Ca-Fe and Alkali-Halide Alteration of an Allende Type B CAI: Aqueous Alteration in Nebular or Asteroidal Settings?

D. K. Ross[1,2], J. I. Simon[2], S. B. Simon[3] and L. Grossman[3], [1]Jacobs Technology-ESCG, 2224 Bay Area Blvd. Houston TX, 77058. daniel.ross@nasa.gov, [2]NASA-ARES, JSC, Houston TX 77058, [3]Univ. of Chicago, Dept. of Geophys. Sci., 5734 S. Ellis Ave. Chicago IL, 60637.

Introduction: Ca-Fe and alkali-halide alteration of CAIs is often attributed to aqueous alteration by fluids circulating on asteroidal parent bodies after the various chondritic components have been assembled, although debate continues about the roles of asteroidal vs. nebular modification processes [1-7]. Here we report detailed observations of alteration products in a large Type B2 CAI, TS4 from Allende, one of the oxidized subgroup of CV3s, and propose a speculative model for aqueous alteration of CAIs in a nebular setting.

Ca-Fe alteration in this CAI consists predominantly of end-member hedenbergite, end-member andradite, and compositionally variable, magnesian high-Ca pyroxene. These phases are strongly concentrated in an unusual "nodule" enclosed within the interior of the CAI (Fig. 1). The Ca, Fe-rich nodule superficially resembles a clast that pre-dated and was engulfed by the CAI, but closer inspection shows that relic spinel grains are enclosed in the nodule, and corroded CAI primary phases interfinger with the Fe-rich phases at the nodule's margins. This CAI also contains abundant sodalite and nepheline (alkali-halide) alteration that occurs around the rims of the CAI, but also penetrates more deeply into the CAI. The two types of alteration (Ca-Fe and alkali-halide) are adjacent, and very fine-grained Fe-rich phases are associated with sodalite-rich regions. Both types of alteration appear to be replacive; if that is true, it would require substantial introduction of Fe, and transport of elements (Ti, Al and Mg) out of the nodule, and introduction of Na and Cl into alkali-halide rich zones. Parts of the CAI have been extensively metasomatized.

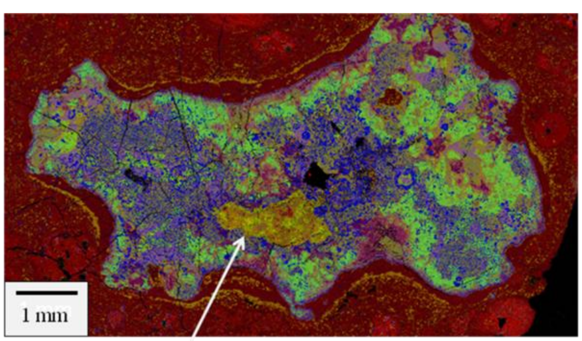

Figure 1. X-ray map of a large Type B2 CAI from the Allende chondrite. Si shown in red, Ca in green and Al in blue. The secondary hedenbergite-, and andradite-bearing nodule is surrounded by primary Al-Ti pyroxene. Spinel is blue and melilite is green.

Mineralogy and Mineral Compositions: The primary mineralogy of the CAI consists of melilite, end-member spinel ($MgAl_2O_4$), Ti-Al rich diopside (9-11 wt. % TiO_2 and ~19.5 wt. % Al_2O_3) and near end-member anorthite. The Ca-Fe rich nodule contains magnesian high-Ca pyroxene (Mg # 93-51) with variable alumina (3.8 to 15.7 wt% Al_2O_3) and virtually no Ti. The nodule also contains hedenbergite, andradite, and minor Ni-Fe metal. The textures of the nodule, and its enclosing CAI are shown in close-up in Figure 2. Figure 3 shows an x-ray map of Fe, Na and Cl, in which the distribution of alteration phases can be seen clearly. Rare phases in the nodule include relic spinel, wollastonite, a rounded magnesian olivine grain, minor and localized magnesian low-Ca pyroxene and one small, porous, amphibole-bearing patch. No sodalite is observed inside the nodule. The Ca-Fe nodule appears to be near the center of the CAI. Al-Ti diopside with abundant included spinel is the dominant primary phase assemblage at the contact between the nodule and host CAI (Figs. 1 and 2). Nepheline grains locally decorate the margin between the nodule and CAI. The replaced minerals were undoubtedly a mixture, but it is uncertain in what proportions they occurred.

Elemental Mobility: The composition of the Ca-Fe nodule requires the introduction of substantial Fe^{2+} and Fe^{3+}, assuming that it formed by replacement of the primary phases in the CAI and not as an enclosed mafic clast. We emphasize the presence of multiple grains of relic spinel inside the nodule, strongly supporting a replacive origin for the nodule. A vein of Fe-bearing phases extends out of the nodule, further into the interior of the CAI. The presence and abundance of andradite indicate that conditions must have been quite oxidizing relative to conditions at the time of formation of the CAI. The formation of sodalite and nepheline requires the introduction of abundant Na and Cl into the CAI. Compositional maps of the nodule suggest that Mg and Al were partially removed, and Ti almost wholly removed from the nodule region. The mobility of Na, Cl and Fe^{3+} suggest that aqueous fluid promoted elemental transport, and could have imposed more oxidizing conditions during alteration. The sodalite-rich vein that extends from the CAI margin and terminates adjacent to the nodule boundary suggests that the fluids that brought in Na and Cl could have transported Fe and promoted formation of the nodule. While the sodalite-rich veins and Ca-Fe nodule consist overwhelmingly of anhydrous phases, minor amphibole has been observed locally, within the nodule.

