Estimation of atmospheric oxygen levels during the Paleoproterozoic by weathering model

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It is widely accepted that the atmospheric oxygen level increased between 2.5 and 2.0 Ga. However, the exact quantitative pattern of the increase has remained highly elusive. Paleosols, containing records at the time of weathering, can be a powerful tool to estimate atmospheric oxygen levels quantitatively. In the present study, the behavior of Fe, sensitive to redox state, during weathering was modelled, the relationships between Fe concentrations in a weathering profile and atmospheric oxygen levels was derived from the model, and finally, the model was applied the relationships to Fe(II) and Fe(III) concentrations in paleosols to estimate atmospheric oxygen levels between 2.5 and 2.0 Ga.

The major factors that affect dissolved Fe(II) concentrations in a weathering profile are: i. dissolution rates of Fe(II)-bearing primary minerals, ii. oxidation rates of dissolved Fe(II), and iii. flow rates of ground water, which were modeled and expressed as differential equations. The relationships between phi values and atmospheric oxygen levels were derived from the differential equations where phi is defined as a ratio of a total amount of oxidized Fe(III) from dissolved Fe(II) to that of Fe(II) dissolved from primary minerals. The assumptions for the model are: (a) a weathering profile is formed horizontally and weathering proceeds normal to the surface, (b) ground water and thus Fe(II) flow one-dimensionally and horizontally, (c) Fe(II) dissolved from primary minerals remains in the profile as oxidized and instantaneously precipitated Fe(III) or flows out of the profile as dissolved Fe(II), and (d) rate-controlling factor of the formation of Fe(III) secondary minerals is the oxidation of dissolved Fe(II).

Considering the three major factors, a change in Fe(II) concentration in a weathering profile is expressed by d[Fe(II)]/dt = f + g + z (f: oxidation term, g: ground water flow term, z: dissolution term) (1). The total amounts of dissolved Fe(II) dissolved and flowing out were calculated based on equation (1), and then, the relationships between phi values and atmospheric oxygen levels were derived. The calculated relationships were applied to those observed in laboratory (Sugimori, 2007), which verified the validity of the model. Then sensitivity analysis of the model by changing the parameter values was carried out, which reveals that pH and ground water flow rate are the main factors that affect Fe behavior during weathering. The model applied to the phi-age relation obtained from paleosols reveals that the atmospheric oxygen levels increased gradually, linearly on the logarithmic scale, from about 10^{-6} to 10^{-3} atm between 2.5 and 2.0 Ga. The present model did not use any constraints of geological records and the conclusion is consistent with geological records such as sulfur isotopic ones.