In-situ Discovery of a Cluster of Refractory Grains in an Allende Ferromagnesian Chondrule

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Introduction: During our nano-mineralogy investigation of the Allende meteorite, we discovered a unique corundum-rich cluster of irregular micrometer-sized refractory grains in a type IA chondrule. The presence of relatively oxidized (rutile) and highly reduced (a new mineral Ti_2O_3, khamrabaevite) phases in the same cluster reflects distinctly different environments prior to incorporation of the cluster into the chondrule. To our knowledge, this is the first occurrence of such a cluster. Investigation of phases that are clearly exotic to the host chondrule and may predate its formation can provide not only important constraints on the materials present when chondrules formed and the enviroments within or outside the Protoplanetary disk, but also on the chondrule formation event. Herein we report our prelimary results on the mineralogy of these grains and the overall petrology of their host chondrule.

Experimental: Electron probe microanalyzer (EPMA), high-resolution SEM, electron backscatter diffraction (EBSD), EDS and micro-Raman analyses at Caltech were used to characterize the cluster grains and their host chondrule. EBSD is used for mineral phase identification and crystal structure determination. The Caltech NanoSIMS was employed for preliminary O isotope analysis of two corundum grains.

Occurrence, Chemistry, Structure: The corundum-rich cluster is a ~130 µm diameter object enclosed in a 1.3 mm × 1.4 mm portion of a type IA chondrule in section USNM 3510-6 (Figs. 1-2). The host chondrule consists of a core containing Mg-rich olivine ($Fo_{99\sim93}$) with a rim of enstatite and more Fe-rich olivine ($Fo_{81\sim61}$). Altered areas contain hedenbergite, diopside, enstatite, wollastonite, sodalite, pentlandite, and Fe-rich olivine ($Fo_{69\sim62}$).

The corundum-rich cluster consists of an aggregate of irregular 5-10 µm diameter corundum grains with an assortment of similarly sized interstitial grains of refractory and non-refractory phases within the cluster. The cluster consists of ~30 Ti-bearing corundum grains (Al_2O_3), one or two grains each of the new mineral Ti_2O_3, khamrabaevite (TiC), rutile (TiO_2), mullite ($Al_6Si_2O_{13}$), an Fe-Si alloy and olivine.

Refractory grains. Corundum is Ti-rich with 0.43~3.21 wt% Ti_2O_3, extending to much higher concentrations than previously described meteoritic occurrences (0.2-0.7, e.g., [1-2]) and this suggests a reducing environment. FeO contents are, however, also fairly high (0.21~0.72 FeO (total Fe)), consistent with some low-temperature alteration of the original chemistry. Preliminary O isotope analyses of two corundum grains reveal that the grains have compositions well above the terrestrial fractionation line but on the CCAM line (Fig. 3), consistent with formation or alteration in an O^{16}-depleted reservoir within the solar system; such an oxygen reservoir predated or was contemporaneous with chondrule formation.

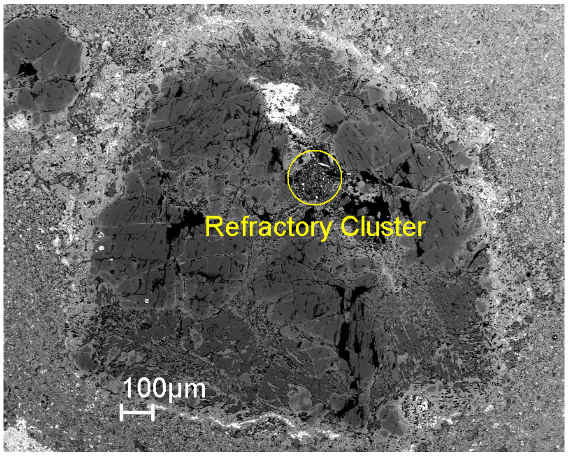

Fig. 1. Backscattered electron (BSE) image of the Allende chondrule containing a refractory cluster.

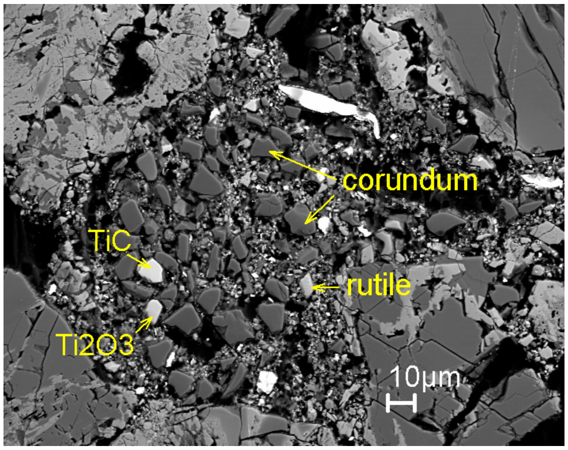

Fig. 2. BSE image showing the cluster of irregular, non-contact grains.

