

CHEMICAL STUDY OF AN ISOTOPICALLY-UNUSUAL ALLENDE INCLUSION, T. Tanaka¹, A.M. Davis^{1,*}, L. Grossman^{1,2}, J.M. Lattimer³, J.M. Allen^{1,†}, T. Lee² & G.J. Wasserburg⁴, ¹Dept. Geophys. Sci. & ²Enrico Fermi Inst., Univ. Chicago, Chicago, IL 60637. ³Dept. Astron., Univ. Illinois, Urbana, IL 61801. ⁴Div. Geol. Planet. Sci., Caltech, Pasadena, CA 91125. Present addresses: *James Franck Inst., Univ. Chicago; †Dept. Geol., Univ. Toronto.

Lee et al. [1] reported results of isotopic measurements on HAL, a hibonite-rich Allende inclusion. Large, mass-dependent Ca isotopic fractionations favoring the heavy isotopes, as well as small nuclear effects, were found in its hibonite core and surrounding rim. Despite high $^{27}\text{Al}/^{24}\text{Mg}$ ratios of some samples, no ^{26}Mg excesses were detected. In a detailed mineralogical study by SEM and electron microprobe, Allen et al. [2] found that unique phases, phase assemblages, textures and mineral compositions accompany the unique isotopic features of HAL. In this work, we attempted to ascertain if HAL contains unusual chemical characteristics as well, using INAA for the determination of 35 elements.

Seven samples of HAL were analysed (see [2] for mineralogical and textural details): the frosty core of one of the interior hibonite crystals, the clear rim of the same crystal, the black, compact rim on the hibonite, friable rim layer III, two samples of friable rim layer IV and a bulk sample containing material from friable rim layers I-IV.

Refractory lithophiles are moderately to strongly enriched, but highly fractionated from one another, relative to C1 chondrites in both hibonite samples. Sc, Hf and Ti are enriched by factors of 67, 15 and 10, resp., in the clear rim of the hibonite crystal which is also enriched in these and REE relative to its frosty core by a factor of two to three. One possible explanation for the distribution of these elements in the hibonite is that they are concentrated in the hibonite relative to the needles which make the core frosty and that lower core concentrations are due to the higher concentration of needles there. This is ruled out, however, by the fact that the needles constitute far less than 50% of the core by volume. Either the lithophiles reside in the hibonite crystal structure or they are concentrated in another phase which is more abundant in the rim than the core. The only other phases seen by SEM are feldspathoids [2]; however, the rim sample is not significantly different in Na content than the core. The hibonite is thus the host for the refractory lithophiles and is zoned in their concentrations.

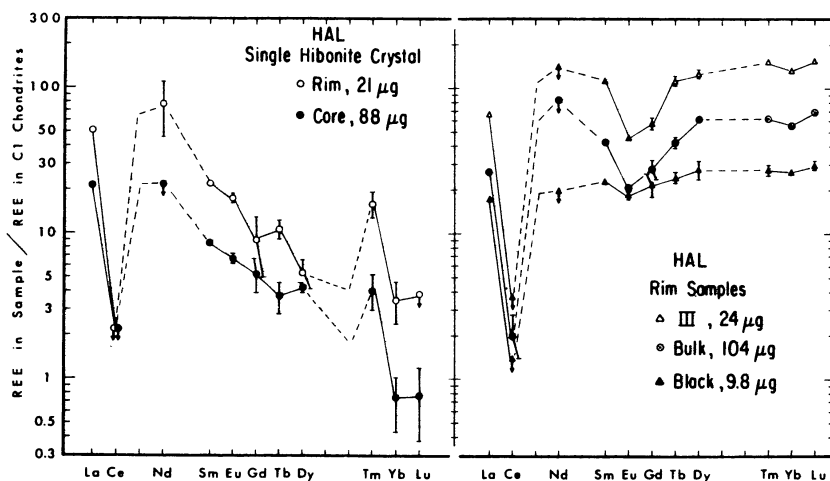
Refractory siderophile concentrations in the rim of the hibonite crystal, 2.6 ppm Ir and 1.6 ppm Os, approach those of coarse-grained inclusions [3]. These elements are enriched in the rim relative to the core of the hibonite by a factor of ten, suggesting that they do not reside in the same phase as the lithophiles. Perhaps refractory noble metal-rich grains are present [4].

A remarkable feature of the hibonite is its extremely low abundances of volatile elements. This is particularly true of the core which contains 684 ppm Fe, 0.76 ppm Co and <5.1 ppb Au, lower than the lowest concentrations ever encountered by this laboratory in coarse-grained Allende inclusions, and 334 ppm Na, 15.4 ppm Cr and 12.9 ppm Mn, very close to the lowest abundances we have seen. This material was strikingly fractionated from volatiles during its formation and has been minimally altered since then.

The hibonite samples have concentric REE patterns characterized by light REE enrichment, extraordinary negative Ce anomalies, sharp positive Tm anomalies and no Eu anomaly. The La/Ce ratio for the rim sample is >24 times the C1 value. This is reminiscent of the factor of three depletion of Ce in C1-S2, but that inclusion also contains a small Eu excess, no light REE enrichment and no Tm anomaly [5]. In HAL, the Tm excess and slope of the pattern through the heavy REE are similar to features characteristic of Allende group

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II REE patterns which are thought to result from condensation of the gas remaining after removal of an earlier, higher-temperature condensate containing the most refractory REE [6,7]. Boynton [8] showed that Ce and Eu depletions can be produced by partial condensation of REE from an oxidizing gas such as may be found in an outer shell of a supernova envelope.

