

The composition of early Earth's seawater: the results of thermodynamic modeling

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The seawater composition is very stable through geologic time. There is a point of view that the one's cation compound was formed very quickly directly after the liquid ocean origination on the Earth's surface [e.g. Vinogradov, 1967]. The isotope composition of the Hadean detrital zircons evidences the liquid water existence on the Earth's surface as early as 4.4 Ga [e.g. Mojzsis et al., 2001; Cavosie et al., 2005; Watson and Harrison, 2005]. In this investigation we offer a possible scenario to form the seawater salt composition of early Earth's ocean.

A number of models for the early Earth suggest a surface magma ocean was formed during accretion with the accumulation of most of the planets volatiles in the atmosphere [e.g. Ozima and Podosek, 2002; Lammer et al., 2004; Elkins-Tanton and Seager, 2008]. The magma ocean(s) would cool under a dense atmosphere that contained most of modern Earth's volatile inventory (currently divided between the atmosphere + hydrosphere + rock). This atmosphere was largely water and carbon dioxide (~80-90% H₂O and 8-18% CO₂; [Denlinger, 2005; MacKenzie and Lerman, 2006; Maurette, 2006]) and the pressure at Earth's surface was ~330 bars [Ozima and Podosek, 2002; Maurette, 2006]. The magma ocean would have solidified within a few million years [Sleep et al., 2001; Elkins-Tanton, 2008]. After magma ocean solidification the surface temperature (and, as a consequence, the water content of atmosphere) is expected to have been a simple function of solar luminosity, which increases, and greenhouse effect. Draw-down of CO₂ from the atmosphere, reducing the greenhouse effect, would occur through 'weathering' reactions producing carbonate minerals. As soon as a liquid ocean started to condense, the alteration of surfaces rock began; as a result the first sedimentary rocks could have formed. At the same time vigorous hydrothermal systems would have been set up mining the heat from the crust and leading to metamorphic reactions changing the composition of the crust and proto-ocean. Submarine hydrothermal systems were probably much more common than today due to more vigorous volcanism than today. In the course of our investigation we examined the next sequence of processes: (1) the hydrothermal alteration of the surface rocks by the hot dense atmosphere, (2) the submarine weathering of the surface rocks by interaction with resulted cold oceanic water, and (3) the hydrothermal alteration of komatiitic protocrust. These processes had to produce the early Earth's seawater composition.

The modeling approach

The quantitative geochemical modeling of weathering and hydrothermal rock alteration was implemented by dint of thermodynamic calculations with accounting of the minerals dissolution kinetics using the approach described in [Zolotov and Mironenko, 2007]. Thermodynamic calculations have been performed on a basis of the program complex for thermodynamic calculations Geocheq [Mironenko et al., 2008] using the thermodynamic database derived from Supcrt92 [Johnson et al., 1992].

The initial model compounds

We modeled interactions in the O-H-K-Mg-Ca-Al-C-S-Si-N-Na-Cl-Fe system. The composition of early Earth's crust was simulated by the basaltic komatiite from the Archean greenstone belt Munro Township, Canada [Arndt, Nesbitt, 1982], wt. %: SiO₂ = 48.76, Al₂O₃ = 9.36, Fe₂O₃ = 3.07, FeO = 8.04, MgO = 21.65, CaO = 8.05, Na₂O = 0.90, K₂O = 0.16. The primary atmosphere composition has been used the same as calculated in [MacKenzie and Lerman, 2006], vol. %: H₂O = 90.58, CO₂ = 7.40, N₂ = 0.20, HCl = 1.39, H₂S = 0.44. The initial atmospheric pressure was 330 bar and temperature - 600°C.

