

**EXPERIMENTAL AND THERMODYNAMIC APPROACH TO STUDY AQUEOUS ALTERATION OF CHONDRITE AT LOW TEMPERATURE.** S. Kikuchi<sup>1</sup> and T. Shibuya<sup>1</sup>, <sup>1</sup>Japan Agency for Marine-Earth Science and Technology (JAMSTEC)

**Introduction:** It is becoming well recognized that aqueous alteration could be a widespread process in the primitive solar system materials [1]. The typical evidence of this process is the common presence of hydrous minerals (e.g., serpentine, smectite, oxyhydroxide) in carbonaceous chondrites. In addition to these direct observations, indirect analytical methods such as infrared spectrometer revealed the presence of phyllosilicates in various small asteroids (e.g., Ceres [2], Ryugu [3]) that might be the parent bodies of the carbonaceous chondrites.

These observations provide an important evidence that water played an important role in the evolution of early solar systems. However, the physicochemical properties of water (e.g., temperature, pH, water/rock ratio, redox potential) which reveal the alteration history of parent body, asteroid size, and the location where alteration took place, are still poorly constrained. One of the reasons for this poor understanding is that alteration processes and secondary mineral assemblages under various temperature and water (e.g., pH) conditions remain unsolved and very few relevant experimental data are available.

In this study, we studied alteration process and secondary mineral assemblage of chondrite by the combination of alteration experiments and thermodynamic modeling. We especially focused on aqueous alteration under anoxic and low temperature (<100°C) condition, which was indeed suggested to occur in some carbonaceous chondrites [1] but has been rarely experimentally examined in previous studies.

**Experimental Methods:** As a starting material for the alteration experiments, we used synthetic chondrite that has a mean chemical composition of CI chondrite [4] except for C concentration. The synthetic chondrite composed predominantly of olivine, troilite, Fe<sub>metal</sub>, pyroxene, and glass.

The alteration experiments were conducted in an anoxic chamber. The synthetic chondrite (particle size < 90 μm) were mixed with NH<sub>4</sub>-containing solutions at a water to rock mass ratio (W/R) of 10. The samples were heated in an oven at 25 and 80 °C for 1 day to 200 days. After the experiments, solid phase was characterized by X-ray Diffraction (XRD), scanning electron microscope (SEM), and transmission electron microscope (TEM). The fluid was collected for the measurements of dissolved ion concentration by ion chromatograph and ICP-OES.

**Modeling Methods:** We use the program EQ3/6 computer code [5] which can simulate mineral-fluid equilibria to provide altered mineral assemblage and co-existing water chemistry (e.g., dissolved ion concentration, pH). The thermodynamic database required for the calculation (e.g. equilibrium constant) were generated by SUPCRT 92 [6]. For the modeling, the W/R, initial dissolved ions in reactant water, and the composition of the starting rock was set to the same conditions as were used in the alteration experiments. The temperature was set between 0 to 100 °C.

**Results: Changes in solution chemistry.** Immediately after the beginning of the experiment, the oxidation-reduction potential (ORP) rapidly decreased from -471 mV (initial) to -578 mV and to -700mV at 25°C and 80°C, respectively. The ORP was below the thermodynamic stability of H<sub>2</sub>O(l) at 80°C, which is corresponding to the production of H<sub>2</sub> in the system. Concomitantly with the rapid redox potential change, the concentration of major ions (Si, Na, H<sub>2</sub>S) also rapidly changed in the first few days of the experiment followed by the relatively steady state.

**Formation of secondary minerals.** Two different secondary mineral phases were formed in the 7-month experiments at 80 °C (Fig. 1). One is pyrrhotite that formed within a day after the start of the experiment. The formation of this phase was correlated with a decrease of troilite. The other secondary mineral phase

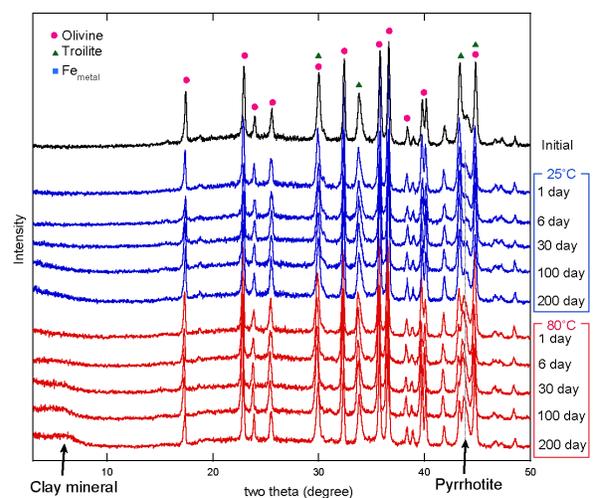


Fig. 1. XRD patterns of initial and altered synthetic chondrite.

was smectite that is shown in the existence of a broad XRD peak at  $2\theta = 6.4^\circ$  after 100-day of the experiment.

