

# Pristine GEMS, Altered GEMS, and GEMS-like Material

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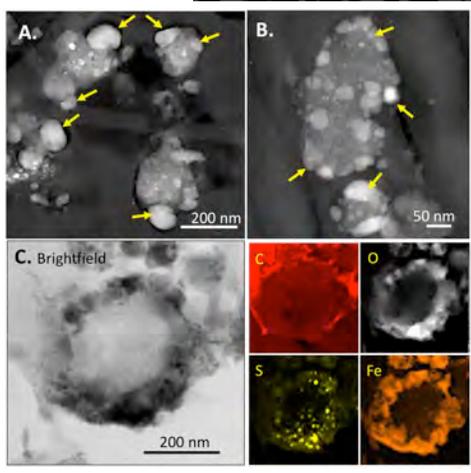
## Introduction

New evidence from electron, secondary ion and optical spectroscopies place the origin of GEMS (glass embedded with metal and sulfides) and associated organic carbon in an extremely cold (<50K) environment, like the outer solar nebula, presolar molecular cloud, and interstellar medium [1]. The common cold origin of GEMS and organic matter reinforces the importance of GEMS in understanding the nature of the original solids in the outer nebula environment and tracing them into parent bodies. To date, GEMS have been positively identified in chondritic interplanetary dust particles (IDPs) and their larger counterparts, ultracarbonaceous (Antarctic) micrometeorites (UCAMMs), believed to originate in small icy bodies [1-3]. GEMS are logical precursors of the fine-grained matrices of carbonaceous chondrites (CCs) but have yet to be rigorously identified there. They also have yet to be confirmed in the returned sample from Kuiper Belt comet 81P/Wild 2 [4]. Confirmation of GEMS in CCs and/or 81P/Wild 2 would have implications for radial mixing in the solar nebula, the state of preservation of CC fine-grained matrices, and the influence of parent body alteration on primordial organic chemistry. Most published data make no distinction between pristine and terrestrially altered GEMS, so we are currently collecting data specifically from minimally-altered GEMS. Here, we review the **properties of pristine and altered GEMS** with the goal of **facilitating their identification in other classes of primitive meteoritic materials, including primitive CC matrices.**

## Altered GEMS

The average bulk GEMS composition is near solar, with element/Si (e/Si) ratios that are systematically depleted from solar ratios, i.e. Si is systematically enriched. (Individual GEMS can vary by as much as ~10x.) Elevated Si in IDPs was viewed with suspicion as early as 1981 [8] and subsequently shown to be due to terrestrial alteration [e.g. 9]. There are at least three causes of elevated Si: heating during **atmospheric entry, silicone oil contamination and aqueous alteration.** Evidence of heating is widespread among GEMS (e.g. Fig. 3) [10]. In-situ TEM heating of pristine IDPs indicates that sulfides in GEMS begin to mobilize and oxidize at ~300°C [9]. Heating lowers e/Si ratios in GEMS through loss of S, Mg, and Fe. The effects of heating are complex, and their detailed impact on individual GEMS likely depends on temperature, kinetics and locally induced redox gradients within individual IDPs or UCAMMs. Low porosity and high organic carbon content inhibit oxidation of sulfides (to Fe<sub>2</sub>O<sub>3</sub>), but not migration of sulfides to the surfaces of GEMS. It is well established that IDPs collected in the stratosphere are contaminated to varying degree with silicone oil that also lowers e/Si ratios [e.g. 1,8,11], and even mild aqueous alteration of UCAMMs in snow and ice lowers element/Si ratios [12]. In general, significant Fe<sup>II</sup> in the amorphous silicate matrices of GEMS is a likely indicator of alteration. As a consequence of their high susceptibility to any alteration, **GEMS grains in a single particle have experienced a range of alteration, and pristine GEMS are rare.**

