larger coercivity is probably due to the large density of structural defects that assist in domain wall pinning. Thicker films have yielded a larger value of remanent polarization. The dielectric constants of the films are in the range of 130 to 180, and a loss tangent of about 2% has been obtained in the best heterostructures. Similar properties have been obtained with  $YBa_2Cu_3O_{7-x}$  and  $Bi_2Sr_2CaCu_2O_{8+x}$  as the bottom electrode layers.

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# Calcic Micas in the Allende Meteorite: Evidence for Hydration Reactions in the Early Solar Nebula

## LINDSAY P. KELLER\* AND PETER R. BUSECK

Two calcic micas, clintonite and margarite, have been identified in alteration products in a calcium- and aluminum-rich inclusion (CAI) in the Allende meteorite. Clintonite replaces grossular in alteration veins, and margarite occurs as lamellae in anorthite. Their occurrence suggests that, in addition to undergoing high-temperature alteration by a volatile and iron-rich vapor that produced the grossular and anorthite, some CAIs underwent alteration at moderate temperatures ( $\leq$ 400 kelvin). Petrographic evidence suggests that the calcic micas formed before accretion but after the formation of the layered rim sequences that surround the CAI. These calcic micas provide strong evidence that, contrary to theoretical calculations, some hydration reactions occurred in the early solar nebula.

A- AND AL-RICH INCLUSIONS (CAIS) are refractory objects that formed at high temperatures in the early solar nebula (1) and are prominent in the Allende CV3 carbonaceous chondrite. Many CAIs, however, contain features such as veins and complex rims that suggest extensive alteration by vapor or aqueous fluids (2-6). All CAIs in Allende have apparently undergone some alteration that has primarily affected melilite (4). Of particular interest among the alteration products are the phyllosilicates. The coexistence of low-temperature hydrated phases with highly refractory minerals poses intriguing questions regarding the thermal evolution of CAIs, the conditions for the formation of hydrous phases, the processes involved, and the relative timing of the alteration event or events.

We studied the alteration features in a coarse-grained CAI from Allende, using scanning electron microscopy (SEM), highresolution transmission electron microscopy (HRTEM), and analytical electron microscopy (7). Earlier TEM studies identified several phases in alteration products in Allende CAIs (8). However, those observations were from mineral separates; therefore, textural relations among phases were lost. We studied ion-thinned samples in which textures and intergrowths are preserved and identified two calcic micas, clintonite [ideally Ca(Mg,Al)<sub>3</sub>(Al<sub>3</sub>Si)O<sub>10</sub>-(OH)<sub>2</sub>] and margarite<sup>-</sup> [ideally CaAl<sub>2</sub>(Al<sub>2</sub>- $Si_2OO_{10}(OH)_2$ ]. The occurrence of these minerals allows constraints to be placed on the thermal history of CAIs and on reactions in the early solar nebula.

Clintonite and margarite are the trioctahedral and dioctahedral members, respectively, of the calcic brittle mica group. Clintonite is rare in terrestrial rocks; it typically occurs in calc-silicate rocks that have undergone extensive metasomatism (9-11). Experimental studies of phase equilibria and of fluid compositions from natural mineral assemblages suggest that water-rich fluids and appropriate bulk compositions are required for the formation of clintonite (1113). Margarite is common in low- to medium-grade metamorphic rocks (14); its stability and compatibility relations are well constrained by experimental phase equilibria studies (15-17).

The CAI we studied is a type-A inclusion, with an interior composed of coarse-grained gehlenite (Ca2Al2SiO7) and minor fassaitic clinopyroxene. The gehlenite grains (80 to 90% gehlenite component) contain kink bands. Spinel, perovskite, hibonite, and FeNi metal occur as inclusions in the silicates. Opaque assemblages (fremdlinge) of FeNi metal, iron sulfides, calcium phosphates, V-rich spinels, and other phases occur in large (up to 300 µm) aggregates. The CAI is surrounded by a poorly developed Wark-Lovering (W-L) rim sequence that is 100 µm wide. W-L rims are believed to have formed during a rapid heating event that vaporized material from the surfaces of CAIs, leaving behind a refractory residue (2).

