論文題目：Kinetics and mechanisms of silicate weathering and Fe behavior under low O_2 conditions
（低酸素環境における珪酸塩鉱物の風化とそれに伴う鉄の挙動に関する速度論的・機構論的研究）

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Kinetics and mechanisms of chemical weathering processes under low O_2 conditions were systematically studied through laboratory experiments for better understandings of weathering in the Precambrian. Iron behavior during weathering was especially investigated extensively because Fe is a good indicator of the redox environment.

Chapter 1. In chemical weathering, Fe-bearing silicates react with solution and release Fe and other constituents to the solution. Firstly, I carried out dissolution experiments under the present oxic conditions using five biotites, muscovite, and two chlorites whose compositions (especially Fe/Mg ratios) are different, in order to investigate the role of Fe and its oxidation within the silicate structure during dissolution. The dissolution experiments were conducted at pH 3.0 and 2.0, and at 25 °C using continuous flow-through reactors. Comparison of the dissolution rates normalized to the initial BET surface areas has indicated that Fe promotes the dissolution rate of biotite. Fluorine content in the structure is also a rate-controlling factor

of biotite dissolution. Chlorite showed the opposite relationship between dissolution rate and Fe content. Because the brucite-like interlayer in Fe-rich chlorite was more stable than that in Fe-poor chlorite, the dissolution rate of Fe-rich chlorite is slower than that of Fe-poor chlorite.

Chapter 2. Referred to the results under oxic conditions, the kinetics of biotite dissolution under low O_2 conditions was examined. The experiment was carried out in a glove box under low O_2 conditions ($Po_2 \leq 6 \times 10^{-4}$ atm) using a continuous flow-through reactor at 25 °C and pH 6.9. For comparison, a similar experiment of biotite
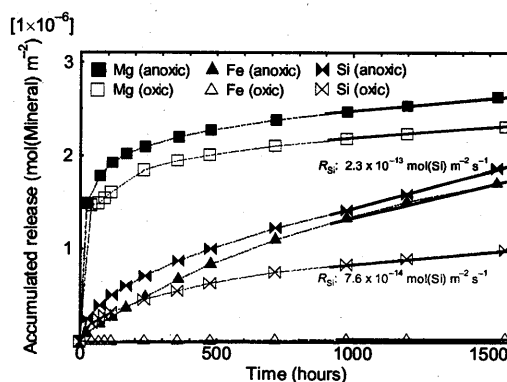

Fig. 1. Accumulated releases of Mg, Fe, and Si during biotite dissolution under low O_2 (referred to as 'anoxic') and oxic conditions.

dissolution was conducted under the present, ambient air (0.2 atm of Po_2). Iron-poor biotite (phlogopite) dissolution experiments were also carried out under low O_2 and oxic conditions to examine the effect of Fe content on biotite dissolution. The release rate of Si (R_{Si}) of biotite under low O_2 conditions was faster by three times than that under oxic conditions (Fig. 1). Phlogopite showed the similar tendency, suggesting that there is no direct effect of Fe content on the difference of the biotite dissolution between under low O_2 and oxic conditions. The results indicate that biotite dissolves faster in anoxic weathering than in modern weathering. Fe was released to the solution at a similar rate to that of Si under low O_2 conditions whereas the release rate of Fe was approximately one order of magnitude slower than that of Si under oxic conditions. After 65-day reactions, 60% of whole dissolved Fe remained in the reactor and 40% flowed out under low O_2 conditions whereas 99% remained and 1% flowed out under oxic conditions. We conclude that the different redistribution of Fe between the two conditions is caused by the difference in oxidation rate of Fe(II) that is a function of Po_2.

Chapter 3. The Fe(II) oxidation rate which affects the Fe behavior during Fe-bearing silicate dissolution is given as:

$$\frac{-d[Fe(II)]}{dt} = k[Fe(II)][O_2]^x[OH^-]^y$$

where the effect of dissolved O_2 (DO) concentration is described in the term of $[O_2]$ with the power of x. The effect of DO concentration on Fe(II) oxidation rate was investigated at a neutral pH region and room temperature, with the P_{O_2} range of 8×10^{-5} atm to 0.2 atm. To achieve the low P_{O_2} conditions and control the DO concentration in solution, the experiments were conducted in the glove box and solution was continuously bubbled by the mixed gases of Ar and O_2. The experimental data of the modified rate constants ($k' = k[O_2]^x$) plotted against P_{O_2} in logarithmic scale deviate from the linear dependence, i.e., $x = 1$ (Fig. 2). The power of $[O_2]$ in the rate law of Fe(II) oxidation rate (x) depends on P_{O_2} and to be below 1. The data points at 8×10^{-5} atm of P_{O_2} (-4.1 in logarithmic scale) are underestimate because the rate of DO consumption by the Fe(II) oxidation was faster than that of O_2 supply to the solution, and the actual DO concentration in the exact reaction area was probably lower than that estimated.
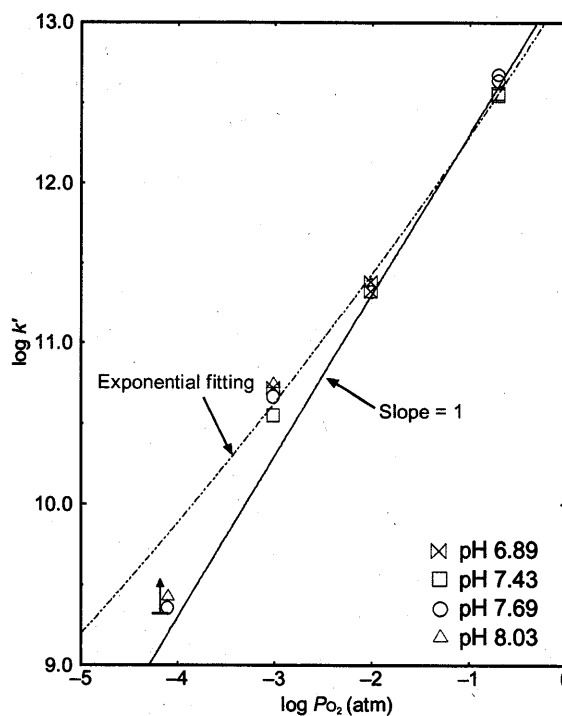

