THE ORIGIN OF ALKALI-HALOGEN ZONAL SEQUENCE IN AN ALLENDE TYPE C CAI.

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Introduction: Aqueous alteration processes played an important role in modifying chondritic meteorites in the early Solar System. However, the mechanisms and environments are still not completely understood [1]. Calcium-Aluminum-rich Inclusions (CAIs) are the oldest materials in the solar system [2]; thus they contain important information about high-temperature events in the early solar nebula. However, due to the sensitivity of the CAI phases to secondary alteration processes, their primary records of the earliest solar system processes have been modified to various degrees. Here, we report detailed SEM and STEM observations on a Type C CAI 04 from Allende CV3 chondrite. This CAI reveals a unique zonal alteration sequence [3] and complex alteration textures resulting from the replacement of primary anorthite grains.

Method: Detailed petrological and mineralogical observations of CAI 04 were described in [3]. In this study, a region of an altered anorthite grain in contact with Al-Ti-bearing diopside, in the mantle of the CAI, was sectioned using the FIB technique and then studied in detail using STEM techniques. EDS measurements were also conducted to identify different phases.

Results: CAI 04 has a spherical shape, indicating that it was once molten. Major minerals include anorthite, Al-Ti-bearing diopside, spinel, forsterite, and secondary phases (e.g., nepheline and sodalite). This CAI shows a mantle-core structure, as demonstrated by the distinct grain sizes and textures exhibited by the two different regions.

Of particular interest in this CAI is the alkali-halogen zonal sequence, with nepheline being present as an alteration product of anorthite in the mantle of the inclusion and sodalite dominating the core. Minor amounts of both nepheline and sodalite, are however, present in both zones. Anorthite throughout the CAI has undergone replacement to varying degrees along grain edges and cross-cutting fractures. The degree of alteration of anorthite generally decreases towards the interior of the CAI and is more advanced in the finer-grained mantle. In order to fully understand the mechanisms of the replacement of anorthite, we extracted a FIB section from a grain boundary between Al-Ti-bearing diopside, anorthite and its alteration products. High resolution FEGSEM imaging shows that the grain boundary region consists largely of sodalite, but with a distinct layer of a high-Z phase, possibly grossular, running parallel to the interface of the unaltered anorthite. Dark-field STEM imaging and EDS analysis of the FIB section shows considerable complexity at the submicron scale. Although there appears to be no evidence of replacement of Al-Ti-bearing diopside, the surface of the pyroxene is decorated by Fe-bearing spinel grains, as well as localized, irregular overgrowths of Ca-Fe pyroxene. The main part of the alteration zone consists of sodalite which contains a few randomly distributed submicron pores, as well as anhedral grains of Ca-rich nepheline and Mg-spinel. Sodalite is in direct contact with anorthite, forming an irregular, curved interface and locally, regions of Ca-rich nepheline are also present directly in contact with the anorthite. Anorthite close to the interface with the Ca-rich nepheline shows the development of irregularly-shaped pores, but the nepheline itself is pore-free.

Discussion: A zoned distribution of secondary Na- and Cl-bearing minerals (nepheline, sodalite and wadalite) in an Allende Type B1 CAI was described by [4], and could be partly attributed to the primary mineralogical zoning. However, the zoning pattern observed in CAI 04 cannot be explained by a primary mineralogical zoning due to the similar mineralogy in the these regions. A more reasonable scenario involves a two-stage alteration process. First, sodium and chlorine were introduced by the fluid into the CAI interior, forming sodalite as a direct replacement product of anorthite, resulting in complete loss of Ca from the anorthite in the replacement reaction. After Cl in the fluid was consumed producing sodalite, nepheline became the stable phase, replacing anorthite directly, but retaining significant Ca in the nepheline structure. Nepheline does not show clear textural evidence of replacement of sodalite in the altered region of anorthite that we have studied. However, we infer that the dominance of nepheline in the outer part of the inclusion is indicative of replacement of sodalite by nepheline at a late stage in the modification of the inclusion, perhaps when fluid availability had decreased significantly. Further work related to the textural relationship between these two phases is needed to understand fully the relationship between them. The bulk Na/Cl weight ratio of CV chondrites (~15.7; [5]) is much higher than the Na/Cl ratio of sodalite (~2.5), consistent with this two-stage hypothesis that involves the removal of Cl from the altering fluid to form sodalite, eventually resulting in a fluid which was dominantly Na-bearing and able to stabilize nepheline.

References: [1] Brearley, A. J. (2014) *Meteorites and Cosmochemical Processes* 309-334. [2] Jacobsen, B. et al. (2008) *Earth and Planetary Science Letters* 272(1): 353-364. [3] Che, S. and Brearley, A. J. (2017) *LPSC XLVIII*, Abstract #2414. [4] Brearley, A. J. and Krot, A. N. (2013) *Metasomatism and the chemical transformation of rock* 659-789. [5] Wasson, J. T. and Kallemeyn, G. W. (1988) *Philosophical Transactions of the Royal Society of London A: Mathematical, Physical and Engineering Sciences* 325(1587): 535-544.