## Constraint on atmospheric hydrogen based on magnetite for the Archean Earth

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Determining environment of the early Earth would provide guidance for the condition under which life began and spread in addition to the evolution of the Earth. According to previous works, detrital magnetite is found in Archean riverbeds (e.g., Donaldson & de Kemp, 1998). Such existence of magnetite has been treated as a proxy constraining partial pressure of atmospheric  $CO_2$  ( $pCO_2$ ) and  $H_2$  ( $pH_2$ ) because it converts to other minerals in the atmosphere with high pCO2 and/or high pH2 considering a thermal equilibrium state (e.g., Rosing et al., 2010). However, since the conversion takes specific time, magnetite may be preserved even in the atmosphere with high  $pCO_2$  and/or high  $pH_2$ . We built a kinetic model of magnetite conversion in addition to a thermal dynamic model in order to estimate the time for which magnetite is preserved and to constrain atmospheric components in Archean. Considering river water with low pH owing to flowing, magnetite conversion is controlled by dissolution of magnetite rather than by siderite formation. And the magnetite conversion takes place through three steps: first, it releases hydrogen ion and converts to maghemite (White et al., 1994); second, the maghemite is reduced to wustite by H<sub>2</sub>; and third, the wustite dissolves into the surrounding water (Jang et al., 2009). Here, the reduction rate of magnetite under gaseous condition (Barde et al., 2016) is applied as the reduction rate of maghemite owing to a lack of literal information. Calculating the conversion time of magnetite under various conditions of pCO<sub>2</sub> and pH<sub>2</sub>, it is indicated that the conversion time depends on pH<sub>2</sub> rather than on pCO<sub>2</sub>. Assuming an initial radius of a magnetite particle is 1 mm according to Donaldson & de Kemp (1998), the conversion time is 100 kyr for  $pH_2 = 0.01$  bar. Considering the residence time of a particle in a river is 100 kyr (Johnson et al., 2014), this indicates that the existence of detrital magnetite constrains pH<sub>2</sub> under 0.01 bar. The constraint is consistent with theoretical predictions based on methanogen (e.g., Kharecha et al., 2005). Since a gaseous reaction tends to be slower than an aqueous reaction, this limit should be treated as the upper limit of pH<sub>2</sub>. Further investigation on magnetite dissolution, especially on maghemite reduction, will give more information for pH<sub>2</sub> in the early Earth.

キーワード:太古代、マグネタイト、大気組成

Keywords: Archean, Magnetite, Atmospheric composition

