

TRACE ELEMENT FRACTIONATIONS IN HIBONITE-BEARING EVAPORATION RESIDUES: COMPARISON WITH HAL-TYPE HIBONITE INCLUSIONS. C. Floss¹, G. Kransel², E. Zinner³, H. Palme², W. Rammensee², and A. El Goresy¹. ¹Max-Planck-Institut für Kernphysik, 69029 Heidelberg, Germany; ²Mineral.-Petrograph. Institut, Universität Köln, 50674 Köln, Germany; ³McDonnell Center for the Space Sciences, Washington University, St. Louis, MO 63130, U.S.A.

Diverse processes have been proposed to account for the origin of Ca-Al-rich refractory inclusions (CAIs) from carbonaceous chondrites. For many inclusions multi-stage processes, including condensation, distillation and igneous differentiation, are required to account for all compositional and petrographic features. Among the CAIs is a group of four hibonite-bearing inclusions for which an origin through Rayleigh distillation appears to be well-established [1]. These so-called HAL-type hibonite inclusions (HAL from Allende, DH-H1 from Dhajala, and 7-404 and 7-971 from Murchison) have Ca and Ti isotopic compositions that are mass-fractionated with enrichments in the heavy isotopes; two also have isotopically heavy Mg [2, 3]. Furthermore, they have very low Mg and Ti concentrations compared to other meteoritic hibonites and exhibit large Ce and V depletions. Through evaporation of the Allende carbonaceous chondrite we have produced two distillation residues that contain large crystals of hibonite set in a matrix of Ca-Al-rich glass. Like the HAL-type hibonites, these hibonites have low Ti concentrations and are virtually devoid of Mg. REE and other refractory trace element (RTE) compositions also show remarkable similarities to those of the HAL-type hibonites, including depletions in Ce, V and Ba, indicative of distillation under oxidizing conditions [4], and a smooth depletion of the HREE relative to the LREE (observed in HAL and DH-H1 [5]) produced through igneous fractionation. Eu anomalies in some of our residues and in three of the HAL-type hibonites, together with the Ce depletions, provide evidence for a change from oxidizing to reducing conditions during evaporation and show that multi-stage processes are not required to produce this association; both anomalies can result from a single evaporation episode.

As part of a series of evaporation experiments designed to better understand the processes responsible for isotopic and elemental fractionations, we have suspended samples of powdered bulk Allende from Re wire loops and partially evaporated them from the liquid state in a high vacuum ($\sim 10^{-8}$ bar) oven under different temperatures and run durations. In this way we most recently produced two hibonite-bearing residues. Residue 44-32 was produced by evaporation at 2050 °C and residue 50-5 at 2100 °C. Both samples have lost approximately 99% of their original mass and contain large (up to 1.3 mm long) lathe-shaped hibonite crystals embedded in a Ca-Al-rich glass. Hibonite makes up 33 vol.% of residue 44-32 and 82 vol.% of residue 50-5. The major element compositions of our hibonites strongly resemble those from the HAL-type inclusions (Table 1). Inclusion 7-404 is compositionally similar to the others [1]. Hibonite from 44-32 contains an average of 0.43 wt.% TiO₂, whereas hibonite from 50-5 only contains 0.03 wt.% TiO₂. MgO, SiO₂, FeO, MnO, V₂O₃ and Cr₂O₃ concentrations are below the detection limits of the electron probe in both residues. Hibonite produced through distillation of kaersutite [6] has a composition similar to ours, but somewhat higher TiO₂ contents (~ 1

Table 1. Average Hibonite Compositions (wt.%)

	44-32	50-5	HAL [7]	DH-H1 [2]	7-971 [8]
Al ₂ O ₃	87.19	89.47	89.95	90.8	91.48
CaO	8.67	8.36	8.71	8.9	8.38
TiO ₂	0.43	0.03	0.71	<0.05	n.d.
SiO ₂	n.d.	n.d.	<0.02	0.26	n.d.
MgO	n.d.	n.d.	<0.01	<0.02	0.14
FeO	n.d.	n.d.	0.32	0.44	n.d.
MnO	n.d.	n.d.	n.a.	n.a.	n.a.
Cr ₂ O ₃	n.d.	n.d.	<0.02	<0.08	n.a.
V ₂ O ₃	n.d.	n.d.	<0.02	n.a.	n.a.

n.d. = not detected; n.a. = not analyzed.

