ALTERATION OF CALCIUM ALUMINUM-RICH INCLUSIONS IN THE WARRENTON CO3.6 CHONDRITE: INSIGHTS INTO THE ROLE OF AQUEOUS FLUIDS DURING FLUID-ASSISTED METAMORPHISM. S. E. Mielke[1] and A. J. Brearley[1]. [1]Department of Earth and Planetary Sciences, MSC-03-2040, 1University of New Mexico, Albuquerque, NM87131 (semielke17@unm.edu)

Introduction: The CO3 carbonaceous chondrites are unique among the different carbonaceous chondrite groups in having a well-defined petrologic sequence that has been widely interpreted as the result of thermal metamorphism [1-4]. The progressive mineralogical and textural changes that occur through the CO petrologic sequence have been well-documented and are, in general, relatively well understood [1-4]. One notable feature of the CO3 chondrites is that they record evidence of fluid-assisted thermal metamorphism that shares affinities with the behavior of the oxidized Allende-like CV3 chondrites [5,6]. The role of fluid during metamorphic heating is indicated by, for example, the formation of ferroan olivine, similar to that observed in Allende and the replacement of CAIs by secondary phases [5-7]. Although the general characteristics of the CAI alteration have been documented [7], the alteration reactions and the fine-grained replacement phases have not been studied in detail. Previous studies of alteration in CAIs in CV3 chondrites using TEM techniques have shown that the replacement reactions are extremely complex and involve a variety of dissolution/precipitation reactions [8]. In this work, we report preliminary results of a study of alteration of CAIs in the Warrenton CO3.6 chondrite in an effort to constrain the mechanisms and conditions of alteration, particular the role of fluids.

Methods: BSE-SEM and EDS X-ray mosaics of a thin section of Warrenton were collected using a FEI Quanta 3D FEGSEM to identify the locations of CAIs. Over 80 CAIs were identified and studied using BSE imaging on a FEI Helios 650 SEM/FIB instrument and X-ray maps of individual CAIs were obtained on a Tescan VEGA SEM. One focused ion beam section was extracted from a region of alteration using the Helios instrument and was analyzed using a JEOL NEOARM aberration corrected TEM/STEM instrument operating at 200 kV. Bright- and dark-field TEM/STEM images and X-ray maps of the FIB section were obtained.

Observations: Over 80 individual CAIs were located and imaged in the thin section. They are typically <200 μm in size and are usually irregularly-shaped, although subrounded to rounded CAIs are also present. Previous studies of CAIs in CO3 chondrites have distinguished three different groups: melilite-rich, spinel-rich, and hibonite-rich. No melilite-bearing CAIs have been identified in this study but based on the textural characteristics of many of the CAIs, we infer that they were originally melilite-bearing, but melilite has been altered. Spinel-rich CAIs are common and hibonite-bearing CAIs are also present.

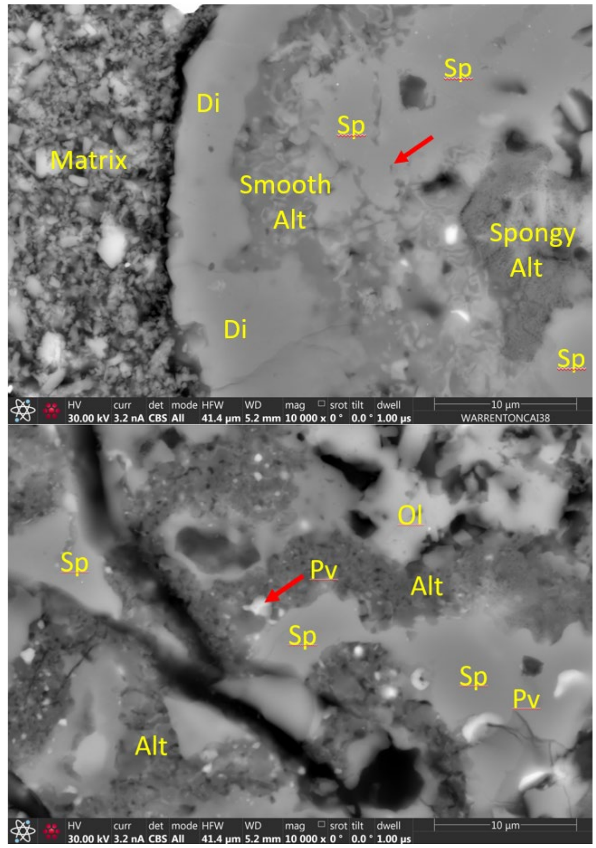

Figure 1 - BSE SEM images of alteration in CAIs in Warrenton. Top: smooth and porous regions of alteration in a spinel-rich CAI with a diopside rim. Bottom: Porous alteration in a nodular CAI similar to a fluffy type A inclusion consisting of spinel, perovskite and porous alteration products.

