

論文の内容の要旨

論文題目

Atmospheric evolution in the Precambrian: Constraints from water-rock-atmosphere interactions
(先カンブリア時代の大気進化：水-岩石-大気相互作用からの制約)

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Atmospheric evolution of the Earth is considered to be correlated with the physicochemical and biological evolutions of the surface environment, and thus is important for understanding the Earth's system. Special interests have been given for the evolutions of atmospheric O₂, CO₂ and CH₄. From accumulating isotopic and mineralogical data in sediments, it is accepted by most researchers that there were two major events of great increases in oxygen in the Precambrian: the Great Oxidation Event (GOE) at ~2.5–2.0 Ga and the Neoproterozoic Oxygenation Event (NOE) at ~0.8–0.6 Ga. At almost the same timings as the GOE and NOE, there were global glaciation events where greenhouse gases, CO₂ and CH₄, are considered to have fluctuated. Although the timings of these major events and qualitative information on surface environments in the events are becoming clearer than ever, quantitative constraints on atmospheric compositions throughout the Precambrian are still scarce. The present thesis gives constraints on atmospheric compositions, mainly CO₂ and O₂, in the Precambrian from water-rock-atmosphere interactions.

In order to precisely estimate atmospheric CO₂ levels in the Precambrian, I developed a new method that calculates CO₂ levels from the chemical compositions of paleosols. The new method (i) calculates the cation concentrations in porewaters at the time of weathering from those of paleosols, (ii) describes the relationships between partial pressure of atmospheric CO₂ (P_{CO_2}), pH and cation concentrations based on the charge balance between the cations and anions including carbonate species in porewaters, and (iii) finally calculates P_{CO_2} levels at a given temperature constraining pH by thermodynamics of weathering secondary-minerals. By applying the new method to modern weathering profiles, I obtained a good agreement between the calculated and observed P_{CO_2} levels. The weathering rate deduced from the new method was proportional to P_{CO_2} with fractional dependence of 0.18 and the apparent activation energy of weathering was 40–55 kJ mol⁻¹, which is consistent with the laboratory and field results. The application to modern weathering and the formulated characteristics of weathering strongly indicate that the new method is valid and robust. The new method was then applied to eight paleosols formed in the Neoproterozoic. I first made constraints on the local temperatures, at which the paleosols were formed, mainly by the temperature-solute concentration relationships in the literature, because local temperatures should have been different between the paleosols and from the average global surface temperatures. Under the constrained local temperatures, the P_{CO_2} levels were calculated to be 85–510 of the present day

atmospheric level (PAL) at ~2.77 Ga, 78–2500 PAL at ~2.75 Ga, 160–490 PAL at ~2.46 Ga, 30–190 PAL at ~2.15 Ga, 20–620 PAL at ~2.08 Ga and 23–210 PAL at ~1.85 Ga. The estimated P_{CO_2} levels are higher than those to maintain the average global surface temperature of the Earth above the freezing point of water only by CO_2 itself. The newly estimated P_{CO_2} levels imply that atmospheric CO_2 decreased gradually in long term in the Neoproterozoic-Paleoproterozoic and that the wide-spread glaciations at ~2.9 and ~2.4–2.2 Ga were differently triggered.

To estimate the partial pressure of atmospheric O_2 (P_{O_2}) in the Precambrian, Fe redistributions recorded in paleosols are useful. To interpret Fe records in paleosols, the relationship between P_{O_2} and Fe(II) oxidation rate is essential according to the previous studies. Because there is no experimental data on Fe(II) oxidation rate under low O_2 conditions ($P_{\text{O}_2} < 10^{-3}$ atm), I first experimentally obtained the Fe(II) oxidation rate law under low O_2 conditions down to 10^{-5} atm of P_{O_2} . All oxidation experiments were carried out in a glove box by introducing Ar gas at $\sim 10^{-5}$ – $\sim 10^{-4}$ atm of P_{O_2} , pH 7.57–8.09 and 22 °C. Luminol chemiluminescence was adopted to measure low Fe(II) concentrations (down to ~2 nM). Combining previous data under higher P_{O_2} conditions (10^{-3} –0.2 atm) with the newly obtained data, the rate law for Fe(II) oxidation over a wide range of P_{O_2} (10^{-5} –0.2 atm) was found to be written as:

$$\frac{d[\text{Fe(II)}]}{dt} = -k[\text{Fe(II)}][\text{O}_2]^x[\text{OH}^-]^2$$

where the exponent of $[\text{O}_2]$, x , and the rate constant, k , change from $x = 0.98$ (± 0.04) and $\log k = 15.46$ (± 0.06) at $\sim 6 \times 10^{-3}$ –0.2 atm of P_{O_2} to $x = 0.58$ (± 0.02) and $\log k = 13.41$ (± 0.03) at 10^{-5} – $\sim 6 \times 10^{-3}$ atm of P_{O_2} . The most plausible mechanism that explains the change in x under low O_2 conditions is that, instead of O_2 , oxygen-derived oxidants, H_2O_2 and to some extent, O_2^- , dominate the oxidation reactions at $< \sim 10^{-3}$ atm of P_{O_2} .

Then, I developed a new weathering model, which considers the steady-state weathering of Fe, in order to constrain P_{O_2} in the Precambrian from paleosols. The model calculates the ratio of the precipitated Fe(III)-(oxyhydr)oxides from dissolved Fe(II) to the total dissolved Fe(II) during weathering (ϕ), as a function of P_{O_2} . For the calculation of the ϕ - P_{O_2} relationship, the kinetic law for Fe(II) oxidation by O_2 obtained above was adapted. The law was further modified to include the effects of both the Fe(II)-hydroxyl and Fe(II)-carbonate species on Fe(II) oxidation from the kinetic data in the literature. The model's validity was confirmed by the consistency of the calculated ϕ - P_{O_2} relationships with those by the weathering model in the literature whose validity has already been verified. Once a ϕ value, and the values for the parameters relevant to weathering, namely, pH of porewater, P_{CO_2} , water flow, temperature and O_2 diffusion into soil, are obtained for a paleosol, the model can estimate P_{O_2} from the paleosol, in theory. The values for the parameters relevant to weathering were scrutinized for five Paleoproterozoic paleosols. The observed values of ϕ were obtained from the literature on the Paleoproterozoic paleosols. The values of pH, P_{CO_2} and temperature for the Paleoproterozoic paleosols were estimated during the P_{CO_2} estimation from the paleosols, as described above. The parameter value for water flow was estimated for each paleosol

based on the mass balance of Si, the relationships between weathering fluxes and runoff and the relationship between water flux and hydraulic conductivity. The parameter value for O₂ diffusion into soil was assumed in a reasonable range. Then, by incorporating the constrained values for the weathering-relevant parameters into the model and applying the model to the Paleoproterozoic paleosols, the *P*O₂ levels in the Paleoproterozoic were estimated: 10^{-6.7}–10^{-5.4} atm at ~2.46 Ga, 10^{-5.2}–10^{-3.2} atm at ~2.15 Ga, 10^{-3.9}–10^{-1.2} atm at ~2.08 Ga and more than 10^{-4.6}–10^{-2.5} atm at ~1.85 Ga. Comparison of the calculated results to the estimates of *P*O₂ in the literature suggests that a drastic rise of oxygen would not have occurred at ~2.4 Ga, supporting a slightly rapid rise of oxygen at ~2.4 Ga and a gradual rise of oxygen in the Paleoproterozoic in long term.

Besides the constraints on *P*CO₂ and *P*O₂ in the Precambrian from paleosols, I also considered the theoretical relationships between silicate weathering, atmospheric compositions (CO₂ as well as CH₄ and O₂) and climates (surface temperatures) in the Precambrian. Atmospheric CO₂ is a greenhouse gas and thus regulates the surface temperature of the Earth together with silicate weathering, which is a major sink of CO₂. The apparent activation energy of natural silicate weathering is thus a determinant factor of the regulation of the surface temperature of the Earth. Although it has long been suggested that the apparent activation energy of silicate weathering can be affected by solution compositions in natural weathering systems, the relationships between the apparent activation energy and solution composition are not fully understood. I formulated the apparent activation energy of silicate weathering, including solution composition effects, in three different scales: (i) each mineral-reaction in a weathering profile, (ii) elemental loss from the profile and (iii) weathering flux, based on the rate expressions in the three scales. It was found that the apparent activation energy of silicate weathering consistent between the three scales is affected by, and thus is a function of, the temperature dependence of atmospheric CO₂ ($\Delta H'_{CO_2}$). By introducing the general rate law for total cation flux by silicate weathering (*F*CO₂) in the Arrhenius expression and the compensation law, which represents the relationships between the apparent activation energy and the pre-exponential factor, the relationships between $\Delta H'_{CO_2}$, temperature (*T*) and *F*CO₂ were established. Based on the relationships between $\Delta H'_{CO_2}$, *T* and *F*CO₂, I discussed the effects of atmospheric CO₂ as well as those of CH₄ and O₂, on the silicate weathering, and their implications for the atmospheric compositions and surface temperatures in the Precambrian.

