*American Mineralogist, Volume 98, pages 163–180, 2013*

# Berthierine-like mineral formation and stability during the interaction of kaolinite with metallic iron at 90 °C under anoxic and oxic conditions

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## Abstract

The interaction between metallic iron and kaolinite was studied in conditions relevant to those that may be encountered in a high-level radioactive waste disposal facility in geological formation. Experiments were carried out under anoxic atmosphere at 90 °C and in chloride solutions to simulate conditions close to disposal facilities. KGa-2 kaolinite was put in contact with powdered metallic iron in batch experiments for durations of 1, 3, and 9 months. Solutions extracted from the end-products were analyzed (pH, Eh, conductivity, and cation concentrations). End-products were characterized by a set of chemical (oxide analyses, CEC, EDXS) and mineralogical techniques (SEM, TEM, XRD, and FTIR), textural analyses (nitrogen adsorption and low-pressure argon adsorption), XPS, and Mössbauer spectroscopy. In another set of experiments the system was changed from anoxic to oxic conditions to evaluate the stability of the system in the presence of $O_2$.

The interaction between metallic iron and kaolinite led to a fast initial reaction as major modifications took place during the first month. The partial oxidation of metallic iron resulted in a pH increase and negative Eh values. Iron was not found in solution but in two new Fe-rich phases: magnetite in very low amounts and a Fe-rich clay phase, belonging to the berthierine family. The Si and Al of the berthierine are derived from the partial alkaline dissolution of kaolinite, mostly along edge faces. TEM-EDXS local analyses showed that the composition of resulting particles consisted in mixtures of berthierine and kaolinite layers. Clay particles became thicker with the epitaxial growth of berthierine layers on the basal surfaces of pristine kaolinite.

Neoformed berthierine was not stable in the presence of $O_2$ at 90 °C. Berthierine layers dissolved, iron was mobilized to form iron oxides and oxyhydroxides while kaolinite layers recrystallized from released Al and Si.

**Keywords:** Kaolinite, metallic iron, Fe-rich serpentine, berthierine, stability