

MINERALOGICAL STUDY OF AN ISOTOPICALLY-UNUSUAL ALLENDE INCLUSION, J.M. Allen<sup>1,\*</sup>, L. Grossman<sup>1,2</sup>, T. Lee<sup>2</sup>, <sup>1</sup>Dept. of Geophysical Sciences and <sup>2</sup>Enrico Fermi Institute, University of Chicago, Chicago, IL 60637 and G.J. Wasserburg, Div. of Geological and Planetary Sciences, Caltech, Pasadena, CA 91125. \*Present address: Dept. of Geology, University of Toronto.

Hibonite ( $\text{CaAl}_{12}\text{O}_{19}$ ) has been proposed to be one of the highest temperature, major element condensates from the solar nebula, based on its estimated  $\Delta G^\circ$  [1] and its textural relations in Ca-Al-rich inclusions [2]. Studies of hibonite-rich Allende inclusions may thus reveal important information about chemical processes which took place at the initiation of condensation and which may not be recorded in hibonite-free inclusions. HAL, an Allende inclusion dominated by hibonite, was found by Lee *et al.* [3] to have isotopic characteristics which differ from other inclusions in this meteorite: no  $^{26}\text{Mg}$  excesses were detected in spite of enormous  $^{27}\text{Al}/^{24}\text{Mg}$  ratios in some samples, but large mass fractionation effects, coupled with small nuclear effects, were discovered in its Ca. We report here the results of a detailed mineralogical study of HAL in order to determine if the unusual history of this inclusion indicated by its isotopic composition has imprinted any other peculiarities upon it. A detailed chemical study has also been completed [4].

HAL is a sub-spherical inclusion with a maximum diameter of 5 mm. It consists of three mineralogically and texturally distinct portions: (1) a coarsely-crystalline, white interior, with (2) a narrow, black, compact rim, and (3) a thick, layered, fine-grained and friable outer rim.

Interior. The interior portion of HAL has a maximum diameter of 1.9 mm and consists almost entirely of three large (up to 1 mm) crystals of hibonite. Each crystal is roughly hexagonal in outline and consists of a white, frosty core containing abundant, fine needles of a Ca-Ti-rich phase, surrounded by a colorless, transparent rim. The needles are oriented in three directions in the 0001 plane of the hibonite, suggesting they are exsolution products. In one hibonite grain examined by SEM, a crystal surface was seen to contain numerous hexagonal pits, 2-6  $\mu\text{m}$  in size, defined by negative crystal faces. Alkali-rich phases, possibly nepheline and sodalite, which sometimes exhibit crystal faces, have been deposited as thin films on the crystal surface and partially overgrow the pits. We envisage a period of vapor phase alteration when hibonite crystal faces were etched and secondary phases deposited.

Black Rim. Adhering to the external surface of hibonite grains is a compact, glassy, black rim, 60-200  $\mu\text{m}$  thick. Its inner surface is in contact with hibonite and is irregular with numerous protuberances of black rim into hibonite and *vice versa*, indicating that the black material has partially replaced the hibonite. From SEM and microprobe study, the black material is seen to consist of an extremely fine-grained mixture of an unidentified, birefringent Al-Fe oxide, sodalite and nepheline. Complex, mottled and feathery textures seen by SEM are reminiscent of textures in devitrified glasses.

Friable Rim. The outer portion of HAL consists of a thick (up to 2 mm) and friable rim sequence with a grain size of 0.5-10  $\mu\text{m}$ . The rim is unusual and complex and differs substantially from those on Type A and B inclusions described by Wark and Lovering [5] in both mineralogy and texture. Five distinct layers can be distinguished on the basis of mineralogy. The thickness, in  $\mu\text{m}$ , and minerals, in decreasing order of approximate abundance, of each layer from I (interior) to V (exterior) are given in the table.

The Al-Fe oxide is similar to that in the black rim layer and occurs in masses up to 45  $\mu\text{m}$  in size. It is altered to nepheline which forms series of parallel streaks across its surfaces. Pyroxene and garnet each occur as irregularly-shaped masses up to 100  $\mu\text{m}$  in size. Ca-phosphate occurs as irregular grains up to 5  $\mu\text{m}$ . The other minerals all have euhedral to rounded form

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I < 70	II 60-270	III 15-35	IV 35-55	V < 1700
nepheline sodalite Ti-Fe oxide	nepheline perovskite Al-Fe oxide Ti-Fe oxide sodalite pyroxene	Ca-phosphate nepheline perovskite grossular andradite pyroxene Ti-Fe oxide	grossular andradite pyroxene hibonite perovskite nepheline Al-Fe oxide Ti-Fe oxide Ti-Sc-Zr oxide	nepheline olivine pyroxene andradite grossular Al-Mg-Fe oxide pentlandite Ni-Fe metal

and are partially or completely enclosed poikilitically in fractured nepheline and subordinate sodalite. Clearly, nepheline and sodalite crystallized after the perovskite, Ti-Fe and Ti-Sc-Zr oxides, olivine, pyroxene and garnet which they enclose. The friability of the rim is due to moderate amounts of void space, but the porosity varies from layer to layer.

**Mineral Chemistry.** Hibonite in the interior is almost pure  $\text{CaAl}_{12}\text{O}_{19}$ . Minor constituents are <0.03-0.09%  $\text{Sc}_2\text{O}_3$ , 0.6-1.1%  $\text{TiO}_2$  and 0.2-0.4%  $\text{FeO}$ . V, Cr, Y and Zr were not detected. It is highly unusual in containing only trace amounts of Mg (<100 ppm). There is a small increase in Fe and decrease in Sc and Ti toward the crystal edges. Hibonite from rim layer IV is richer in both refractory and more volatile elements than that in the interior of HAL: 0.4%  $\text{MgO}$ , 0.33%  $\text{Sc}_2\text{O}_3$ , 1.6%  $\text{TiO}_2$ , 0.8%  $\text{FeO}$  and 0.08%  $\text{ZrO}_2$  (mean of four analyses).