Millimeter-sized laths of gehlenite in the interior of the inclusion show the effects of alteration along cracks, cleavage planes, and grain boundaries. The veins of alteration extend from the surface of the inclusion, through the W-L rim, and into the interior. Grossular (Ca<sub>3</sub>Al<sub>2</sub>Si<sub>3</sub>O<sub>12</sub>), anorthite (CaAl<sub>2</sub>-Si<sub>2</sub>O<sub>8</sub>), clintonite, and an unidentified, finegrained Na-Mg-Ca-Fe-Al-silicate occur in the altered areas. Relict grains of gehlenite with a high density of crystal defects also occur in the veins. Polysynthetic twinning in the gehlenite is common and increases toward the rim of the CAI. Polysynthetic twinning has been observed in metamorphic but not in igneous gehlenite (18).

Clintonite partially replaces grossular in one of the alteration veins in gehlenite. Individual clintonite crystals are 10 to 40 nm wide parallel to the c axis, are 100 to 500 nm long, and occur in pods up to 600 nm in diameter (Fig. 1). Energy-dispersive x-ray spectrocopy



**Fig. 1.** Low-magnification TEM image of a clintonite (Cn) pod surrounded by grains of grossular (Gr).

Departments of Geology and Chemistry, Arizona State University, Tempe, AZ 85287.

<sup>\*</sup>Present address: Mail code SN14, National Aeronautics and Space Administration, Johnson Space Center, Houston, TX 77058.



**Fig. 2.** High-resolution TEM image of clintonite crystals with 1-nm fringe spacing. (Inset) An SAED pattern of the clintonite.

(EDS) analyses yield stoichiometries (7) that correspond to an Al-bearing clintonite:  $(Ca_{0.95}Na_{0.05})(Mg_{2.5}Al_{0.3}Fe_{0.05}Ti_{0.05}\Box_{0.1})$   $(Si_{1.6}Al_{2.4})O_{10}(OH)_2$ , where  $\Box$  represents a vacancy in the octahedral sites. The crystals show strain contrast and contain terminated layers and defects. There are regions where it is possible that an orientation relation exists between the clintonite laths and the host grossular, but it was not possible to obtain confirming diffraction data. HRTEM images and selected-area electron diffraction (SAED) patterns (Fig. 2) show that the clintonite in Allende is the 1M mica polytype, with a 1-nm fringe spacing.

In the outer parts of the inclusion, gehlenite is replaced by a network of fine-grained, lath-shaped, polysynthetically twinned anorthite and lesser feldspathoids. Margarite occurs as a lamellar intergrowth in the anorthite (Fig. 3). On the basis of TEM-EDS



**Fig. 3.** Low-magnification TEM image of margarite (Ma) lamellae in anorthite (An). The area outlined by the box is enlarged in Fig. 4. (Inset) An SAED pattern showing the orientation relation between Ma and An.

analyses, the margarite contains significant Fe and Mg in octahedral sites: [(Ca<sub>0.95</sub>- $Na_{0.05})(Al_{1.65}Fe_{0.2}Mg_{0.15}) (Si_{1.8}Al_{2.2})O_{10}$ (OH)<sub>2</sub>]. Individual margarite lamella are 20 to 500 nm wide and oriented with  $c^*$  parallel to the  $(11\overline{3})$  direction of anorthite. HR-TEM images showing disordered fringe spacings of 1 and 2 nm and heavy streaking along the (001) direction in SAED patterns indicate that either different margarite polytypes are present or the mica layers are randomly stacked (Fig. 4). A margarite polytype with 1-nm layers has been observed in synthetic material (19, 20) but not in natural samples. The widths of individual packets of 1- or 2-nm polytypes seldom exceed 15 nm; the average number of layers is approximately four for the 2-nm and six for the 1-nm layers.