The effects of CO₂ on silicate weathering were firstly discussed based on the relationships between $\Delta H'_{CO_2}$, *T* and *F*CO₂ and the greenhouse effect of CO₂. In the global scale, the greenhouse effect of atmospheric CO₂ represents $\Delta H'_{CO_2}$, and thus determines silicate weathering. From the greenhouse effects of CO₂ in the literature, I calculated the ratio of the change in *F*CO₂ to the corresponding change in *P*CO₂, as an indicator of the feedback of silicate weathering on CO₂. The calculation of the feedback indicator revealed that the feedback is negative and independent of both *P*CO₂ and *T* when *P*CO₂ > 10^{-0.5} atm. Thus, the conditions of *P*CO₂ > 10^{-0.5} atm are stable with respect to silicate weathering. On the other hand, when *P*CO₂ < 10^{-0.5} atm, the feedback is *P*CO₂-independent but temperature-dependent; at low (< ~30 °C) and high (> ~30 °C) temperatures, the feedback is

negative and positive, respectively. Due to the positive feedback, the conditions of $P_{\text{CO}_2} < 10^{-0.5}$ atm and $T > \sim 30$ °C are unstable, and immediately change, with a slight change in CO_2 , to either the conditions of $P_{\text{CO}_2} > 10^{-0.5}$ atm or those of $P_{\text{CO}_2} < 10^{-0.5}$ atm and $T < \sim 30$ °C. When $P_{\text{CO}_2} < 10^{-0.5}$ atm and $T < \sim 30$ °C, the feedback is not only negative, but also becomes more negative as temperature decreases. Therefore, the global glaciations hardly occur by CO_2 alone. The stable climates in the Precambrian excluding the periods of glaciations (especially the stable climate in the Mesoproterozoic) may be explained by the stability of low CO_2 conditions ($P_{\text{CO}_2} < 10^{-0.5}$ atm and $T < \sim 30$ °C) against glaciations.

Atmospheric CH_4 affects the greenhouse effect of CO_2 , and thus the feedback of weathering on CO_2 . I calculated the feedback indicator under the presence of CH_4 , using the relationships between $\Delta H'_{\text{CO}_2}$, T and F_{CO_2} and the greenhouse effects of CH_4 in the literature. It was found that with a limited range of CH_4/CO_2 ratio ($< \sim 0.15$ and $> \sim 0.03$), positive feedback operates at low temperatures ($< \sim 5$ °C). Thus, with such CH_4/CO_2 ratios, global glaciations can occur. The emergence of CH_4 to make such CH_4/CO_2 ratios can be one of the triggers of the glaciations in the Precambrian, especially that in the Mesoarchean.

Atmospheric O_2 , when increasing from extremely low P_{O_2} to $\sim 10^{-6}$ – 10^{-3} atm, changes the apparent activation energy of weathering by involving oxidation reactions in weathering, and can increase F_{CO_2} at low temperatures, according to the general rate law. Thus, it is possible that the P_{O_2} increase from almost nil to $\sim 10^{-6}$ – 10^{-3} atm, can cause global glaciations, which may explain the glaciations in the Paleoproterozoic.

I finally calculated the temperature and P_{CO_2} transitions in the Precambrian based on the relationships between $\Delta H'_{\text{CO}_2}$, T and F_{CO_2} and the greenhouse effects of CO_2 in the literature. The results show that the temperature can have been maintained at > 0 °C only by CO_2 itself through the Precambrian, confirming that CO_2 was the dominant greenhouse gas in the eon. The argument is supported by the consistency of the calculated results with the P_{CO_2} estimates from paleosols in the Precambrian. From the calculated temperatures, it is also suggested that the Earth might have been hot ($> \sim 40$ °C) until around the end of Archean.