The Al-Fe oxide in the black rim layer is intimately mixed with nepheline and sodalite, making chemical analysis difficult. An X-ray powder pattern shows lines corresponding to these last two phases as well as lines close to those of spinel. The Al-Fe phase could be hercynite, but analyses corrected for the presence of impurities have excess Al such that Fe:Al is ~5:12.

Perovskite contains 0.09-0.14%  $\text{Sc}_2\text{O}_3$ , 0.08-0.10%  $\text{Y}_2\text{O}_3$  and 0.58-0.83%  $\text{ZrO}_2$ . An associated Ti-Fe phase is too small to be analyzed. Very rare grains of a Ti-Sc-Zr phase occur in rim layer IV. Good analyses are not available because of their fine grain size but the atomic ratio Ti:Sc:Zr is ~10:7:3. This is a new mineral, the first record of a scandium phase in a meteorite, reflecting the highly refractory nature of this inclusion.

The phosphate phase consists primarily of Ca and P in the ratio 10:6, as in apatite. However, F was not detected (<0.2%) and Cl is minor (0.2%), indicating the presence of significant  $\text{H}_2\text{O}$  or  $\text{CO}_2$  if the phase is apatite.

Nepheline, sodalite, grossular and andradite compositions are similar to those in other Allende inclusions [2,5,6]. Pyroxenes range from aluminous diopside with only minor Ti to hedenbergite, like those found in outer rim zones of Type A and B inclusions [2,5].

About 30% of rim layer V consists of a mineral which is probably olivine, Fa22-34. It has an unusual habit with rectangular cross-sections, distinctly different from olivine in the Allende matrix which has a barrel-shaped or platey form. It also differs in containing a finely-disseminated Al-Fe phase.

**Origin.** Hexagonal etch pits on the surface of hibonite in the interior of HAL and the deposition thereon of alkali-rich phases suggest that hibonite was etched and altered by a vapor phase after its formation. However, evidence as to whether the hibonite itself condensed from a vapor or crystallized from a melt is lacking. The textural relationships described indicate clearly that the black rim on hibonite is a later replacement product. The compact nature, fine grain size, distinctive mottled and feathery textures and smooth exterior surface of this black material combine to suggest that it may be a devitrified glass. If the interior were once molten, the black rim cannot simply be the remains of the original melt from which the hibonite crystallized because it replaces the hibonite. It is conceivable that the hibonite

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crystallized from a melt which underwent wholesale exchange with a gas phase while still molten and that that melt began to replace the hibonite and then froze to form the black rim. Alternatively, perhaps the hibonite crystals were partially melted around their margins, together with unknown surrounding phases, by a thermal or shock event, the melt froze to a glass and then both the hypothetical glass and the hibonite underwent vapor phase alteration to form nepheline and sodalite.

The absence of glass from and loosely-packed, porous nature of rim layers I-V suggest that these layers did not crystallize from melts. One possibility is that the friable rim accreted, grain-by-grain, around the coarse interior hibonite and its black rim while the latter were suspended in the nebula. That the rim is made of condensates is supported by the presence of perovskite, hibonite, pyroxene, olivine and Ni-Fe, predicted from thermodynamic calculations to be solar nebular condensates [1,7] and of nepheline, sodalite, grossular and andradite, inferred to be condensates from their textural relations and mode of occurrence in other Allende inclusions [2,5,8]. Even though the latter four phases probably cannot condense from a gas of solar composition under any set of equilibrium conditions, their coexistence within individual rims with phases which can also suggest that they, too, are condensates. In this interpretation of the rim layers, the presence of oxidized iron in the interior hibonite and in rim phases which coexist with others thought to be refractory condensates and the coexistence of phosphate, rather than phosphide, with perovskite suggest that the phases in HAL condensed from a gas far more oxidizing than one of solar composition. Nepheline post-dates all other rim phases and may also be later than the assembly of the rim. Thus, the rim could have been altered in the nebula at relatively low temperatures, but there is no evidence that oxidation of the rim accompanied this event.

It is hard to rule out another possibility, that the friable rim is a reaction corona [3], from which unknown primary phases have been dissolved and secondary ones deposited during nebular gas phase reactions under low-temperature, oxidizing conditions. Whether this can be done in a gas of solar composition is still moot. In that case, non-equilibrium would be required for reasons mentioned above but, even then, it is difficult to explain how Na-rich phases texturally post-date FeO-bearing ones. Also troublesome is the fact that textures indicative of gas-solid reactions found in alteration assemblages in other inclusions [2] are absent from HAL.

The only petrographic evidence for a melt at any time in the history of HAL is the resemblance of the black rim to a devitrified glass. If present, it must have formed prior to formation of the friable rim.

The unusual mineralogy of the core of HAL, unusual composition of its hibonite and the unique minerals and mineral assemblages of its rim layers all distinguish HAL from other inclusions. The isotopic composition is thus not the only unusual feature of HAL. Perhaps both the odd mineralogical and odd isotopic characteristics of HAL are due to the same thing--that HAL condensed from a gas phase of different chemical and isotopic composition than most other inclusions. Recognition of other refractory Allende inclusions with unusual mineralogy may provide additional samples with special isotope anomalies.

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