HIBONITE TRACE ELEMENT FRACTIONATIONS Floss C. *et al.*

wt.%). Glass in the residues contains more Ca than the hibonite, with CaO = 25.6 wt.% in 44-32 and 31.2 wt.% in 50-5.

The REE and other RTE have been measured in hibonite and interstitial glass from one of the residues, 44-32 (Fig. 1). Both phases are enriched in these elements, with abundances ranging up to 80 x C1, and show the same volatility-related depletions in V, Ba, Ce and, to a lesser extent, Pr that we have observed in other evaporation residues [9]; these depletions indicate oxidizing conditions [4] during distillation, due to the release of O during evaporation of major-element oxides. In addition, Eu is slightly depleted in the glass and, based on mass balance considerations, in the bulk residue ($\text{Eu}/\text{Eu}^* = 0.65$). We have observed a similar anomaly in one other residue, 44-12, which consists of a fine-grained mixture of less refractory Ca-aluminates (average Ca/Al = 0.55 vs. 0.12 for hibonite). The Eu anomaly in these residues cannot be explained through volatility-related depletion under oxidizing conditions, as Eu becomes more refractory under these circumstances [4]. Its presence suggests a change to more reducing conditions at later stages of evaporation. Refractory element fractionations in the HAL-type hibonites strongly resemble those observed in our residues, providing further evidence for a distillation origin of these inclusions. All have strong depletions in V, Ba (except for HAL) and Ce, and all (again, except for HAL) have smaller Pr depletions. Three of the four inclusions also have Eu anomalies, along with Yb anomalies not observed in our residues. Yb, like Eu, is volatile under reducing but not under oxidizing conditions. The presence of both Eu and Ce anomalies in some of our residues shows that redox conditions can change significantly during a single evaporation event under constant external conditions, implying that multiple distillation episodes may not be required to produce the trace element patterns seen in these inclusions.

In addition to the volatility-related fractionations, residue 44-32 exhibits an igneous fractionation between hibonite and glass. Hibonite is depleted in the HREE (and Y) relative to the LREE and does not have a Eu anomaly; the glass has a complementary HREE-enriched pattern. Calculated hibonite/glass distribution coefficients are qualitatively, but not quantitatively, in agreement with equilibrium hibonite/melt D values previously determined [10]. However, we do not expect quantitative agreement as our hibonite clearly did not grow under equilibrium conditions. HAL and DH-H1 are also depleted in the HREE and Y, and have no or very small Eu anomalies. Thus, the REE partitioning seen in these two inclusions can also be produced during a single distillation episode, if evaporation occurred from the liquid state.

The four HAL-type hibonite inclusions have mass-fractionated Ca and Ti isotopic compositions, ranging from +2 to +13 ‰/amu and +4 to +19 ‰/amu, respectively [1]. We have not yet made isotopic measurements on our two hibonite-bearing residues. However, our most refractory residue previously analyzed, 44-12, has enrichments of 9.5 ‰/amu in the heavy isotopes of Ca but isotopically normal Ti. The differences in Ca and Ti isotopic compositions, combined with the less refractory nature of this residue (see above), suggest that at least some of the HAL-type inclusions formed from a different precursor material than that used in our experiments.

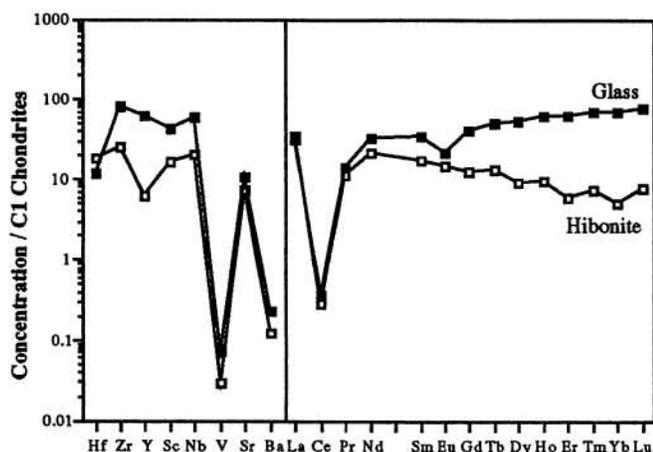


Figure 1

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