Localization of magnetite from Fe-rich brucite induced by pH changes during serpentinization

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H_2-rich fluids from ultramafic-hosted hydrothermal vent is important for understanding generation of hydrocarbon and biosphere in deep sea floor. Key to the formation of hydrogen in such system is magnetite formed serpentinization reaction. Magnetite distribution in serpentinized peridotite is usually heterogeneous; randomly scatted, and/or localized at former olivine-grain boundaries. However, formation mechanism of magnetite segregation during serpentinization remain poorly understood.

In this study, hydrothermal experiment of olivine –H_2O system was conducted with varying initial solution pH from under conditions of 250 ˚C and vapor-saturated pressure of 3.98 MPa. In the autoclave, 1.0 g of olivine powder (Fo91;38-75 μm) were set with solutions. Six solutions with varying initial solution pH at room temperature were used; pH at room temperature is 5.7, 6.8, 9.0, 10, 11, and 12. pH were adjusted by diluting NaOH solutions. The run time up to 63 days.

After the experiments, for solutions of initial pH = 5.7-9.0, pH increased to around 10. In contrast, for solutions of initial pH >10, the pH after experiments weren't changed. SEM observation revealed that Serpentine + Brucite + Magnetite were formed and no significant difference was not observed by changing pH of initial solution. Magnetite occurred with 5-10 μm, and seems that no localization of magnetite occur. After 63 days experiments, amount of serpentine and brucite, measured by thermogravity, were increased with increasing the pH of initial solutions. Amount of magnetite, which was measured by Alternating Gradient force Magnetometer, was increased with increased with increased with increasing initial pH up to 11. At initial pH = 12, the amount of magnetite after 63 days reaction was lower than that of initital pH = 11.

From EPMA analysis, the presence of ferric ion in serpentine and brucite were not observed. the iron content of the serpentine was almost similar with varying initial pH. In contrast, the iron content of the brucite roughly increased as pH was increased. The amount of products were almost proportional to reaction progress, indicating that reaction rates were approximately constant during the experiments. Mass balance calculation revealed that iron partitioning varies with pH; at initial pH = 6.8, the Fe partition ratio ween brucite and magnetite was 3:7. With increasing the initial pH, the ratio gradually decreased to 6:4 at initial pH = 12.

Klein et al. (2013) suggests that magnetite was formed at >200 ˚C by breakdown of Fe-rich brucite formed at <200 ˚C. Our experiments revealed that Fe-rich brucite could be formed by reaction with alkaline solution (pH>11). This indicates that pH changes from alkaline to neutral could from magnetite from Fe-rich brucite. To test this hypothesis, further hydrothermal experiments were conducted. The solid samples, which reacted with initial pH = 12 for 27 days, was reacted with water for 14 days. As a result, two type of magnetite were observed; magnetite with 5-10 micro and magnetite with < 1 μm. The later magnetite was occur within brucite grains, which was not observed reaction with initial pH = 12 for 27 days.

Our experiments revealed that, by changing pH in solution from alkaline to neutral, magnetite were formed from Fe-rich brucite. Two stage process of magnetite formation were suggested; (1) low fluid-flux serpentinization of olivine changes the fluid to alkaline to form serpentine and Fe-rich brucite. (2) Reaction with fresh fluid which were transported via newly-formed cracks to form magnetite and hydrogen

is generated.

References
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