DISCOVERY OF VESUVIANITE AND KAOLINITE FORMED DURING THE ALTERATION OF MELILITE IN AN ALLENDE TYPE A CAI: CHARACTERIZATION BY FIB/TEM. R. L. Ford and A. J. Brearley, Dept. of Earth and Planetary Sciences, MSC03-2040, 1University of New Mexico, Albuquerque, NM 87131 (rford@unm.edu)

Introduction: Calcium-aluminum-rich inclusions (CAIs) in the Allende CV3 chondrite have been the focus of intense study since the fall of this meteorite in 1969 [1-4]. These studies have revealed both diversity in the types of CAIs that are present, as well as variable formational and thermal histories. Although Allende CAIs contain a remarkable isotopic and petrologic record of early solar system processes, it has been widely recognized that the CAIs in Allende are not completely pristine [3,4]. Studies have shown that essentially all Allende CAIs show evidence of secondary alteration, ranging from incipient to extremely extensive, with more than half of the original mineralogy replaced by alteration products [5]. Understanding the nature of this alteration can provide important constraints on the timing and location of the processes that have affected CAIs [6-11].

Although key aspects of the alteration of Allende CAIs are now well understood, there are many questions that remain. One vital issue is the role of fluids in the alteration of CAIs. Evidence that hydrous fluids were involved in the alteration process is indicated by the presence of rare phyllosilicate phases in CAIs and chondrules [8, 12]. However, due to the fine-grained nature of CAI alteration products and their occurrence as complex intergrowths of phases, it is not known whether hydrous phases are more widespread. With the exception of [8] there have been almost no TEM studies to address this important question. Here we present the results of a detailed TEM study of the secondary alteration products of a type A CAI from Allende, in an effort to improve our understanding of the mechanisms of alteration of CAIs.

Methods: TEM samples were prepared from a type A CAI which had been characterized previously by SEM and EPMA [5, 13]. Site specific samples were prepared by focused ion beam techniques using an FEI Quanta 3D FEGSEM/FIB instrument. The FIB sections were removed from the thin section by the in situ lift out technique using an Omniprobe 200 micromanipulator. FIB TEM samples were studied using bright field TEM, HRTEM, electron diffraction and analytical electron microscopy using a JEOL 2010 TEM operating at 200 kV. Individual phases were identified using combination of HRTEM images, electron diffraction patterns and EDS data. Zone axis diffraction patterns from individual phases were compared to theoretical diffraction patterns calculated using SingleCrystal software.

Results: We studied a type A CAI from Allende that had experienced significant amounts of alteration (>35% secondary phases) [13]. In Figure 1, melilite, which occurs as large, blocky crystals in type A CAIs, has been extensively replaced by fine-grained alteration products. Unaltered melilite is typically in direct contact with grossular which occurs as a fine-grained mass, 10-20 µm in thickness rimming the melilite crystals. The layer of grossular is itself embayed by a zone that consists of fibrous, elongated crystals of a phase that has been previously characterized as anorthite [14]. FIB sections were prepared that crosscut the interface from the melilite into the grossular and also sampled the fibrous, elongated phase.

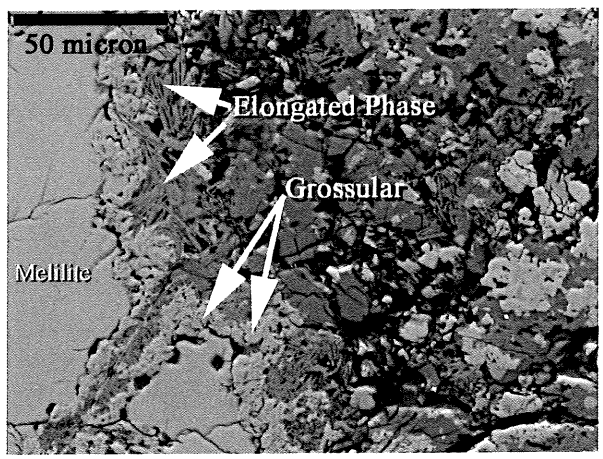

Figure 1. *SEM backscattered electron image of a region of alteration in the type A CAI studied by TEM. Primary melilite (left) has altered progressively to a porous layer of grossular, followed by a layer of a fine-grained platy, elongate phase,, commonly been identified as anorthite [14].*

