

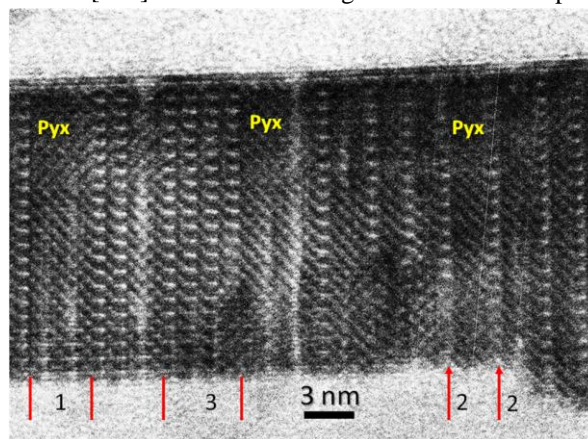
**FIB-TEM CHARACTERIZATION OF DMISTEINBERGITE WITH INTERGROWN BIOPYRIBOLES IN ALLENDE Ca-AL-RICH INCLUSIONS: EVIDENCE FOR ALTERATION IN THE PRESENCE OF AQUEOUS FLUID** A. J. Brearley<sup>1</sup>, T. J. Fagan<sup>2</sup>, M. Washio<sup>2</sup> and G. J. MacPherson<sup>3</sup>. <sup>1</sup>Department of Earth and Planetary Sciences, MSC03-2040, University of New Mexico, Albuquerque, NM, USA. E-mail: brearley@unm.edu. <sup>2</sup>Department of Earth Sciences, Waseda University, 1-6-1 Nishiwaseda, Shinjuku, Tokyo 169-8050, Japan. E-mail fagan@waseda.jp. <sup>3</sup>Department of Mineral Sciences, Smithsonian Institution, Washington, DC, USA. E-mail: macpher@si.edu.

**Introduction:** Ca-Al-rich inclusions from the Allende CV3 carbonaceous chondrite contain a complex record of early solar system processes that have been overprinted by a later period of alteration [1-4]. The primary high temperature Ca-Al-rich phases have been replaced to variable degrees by a wide range of secondary minerals [1-4]). A full understanding of the nature of the alteration has been hindered by the fine grain sizes of the secondary minerals. As a consequence, the nature of the alteration products, as well as the timing, location (nebular vs. asteroidal) and conditions of the alteration continue to be a topic of considerable discussion [1-4]. Several different textural occurrences of secondary minerals have been recognized within CAIs including: (1) an alkali-FeO domain located near CAI rims and (2) grossular-rich veins, extending into CAI interiors [2-5]. Here we present new FIB-TEM data from alkali-FeO alteration domains from one fluffy type A (FTA) CAI (3529-47) and one type B2 CAI (4022) from the Allende CV3 chondrite that have been described previously by [3]. Both CAIs have undergone extensive replacement of primary phases by an elongate secondary phase that has commonly been identified as anorthite, associated with grossular, Fe-bearing spinel, nepheline and sodalite.

**Samples and Methods:** We extracted one FIB section from regions of the elongate phase in each of the two CAIs. CAI 4022 shows evidence of alteration around its periphery in a zone that extends ~200  $\mu\text{m}$  into the interior of the inclusion. The FIB section was removed from a region of alteration consisting of grossular, nepheline, sodalite and the elongate phase. The section was located to cut across the elongate phase into a grain of grossular. CAI 3529-47 shows much more extensive alteration. Primary melilite with inclusions of spinel has been extensively replaced by fine-grained grossular, feldspathoids and the elongate phase. The FIB section transects a region of grossular into a region of the elongate phase. Each FIB section has been investigated by a variety of TEM techniques (HRTEM, DF-STEM, EDS, electron diffraction).

**Results:** In the FIB section of 4022, the elongate phase occurs as subparallel grains varying from 0.2-1  $\mu\text{m}$  in width. This phase has an extremely complex microstructure. Abundant submicron pores are heterogeneously distributed throughout individual grains. These pores are irregular to faceted in shape and can be oriented parallel to the elongation direction of the

grains. EDS analytical data from the elongate phase show that it is close to stoichiometric  $\text{CaAl}_2\text{Si}_2\text{O}_8$  in composition, but does show variations in  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$  and  $\text{CaO}$  contents. Minor  $\text{MgO}$  is also present in some analyses. Dark-field STEM imaging shows that the grains are compositionally heterogeneous, containing rare, thin lamellae of a second phase with a distinct Z contrast, demonstrating that each grain is a disordered intergrowth of at least two distinct phases. The compositional variability observed in our EDS data is consistent with the fact that the elongate phase is an intergrowth of two or possibly more phases. Our previous efforts to identify the main phase in these intergrowths were ambiguous [6]. However, the recent discovery of the hexagonal polymorph of  $\text{CaAl}_2\text{Si}_2\text{O}_8$ , dmisteinbergite, as a CAI alteration product in the NWA 2086 CV3 chondrite, has indicated a plausible solution to this problem. Zone axis electron diffraction patterns obtained from several elongate grains within the 4022 FIB section show that the dominant phase can be indexed unambiguously as dmisteinbergite, rather than anorthite. [010] zone axis patterns of dmisteinbergite show that the grains are elongated parallel to [100] and that the intergrown lamellae are par-



