (Figure 4.15). The kernels of future continental massifs were being formed in the centers of these zones. Their elevations reached 6 km (see Figures 4.9 and 4.16).

The high continent stand level in the Archaean time was determined by the high heat flows. This resulted in thick and heavy lithospheric plates, which could not form underneath the heavy continental shields. The continental crust, because of a lighter density (buoyancy), rose high over the average mantle surface. Today, the present-day continental crust is underlain by a thick (up to 200 km) and dense (≈ 3.3 g/cm^3 ultramafic lithosphere), which substantially sinks the continents into the upper mantle (see Figure 4.17).

The high stand of the continental shield during the Archaean time resulted in intense physical erosion of its surface (Sorokhtin *et al.*, 2011). This is observed in many of today's Archaean shields on whose surface are deeply exposed, metamorphosed amphibolite and granulite facies that were formed at depths of 5–10 km. There are also examples of deeply metamorphosed epidote-amphibolite facies, e.g., in the Kola Peninsula Keiva

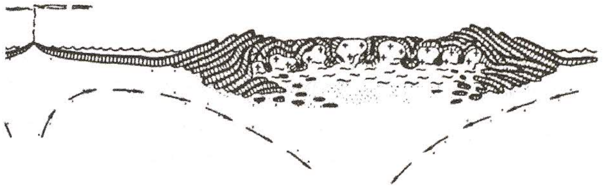

Figure 4.15 Image of the continental crust formation in Archaean time. (After Sorokhtin *et al.*, figure 7.5, p. 247.)

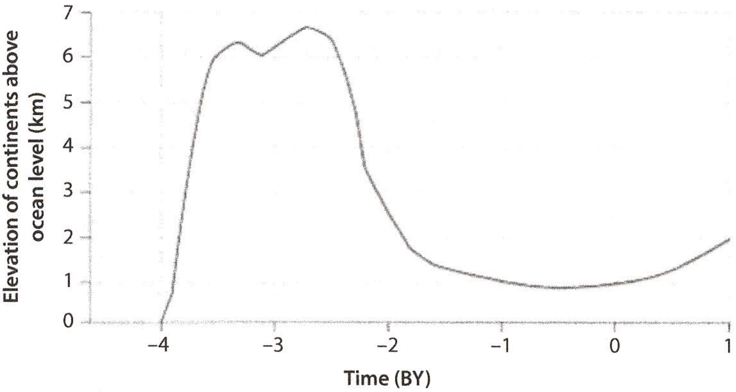

Figure 4.16 Average stand (elevation) of continental massifs over the rift zones in the Archaean time and over the ocean surface in Proterozoic and Mesozoic. (After Sorokhtin *et al.*, 2011, figure 7.10, p. 353.)

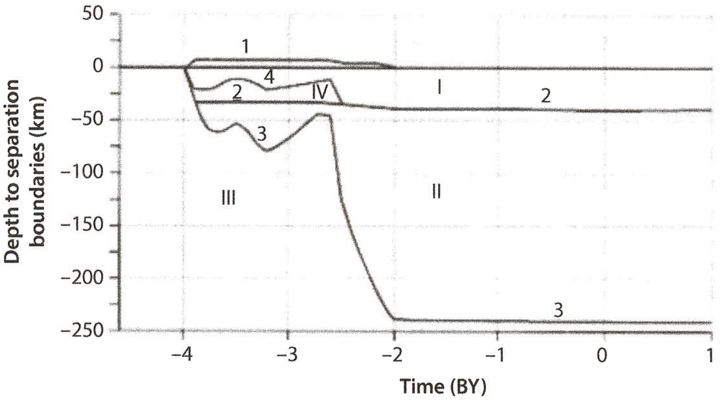

Figure 4.17 Evolution of the structure of the continental plates: *Area I* – continental crust; *Area II* – continental lithosphere; and *Area III* – sublithospheric (hot) mantle. *Curve 1* – surface of the continents; *Curve 2* – continental crust base (Mohorovicic boundary); and *Curve 3* – base of the continental lithosphere. (After Sorokhtin *et al.*, 2011, figure 7.9, p. 252.)

block. Huge masses of sedimentary rock had to be deposited on the ocean floor during the high stand of the Archaean continental blocks, after they remelted in the oceanic plate pileup zones and converted to massive granitoid intrusions of Archaean granite-greenstone belts Figure 4.15).

At the end Proterozoic, the surface of the growing ocean had risen to the average elevation of the continental planes. In the Phanerozoic, the first global marine transgressions on the continents occurred, which noticeably shrank the river discharge and continental rock erosion dump areas in the oceans.

If water dissociation occurred during the Archaeon time within the Earth's matter differentiation zone, then the mass of water in the hydrosphere would have exceeded the current amount by 1.5 times: $\approx 3 \times 10^{24}$ g rather than the $\approx 2.2 \times 10^{24}$ g (see Figure 4.11). The ocean surface elevation would then be about 2 km above its current elevation. This would have resulted in the flooding of the Earth in the Archaean and Protozoic time over a large portion of today's continental areas (see Figure 4.9). Only the highest continental areas would have been above the water surface.