Apparently, bulk composition, fluid composition, and temperature were favorable for the formation of calcic micas, and only local differences in bulk composition regulated whether clintonite or margarite formed. Possible alteration reactions for the formation of the micas can be grouped into two categories, depending on which elements were mobile. We first consider the case for margarite. If Ca was the least mobile of the elements involved, then margarite may have formed by the idealized reaction

$$CaAl_2Si_2O_8 + MgAl_2O_4 + H_2O =$$
  
anorthite spinel

 $CaAl_2(Al_2Si_2)O_{10}(OH)_2 + MgO$  (1) margarite

Conversely, if Ca was more mobile, then margarite may have formed by a reaction such as

$$2CaAl_2Si_2O_8 + H_2O_{(g)} =$$

$$CaAl_2(Al_2Si_2)O_{10}(OH)_2 + CaO + 2SiO_2$$
(2)

In order to form margarite by reaction 1, Al from some source (in this case, spinel) in addition to anorthite is required. However, we do not see evidence that the predominantly aluminous minerals (hibonite and spinel) lost Al or participated in the reaction. Rather, there is abundant evidence that Ca, and to a lesser extent Mg, were mobile. The alteration of perovskite and spinel to ilmenite and hercynite, respectively, is common and involved the displacement of Ca and Mg by Fe<sup>2+</sup>. Hibonite grains show stacking defects that are consistent with the alteration of hibonite to spinel. Anorthite has been locally converted to feldspathoids (Na for Ca exchange). Thus, the petrographic observations show that Ca and Mg were more mobile than Al. On the basis of these observations, we favor alteration reac-



Fig. 4. HRTEM image of disordered margarite with 1- and 2-nm fringe spacings. The stacking disorder causes streaking in the SAED pattern (inset).

tions such as reaction 2 for the formation of margarite. The CaO and SiO<sub>2</sub> reaction products are written in oxide form for convenience only; we have no evidence regarding the form of the Ca and Si species that were actually produced. Ca and Si may have been moved elsewhere in the inclusion in the fluid phase and precipitated as a distinct mineral (possibly the unidentified Na-Mg-Ca-Fe-Al-silicate) or were incorporated in other minerals. Other workers have suggested that during alteration Ca diffused out of CAIs and participated in reactions to form Ca- and Fe-bearing silicates in veins or in rims surrounding the inclusions [for example, (5, 21)].

Grossular contains insufficient Mg to form clintonite. Thus, clintonite development required addition of Mg and  $H_2O$ . The Mg may have been introduced into the veins by a vapor phase (22), or it may have been displaced from spinel during its conversion to more hercynitic compositions. We believe the latter hypothesis is more plausible because hercynitic spinel is ubiquitous in veins, whereas the spinel in the interior of unaltered gehlenite grains is pure MgAl<sub>2</sub>O<sub>4</sub>. By analogy to the margariteforming reaction, clintonite probably resulted from a reaction such as

$$2Ca_{3}Al_{2}Si_{3}O_{12} + 2MgAl_{2}O_{4}$$
  
grossular spinel  
$$+ 2Fe^{\circ} + 3H_{2}O_{(g)} =$$
  
$$Ca(Mg_{2}Al)(Al_{3}Si)O_{10}(OH)_{2} + 2FeAl_{2}O_{4}$$
  
clintonite hercynite  
$$+ 5CaO + 5SiO_{2} + 2H_{2(g)}$$
(3)

There is no evidence that spinel provided Al for the formation of clintonite.

Other researchers have described finegrained phases in CAIs that may also be calcic micas. Several unidentified fibrous Ca-Al-(Mg) silicates were reported from a layer of a W-L rim sequence on an Allende type-A CAI (2). These phases also occur in altered plagioclase-rich type-C CAIs (23). Another unknown Ca-Al-Si mineral associated with anorthite and nepheline has also been reported in Allende CAIs. A high-Al phyllosilicate containing ~44% Al<sub>2</sub>O<sub>3</sub> by weight was observed in a CAI from the Kaba CV3 chondrite (24). These unidentified phases are common and occur in essentially the same relative locations and in the same mineral assemblages in which we observe the calcic micas.