The altered samples were further examined by TEM to understand the spatial distribution of secondary minerals. The newly-formed fibrous minerals were notable in the experiment both at 25 °C and 80 °C after 100 days. These minerals encrusted the surface of the original olivine, troilite, pyroxene, and glass (Fig. 2). The fibrous minerals have 1.0 to 1.4 nm basal lattice fringes, indicative of saponite. The saponite coexisted with secondary Si-rich amorphous phases.

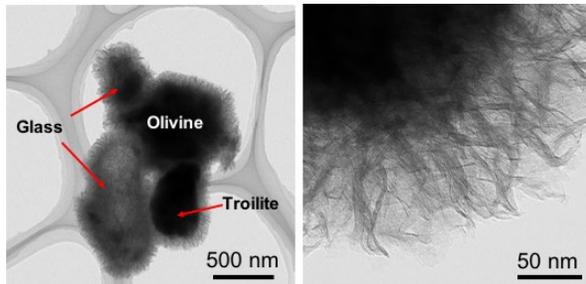


Fig. 2. TEM images of altered chondritic rock at 80 °C, 100 days.

*Secondary mineral assemblage expected from thermodynamic modeling.* At W/R = 10, the altered chondrite are dominated by serpentine and troilite over the modeled temperature range (Fig. 3). Gibbsite, alabandite, and saponite are also observed as minor phases.

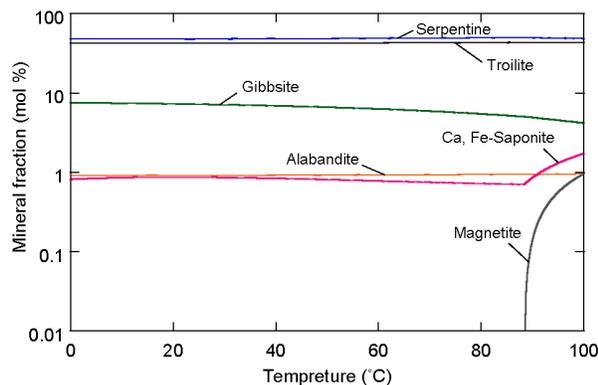


Fig 3. Abundance of alteration minerals between 0 to 100 °C at W/R = 10.

**Discussion:** Our alteration experiments revealed the formation of secondary minerals on several days to months at 80 °C, suggesting quite short timescales providing the mineralogical signature of aqueous alteration. These data provide important insights into the understanding of the earliest alteration process of chondritic rock and the sequence of secondary mineral formation, which are difficult to consider by thermodynamic calculation.

When the chondritic rock (consists of anhydrous minerals and troilite) reacts with anoxic liquid water, the formation of pyrrhotite could be the first alteration mineral observed in the system, which is resulted from the rapid dissolution of troilite. This process also results in the decrease of ORP and corresponding H<sub>2</sub> production. After the formation of pyrrhotite, the formation of saponite appears to be the main process. The saponite develops by encrusting the original rock, which is likely resulted from the dissolution of olivine, glass, and pyroxene followed by the precipitation of saponite. The formation of saponite, however, is inconsistent with the results of thermodynamic calculations that indicate the dominance of serpentine rather than saponite as a main phyllosilicate mineral. It is possible that serpentine precipitates after the precipitation of saponite in our systems, as is observed in the intimate intergrowth of saponite and serpentine during artificial Allende meteorite weathering at 200 °C [7]. Alternatively, serpentine formation might be kinetically much slower than that of saponite at low temperatures (<100 °C). Further alteration experiments will reveal a more detailed processes of the early stage of aqueous alteration of chondritic rock.

We finally note that a part of alteration phases obtained from our experiment is similar to that observed in several carbonaceous chondrites and micrometeorite [8, 9]. For example, Kaba CV3 carbonaceous chondrite lacks serpentine but contains a predominance of fibrous saponite with submicron Fe-Ni sulfides [8]. Although more detailed mineralogical comparison such as the sized of the saponite and the mineral species of Fe-Ni sulfide between Kaba and our experimental results should be done, the dominance of saponite and Fe-Ni sulfide in Kaba CV chondrite might be explained by the alteration of anoxic water at low temperature, and short duration of time. Therefore, our data also provide some constrains on the temperature and timescales of aqueous alteration of chondrites in the primitive solar system.

**References:** [1] Brearley, A. J. (2006) *Meteorites and the early solar system II*, 587–624. [2] King, T. V. et al. (1992) *Science*, 255, 1551–1553. [3] Kitazato, K. et al. (2019) *Science*, 364, 272–275. [4] Lodders, K. (2003) *The Astrophys. J.*, 591, 1220–1247. [5] Wolery, T. W. and Larek, R. L. (2003) *Sandia National Lab.* [6] Johnson, J. W. et al. (1992) *Comput. Geosci.*, 18, 899–947. [7] Jones, C. L. and Brearley, A. J. (2006) *GCA*, 70, 1040–1058. [8] Keller, L. P. and Buseck, P. R. (1990) *GCA*, 54, 2113–2120. [9] Noguchi, T. et al. (2002) *EPSL*, 202, 229–246.