
Introduction: The petrologic texture, constituent minerals and chemical compositions of CM chondrites are very complicated. The complexities are mainly due to various degrees of secondary aqueous alteration before their arrival on Earth. It is important to clarify the aqueous alteration in order to disclose the geological evolution of CM chondrites. The aqueous alteration is recorded in fine-grained materials around coarse-grained materials (chondrule, fragmented mineral and CAIs), which are referred fine-grained rims (FGRs), matrices and chondrules. In this study, we attempted to anatomize FGRs covering chondrules and the chondrules to clarify the aqueous alteration record by using FIB-TEM/STEM technique. This is the first reported investigation of TEM/STEM analysis of the individual grains of FGRs and altered chondrules in CM chondrites.

Experimental methods: The Cold Bokkeveld carbonaceous chondrite (CM2) was selected for our first attempt. Two Type IA chondrules (No. 1 and No. 2) were selected for a FIB-TEM/STEM work. FGRs covering altered chondrules, the altered chondrules and the altered chondrules-FGRs boundary (CFB) were extracted by FIB and characterized by TEM and STEM with EDS subsequent to Raman spectroscopy, FEG-SEM and EMPA.

Results: No. 1 chondrule. No. 1 chondrule consists mainly of forsterite (Fo_{99}) and enstatite, and minor clinoenstatite, diopside, iron oxide and iron sulfide. Forsterite shows the few evidences of aqueous alteration. Most enstatite and clinoenstatite grains show a skeleton or pectinate-like texture, which is indicative of aqueous alteration. Altered pyroxenes are replaced by Fe and Mg-rich silicates. Fe-rich parts were observed on grain boundaries of the altered pyroxenes. FIB-TEM/STEM analyses show that the altered pyroxenes consist mainly of poorly-crystallized (or amorphous) silicates (PCS). Fe-rich part on grain boundaries of the altered pyroxenes is mainly Fe-serpentine (cronstedtite). In some case, a cronstedtite unit layer is detached from cronstedtite crystal along (001). A fibrous-phase is accompanied with cronstedtite. Based on chemical compositions and electron diffraction patterns, the fibrous-phase may be iron sulfate hydrate. FGRs covering No. 1 chondrule appears to have a layered structure because relatively coarse-grained iron-rich phase is distributed preferentially on the outer portion of FGRs. The major components of FGRs are PCS and iron sulfide, and minor iron oxide and cronstedtite. They are randomly scattered in FGRs. Many interstices exist in FGRs compared with chondrule inside. Some PCS appears to be a (amorphous) cluster or pseudomorph and include a few cronstedtite. Small packets of a cronstedtite unit layer detached from a cronstedtite crystal were also observed in FGRs.

No. 2 chondrule. No. 2 chondrule consists of forsterite (Fo_{99}) with minor enstatite, clinoenstatite and augite. The apparent alteration degree of No. 2 chondrule is lower than that of No. 1 chondrule. Only a part of pyroxene near CFB alters with maintaining its original shape. A mesostasis was observed among forsterite, enstatite and clinoenstatite crystals, and it was altered. The altered mesostasis consist mainly of cronstedtite. Some cronstedtite are replaced by PCS. Distinguished sedimentary structure could not be observed in FGRs. The textures of FGRs appear to be porphyritic. FGRs consist mainly of PCS and fragmentary cronstedtite. The detachment of a cronstedtite unit layer from cronstedtite crystal was observed. A few fragmentary fayalitic olivine (Fo_{53}) were observed among cronstedtite grains. Few iron sulfide were contained in FGRs. Alternatively, considerable amount of iron oxide blob were contained in FGRs.

Discussion: FGRs consist mainly of (fragmentary) cronstedtite and PCS (or PCS cluster). The constituent minerals of FGRs are homogeneous, which is likely in the solar nebula. Layering-like structure was observed in FGRs. This mineralogical characteristic may support accretion scenario as the formation process of FGRs ([1], [2]). In case of accretion scenario, the formation of FGRs is induced by the collision of fine-grained materils on chondrules. It is likely that fine-grained materils near chondrules are deformed or...
compressed at least. However, deformation texture could not be observed in FGRs. There were many interstices in FGRs even if near chondrules by contrast. In case of No. 2 chondrule, fragmentary cronstedite is one of major constituent minerals of FGRs. Most cronstedite would be formed as the replacement of fine-grained fayalitic olivine because relic fayalitic olivine were embedded among cronstedite grains. There were some amebiform PCS clusters in the FGRs of No. 1 chondrule, and small amounts of cronstedite were included in them. Considering their aspects, they may originate from glassy material, and they would alter to PCS via cronstedite. It is unlikely that these alterations occurred in the solar nebula by solid-gas reaction in terms of kinetics (e.g., [3]). The mesostasis of the Cold Borkeveld CM chondrite appears to be considerably rich in Fe and Mg, and depleted in Si, Al, Ca and Na compared with those of other CO, CM and CV chondrites [4]. Considerable mass transport is essential for the alteration of the mesostasis. Fluid-rich environment appears to be favorable for the formation of iron sulfate hydrate [5]. Alteration from cronstedite to PCS was observed both in chondrules and FGRs. These evidences propose that the Cold Borkeveld CM chondrite had experienced aqueous alteration on a parent-body alteration. The constituent minerals of FGRs would originate from anhydrous fine-grained materials accreted on a parent-body with chondrules. These anhydrous fine-grained materials and chondrules would be altered on it simultaneously. The altered fine-grained materials around chondrules would become FGRs by brecciation subsequent to cementation (e.g., [6]).

When a chondrule reacts with aqueous solution, mesostasis is altered at early stage because it is very sensitive to aqueous alteration. TEM images show that the mesostasis of the Cold Borkeveld CM chondrite is replaced by cronstedite. According to several synthesis experiments, neutral-alkaline condition is favored for the formation of serpentine (e.g., [7], [8]). Terrestrial cronstedite and greenalite are low-temperature hydrothermal products in sulfide veins or in iron formation ([9], [10], [11], [12], [13]). Abundant iron and neutral-alkaline condition is necessary for the formation of cronstedite. In other words, the chondrules of the Cold Borkeveld CM chondrite would be equilibrated with a Fe-rich fluid with neutral-alkaline condition at the early stage of an aqueous alteration on a parent-body. Cronstedite and iron-sulfate hydrate were formed on the grain boundaries of enstatite, clinoenstatite and diopside. Additional iron is also essential when fine-grained fayalitic olivine and glassy material contained in FGRs alters to cronstedite. These evidences support that aqueous alteration by a Fe-rich fluid occurred at the early stage of an aqueous alteration on a parent-body. An aqueous alteration by an Mg-rich fluid with neutral-alkaline condition, which is ubiquitous on CM chondrites, would become dominant subsequent to the aqueous alteration by the Fe-rich fluid with neutral-alkaline condition. The alteration from enstatite (or clinoenstatite) to PCS and cronstedite to PCS were induced by this aqueous alteration.

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