Much of the alteration in CAIs was accomplished by a vapor that was rich in Si, Fe, alkalis, and other volatile elements [for example, (1, 4, 5, 25)]. The major alteration reactions are known and involve the conversion of gehlenite to grossular and anorthite, Fe enrichment in spinel, and the alteration of anorthite to feldspathoids. These reactions reflect a continuous sequence of alteration with decreasing temperature (25). Thermodynamic calculations show that sodalite and nepheline are unstable in a gas of solar composition above 1100 K (2), which is then a maximum for the initiation of alteration by the volatile- and Fe-rich vapor. Clintonite has a large stability field, ranging from 600 to 1250 K and pressures up to 20 kbar (12). The stability field of margarite lies ~200 K lower than that of clintonite (15). Paragonite solid solution increases the thermal stability of margarite but decreases the stability field of clintonite.

In order to further constrain the temperature of calcic mica formation, we performed thermodynamic calculations following the procedure of Hashimoto and Grossman (25), for the breakdown reaction of margarite into its most stable products by the reaction

$$CaAl_{2}(Al_{2}Si_{2}O_{10}(OH)_{2} =$$
  
margarite  
$$CaAl_{2}Si_{2}O_{8} + Al_{2}O_{3} + H_{2}O$$
  
anorthite corundum (4)

Reaction 4 was used because thermodynamic data for all the phases are available, and calculations based on this reaction constrain the maximum temperature at which margarite is stable. Data for the solid phases were obtained from (26) and data for H<sub>2</sub>O from (27). For a solar nebular water fugacity of  $10^{-6}$  (25), the calculated equilibrium temperature is 390 K. Uncertainties in the thermodynamic data and in the estimate of the water fugacity combined with solid solution and disorder in the margarite suggest

that the uncertainty in the calculated temperature is approximately  $\pm 50$  K. The calculated temperature probably represents a maximum for the formation of margarite in CAIs; solid solution with paragonite would elevate this temperature only slightly (28). We estimate that clintonite would require slightly higher temperatures than margarite, on the order of 400 to 450 K. Still higher temperatures (470 K) were calculated for the formation of Na-phlogopite in Al-rich inclusions (25, 29), which is consistent with phase equilibria studies (12) that show Naphlogopite stable to higher temperatures than either margarite or clintonite.

Petrographic evidence suggests that the calcic micas formed before the incorporation of the CAI into its present setting and after the formation of the W-L rim sequence. The alteration is continuous across the interface between the W-L rim and the interior; thus, the primary minerals in the W-L rim (gehlenite, spinel, perovskite) were altered during the event that formed the alteration veins in the interior of the inclusion. This conclusion is consistent with earlier work on alteration in CAIs (2, 5). The calcic micas are separated from matrix by at least 100 µm, so that formation by reaction with matrix is unlikely. It is also unlikely that CAIs were preferentially altered on a parent body, because any process that would form hydrated phases in the CAI would also be expected to hydrate other materials in the meteorite such as the glass in chondrules and the fine-grained olivine in matrix. The common alteration products of olivines and pyroxenes (amphiboles and chlorites) are thermodynamically stable in the temperature range that we propose for the formation of the calcic micas. However, hydrous minerals were not observed in the matrix adjacent to the inclusion, nor have they been reported from Allende matrix. Hydrous minerals in Allende are restricted to CAIs and amoeboid olivine aggregates (25, 30, 31).

