

A Unique Zoned Wollastonite-bearing Particle from a Giant Cluster IDP of Probable Cometary Origin. D. J. Joswiak and D. E. Brownlee, Dept of Astronomy, Univ. of Washington, Seattle, WA, USA (joswiak@uw.edu)

Introduction: Mineralogical, chemical, isotopic and other studies of materials sampled from comets provide direct evidence on the nature of solid particles that were present in cold regions of the early Solar System(SS) [1-4]. These investigations provide insights into how comets formed and the processes and evolution of the early SS [5]. Ongoing studies of samples from comet Wild 2, as well as a giant cluster interplanetary dust particle (IDP), which has a probable cometary origin [3,6], have shown that many comet materials were formed in relatively hot regions and are similar to high temperature materials in chondrites [3,4,6].

Although most of the cometary particles we and others have examined are composed of moderately refractory materials, typically pyroxenes and olivines, some are more refractory and have chemical and mineralogical similarities to AOs, Al-rich chondrules and fine-grained CAIs (FGIs) [6]. One particle, however, LT43 from a giant cluster IDP, is a mixture of both moderately and more refractory minerals and as such is mineralogically unusual. LT43 is a ~10 μm polymineralic concentrically zoned particle with forsterite overlain by pigeonite, diopside and then wollastonite with submicron grains of perovskite and an amorphous Al,Si phase on the exterior. A small region of melilite and possible anorthite are also present. To our knowledge this assemblage is unknown in other ET materials. Here we discuss this unique particle and a possible scenario for its origin.

Sample Prep and Analysis: Particle LT43 was hand-picked from the interior of a giant cluster IDP that was collected in the stratosphere. The IDP (U2-20 GCA) is a large anhydrous chondritic porous particle consisting of thousands of petrologically unequilibrated grains, submicron to ~40 μm in size, and has chemical and physical properties consistent with an origin from a comet [3,6] including a high presolar grain content [7]. The particle was washed in hexane to remove adhering Si oil and embedded in epoxy resin. 70nm-thick microtome slices were produced with a ultramicrotome and placed on 10 nm C films on TEM grids. The microtome sections were studied with a Tecnai TF20 STEM at the University of Washington by conventional TEM/EDX techniques. The potted butt was additionally observed with a FESEM where BSE images and element maps were acquired.

Results: TEM and SEM observations show that LT43 is composed of a sequence of minerals whose elemental compositions are progressively more refractory from its interior to the rim (Fig. 1). The innermost phase consists of forsterite ($\text{Fo}_{99,6-99,8}$) followed by Fe-poor pigeonite ($\text{En}_{87}\text{Wo}_{11}$). These in turn are overlain

by Fe-poor diopside (ave. $\text{Al}_2\text{O}_3 = 2.1 \text{ wt\%}$, $\text{TiO}_2 = 0.6 \text{ wt\%}$) and then wollastonite, (Fig. 1). Exterior to the wollastonite are submicron rounded grains of perovskite and an Al,Si glass. A single occurrence of submicron melilite (Ak_{21}) and possible anorthite are associated with wollastonite. A number of sub-100 nm inclusions were also found including a single grain of kamacite in forsterite, an Al-rich inclusion in wollastonite and multiple occurrences of subhedral Mg,Al,Cr+/-minor Ti,V,Fe spinels in diopside and pigeonite.

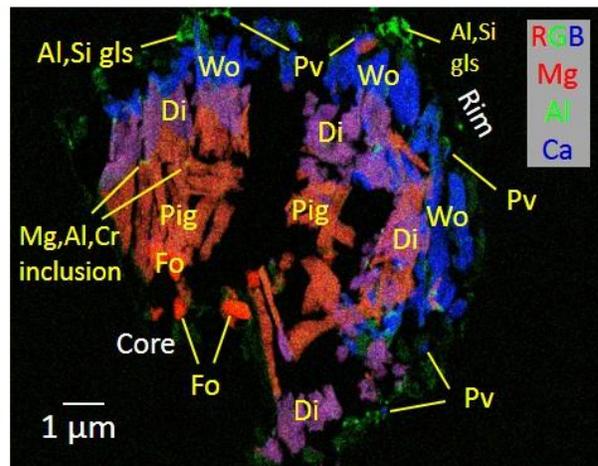


Fig. 1: TEM Mg-Al-Ca element map of a microtomed section of a unique particle from the giant cluster IDP. Mineral sequence from core to rim is: forsterite(bright red), pigeonite(orange-red), diopside(purple) and wollastonite(blue). Small grains of perovskite(not visible) and Al,Si glass(green) occur outward of wollastonite. A submicron kamacite grain is present in the forsterite.

Discussion: LT43 is a most unusual particle in that it contains a mix of minerals that have not previously been observed together. The presence of wollastonite is often interpreted as an alteration phase and is observed in CAIs and other refractory materials in chondrites. [8]. However, the bulk Na_2O (0.17 wt%) and FeO (0.69 wt%) contents of LT43 are low and we have not observed any other alteration phases that are often accompanied with wollastonite in CAIs such as grossular, andradite, monticellite or nepheline. Also, the exterior location of wollastonite, along with the concentrically zoned mineral texture suggests that all the major minerals in LT43 formed in one or more linked processes. This is further reinforced by well-defined monotonically increasing Ca/Mg ratios of core to rim minerals. These observations indicate that wollastonite is likely a primary phase that formed coinciding with the other LT43 minerals. The presence of pigeonite

suggests that the particle may have an igneous origin associated with rapid cooling.

