Geochemical water cycle and evolution of mantle redox state

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A numerical model is constructed to simulate the evolution of gas composition and flux degassing from mantle and that of mantle redox state through geochemical water cycle.

For the evolution of the Earth's atmospheric composition, plausible estimates have been done about CO_2 and O_2 so far (*Kasting*, 1993). However, other gas species such as H_2, N_2, NH_3, CH_4 remain to be studied. It is important to clarify the evolution of atmospheric composition, particularly redox state, for understanding not only the evolution of surface environment of the Earth but also the origin and evolution of life. There exist, however, many uncertainties especially for the early Earth.

The redox state of the atmosphere is controlled by the balance of supply and loss of oxidized and reduced molecules for the atmosphere. Therefore, this study focuses on H and O which are the most abundant volatile elements and the numerical model of H_2 and H_2O degassing from mantle to atmosphere-ocean system is formulated taking into account the change in mantle composition due to redox reaction.

In our model, degassing occurs from mid-oceanic ridge where magma production rate is the highest on the Earth. The ratio of H_2O and H_2 in degassing gas is obtained from the chemical equilibrium calculation between gas and magma generated by partial melting of mantle. Here we consider the reaction $H_2O + 2FeO = H_2 + Fe_2O_3$. A realistic upper mantle composition is given for model mantle while the present concentrations of Fe_2O_3 and H_2O in the mantle are given by observational constraints. The magma production rate is assumed to be equal to the oceanic crust production rate which changes with mantle temperature. Supposing that the volume of seawater is constant (*Kasting and Holm*, 1992), H_2O inflow flux to mantle is balanced with H_2O degassing flux from mantle. In this case, the secular change of H_2O concentration in mantle is equivalent to the integrated amount of degassing H_2.

The H_2 / H_2O ratio of degassing gas rises as the concentration of Fe_2O_3 in mantle is lower. The estimate of Fe_2O_3 concentration in mantle includes uncertainty. In the case of present Fe_2O_3 concentration at 0.1 wt% , which is near the lower estimate from observation, its concentration was as low as 0.04 wt% 4 billion years ago. For 4 billion years, the H_2 degassing flux decreases from 6.5 x 10^{12} mol/yr to the present value 7.8 x 10^{11} mol/yr. During this period, 0.4 ocean mass of H_2O was lost from mantle. In the case of present Fe_2O_2 concentration at 0.4 wt% , which is near the upper estimate from observation, its concentration was as low as 0.38 wt% 4 billion years ago. The H_2 degassing flux decreases from 2.7 x 10^{12} mol/yr to the present value 0.95 x 10^{11} mol/yr. In this case, 0.15 ocean mass of H_2O was lost from mantle for 4 billion years.

These results suggest that the degassing flux of H_2 was 10 - 30 times larger and that atmospheric H_2 concentration might be as high as 2 - 50 vol% 4 billion years ago when the degassing flux is balanced with H_2 escape flux from atmosphere to space (*Tian et al.*, 2005). Hence, the Earth's early atmosphere might have had significantly reduced composition.