

AN UNALTERED GROUP I FINE-GRAINED INCLUSION FROM THE VIGARANO CARBONACEOUS CHONDRITE; Andrew M. Davis*, Glenn J. MacPherson†, Richard W. Hinton‡ and John R. Laughlin◇, *James Franck Inst., ‡Enrico Fermi Inst., ◇Dept. of Chemistry, University of Chicago, Chicago, IL 60637 and †Dept. of Mineral Sci., National Museum of Natural History, Smithsonian Institution, Washington, D. C. 20560.

During examination of polished thin sections of a suite of refractory inclusions from the Vigarano C3V chondrite, one inclusion, USNM 1623-4, attracted attention because of its resemblance to Allende fine-grained spinel-rich inclusions. The latter are interesting because their volatility-fractionated group II rare earth element (REE) patterns require a more complicated gas-solid fractionation history than that of unfractionated group I inclusions [1,2]. Unfortunately, Allende fine-grained inclusions are heavily altered to an assemblage of iron-bearing spinel and silicates, grossular, anorthite, pyroxene and feldspathoids, so that prealteration mineralogy and textures are unknown. Vigarano 1623-4 is virtually devoid of any secondary alteration products, just as Vigarano coarse-grained inclusions are unaltered relative to their Allende counterparts [3].

1623-4 is an irregularly-shaped 1.5x1.8 mm blue object. It was located next to a larger (~5 mm) white inclusion, 1623-3, part of which is contained within the same thin section as 1623-4. This part of 1623-3 has the same texture and mineralogy as 1623-4. A larger portion of 1623-3 is represented in another thin section. A brief examination of that section shows that 1623-3 is inhomogeneous, with some parts melilite-rich and other parts spinel-rich. 1623-4 is mineralogically zoned. Its interior consists of a porous aggregate of 1-10 μm spinel grains, around which are thin (<1 μm) rims of gehlenite. Distributed within this spinel aggregate are irregular clumps of perovskite and hibonite. The clumps also have thin rims of gehlenite. Despite its porous nature, the central zone is virtually free of secondary alteration phases: calcite occasionally occurs in veins and only two tiny grains of sodalite were found. Exterior to the central spinel-rich zone is a dense mantle, 40-80 μm thick, of gehlenite enclosing spinel, hibonite, perovskite, and rare CaAl_4O_7 . There are cavities (5-10% by volume) in mantle gehlenite, some of which are filled with calcite. 1623-4 is rimmed by a 10-20 μm thick band of Fe-free spinel enclosing occasional grains of melilite and a 5 μm thick band of pyroxene grading from Ti-fassaite out to Al-diopside. The concentric zonation is precisely the characteristic that might be expected for the unaltered precursor of Allende fine-grained inclusions. The well-known concentric zonation of the latter [4] is caused by modal abundance variations of secondary minerals which are presumably related to the abundances of primary minerals they replaced. It has been suggested that melilite was once abundant in Allende fine-grained inclusions, even though it is now a rare phase [4,5].

REE concentrations and Mg isotopic compositions were determined by ion microprobe. Perovskite grains in the interior and exterior of 1623-4 and in the interior of 1623-3 show similar REE patterns: uniform enrichments in light REE by $\sim 1000_{\text{C1}}$ (relative to C1 chondrites) and dropping off smoothly in the heavy REE down to 500_{C1} . Each pattern has a 6-fold negative Eu anomaly. Hibonite from the interior of 1623-4 shows uniform enrichment in nearly all REE by 10_{C1} , with no Eu anomaly; La is enriched by only 5_{C1} . Since both major REE-bearing minerals in 1623-3,4 have nearly flat REE patterns, the inclusion is probably group I. Melilite and hibonite in 1623-4 have Al/Mg-correlated excess ^{26}Mg . The isochron diagram yielded an initial $^{26}\text{Al}/^{27}\text{Al}$ ratio of $(3.83 \pm 0.66) \times 10^{-5}$ and an intercept of $\delta^{26}\text{Mg} = +2.1 \pm 9.2\text{‰}$ (2σ), indistinguishable from the ratio and intercept commonly found in many C3V and C3O inclusions. Spinel in the rims and interiors of both 1623-3 and -4 show isotopically light magnesium: $\Delta^{25}\text{Mg} = -5.0 \pm 0.8\text{‰/amu}$. The oxygen isotopic composition of 1623-3 (relative to SMOW) is $\delta^{18}\text{O} = -1.3\text{‰}$ and $\delta^{17}\text{O} = -5.0\text{‰}$ [6]. Fluorination of the sample gave a very low yield of SiF_4 , indicating that a very silicate-poor portion of the inclusion was analyzed. We suspect that little of the melilite in 1623-3 was collected during sampling for oxygen isotopic analysis.

