ALTERATION OF CA- AND AL-RICH INCLUSIONS IN ALLENDE: A TRANSMISSION ELECTRON MICROSCOPE STUDY; Lindsay P. Keller and Peter R. Buseck, Departments of Geology and Chemistry, Arizona State University, Tempe, AZ 85287.

Introduction. Ca- and Al-rich inclusions (CAIs) are common in some carbonaceous chondrites and are widely believed to represent high-temperature condensates from the early solar nebula. Many CAIs, however, contain features such as veins of alteration products and complex rims that suggest extensive alteration [1-5]. We report here our observations from a scanning electron microscopy (SEM) and transmission electron microscopy (TEM) study of alteration features in a coarse-grained CAI from Allende. In addition, we describe the occurrence of two calcic micas, margarite and clintonite, in alteration material. This is the first positive report of these minerals in meteorites; their occurrence places important constraints on the thermal history of CAIs.

Observations. The CAI we studied is a type-A inclusion, with an interior composed of coarse-grained gehlenite and lesser fassaitic clinopyroxene. The gehlenite grains (Gh80-90) have undergone slight deformation, as shown by kink-banding. Spinel, perovskite, hibonite, and FeNi metal occur as inclusions in the silicates. Opaque assemblages (fremdlinge) of FeNi metal, Fe sulfides, Ca phosphates, V-rich spinels, and other phases occur in large (up to 300 μm) aggregates. The CAI is surrounded by a poorly developed, 100-μm-wide Wark-Lovering (W-L) rim sequence.

Millimeter-sized laths of gehlenite ($Ca_2Al_2SiO_7$) show alteration along cracks, cleavage planes, and grain boundaries. The veins of alteration extend into the interior of the inclusion. Grossular, anorthite, clintonite, and an unidentified Na-Mg-Ca-Fe-Al-silicate have been observed in the altered areas. Small relict grains of gehlenite with a high density of crystal defects also occur in the veins. Polysynthetic twinning in gehlenite is common and increases towards the rim of the CAI.

Perovskite ($CaTiO_3$) is concentrated in the rim of the CAI where it occurs as rounded grains intergrown with hercynitic spinel, hibonite, and gehlenite. The perovskite grains are small and commonly twinned on $(1\bar{2}1)$. Perovskite has been partially altered to ilmenite. Evidence from selected-area electron diffraction (SAED) patterns show that the replacement occurred coherently, with [001] of ilmenite coincident with [012] of perovskite. Superstructure reflections are common in Allende perovskite [6].

Hibonite ($CaAl_{12}O_{19}$) has also been altered. SAED patterns of hibonite show streaking parallel to c*, indicating stacking disorder. High-resolution images suggest the presence of extra spinel layers in hibonite grains, indicating a deficiency of Ca. Either there was insuffiсent Ca present during crystal growth, or Ca was lost during an alteration event.

We have observed clintonite [ideally: $Ca(Mg,Al)_3(Al_3Si)O_{10}(OH)_2$], a trioctahedral brittle-mica, replacing grossular in one of the alteration veins in gehlenite. High-resolution TEM images and SAED patterns show that the clintonite in Allende is the 1M mica polytype, with a 1-nm fringe spacing. A small sodic component in solid solution is suggested by EDS analyses. Individual clintonite crystals are 10 to 40 nm wide, 100 to 200 nm long, and occur in pods of up to 400 nm in diameter. There is no apparent crystallographic relationship between the clintonite laths and the host grossular.

In the outer portions of the inclusion, gehlenite is replaced by a network of lath-shaped, polysynthetically twinned anorthite with lesser fine-grained sodalite and nepheline. Margarite [ideally: $CaAl_2(Al_2Si_2)_{10}(OH)_2$], a dioctahedral brittle-mica, occurs as a lamellar intergrowth in the anorthite. Individual margarite lamella vary from 20 to 500 nm in width. The margarite lamellae are oriented with their [001] directions parallel to $[11\bar{3}]$ of anorthite. Stacking disorder in margarite is indicated by abundant strain contrast in TEM images and heavy streaking along the [001] direction of margarite in SAED patterns. High-resolution TEM images show 1- and 2-nm fringe spacings that indicate different margarite polytypes. While 1-nm polytypes have been reported for synthetic margarite [7,8], this is the first report of a natural margarite polytype with a 1-nm spacing.

