

PETROGRAPHY AND ORIGIN OF REFRACTORY INCLUSIONS FROM THE MURRAY AND MURCHISON C2 CHONDRITES; S.B. Simon¹, L. Grossman^{1,2} and A. Hsu³. ¹Dept. of Geophysical Sciences, The University of Chicago, 5734 S. Ellis Ave., Chicago, IL 60637. ²Enrico Fermi Institute, The University of Chicago, 5640 S. Ellis Ave. ³Illinois Math and Science Academy, Aurora, IL 60506.

Abstract. By freeze-thaw disaggregation we have recovered a total of 47 refractory inclusions. New discoveries include a hibonite-pyroxene spherule from Murray; a CaAl_4O_7 -bearing spherule from Murchison; and a Sc-fassaite-bearing ultrarefractory inclusion from Murchison.

Freeze-thaw disaggregation, combined with density separation and hand-picking as described by [1], is a proven method for recovering rare objects from carbonaceous chondrites. This method is especially effective on C2's due to their porosity, and typically results in the discovery of new types of refractory inclusions [e.g., 2, 3, 4]. Because few refractory inclusions from Murray have been described, we studied this meteorite, although only a small amount of material (730 mg) was available for disaggregation. Many refractory inclusions from Murchison have been described [2-6], and we disaggregated a larger amount (~18 g) of Murchison in an attempt to find new types of refractory inclusions, especially corundum-bearing ones.

Murray. Five refractory inclusions were recovered. Two are spinel-pyroxene objects, with interiors composed of Mg-, Al-spinel with many void spaces and trace amounts of perovskite, and rims of aluminous diopside. One object is like the "nodular" type previously found in Murchison [3] while the other is a spherule. One inclusion is best classified as a spinel-hibonite aggregate [4], with ragged hibonite laths 10-20 μm long and much void space, perhaps formed by dissolution during secondary alteration. It does not have a continuous spinel rim like SH-6 [4] but, like SH-6, spinel is present only at the edges of the inclusion and appears to be replacing hibonite. One spinel-hibonite spherule [4], MY92L9, was found in Murray. It is kidney-shaped, $200 \times 125 \mu\text{m}$, and consists of 20 μm -long hibonite (~2.3 wt % TiO_2 , 1.0 wt % MgO) laths and blades in a matrix of spinel, with many void spaces and rare grains of perovskite. Many of the hibonite laths are perpendicular to the rim of the inclusion, consistent with nucleation on the edge of a cooling droplet. Unlike the Murchison inclusions separated by MACPHERSON et al. [3, 4], but similar to those described by MACDOUGALL [5], this inclusion is completely enclosed in a rim of Fe-rich phyllosilicate. Outward from this layer in MY92L9 is a sequence (only partially retained) of aluminous diopside, enstatite and pure diopside. MACDOUGALL [5] also observed outer layers of pure diopside and inner layers of Fe-silicate on hibonite-bearing spherules, but did not report finding enstatite.

The most unusual inclusion among the Murray samples is MY92S3, a hibonite-pyroxene spherule like one in Y791717 (CO3) [7]. The Murray sample is $\sim 70 \times 60 \mu\text{m}$ in size and consists of several isolated hibonite laths ($<10 \mu\text{m}$ across and 10-25 μm long) enclosed in a silicate matrix. The laths are not oriented at high angles to the rim as in MY92L9. Sample MY92S3 consists of 14.4% hibonite (2.4% TiO_2 , 1.1% MgO) and 85.6% pyroxene (6.4% MgO , 28.5% Al_2O_3 , 37.1% SiO_2 , 25.8% CaO and 2.2% TiO_2). This composition is also similar to that of the glass in a Lancé hibonite-glass spherule [8], but the material in MY92S3 consists of 2-3 optically birefringent crystals and has pyroxene stoichiometry (as does the material in Lancé), with four cations (including one Ca) per six oxygen ions. The pyroxene in MY92S3 has a very high CaTs (CaAlAlSiO_6) component (~59.3 mole %). This is not a stable pyroxene composition [9] and must have formed metastably, probably due to rapid cooling. The bulk composition of MY92S3 is spinel-saturated, not hibonite-saturated, and plots in the Sp+An+L field when projected from spinel onto the anorthite-gehlenite-forsterite plane [10], but neither spinel nor anorthite are present in the sample. Although rapid cooling can delay anorthite crystallization [11], this is probably not the case for spinel. The absence of spinel and presence of hibonite suggest that at least some of the hibonite is relict. This spherule may have formed by heating of a hibonite-, silicate (probably Al-diopside)-bearing object to a temperature high enough to melt all of the silicate and some of the hibonite. Upon rapid cooling, the liquid, enriched in Al due to the melting of hibonite, crystallized to a metastable pyroxene. A problem with this model is that we have not observed any other inclusions composed exclusively of hibonite and pyroxene that would represent a likely (unmelted) source. Hibonite always occurs with spinel, and spinel could not be melted completely without hibonite melting completely unless it was finer grained and less abundant than hibonite.