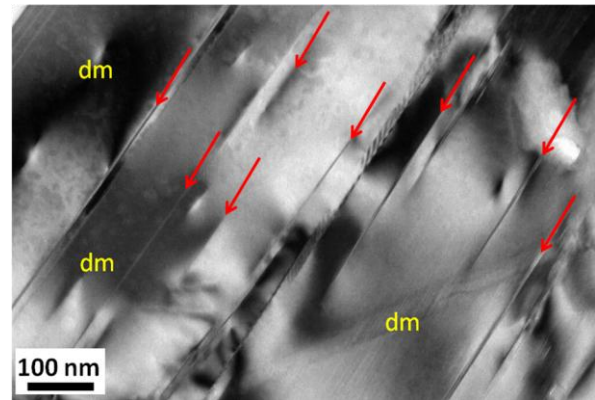
**Figure 1.** HRTEM image of disordered intergrowth of biopyriboles within dmisteinbergite in CAI 4022 viewed down the c-axis of the chain structure (i.e. viewed along the chains). Slabs of single chain pyroxene (Pyx) dominate, intergrown with lamellae of double chain (amphibole-  
arrowed 2) and slabs of triple chain sequence (3).

allel to (001) planes of dmisteinbergite. The dmisteinbergite is highly beam sensitive and amorphizes rapidly during electron beam irradiation. Fortunately, the beam damage affects the

dmisteinbergite preferentially, revealing the distribution of the intergrown lamellae phase because it remains crystalline longer. The lamella phase in dmisteinbergite in 4022 occurs predominantly on the periphery of the grains, although rare lamellae do occur within the grain interiors. The lamellae are typically 15 to 50 nm in thickness and can occur as both ordered and disordered intergrowths of more than one phase. In most lamellae the main basal spacing is  $\sim 0.9$  nm, but spacings of 0.7 nm are also present. One lamellae in a different crystallographic orientation was located within the thin foil which provided key information on the identity of the lamella phase. High resolution TEM imaging of this lamella demonstrated that it is disordered biopyribole consisting of single, double and triple chain units (Fig. 1). The dominant phase is pyroxene (single chain), containing lamellae of amphibole (double chain), typically no more than 1 unit cell in thickness, and slabs of a triple chain phase, probably jimthompsonite or clinojimthompsonite, up to four unit cells in thickness. From these observations we infer that the lamellae that lie parallel to the (001) plane of dmisteinbergite are also disordered biopyriboles, but are oriented with the *b* axes of the pyroxene and amphibole structures parallel to  $[010]_{\text{dmisteinbergite}}$ , an orientation in which the chain width disorder lies normal to the electron beam direction and is not visible. The  $\sim 0.9$  nm spacing observed commonly in the lamellae is therefore likely to be the (020) spacing of amphibole and/or the (010) spacing of pyroxene. We do not yet know if the pyroxene has a monoclinic or orthorhombic structure or is Ca-bearing.

The characteristics of the elongate phase in the FIB section of 3529-47 are distinct from the occurrence in 4022. The elongate phase occurs in a much denser and lower porosity intergrowth than in 4022 and individual grains lack significant pores. Electron diffraction patterns of the elongate phase indicate that both anorthite and dmisteinbergite are present. Very thin (typically just a few unit cells in thickness), discontinuous lamellae of a second phase (Fig. 2) with a basal spacing of  $\sim 0.9$  nm commonly occur parallel to  $(001)_{\text{dmisteinbergite}}$ . These lamellae are distributed throughout individual grains and are separated by distances of no more than 150 nm. Based on these characteristics, we infer that the lamella phase in dmisteinbergite in 3529-47 is also a disordered biopyribole.

**Discussion:** Both [7] and [8] have reported dmisteinbergite in CAIs in CV chondrites, but the genesis of these two occurrences appears to be quite different. [7] proposed that dmisteinbergite in a type B2 CAI is a primary phase that crystallized from a melt, whereas [8] argued that the elongate dmisteinbergite in NWA 2086 is the result of secondary alteration by aqueous fluids. The occurrences in CAIs 4022 and



**Figure 2.** Bright-field TEM image of dmisteinbergite in CAI 3529-47 viewed down the  $[010]$  zone axis. Numerous thin, lamellae of a second phase, probably biopyriboles are distributed throughout the grain (red arrows).

3529-47 are consistent with the latter origin and also support the suggestion of [8] that dmisteinbergite may be a much more common secondary alteration phase than has been previously recognized. They also suggested that dmisteinbergite may have been commonly misidentified as anorthite in altered CAIs. Our observations indicate that both of these predictions are correct, although our data also show that secondary anorthite does occur closely associated with dmisteinbergite, at least in 3529-47. In addition, we have also shown that dmisteinbergite is commonly intergrown with small amounts of hydrous phases, notably disordered biopyriboles, providing definitive evidence that alteration of CAIs and the formation of dmisteinbergite occurred in the presence of an aqueous fluid. Biopyriboles have been previously identified in chondrules in Allende [9], but this is the first documented occurrence in a CAI. However, the mechanisms of formation appear to be quite distinct in these different textural settings. The occurrence of an intergrowth of two metastable phases, dmisteinbergite and disordered biopyribole, implies a kinetic control on the alteration reactions, perhaps as a result of rapid growth in response to a sudden influx of aqueous fluid.

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