We performed a series of calculations to see the effect of prior removal of the most refractory REE during condensation in supernova ejecta. For these calculations, we took the temperature dependence of the partial pressure of oxygen for each supernova shell from the computer programs used by Lattimer et al. [9] to compute condensation sequences in the cooling, expanding ejecta in which $C/O=0.5$. Large Ce anomalies were produced in the explosive H-, He- and C-burning zones but, despite a statement to the contrary by Boynton [8], they were always accompanied by Eu anomalies at least one-fifth as great. Another consequence of condensation under these highly oxidizing conditions is that Tm becomes more refractory than in a gas of solar composition. This causes the Tm anomaly to shrink substantially such that its enrichment factor is predicted to be significantly less than that for Dy. Thus, these models fail to match the observed patterns because they make Eu anomalies and do not produce large enough Tm anomalies, particularly for the rim hibonite. One way to produce the REE pattern of the hibonite by condensation is by removing the most refractory REE in a high-temperature condensate from a reducing gas, conversion of the gas to a much more oxidizing one, complete condensation of the remaining REE including tetravalent Ce and separation of a phase with a selective affinity for that ion. Another way is to evaporate both Ce and Eu into an oxidizing gas from an inclusion with a group II REE pattern which initially had no Eu anomaly. The pattern could be produced in the residue by re-condensation of Eu into it and by removal of tetravalent Ce in a separate phase. Both of these models seem too complex to be correct. Nevertheless, we are convinced that gas-solid fractionation processes in an oxidizing environment were involved in some way in the formation of this hibonite.

The black, compact rim contains relatively high concentrations of volatiles, including 1.8% Na, 8.5% Fe, 6040 ppm Zn and 28 ppm Co. Refractory lithophiles are enriched in the black rim relative to CI chondrites and are fractionated from one another. Enrichment factors are: Zr-70, Ta-48, Hf-48, Ti-35, Al-35, Lu-30, Th-25, Sc-22, La-17, Ca-1.5 and Ce-<1.4. The REE pattern shows slight heavy REE enrichment, a very deep negative Ce anomaly and a slight negative Eu anomaly. Because of the Tm anomaly in the hibonite and the absence of one in this material, no equilibrium relationship exists between them. If the black rim were once molten, it cannot simply be the remains of a melt from which the hibonite originally crystallized, as pointed

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out in [2] from petrographic data. The hibonite, however, could have equilibrated with a melt which later underwent complete exchange of its REE with an oxidizing gas and which then formed the black rim by solidification, alteration by volatile-rich phases and devitrification.

The pink, friable rim layer III is very strongly enriched in the refractory lithophiles Sc, Th, Ti, Lu, Hf and Ta (enrichment factors >100 relative to Cl chondrites). Enrichments of Ce, Al, Ca and La are <3.7, 14, 14 and 66, resp. It is also high in refractory siderophiles, including 1.4 ppm Ir, but rather low in Au, <47 ppb. It is very rich in volatile elements, 5.1% Na, 7.8% Fe, 58 ppm Co and 9.8 ppm Br. Its REE pattern shows moderate heavy REE enrichment, sharp negative Ce and Eu anomalies and a low concentration of Gd relative to Sm and Tb. This pattern is nearly parallel to that of the bulk rim, but REE are concentrated in the pink rim relative to the bulk by factors of 2.2-2.4 (Tm, Yb, Lu) to 2.6-2.7 (La, Sm), indicating slight relative enrichment in light REE in the pink rim. Ti is enriched in the pink rim relative to the bulk rim by the same factor, 2.5, as REE and the rim perovskite is known to have very high Y concentrations [2]. These facts combine to suggest that perovskite, though not the sole REE carrier, may contain a preponderant fraction of the total REE in the rim, despite the presence of other, more abundant, potential host phases, such as Ca-phosphate, pyroxene and hibonite. The ratio of the Ce anomaly to the one for Eu in both the pink rim and the bulk rim is only slightly greater than that achievable in the above calculations. Perhaps the REE components were formed under oxidizing conditions by incomplete condensation or by partial evaporation of REE from something which originally had a flat REE pattern. It is not clear how these processes could cause slight enrichment from Tb to Lu or depletion of La relative to Sm, given the size of the Eu anomaly. We have no explanation for the low Gd/Tb ratios. Perhaps the fact that Gd is determined *via* its p-process isotope, ^{152}Gd , is significant.

The high volatile element concentrations in the pink rim may be consistent with the idea mentioned above and suggested in [2] that the rim condensed from a gas whose chemical composition was significantly non-solar in that, depending on its exact composition, elements normally thought of as volatile may be able to condense from it at higher temperatures than from a gas of solar composition. Also, the late, low-temperature alteration of the rim suggested by textural evidence [2] provides another mechanism for the introduction of volatiles. High concentrations of volatiles would also be expected if, as suggested in [1] and [2], the entire rim sequence were composed of low-temperature alteration products of more refractory material.

The extremely low volatile element concentrations in the hibonite, huge enrichments of refractory elements in the pink rim layer, large negative Ce anomalies and strong fractionations of refractory lithophiles from one another are only some of the chemical peculiarities which distinguish HAL from other Allende inclusions. Thus, in addition to its unusual mineralogical features and isotopic composition, HAL has a most unusual chemistry. This coincidence of unique characteristics undoubtedly reflects a unique formation environment or unique formation processes or both.

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