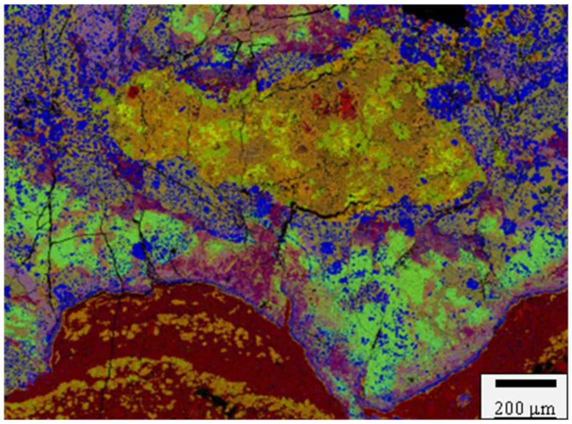

Figure 2. Close-up view of alteration zones in the Allende CAI. Colors as in Fig. 1. The magenta region in the center is a sodalite-rich vein that extends from the CAI margin, towards the Ca-Fe rich nodule. Blue grains are end member-spinel, abundantly enclosed in Al-Ti rich diopside. Relic grains of spinel are observed within the nodule. The bright red grain in the far left portion of the nodule is olivine, and the red region at center-right is low-Ca pyroxene.

Among the most puzzling aspects of the Ca-Fe nodule are the presence of very rare magnesian olivine, low-Ca pyroxene, as well as amphibole. The nodule is depleted in Mg relative to the bulk CAI, and relative to the chondrite matrix and chondrules.

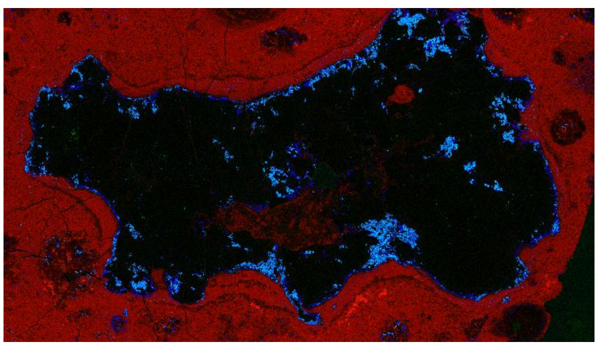

Figure 3. X-ray map of CAI. Fe is red, Cl is green and Na is blue. This map shows the distribution of sodalite, in pale blue, nepheline, in deep blue, and Fe-rich alteration in deep red, within the CAI. Scale as in Fig. 1

Micro-faults at the margins of this and other CAIs cut and offset the W-L rims, and also offset sodalite alteration zones within the CAI, but do not offset the margin between the accretionary rim and matrix of the chondritic host (Fig. 4). Exposed interiors of the CAI were not converted to sodalite after faulting, suggesting that the micro-faulting and alkali-halide alteration predated incorporation of the CAI into its chondritic parent body, in agreement with observations in earlier studies [3,8].

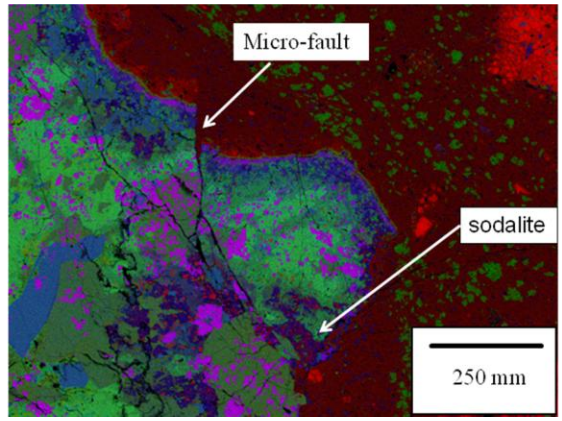

Figure 4. Micro-fault offsetting secondary sodalite (dark blue) in the CAI, and exposing primary melilite (pale green) and Al-Ti diopside (dark green). Mg in red, Ca in green and Al in blue. The lack of contiguous alteration is difficult to explain if sodalite formed by aqueous fluids *in situ*.

Concluding Remarks: The often-expressed view [4,6-7 and references therein] has been that aqueous or other fluid assisted alteration of CAIs takes place in an asteroidal setting. We suggest that some aqueous alteration could occur in a nebular setting. It is known that some CAIs were transported to regions where water ice condensed from the nebula [9]. We envision a stage in the histories of some CAIs where they formed the core of small, dirty snowballs, and that the ices in these small bodies could have been re-melted as the CAIs were transported through the protoplanetary disk [10]. Liquid water and-or water vapors could have been generated that led to aqueous alteration of the CAI, with low fluid-rock ratios. Dirty snowballs could have included NaCl that provided these elements during alteration. Fine-grained, Fe-bearing silicates incorporated in the dirty snowballs could have provided the iron needed to form the Ca-Fe nodule. In proposing this speculative model, we do not discount the possibility that Ca-Fe and alkali-halide alteration could form by a variety of processes, perhaps both before and after assembly of the chondritic parent bodies.

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