The similarities in mineralogy, texture, Mg isotopes and trace element composition between 1623-3 and -4 make it clear that both are part of the same inclusion. Vigarano inclusion 1623-3,4

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Davis, A. M., MacPherson, G. J., Hinton, R. W. and Laughlin J. R.

has an unusual chemistry. Unlike Allende fine-grained inclusions, it does not have a group II REE pattern but, rather, is group I. Either this inclusion is not a precursor to the Allende inclusions or else the group II REE signature in Allende fine-grained inclusions is imposed by the secondary alteration process. The latter possibility seems unlikely, as highly altered Allende coarse-grained inclusions retain the group I REE patterns of their less-altered counterparts. The porous nature of 1623-4 strongly indicates that it cannot have crystallized from a melt. This view is supported by the REE patterns in hibonite and perovskite. Coexisting perovskite and hibonite have been analyzed in several inclusions [7,8]. In each case, REE partitioning between the two phases is a strong function of ionic radius, such that the La/Lu ratio of hibonite is 50-100 times that of perovskite. In 1623-3,4, hibonite and perovskite both have nearly flat REE patterns, indicating that, despite their close proximity, the minerals have not equilibrated with one another.

The oxygen isotopic composition of 1623-3 presents a dilemma. Spinel separated from bulk Murchison by acid demineralization and spinel mineral separates from Allende coarse- and fine-grained inclusions show a tight cluster at $\delta^{18}\text{O} \approx -40\text{‰}$, $\delta^{17}\text{O} \approx -41\text{‰}$. It is very unusual to find a spinel-rich sample displaced so far from the oxygen isotopic composition of "normal" inclusion spinel and so close to the most ^{16}O -poor components along the Allende ^{16}O mixing line. The Allende mixing line is believed due to the later exchange of initially ^{16}O -rich primary phases with a ^{16}O -poor (*i.e.* solar) reservoir, the degree of exchange being controlled by the crystal structure of the different phases [9]. Melilite has an oxygen diffusion coefficient 10 orders of magnitude greater than spinel [10]. For this reason, melilite in inclusions is believed to have exchanged almost completely with a gaseous reservoir, while spinel preserves the composition of the original solid starting material. Secondary alteration involves dissolution of primary minerals and vapor-phase growth of secondary minerals. The oxygen isotopic composition of the secondary minerals should reflect the composition of the reservoir from which they formed. Secondary phases in Allende inclusions are known to have more nearly normal oxygen isotopic compositions, so secondary alteration must have taken place in a near normal oxygen isotopic reservoir. Since easily-exchanged melilite has essentially the same oxygen isotopic composition as secondary phases, it has been assumed that the oxygen exchange in primary minerals occurred during secondary alteration.

Vigarano 1623-3 is unaltered and consists largely of spinel, yet it has an oxygen isotopic composition similar to melilite and secondary minerals in Allende inclusions. There are two possible explanations for this: (1) oxygen exchange in primary minerals predated secondary alteration or (2) 1623-3,4 condensed from an ^{16}O -poor reservoir similar in isotopic composition to the bulk inclusion. There are problems with the first explanation. The time required for oxygen exchange in a 5 μm radius spinel at 1400K is 6 months and at 1000K is 8000 years, yet there is no chemical or mineralogic evidence for later exchange with a gaseous reservoir. Hibonite and perovskite in close proximity to one another in 1623-4 have not equilibrated REE with one another. Although diffusion coefficients for REE in these minerals are not known, it seems unlikely that they can have coexisted at high temperature for a long period of time. Secondary alteration and oxygen exchange in Allende inclusions is believed to have taken place at 800-1000K (see [10]). If the second explanation is correct, there may have been higher temperature processes in the isotopic reservoir in which secondary alteration and exchange of primary minerals took place.

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