A similar, but more refractory object, known as the 'White Angel' was reported in a Type A CAI from the CV3 chondrite Leoville [9]. Composed of melilite, wollastonite, fassaite, perovskite and minor Fe,Ni metal this CAI was shown to have a complex formation history involving melting of precursor materials, evaporation and isotopic exchange in one or more nebular reservoirs. Mineralogical and chemical differences with LT43, however, are significant. LT43 has only trace melilite, higher bulk SiO₂ (56.4 wt% vs 29.6 wt%), much lower bulk Al₂O₃ (2.1wt% vs 24.7 wt%) and also contains pigeonite.

The major elements comprising the core to rim sequence of minerals in LT43 - forsterite-pigeonite-diopside-wollastonite-perovskite - show a progressive increase in more refractory (higher condensation temperature) elements. Ca/Mg and Ca/Si ratios increase across the mineral sequence while perovskite, a Ca-Ti oxide, is concentrated on the exterior of the grain. This suggests that LT43 could have formed via a volatility-related process such as condensation in the early solar system. However, the observed minerals are not those predicted from condensation calculations for typical solar gas [10]. Wollastonite is not a predicted condensation phase unless the gas is nonsolar with subchondritic Mg/Si ratios (Mg/Si = 0.63) [11] and pigeonite generally forms via igneous processes. Also, the core to rim element concentrations in the mineral sequence is the reverse of that expected for objects forming by condensation. These observations indicate a complex formation history for LT43.

In order to account for most of the mineralogical, chemical and textural properties a scenario involving flash heating, partial melting, volatile loss, rapid cooling and collisional fragmentation is necessary. SiO₂, MgO and CaO comprise 97.5% of the total oxides in LT43. The primary bulk composition along with its low bulk Al concentration suggests a precursor such as an Al,Ti-bearing pyroxene + olivine grain.

The bulk composition of LT43 plots in the Di field on a SiO₂-MgO-CaO liquidus phase diagram [12], however, it is apparent from the fractured texture (Fig. 1) that more forsterite was likely present in the original grain than currently exists. This would change the bulk composition to a more Mg-rich composition and likely place the grain into the Fo rather than Di field. A moderately refractory grain with this bulk composition that was flash-heated in the nebula would initially crystallize forsterite followed by the pyroxenes pigeonite and diopside around 1350-1400 °C as indicated in a SiO₂-MgO-CaO phase diagram. Because the condensation temperatures of Mg and Si are significantly lower

than the crystallization temperatures, it is likely that the residual liquid whose composition was near the Di-Fo-Pig reaction point on the SiO₂-MgO-CaO diagram, would partially lose more volatile Mg and Si from evaporative loss during crystallization. The loss of Mg and Si would drive the residual Di-Fo-Pig liquid toward a Ca-rich composition (wollastonite on the phase diagram). This compositional change toward wollastonite would be further enhanced from the simultaneous crystallization of forsterite, pigeonite and perhaps diopside which would deplete the same liquid of Mg, thus an unusual residual composition largely composed of CaO and SiO₂ could allow the late stage crystallization of wollastonite, an unusual igneous phase. The residual Ti that was not previously incorporated into pigeonite would combine with some of the remaining CaO in the liquid to form perovskite which is observed on the outer rim of the assemblage. The SiO₂-MgO-CaO phase diagram shows that no simple igneous crystallization process producing both forsterite and wollastonite is possible, however, an evaporative loss of Mg and Si during crystallization of a nebular melt from a pre-existing moderately refractory object (such as an Al,Ti-bearing pyroxene + olivine) could provide a path where both forsterite and wollastonite occur in the same assemblage. It is notable that Cr and Mn, relatively volatile elements, are low in the LT43 bulk. This scenario for the origin of LT43 could create a mineralogically and concentrically zoned grain whose minerals contain progressively more refractory elements on its exterior. Fracturing, perhaps in a grain-to-grain collision, likely occurred prior to accretion into the giant cluster IDP parent body.

Conclusions: The genesis of LT43 from the giant cluster IDP appears to have involved a multitude of processes including flash heating, partial melting, fractional crystallization, rapid cooling, volatile loss and fragmentation. This resulted in a concentrically zoned sequence of refractory and moderately refractory minerals that have not here-to-fore been observed together and provides additional evidence that comets accreted materials from hot dynamic regions in the early SS.

References: [1] Joswiak et al. (2012) *MAPS* 47: 471-524. [2] Frank et al. (2014) *GCA* 142: 240-259. [3] Zhang et al. (2021) *EPSL* 564: 1-11. [4] Defouilloy et al. (2017) *EPSL* 465: 145-154. [5] Brownlee (2004) in *Met. Comets & Planets, Treat. on Geochem 1*, 663-688. [6] Joswiak et al. (2017) *MAPS* 52: 1612-1648. [7] Nguyen et al. (2020) *51st LPSC*, abstract #2487. [8] MacPherson (2004) in *Met. Comets & Planets, Treat. on Geochem 1*, 201-246. [9] Komorowski et al. (2007) *MAPS* 42: 1159-1182. [10] Wood et al. (2019) *Am. Min.* 104: 844-856. [11] Unterborn and Panero (2017) *ApJ* 845: 1-9. [12] Huang et al. (1995) *Met. Trans. A* 26A: 2293-2309.