Discussion. It is well documented that much of the alteration in CAIs was accomplished by a vapor that was rich in alkalis, other volatile elements, and Fe [e.g., 3,4,9]. The initial phase of alteration resulted in 1) the formation of anorthite and grossular from gehlenite; 2) the replacement of perovskite by ilmenite; and 3) the alteration of hibonite to spinel. Continued alteration by the vapor converted anorthite to nepheline, sodalite, and margarite; spinel to hercynitic-spinel; and grossular to clintonite. Two possibilities present themselves for the formation of the calcic micas, depending on which elements were mobile. If Ca was the least mobile of the elements involved, then margarite and clintonite may have formed *via* reactions [1] and [2].

$$\underset{\text{anorthite}}{CaAl_2Si_2O_8} + \underset{\text{corundum}}{Al_2O_3} + H_2O = \underset{\text{margarite}}{CaAl_2(Al_2Si_2)O_{10}(OH)_2} \quad [1]$$

$$\underset{\text{grossular}}{Ca_3Al_2Si_3O_{12}} + \underset{\text{spinel}}{5MgAl_2O_4} + Mg_{(g)} + 4H_2O_{(g)} = \underset{\text{clintonite}}{3Ca(Mg_2Al)(Al_3Si)O_{10}(OH)_2} + H_{2(g)}. \quad [2]$$

Conversely, if Ca was mobile, then the micas may have formed by:

$$2CaAl_2Si_2O_8 + 3H_{2(g)} = CaAl_2(Al_2Si_2)O_{10}(OH)_2 + Ca + 2SiO_{(g)} + 2H_2O \quad [3]$$

$$2Ca_3Al_2Si_3O_{12} + 8H_{2(g)} + 2Mg_{(g)} = Ca(Mg_2Al)(Al_3Si)O_{10}(OH)_2 + 5Ca + 5SiO_{(g)} + 7H_2O. \quad [4]$$

On the basis of the alteration of perovskite to ilmenite, and the alteration of hibonite to spinel, Ca appears to have been somewhat volatile, a fact that is difficult to reconcile with known element volatilities [10]. However, Hashimoto and Wood [11] showed that in a gas of solar composition at moderate temperatures (800K), Ca could form a gaseous species, $Ca(OH)_2$, that is more volatile than the Mg and Si vapor. Thus, we favor reactions [3] and [4] for the formation of margarite and clintonite in CAIs.

The observed phases in alteration products allow constraints to be placed upon their temperatures of formation. Thermodynamic calculations show that sodalite and nepheline are unstable above 1100K [1], which is then a maximum for the initiation of alteration by the volatile- and Fe-rich vapor. The presence of calcic micas suggests that the alteration continued to lower temperature. We have performed thermodynamic calculations for the first appearance of margarite from its most stable breakdown products at nebular water fugacities. The calculated equilibrium temperature is 345K, which represents a maximum for the formation of margarite in CAIs. Clintonite would probably require slightly higher temperatures (say 350 to 400K).

Conclusions. 1) On the basis of our TEM observations, Ca appears to have been mobile during the alteration of CAIs. 2) Two calcic micas, clintonite and margarite, occur in a coarse-grained CAI in Allende. Their occurrence suggests that, in addition to the high-temperature, volatile- and Fe-rich vapor alteration experienced by CAIs, some CAIs underwent alteration at moderate temperatures (300 to 500K). 3) The alteration assemblages probably reflect a continuous sequence of alteration with falling temperature, with grossular and anorthite as the first products, followed by hercynite, nepheline, and sodalite, and finally the formation of the calcic micas.

Acknowledgements. Supported by NASA Grant NAG 9-59. We thank Dr. C. Moore and Mr. C. Lewis of the Center for Meteorite Studies, ASU, for samples of Allende CAIs. We thank Mr. J. Clark for help with the SEM and Dr. R. Sharma and Mr. J. Wheatley for assistance with the JEOL 4000EX. Electron microscopy was performed at the HRTEM facility in the Center for Solid State Science at ASU, established with support from NSF Grant # DMR-86-11609. The microprobe was obtained with funds provided by the Earth Science Division of the NSF (Grant #EAR-8408163).

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