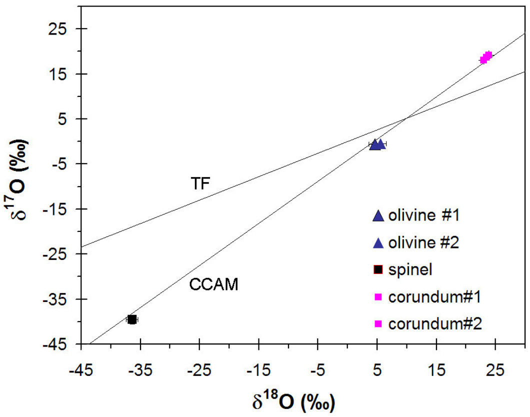

Fig. 3. $\delta^{18}O_{SMOW}$- $\delta^{17}O_{SMOW}$ plot of two corundum grains, host olivine, and spinel from a nearby CAI. The CCAM and terrestrial fraction lines are also shown.

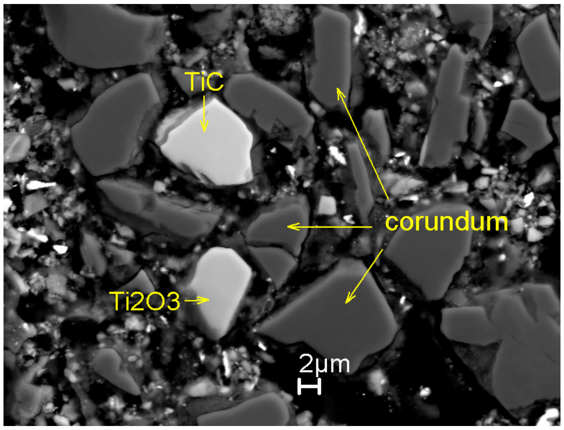

Fig. 4. BSE image showing Ti_2O_3, TiC, and corundum grains.

The new mineral Ti_2O_3 belongs to the corundum-hematite group ($A^{3+}{}_2O_3$), showing a formula $(Ti^{3+}{}_{1.90}Mg_{0.07}Al_{0.04}Zr_{0.01})_{\Sigma 2.02}O_3$. Ti_2O_3 is stable only under highly reducing conditions, subsolar if it equilibrated at temperatures below ~1200°C.

The 9 µm TiC grain is close to but not in contact with the Ti_2O_3 grain (Fig. 4) and has a formula $(Ti_{0.988}Al_{0.004}V_{0.003}Fe_{0.003}Zr_{0.001})_{\Sigma 0.999}C$. It is likely the largest TiC grain reported in a meteorite.

The rutile grain shows a mean formula $Ti_{0.96}Mg_{0.03}Al_{0.02}Fe_{0.01})_{\Sigma 1.02}O_2$. It contains nano-inclusions of carbon and, probably, $MgAl_2O_4$ spinel. Although it may seem intuituive that rutile indicates oxidizing conditions, rutile is actually stable at solar fO_2s if the temperature is below ~800°C (i.e., rutile does not necessarily imply oxidizing conditions). The mullite grain has a formula $(Al_{5.83}\ Ti_{0.07}\ Mg_{0.07}\ Fe_{0.02})_{\Sigma 5.99}\ (Si_{1.66}\ Ti_{0.34})_{\Sigma 2.00}O_{13}$. To our knowledge, this is the first occurrence of mullite in a meteorite.

Non-refractory grains within the cluster. One 8 µm olivine grain (Fo_{95}) is present, showing a weak EBSD pattern compared to the host olivine of the chondrule. There are three smaller 2~3 µm olivine grains ($Fo_{57\sim53}$) that contain unknown nano-inclusions but these grains may be contaminants introduced during sample preparation.

Two Fe-Si grains ($Fe_{96}Si_4$) occur near the edge of the cluster, having a disordered crystal structure as revealed by EBSD. The Si contents of these Ni-poor alloys are comparable to values observed in enstatite chondrites [e.g., 3]. The compositions are indicative of reducing conditions.

Sub-micrometer to nano-sized particles in the interstices between large grains in the cluster are mainly Fe-rich olivine and pentlandite. These were likely introduced during sample preparation.

Origin and Significance: Multiple refractory phases are potentially useful as probes of their formation environments. All of these grains either indicate or are consistent with extremely reducing conditions. The fragmental nature of the grains and clear example of disequilibrium between rutile and Ti_2O_3, however, suggests multiple sources and, therefore, multiple environments were sampled. Our current limited isotope measurements suggest that the corundum is probably not presolar but may have formed in a ^{16}O-depleted reservoir during the earliest stages of the solar system. This is consistent with even more extreme isotopic compositions of nano magnetite particles that [4] interpreted to be the product of low temperature oxidation of alloys in an ^{16}O-depleted nebular or asteroidal reservoir. It may be tempting to attribute the refractory grains to condensation. Corundum is an early condensing phase in a cooling gas of solar composition [5] but a more complex origin is also possible.

We emphasize possible implications of the corundum cluster for environments associated with formation of the constituent grains but it is also important to note that the cluster is hosted by a chondrule and it therefore survived a chondrule melting event which heated the object to temperatures likely in excess of 1500ºC. This has a number of potential implications. For example, survival of the corundum and other phases can be used to establish constraints on the chondrule formation event, as given sufficient time, all of the corundum would have dissolved into the melt. The corundum cluster may also be a rare surviving example of the refractory component of chondrules.

References: [1] Kurat G (1970) EPSL 9, 225-231. [2] Simon SB et al. (2002) MPS 37, 533-548. [3] Keil K. (1968) JGR 73, 6945-6976. [4] Sakamoto N. et al. (2007) *Science* 317, 231-233. [5] Ebel D.S. (2006) In *Meteorties and the early Solar System II*, 253-277.