There are objections to the formation of hydrous minerals by gas-solid interactions in the nebula. Prinn and Fegley (32), for example, suggested that the formation of phyllosilicates (such as serpentine and talc) in the nebula at temperatures below ~300 K should be kinetically inhibited (32). Some hydrous phases could form in the nebula (Na-phlogopite, tremolite), but at temperatures higher than 300 K (32). Even at temperatures above 300 K, the only type of hydration reaction that was considered to be possible was one involving only a single solid phase and H<sub>2</sub>O as reactants, a situation similar to the margarite-forming reaction we propose above. The formation of clintonite, however, involved not only grossular but a simultaneous reaction converting spinel to

more hercynitic compositions. Thus, even at 400 K, limited diffusion occurred between at least two minerals involving diffusion path lengths on the order of several micrometers.

Other workers have proposed that some hydrated phases in CAIs (notably Na-phlogopite) formed in a nebular setting (25). This work extends the estimated formation temperatures for gas-solid interactions downward to ~400 K. The occurrence of the calcic micas provides strong evidence that alteration of some CAIs continued to low temperatures in the early nebula.

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- 7. Petrographic thin sections were made from a fragment of an Allende CAI having a diameter of 1.5 cm. Backscattered SEM images and quantitative chemical analyses of the thin sections were obtained with the use of a JEOL JXA8600 electron microprobe analyzer equipped for SEM. Quantitative analyses were obtained by wavelength-dispersive x-ray spectroscopy and reduced with an unmodified Tracor-Northern ZAF correction procedure. Specimens for TEM analysis were extracted from thin sections, mounted on a Cu support grid, and thinned with Ar ions. High-resolution images were obtained with Philips 400T (120 kV) and JEOL 200CX (200 kV) transmission electron microscopes. EDS analyses and SAED patterns were obtained with the Philips 400T. EDS spectra were accumulated for 150 s, and the detector deadtime was 15 to 30%. The EDS analyses, although semiquantitative, allow the determination of approximate mineral stoichiometries that aid in confirming mineral idenstolcholichers inta au m comming inner a derivation der state auf der state au der state auf der state au
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# Samarium-Neodymium Direct Dating of Fluorite Mineralization

## J. T. CHESLEY, A. N. HALLIDAY, R. C. SCRIVENER

The direct dating of many styles of hydrothermal mineralization has proved difficult, limiting understanding of the geological processes that lead to crustal fluid flow and the formation of major ore deposits. The hydrothermal mineral fluorite  $(CaF_2)$ displays large variations in rare earth element (REE) abundance and samarium/ neodymium ratios within a single vein. Samarium-neodymium dating of fluorite from the classic granite-hosted tin deposits of southwest England demonstrates its use as a precise chronometer of mineralization. The concentrations of light rare earth elements (LREEs) in the fluorites are highly variable and suggest the coeval precipitation of an LREE-rich phase as the most likely cause of the extreme variation in samarium/ neodymium ratios.

ANY HYDROTHERMAL ORE DEposits lack minerals that are suitable for isotopic dating. The most readily applicable techniques, such as U-Pb dating of pitchblende and K-Ar dating of sericite, are compromised by susceptibility to continuous or episodic chemical and thermal disturbances associated with hydrothermal activity along fracture systems. Furthermore, isotopic techniques used to date ore deposition commonly utilize alteration products, gangue minerals, or fluids that may not be coeval with ore-forming minerals. We need to be able to date mineralization directly and accurately in order to understand fully the many different products of crustal fluid flow, such as Mississippi Valley Type (MVT) deposits (1). Similarly, because it has not been possible to resolve the age of specific stages of ore deposition, most researchers have commonly concluded that granite-related hydrothermal mineralization is concurrent with or immediately follows magma emplacement ( $<10^6$  years) (2, 3), whereas it has recently been demonstrated that mineralization can postdate the host granite by as much as 3 million to 25 million years (4-6).

Fluorites display highly variable rare earth element (REE) patterns, the causes of which are poorly understood (7-10). In this report, we demonstrate that the large range of Sm/Nd ratios in fluorite from southwest England permits the determination of highprecision Sm-Nd isochron ages. This technique allows the accurate dating of a variety of ore deposits and thus the timing of major fluid movements in the crust that have hitherto proved undatable with the use of other geochronological methods.

