THE ROLE OF FLUID IN THE FORMATION OF THE IRON-ALKALI-HALOGEN ZONING SEQUENCE IN AN ALLENDE TYPE C CAI. S. Che and A. J. Brearley, Department of Earth and Planetary Sciences, MSC03-2040, 1University of New Mexico, Albuquerque, NM 87131, USA. (E-mail: shaofan-che@unm.edu; brearley@unm.edu).

Introduction: Metasomatism is a widespread phenomenon in Vigarano-type (CV) carbonaceous chondrites, and can also be found, though less commonly, in Ornans-type (CO) carbonaceous chondrites and uneqilibrated ordinary chondrites (UOCs) [1]. It is characterized by replacement reactions that produce anhydrous secondary minerals such as feldspathoids, Fe-rich pyroxenes, garnets and olivines [2-3] from primary mineral phases. Although a variety of phyllosilicates have been identified in these chondrite groups [e.g., 3-4], implying that aqueous alteration obviously occurred at some stage, these hydrous phases are minor compared to other secondary phases. Therefore, it is unclear what role fluids played during the alteration processes experienced by the above chondrite groups. Here we present detailed mineralogical and petrological observations on a metasomatized fosterite-bearing type C Calcium-Aluminum-rich Inclusion (CAI) from the Allende CV3 chondrite. Metasomatic iron-alkali-halogen zonal sequences have been reported previously in Allende CAIs and chondrules [3,5]. However, this CAI (ALNH 04) shows a zonal sequence which is unusual and thus may provide additional information about the fluids involved in the metasomatic processes.

Methodology: Backscattered electron (BSE) images and X-ray maps of selected areas of interest were obtained using a FEI Quanta 3D FEG-SEM/FIB instrument fitted with an EDAX Apollo 40 SDD Energy Dispersive Spectroscopy (EDS) system. The compositions of some fine-grained phases were characterized semi-quantitatively using EDS. Two focused ion beam (FIB) sections were extracted from regions of altered anorthite in contact with Al-Ti-bearing diopside, in the outer part of the CAI and then studied by transmission electron microscopy (TEM) using a JEOL 2010F FEGSTEM instrument operating at 200 kV.

Results: The general textural and petrological features, and mineral compositions of ALNH 04 was reported in our previous study [6]. This inclusion has a compact igneous texture, and is composed of anorthite (~45vol%), Al-Ti-bearing diopside (~35vol%), spinel (~15vol%), and a minor amount of forsteritic olivine grains (~5vol%), as well as some secondary phases. Most anorthite (~200×50μm) and diopside (~100×50μm) grains in this CAI are coarse-grained, with a radiating orientation from the periphery to the core region. However, in some regions adjacent to the periphery, the grain sizes decrease significantly and abruptly, and these regions are separated from the remaining part of the inclusion by an extensively altered zone composed of sodalite, salitic diopside, Fe-Ni sulfides, and minor nepheline.

The most unique feature of this spherical inclusion is the iron-alkali-halogen zoning sequence represented by the distribution of Fe-rich phases, nepheline, and sodalite. The general distribution of nepheline and sodalite are obvious on the X-ray elemental maps, with sodalite dominating the inner core region, giving way to nepheline + sodalite in the outer part of the CAI. However, the replacement relationship between these two types of feldspathoids is unclear from the high-resolution BSE images. In the first FIB section (FIB 01) we made, we observed that both nepheline and sodalite have a direct contact with the primary anorthite, and there is no clear replacement relationship between them [7].

The Fe-rich secondary phases, on the other hand, are less abundant than feldspathoids. The main secondary Fe-rich phases in the inclusion include salitic diopside (~2μm), hedenbergite (~3μm), Fe-Ni sulfide (<1μm), hercynitic spinel (~5μm), fayalitic olivine (~Fo_{56}) (<1μm), and an unidentified phase (~2μm). Salitic diopside is a ubiquitous secondary phase growing on primary Al-Ti-bearing diopside along the grain boundaries between diopside and anorthite, and sometimes is associated with a Fe-Al-rich oxide (possibly hercynite based on the EDS spectrum). Hedenbergite is only present as nodules with wollastonite replacing diopside, and there appears to be a replacement relationship between these two altering phases. Iron-nickel sulfides are concentrated in the extensive alteration zone noted above at the periphery of the CAI, associated with fayalitic olivine grains with textures and compositions similar to those in the surrounding matrix. From the BSE images, spinel grains show a range of Fe-enrichment, with most of them exhibiting Fe-rich rims enclosing Mg-rich cores. Fayalitic olivine is replacing the primary forsterite grains in the inner part of the CAI. The unidentified phase is compositionally similar to salitic diopside, but has higher Fe and Al contents, and is replacing anorthite, rather than Al-Ti-bearing diopside. This unknown phase is also closely associated with feldspathoids. In the second FIB section (FIB 02) from an anorthite grain extensively replaced by the unidentified phase and feldspathoids, we observed the presence of olivine grains (~Fo_{52}) that are in direct contact with sodalite and have a high dislocation density. Combined with the electron diffraction pattern, this observation indicates that the unidentified phase is related to fayalitic olivine.