In the FIB sections, the most abundant phase present is margarite, followed by grossular, sodalite, kaolinite and finally vesuvianite. Margarite occurs as lath shaped crystals ~1 µm wide and extending from grossular and vesuvianite-bearing regions to kaolinite and sodalite dominated regions where the ~1µm wide crystals taper off to thin (<0.1 µm) pieces. Vesuvianite is a minor phase occurring as both discrete crystals up to 1 µm in diameter and as 20 nm layers within the euhedral, 3µm grossular crystals. Sodalite occurs as a fine-grained mass of apparently randomly oriented crystals ~50-200 nm. Kaolinite appears to have replaced sodalite, and EDS data indicate that some kaolinite crystals have elevated amounts of chlorine (<5 wt%).

Discussion: Our TEM observations have implications for several aspects of CAI alteration. We first consider the issue of secondary anorthite in CAIs. As well as being a primary phase in all three major types of CAI (A, B, and C) in Allende, anorthite has commonly been reported as a secondary phase in compact type A CAIs [14]. Secondary anorthite is generally an alteration product after either grossular or melilite. In this study, an elongate phase is present in contact with grossular which, based on previous studies, is texturally consistent with anorthite [12]. However, our EDS and electron diffraction data show instead that this phase is most consistent with the Ca-rich mica, margarite, not anorthite. There is no evidence of secondary anorthite in the FIB sections that we have studied. We suggest that the identification of anorthite as an alteration product of CAIs should be reexamined.

Our observations provide new constraints on the mechanisms and conditions of alteration. In Allende, CAI alteration progresses from high-Ca primary phases, such as melilite, through a sequence of phases which have lower Ca contents [5]. First, melilite alters to grossular, a reaction that has been reported extensively in Allende CAIs [3-11]. Our observations suggest that rather than altering to anorthite, grossular is replaced by margarite. Based on the textural relationships, grossular has undergone partial replacement to vesuvianite. Vesuvianite, a contact metamorphic phase in terrestrial rocks, may be stabilized by the presence of Mg and Fe that are not readily incorporated into other phases. We infer that margarite is replaced by nepheline and sodalite based on the juxtaposition of layers containing these phases. The formation of feldspathoids involves a transition from Ca-rich alteration products to highly sodic, Si-poor phases The last stage of alteration is represented by the replacement of sodalite by kaolinite. In this reaction, chlorine released from sodalite hydration is taken up by the kaolinite, presumably substituting for OH^-.

The role of aqueous fluids in the alteration of CAIs has been the subject of considerable debate. The rarity of hydrous phases is usually interpreted as evidence of preaccretionary alteration of CAIs. However, the presence of significant quantities of margarite in this CAI demonstrate unequivocally that aqueous fluids played a significant role in the alteration process. Although less abundant, the occurrence of kaolinite confirms that the late stages of alteration also involved aqueous fluids. Hydrous phases in other Allende components have been noted before, specifically talc replacing enstatite in chondrules [12]. Similar processes recorded in different components of Allende is a strong indicator that alteration occurred after accretion within a parent body environment.

The sequential alteration observed in this CAI could have been accomplished through continuous or intermittent exposure to fluids. Our textural data do not allow us to constrain which possibility is correct. However, it is clear that in the initial stages of the alteration the fluids appear to act solely as a mass transport agent, but in the later stages, the fluids themselves are incorporated into the alteration products. We infer that such a sequence of reactions may represent the evolution of a hydrothermal system from high temperature, anhydrous phases to more hydrated phases as cooling proceeds. In the final stages of evolution of the system, any remaining fluid is consumed by reactions that produce highly hydrated phyllosilicates such as kaolinite and talc.

In terrestrial instances, vesuvianite is commonly found in skarns and low pressure contact metamorphism of calcsilicate rocks. Vesuvianite formation in terrestrial rocks occurs over the temperature range from ~250°C to >500°C [15]. The occurrence of vesuvianite as an alteration product in CAIs therefore provides an additional constraint on the conditions of alteration and is also consistent with temperatures for grossular to margarite alteration of 500 K [8].

Conclusions: Our TEM observations show that alteration of Allende CAIs is more complex than previously recognized. Development of hydrous phases, at least in the CAI that we have studied, is more pervasive than previously recognized and suggests that a reevaluation of CAI alteration may be warranted. The presence of hydrous phases in high abundances supports previously suggested hydrothermal type alteration on the Allende parent body [5, 12, 13].

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