1. Modeling of interactions in the protocrust – hot dense atmosphere system (600° - 50°C)

According to the received data the interactions in the protocrust – hot dense atmosphere system result to the next secondary mineral associations: pyroxenes + albite + olivine + amphiboles (600° - 500°C); amphiboles + talc + albite + chlorites (450° - 300°C); carbonates + quartz + clay

minerals + pyrite (250° - 50°C). The model system cooling is accompanied by the dramatic decrease of atmospheric CO₂ content from 48 to 9 bars. At T = 350°C the liquid water condenses and the water vapor content in the atmosphere declines gradually (up to 0.05 bars at 50°C). The nitrogen portion grows (but the partial pressure is stable in the course of the temperature reduction, it's about 0.8 bars). The reduced gases (H₂, CH₄, H₂S) pressure comes down. With the temperature decrease the cation composition of the hydrosphere originated as a result of the primary hot atmosphere condensation changes drastically. At T = 350° – 200°C calcium is the dominated cation of solution. The magnesium content increases gradually and this cation becomes the prevailing at low temperature (200° – 50°C). Chlorine- and sulfate-ions dominate in the anion compound. The dissolved CO₂ is the most abundant solution species.

2. The submarine weathering of surface rocks

Firstly the simulation of submarine weathering and hydrothermal alteration of the early Earth's protocrust has been described in our previous work [Novoselov and Silantyev, 2010]. The long-term low temperature (15°C) interaction of seawater received in the previous model block with komatiitic substratum produces the secondary mineral association consisted from amorphous silica, pyrite, carbonates and clay minerals. The carbon dioxide draw-down from atmosphere continues gradually. The calculated seawater pH grows from 4 to 5.5. The anion composition of the solution doesn't change. Magnesium remains the dominant cation, but the concentration decreases slightly. Sodium is the second most abundant cation and its content grows slowly, but it is in order of magnitude lower than in modern seawater. The calcium concentration is limited by carbonation precipitation and this one is equal to the modern seawater content. The calculated high content of dissolved iron and silica is a feature of early Earth's seawater [e.g. Holland, 1984]. The characteristics of received seawater may fluctuate as a result of different water-rock ratios (sodium becomes the dominant cation at low water-rock ratios – less then 0.1), but the general picture maintains the same.

3. The hydrothermal alteration of komatiitic protocrust

In this investigation we used the same concept of the hydrothermal circulation system of mid-oceanic ridges as in our previous work [Silantyev et al., 2009]. It was suggested that the hydrothermal fluid circulates through the komatiitic crust in the T - P range from 15°C - 400 bar up to 500°C – 2000 bar. Due to hydrothermal alteration the next secondary mineral associations form with the depth increasing: quartz + carbonates + clay minerals + pyrite + goethite/hematite (15° - 75°C); amphiboles + albite + chlorites + serpentine + magnetite (100° - 350°C); amphiboles + pyroxenes + talc + albite + olivine + magnetite (375° - 500°C). At temperature range 100° - 150°C the intense producing of reduced dissolved gases (H₂S, CH₄, H₂) occurs. At the same time carbonate- and sulfate-ions drastically remove from the hydrothermal fluid. The sharp decrease of magnesium content in solution is a feature of oceanic hydrothermal systems. Magnesium removes from the hydrothermal fluid in the temperature range 100° - 150°C. The concentration of other cations fluctuates, but doesn't change drastically. Sodium becomes the dominant cation of hydrothermal fluid. The general solution mineralization grows as a result of the water consumption for hydration reactions.

As a result of the seawater and hydrothermal fluid mixing the mineral association consisted from dolomite + amorphous silica + pyrite deposits. The carbonate- and sulfate-ions content decreases. Sodium becomes the dominant cation of seawater. Generally the model seawater composition comes to the modern one. However silica and iron is sufficiently more abundant as well as dissolved CO₂.

Conclusions

1. Due to the magma ocean solidification and consecutive cooling of Earth's surface the hot dense atmosphere consisted from water vapor and carbon dioxide should be reduced from 330 bar up to 10 bar as a result of the liquid ocean condensation and hydrothermal alteration of surface rocks.
2. If the main carbon species of early Earth's atmosphere was carbon dioxide, the abundant carbonate deposits should be formed as soon as the liquid water originated on Earth's surface.
3. Magnesium was the dominant cation of seawater before the hydrothermal circulation beginning through the oceanic crust.

4. The seawater composition has been resulted by both submarine weathering and hydrothermal alteration of komatiitic crust. It was very similar to the modern seawater, but dissolved CO₂, silica and iron were more abundant.

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