Murchison. We recovered 42 refractory inclusions. Of these, 18 are spinel-pyroxene objects, 17 are spinel-hibonite spherules (or fragments thereof), and five are simply hibonite plates \pm attached alteration products, such as calcite. One of the spinel-hibonite spherules, M92B6, is unusual in that it contains an ~10 μm -wide mantle of spinel, an ~20 μm -thick inner zone of spinel + hibonite laths (5.1 wt % TiO_2 , 3.3% MgO) and a core of CaAl_4O_7 + perovskite. This is the first report of CaAl_4O_7 from Murchison. Bulk trace element abundances for this inclusion, determined by INAA, are reported in [12]. In thin section, the sample is a wedge-shaped piece of a spherule whose original radius was ~85 μm . This does not include the rim sequence, which consists of monomineralic layers of melilite (~ $\text{\AA}k_5$), anorthite and aluminous diopside outward from the spinel mantle. The melilite and anorthite layers are each ~2-5 μm thick and the pyroxene layer is ~10 μm thick. The silicate rims on this SiO_2 -free, unaltered inclusion were either deposited upon the spherule in different physico-chemical regimes within the solar

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nebula, or formed by metasomatic reaction of the spherule with the gas, as has been suggested for some Allende inclusions [13]. If we now ignore these layers and the perovskite and normalize the bulk composition to 100% $\text{CaO}+\text{MgO}+\text{Al}_2\text{O}_3$, the result is 6.0, 18.4 and 75.6 wt %, respectively. According to the phase equilibria of this system [14, 15], a liquid of this composition should begin crystallizing spinel at $\sim 2100^\circ\text{C}$ and continue until the spinel-hibonite cotectic is reached at $\sim 1750^\circ\text{C}$. These phases should be joined by CaAl_4O_7 at $\sim 1700^\circ\text{C}$ [16]. The textural relationships of the phases in the inclusion are thus consistent with this crystallization sequence, assuming sequential crystallization, from the outside inward, by cooling from the surface of a liquid droplet. The round shape of the inclusion also supports a liquid origin. Substitution of $\text{Mg}+\text{Ti}$ into hibonite lowers its melting point [3], so taking into account the TiO_2 in the system and the 5 wt % TiO_2 in the hibonite in M92B6, the above liquidus temperatures could be lowered by $\sim 150^\circ\text{C}$ (proportional to a 230°C depression in hibonite with 7 wt % TiO_2 [3]). Even so, assuming that all the hibonite in M92B6 crystallized from a liquid would require a temperature of at least 1600°C , perhaps the highest temperature yet inferred for a refractory inclusion. MACPHERSON et al. [3] reported a SiO_2 -free, spinel-, hibonite-, perovskite-bearing inclusion from Murchison, BB-2, in which, based on the inclusion's bulk composition and the relevant phase equilibria, CaAl_4O_7 should have, but did not, crystallize after spinel + hibonite. They attributed the absence of CaAl_4O_7 in that inclusion to the presence of TiO_2 , which presumably stabilized Ti-, Mg-bearing hibonite at the expense of CaAl_4O_7 [3]. The sample we studied has virtually the same CaO , MgO and Al_2O_3 contents as BB-2, but less TiO_2 (0.9 vs. 3 wt %) and does contain CaAl_4O_7 . This supports the conclusion of [3] that the presence of TiO_2 expands the stability field of hibonite at the expense of CaAl_4O_7 . This effect may account for the rarity of the latter phase in refractory inclusions.