Discussion: We infer from the replacement textures that fluid was present during the alteration. The preservation of the original morphologies of anorthite grains indicates that the alteration is a pseudomorphic transformation. In addition, the porosity in the alteration products is consistent with a dissolution-precipitation metasomatic mechanism [e.g., 8]. The sharp compositional boundaries, even at the TEM scale, between the host anorthite and the alteration products are evidence against a solid-state diffusion mechanism [e.g., 9]. The presence of Ca-Fe-rich halos in the matrix surrounding CAIs in [10] and this study also attest to a fluid-assisted process. The distribution of discrete nepheline grains with minor sodalite in the matrix, forming another halo, may be caused by redissolution of feldspathoids and subsequent precipitation outside the inclusion.

From the Ca-Na-Cl X-ray elemental map of the whole CAI, we proposed [7] that the dominance of nepheline in the outer part and of sodalite in the inner part of the inclusion could be attributed to a two-stage alteration process: (i) a fluid initially enriched in sodium and chlorine was introduced into the CAI along fractures and grain boundaries, and then reacted with primary anorthite grains, dissolving them while precipitating sodalite; (ii) the production of sodalite should have depleted the fluid in chlorine, and the resultant fluid saturated with respect to nepheline replaced the sodalite by nepheline. The outer part of the CAI was where the alteration started preferentially, and thus has experienced more extensive alteration than the interior of the CAI, producing more nepheline. However, in the FIB section we examined [7], we did not observe an unambiguous replacement relationship of sodalite by nepheline.

An alternative mechanism is that the fluid composition was changing progressively during the alteration process. In this case, the earlier precipitant is nepheline, which decreased the Na/Cl ratio of the fluid; the resultant fluid was then able to stabilize sodalite. If we assume that the initial fluid had a Na/Cl weight ratio similar to the bulk CV chondrites (~15.7; [11]), the much higher ratio compared to that of sodalite (~2.5) may have preferentially stabilized nepheline, rather than sodalite, which appears to be consistent with this hypothesis. However, there are several issues with this mechanism. First, since the outer part of the inclusion represents the most extensively altered region, it is difficult to explain why this region contains only a small amount of sodalite, while the alteration products in the inner core region are almost exclusively sodalite grains. Second, this fluid evolution mechanism would require nepheline being replaced by sodalite, but no such textures are observed. More FIB/TEM work will be needed to better understand the relationship between the two types of feldspathoids.

The presence of fayalitic olivine in FIB 02 is reminiscent of the assemblage of ferroan olivine and Al-rich chlorite in a Na-Cl-rich chondrule reported by [5]. The Al-rich chlorite is in the form of lamellae with a thickness of only one to two unit cells. Based on the compositional similarity and the observation that the Fe-rich phase described by [5] is also closely associated with nepheline, we speculate that the unknown phase in our inclusion may also be a mixture of olivine and chlorite, though further high resolution TEM studies are needed to confirm this hypothesis. Another problem is that in the chondrule studied by [5], the primary phase that olivine and chlorite have completely replaced may not be anorthite. More work will be needed to understand the relationship between this unknown phase and feldspathoids.

Conclusions: Two possible metasomatic mechanisms are proposed to explain the alkali-halogen zonation observed in the Allende CAI ALNH 04. The key factor for distinguishing them is the relationship between nepheline and sodalite. The nature of the unidentified Fe-rich phase associated with feldspathoids in this CAI and its relation with other phases is unclear.

Acknowledgements: This work was funded by NASA grant NNX15AD28G to A.J. Brearley (PI).

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