The Cornish Sn deposits are a classical, although complex, example of granite-related hydrothermal mineralization (11-13). Mineralization is spatially related to the Cornubian batholith, a series of peraluminous biotite-muscovite granites, intruded into polydeformed sedimentary and volcanic rocks of Devonian and Carboniferous age, at 280 to 290 Ma (million years ago) (5). The plutons are intruded by medium- to fine-grained granitic or aplitic dikes and, locally, by late-stage Li-rich or topaz-bearing granites. The final stage of magmatism, 270 to 280 Ma (5), is represented by a series of fine-grained, felsic dikes crosscutting the major plutons.

Mineralization is expressed as multiple, steeply dipping veins that cut both the granites and the country rocks and has been broadly classified into three main stages: (i) stage 1, early Sn- and W-bearing pegmatite deposits and Sn-bearing, greisen-bordered veins with fluid-inclusion homogenization temperatures  $(T_h)$  of 300° to 500°C, (ii) stage 2, polymetallic (Cu, Pb, Zn, Sn) quartz veins with  $T_h$  of 200° to 380°C, and (iii) stage 3, late polymetallic (Cu, Pb, Zn, Ag) sulfide veins, locally termed "crosscourses," with  $T_{\rm h}$  of 105° to 180°C (14–17). Stage 2 veins represent the major episode of Sn and Cu mineralization. The classic mineralogical zoning and structures of these ore bodies, together with their apparent spatial relationships with the granites, has led to the traditional view that this stage of mineralization was directly linked to plutonism. The fluid inclusions analyzed from stage 3 crosscourse mineralization are similar in composition to Na-Ca-Cl-rich deep sedimentary brines and are probably from a younger regional event, unrelated to the intrusion of the Cornubian batholith (16).

Fluorite samples analyzed in this study were collected at the Wheal Jane and South Crofty mines in the vicinity of the Carnmenellis pluton (11, 18). Mineralization at the Wheal Jane Mine is hosted by Upper Devonian slate, and shale of the Mylor Formation and biotite-muscovite granite are not exposed in the mine or recorded in drill core. At South Crofty, however, similar mineralization crosscuts both the granite and the Mylor Formation. Samples from the South Crofty Mine were collected only from granite-hosted veins because of limited mine access.

Sm and Nd concentrations for fluorites and spatially associated hydrothermal alteration products from the Wheal Jane and South Crofty mines vary over more than two orders of magnitude (Table 1). The <sup>147</sup>Sm/<sup>144</sup>Nd ratios range from 0.12 to 0.95 and have a spread of as much as 0.12 to 0.37 within a single hand specimen. In the fluorite from the South Crofty, stage 2, Snbearing polymetallic veins there is a clear relation between the intensity of the color, Sm and Nd concentrations, and Sm/Nd ratios (Table 1).

Sm-Nd isotopic data for fluorites from the Sn-bearing polymetallic veins at South Crofty and Wheal Jane define precise isochrons (Fig. 1, A and B). Data for chloritic hydrothermal alteration products and crosscourse fluorites plot below these isochrons and have been excluded from the regressions. The data for South Crofty fluorites yield a slope corresponding to an age of  $259 \pm 7$  Ma (2 $\sigma$ ) and an intercept of 0.51197 [initial  $\epsilon_{Nd}$  (deviation in parts per  $10^4$  from coeval bulk earth) =  $-6.5 \pm 0.2$ ]; the mean square of weighted deviates (MSWD) is 1.0 (Fig. 1B). The Wheal Jane fluorites define a slope corresponding to an age of 266  $\pm$  3 Ma (2 $\sigma$ ) and an intercept of

J. T. Chesley and A. N. Halliday, Department of Geo-logical Sciences, University of Michigan, Ann Arbor, MI 48109.

R. C. Scrivener, British Geological Survey, Exeter, EX4 6BX, United Kingdom.