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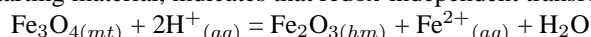
## Mechanisms of Iron Oxide Transformations in Hydrothermal Systems

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Coexistence of magnetite and hematite is observed in various hydrothermal systems (e.g., banded iron formations (BIF), seafloor hydrothermal systems, volcanogenic massive sulfide (VMS) deposits, iron oxide copper gold ore (IOCG) deposits). They have often been used to constrain the redox potential of fluids, assuming that the redox equilibrium is attained among all minerals and aqueous species. However, as temperature decreases, disequilibrium mineral assemblages may occur due to the slow kinetics of reaction involving the minerals and fluids. In this study, we conducted a series of experiments in which hematite or magnetite was reacted with an acidic solution under H<sub>2</sub>-rich hydrothermal conditions (T = 100-250 degree C, P of hydrogen = 0.05-5 MPa) to investigate the kinetics of redox and redox-independent transformations between hematite and magnetite, and the mechanisms of iron oxide transformation under hydrothermal conditions.

The formation of euhedral crystals of hematite in 150 and 200 degree C experiments, in which magnetite was used as the starting material, indicates that redox-independent transformation of magnetite to hematite occurred within 24 hours:



The chemical composition of the experimental solutions was controlled by the redox-independent transformation between magnetite and hematite throughout the experiments. While solution compositions were controlled by the redox-independent transformation in the first 3 days in a 250 degree C experiment, reductive dissolution of magnetite became important after 5 days and affected the solution chemistry. At 100 degree C, the presence of maghemite was indicated in the first 7 days. Based on these results, equilibrium constants of redox-independent transformation between magnetite and hematite and those of redox-independent transformation between magnetite and maghemite were calculated. Our results suggest that the redox transformation of hematite to magnetite occurs in the following steps: (1) reductive dissolution of hematite to Fe<sup>2+</sup>(aq) and (2) non-redox transformation of hematite and Fe<sup>2+</sup>(aq) to magnetite.

We propose that transformation mechanisms observed in the experimental study are applicable to various natural systems involving low-temperature hydrothermal solutions. For example, coexistence of magnetite and hematite is commonly observed in typical oxide-type BIFs. Many geochemical and mineralogical studies (e.g., Hoashi et al., 2009) suggested that hematite is a primary mineral in the BIFs, and that magnetite is a transformation product of primary hematite. Our study showed that redox-independent transformation of hematite to magnetite is a plausible process in the BIFs, by a reaction between primary hematite and Fe<sup>2+</sup>-rich hydrothermal fluids during early diagenesis. An important implication in considering the origin of magnetite in BIFs is that magnetite was likely formed under the conditions where the system was far from redox equilibrium. Therefore, the presence of magnetite in BIFs cannot be used to constrain the atmospheric or oceanic oxygen levels during the deposition of BIFs.

### Reference

Hoashi, M., Bevacqua, D. C., Otake, T., Watanabe, Y., Hickman, A. H., Utsunomiya, S., and Ohmoto, H. Nature Geoscience, 2, 301-306, 2009.

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