Alteration of CAIs. Based on X-ray maps of several CAIs and BSE imaging, all the CAIs that we have studied in Warrenton have undergone secondary alteration. No melilite has been observed in any of the CAIs. Instead, irregularly-shaped regions between spinel or pyroxene grains probably represent the alteration products of melilite. There appear to be at least three different textural styles of alteration, with more than one style sometimes occurring within the same CAI. A common style of alteration consists of fine-grained alteration products with a smooth texture (Fig 1 – top), minor compositional heterogeneities, and low porosity. This style of alteration occurs in altered rims sequences in CAIs with Wark-Lovering rims, in nodular CAIs with textures resembling fluffy type A inclusions, and some spinel-rich inclusions. The second style also occurs in nodular inclusions, and consists of a very porous, heterogeneous material, with anhedral grain shapes and grain sizes <2 µm, often with submicron high-Z inclusions. A third type of alteration that typically occurs in the cores of coarser-grained inclusions, consists of a spongy or fibrous texture with a very fine grain size. EDS X-ray maps of CAIs with the smooth alteration texture show that this material is enriched in Na and Al, and locally shows enrichments in Cl. Previous studies have reported nepheline and sodalite based on EDS analyses [7,9,10] in altered CAIs in CO3 chondrites. To confirm the presence of these two phases, we extracted a FIB section from a region of smooth alteration in a highly altered, spinel-bearing CAI that contains localized enrichments in Cl. This CAI was likely to have been melilite-rich prior to alteration.

TEM observations of the smooth alteration texture show that it consists of a complex intergrowth of secondary and primary phases (Fig. 2). More than 50% of the FIB section is composed of feldspathoids which EDS and electron diffraction analysis confirm are sodalite and nepheline. The feldspathoids occur in polycrystalline regions with sizes ranging from ~0.3 to 1 µm in size. Sodalite dominates the intergrowths. A significant amount of void space, which is not apparent on the surface of the sample is present within the FIB section. Feldspathoid grains which occur on the edge of the void space show weakly-developed facets. The sodalite also contains heterogeneously distributed pores ranging from a few 10s of nm up to 0.8 µm. Some of larger pores have crystallographically controlled facets, whereas the smaller pores are subrounded or irregularly shaped. In some regions of the sodalite the density of small pores is very high, whereas other areas are pore free. Nepheline contains a much lower density of pores. A few submicron inclusions of diopside also occur within the feldspathoids, in addition to coarser-grained primary diopside. Intergrown with the regions of feldspathoids are a number of ferroan olivine grains with irregular to anhedral morphologies and grain sizes of 0.3 to 2 µm. These olivine grains have complex reentrant intergrowth textures with the feldspathoids or occur as isolated grains. A number of primary spinel grains that now have hercynitic compositions Fe/(Fe+Mg)*100 ratios of 49-54 are also present within the FIB sections. Submicron grains of TiO_2 occur along grain boundaries within spinel aggregates, the second reported occurrence in CAIs in CO3 chondrites [10].

Discussion: The microstructural characteristics of this altered CAI show that extensive pore space developed during secondary alteration, strong evidence that significant dissolution of primary phases, presumably melilite, occurred. This is consistent with the role of an aqueous fluid during the alteration process. Although not typically widely developed, our observations show that along with nepheline, sodalite has also formed locally during the alteration of melilite in this CAI from Warrenton. There is no clear reaction relationship between the two phases that would indicate that one replaced the other, although nepheline grains are sometimes found enclosed within sodalite. Sodalite is the dominant phase surrounding pore space in the inclusion, implying that it formed relatively late, after significant dissolution of melilite occurred. Secondary ferroan olivine also formed with textures that suggest it mainly grew interstitially to the feldspathoids. The alteration mineralogy in this CAI resembles the final stages of alteration of CAIs in Allende, that is dominated by feldspathoids [6,8]. However, the abundance of sodalite is much lower, demonstrating that Cl metasomatism was much more limited in Warrenton. However, the formation of ferroan olivine clearly demonstrates that Fe metasomatism also accompanied alkali mobilization during melilite alteration.

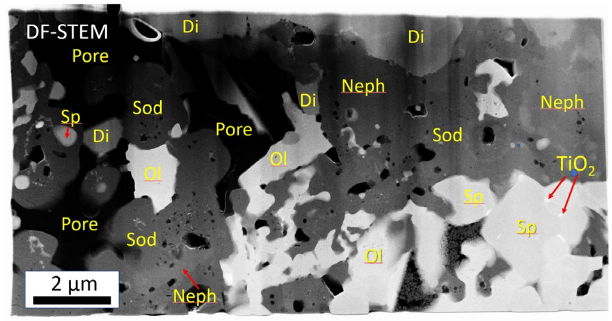

Figure 2 - Dark-field STEM image of FIB section from altered region of a spinel-bearing CAI. The alteration products consist of an intergrowth of nepheline (Neph), sodalite (Sod), ferroan olivine (Ol), with primary diopside (Di) and spinel (Sp). The spinel grain on the lower right contains submicron grains of TiO_2.

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