Fig. 2. Effects of P_{O_2} on Fe(II) oxidation rate.

Chapter 4. Fe behavior in chemical weathering including the processes such as dissolution of Fe-bearing silicate, Fe(II) oxidation in solution, and Fe(III) precipitation was investigated by forsterite dissolution experiments. First, forsterite was reacted with solution at pH 4.5–6.0 and 15–55 °C under oxic conditions to investigate the effects of pH and temperature on Fe behavior during dissolution. A ratio of the amount of precipitated Fe(III) to the total amount of dissolved Fe(II) from forsterite (Φ) was estimated from both the experimental data and a kinetic model calculated by the rate law of Fe(II) oxidation. The pH and temperature dependences of Φ obtained from the experimental data were well-explained by the calculated
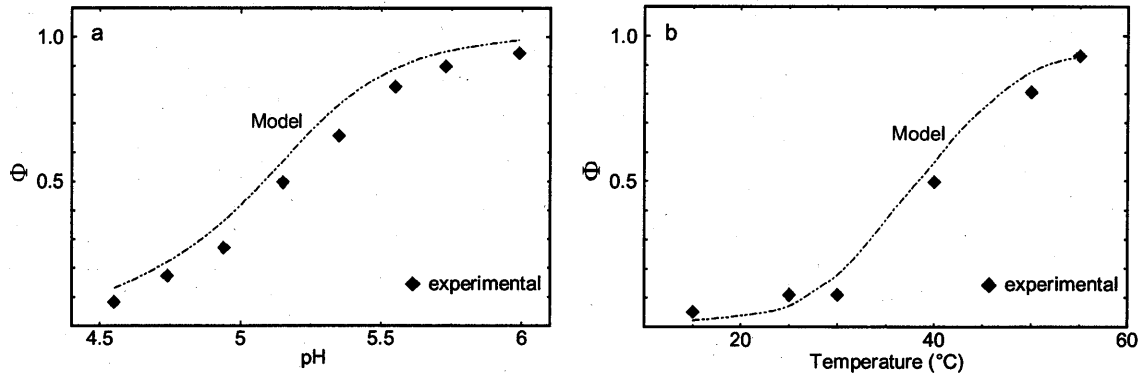
Fig. 3. Variations of Φ estimated from experimental data and a simple kinetic model plotted against pH (a) and temperature (b).

model (Fig. 3), suggesting the kinetics of Fe(II) oxidation mainly controls the Fe distribution between solid and solution during forsterite dissolution.

Chapter 5. Similarly, the effect of DO on Fe behavior represented by the values of Φ was estimated from the forsterite dissolution experiments at the range of 9×10^{-5} to 0.2 atm of P_{O_2}. The values of Φ depend on P_{O_2} and thus Fe(II) oxidation rate (Fig. 4). The kinetic model of Φ calculated from the Fe(II) oxidation rate law can explain the variation of Φ obtained from the experiments when the power of $[O_2]$ in the equation of Fe (II) oxidation rate (x) decreases from 1.00 to 0.75 as P_{O_2} decreases from 0.2 to 9×10^{-5} atm.
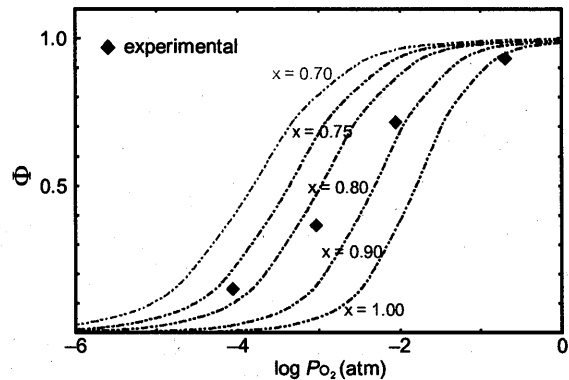

Fig. 4. Variations of Φ estimated from experimental data and a simple kinetic model plotted against P_{O_2}.

The above results provide the basic knowledge of chemical weathering under low O_2 conditions. The weathering model under low O_2 conditions can be complemented by the data of kinetics of silicate dissolution, Fe(II) oxidation, and Fe behaviors under low O_2 conditions. From the model, Fe distribution in paleosols and the relation between Fe retention fractions in paleosols and O_2 evolution in the Precambrian can be precisely discussed.