Another unique inclusion, M92HIB11, is half of a spherule that was originally $\sim 80\ \mu\text{m}$ in diameter. It consists of numerous grains of Mg-, Al-spinel, mostly $\sim 5\ \mu\text{m}$ across, and perovskite, mostly $< 5\ \mu\text{m}$ across (but one grain is $\sim 10 \times 6\ \mu\text{m}$), enclosed in Sc-, Ti-rich pyroxene. Ranges of six electron probe analyses of this pyroxene are: 1.7-5 wt % MgO; 24.8-27.5% Al_2O_3 ; 21.2-26.9% SiO_2 ; 21.5-24.0% CaO; 4.6-10.7% Sc_2O_3 ; 9.2-16.8 $\text{TiO}_2^{\text{tot}}$ (all Ti as TiO_2); $\sim 1.5\%$ ZrO_2 ; 0.5-0.7% V_2O_5 ; and 0.1-0.5% FeO. This composition is similar to that of a Sc-rich fassaite reported by DAVIS [16] in an ultrarefractory inclusion (OSCAR) in Ormans, but the pyroxene in M92HIB11 has less Sc_2O_3 and more $\text{TiO}_2^{\text{tot}}$ than that in OSCAR [17]. Perovskite in M92HIB11 contains ~ 1.6 wt % Y_2O_3 , compared to 5.9% in the OSCAR perovskite [17]. Based on strong depletion of LREE relative to HREE with little isotopic mass fractionation, DAVIS [pers. comm.] has concluded that OSCAR is an ultrarefractory condensate, rather than a volatilization residue. Preliminary ion probe analyses indicate that M92HIB11 has a chondrite-normalized REE pattern similar to that of OSCAR and is therefore also an ultrarefractory inclusion.

Another unusual inclusion is M92HIB9, an oval-shaped, $100 \times 65\ \mu\text{m}$ object consisting of ~ 90 vol % Mg-, Al-spinel with many small (up to $10\ \mu\text{m}$) inclusions of perovskite and gehlenite. Most of the gehlenite is in the interior of the inclusion and several of the grains are near the rim. If the object crystallized from a liquid, it would have begun to crystallize spinel at about 2100°C and would have continued to do so until the spinel-gehlenite cotectic was reached at 1527°C [16]. This sequence should yield an inclusion with a thick spinel mantle and a small, gehlenite + spinel core, and this is essentially what is observed.

We also recovered two blue hibonite crystals that are large enough ($\sim 80\ \mu\text{m}$ across) for investigation of zoning trends with the electron probe. In both grains analyzed, MgO and $\text{TiO}_2^{\text{tot}}$ increase from core to rim. On an atomic basis, there is a slight excess of Ti over Mg. Equal proportions would be expected from the coupled substitution $\text{Ti}^{4+} + \text{Mg}^{2+} \rightleftharpoons 2\text{Al}^{3+}$. The "excess" Ti is probably in the form of Ti^{3+} , which can substitute directly for Al^{3+} . Our analyses indicate that, in both samples, the $\text{Ti}^{3+}/\text{Ti}^{4+}$ ratio remains constant and that $\sim 15\%$ of the Ti is Ti^{3+} . This is at the high end of the range (2-15%) observed in synthetic blue hibonite [18] but a little lower than that (23%) detected in a blue hibonite from a Murchison spinel-hibonite inclusion [18].

This work, in which we sampled a fairly large (and presumably representative) group of inclusions, provides further evidence that refractory inclusions in C2 chondrites represent higher-temperature assemblages than those in C3 chondrites; that new types of inclusions remain to be discovered; and that freeze-thaw disaggregation combined with density separation and hand-picking is an efficient way of finding these inclusions. Corundum is very rare.

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