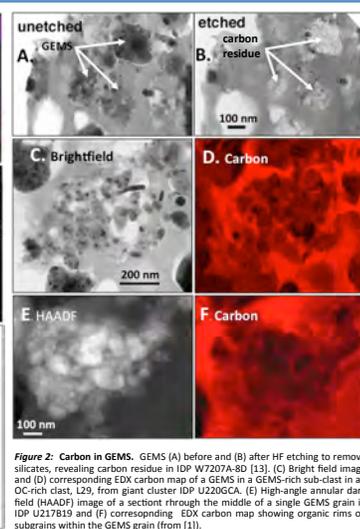
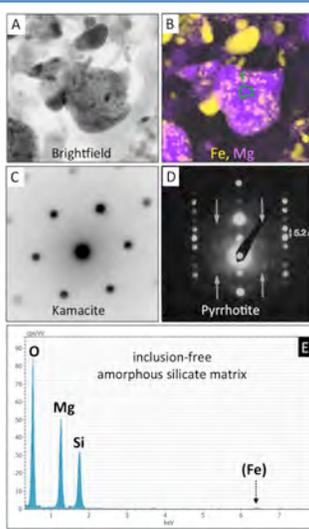
**Figure 3: Altered GEMS.** (A&B) Dark field scanning transmission electron microscopy (STEM) images of altered GEMS decorated with thermally ripened sulfides (arrowed) in UCAMM 0835-21 (Cape Prud'homme). (C) Bright field image and carbon, oxygen, sulfur, and iron maps of a highly (thermally) altered, chemically segregated GEMS grain in the organic carbon-rich clast, L29, from the giant cluster IDP U220GCA. →



## Pristine GEMS

Most GEMS grains are 100 – 500 nm in diameter and have approximately solar composition. They are comprised of three inorganic components: amorphous matrix, Fe,Ni-metal nanocrystals, and Fe,Ni-sulfide nanocrystals. The Mg-silicate matrix is nearly Fe-free (<3 at.% Fe) in the least-altered GEMS, the metal inclusions are kamacite, and the sulfide inclusions are low-Ni pyrrhotite [2,3,5-7]. Figure 1 shows nanodiffraction patterns from kamacite and pyrrhotite inclusions and elemental chemistry of the amorphous matrix from a sample GEMS grain. Metal and sulfide nanocrystals are relatively uniformly distributed in the matrix, with metal grains smaller than sulfide grains, on average. GEMS typically are embedded in organic carbonaceous material, and many also contain carbon throughout their interiors [1]. Figure 2 shows examples of carbon distribution in GEMS grains.

**Figure 1: Inorganic components in GEMS.** (A) Bright field image of a GEMS grain in carbon-rich clast L29 from giant cluster IDP U220GCA. (B) Corresponding element map of Fe (yellow) from pyrrhotite and kamacite inclusions and Mg (magenta) from the amorphous silicate matrix. (C) [111] zone axis nanodiffraction pattern from kamacite inclusion in a GEMS grain [7]. (D) Nanodiffraction pattern (a\*-c\* projection) from a pyrrhotite inclusion [2]. (E) Energy-dispersive x-ray spectrum from region indicated in B shows that the amorphous silicate matrix is ~Fe-free. →

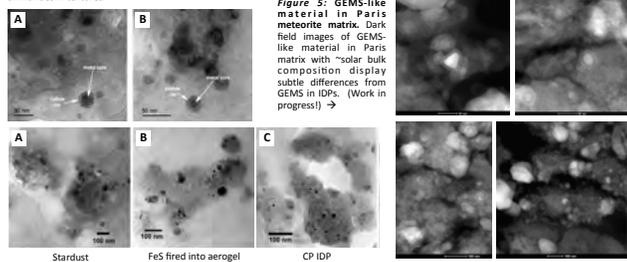


**Figure 2: Carbon in GEMS.** GEMS (A) before and (B) after HF etching to remove silicates, revealing carbon residue in IDP W7207A-80 [13]. (C) Bright field image and (D) corresponding EDX carbon map of a GEMS in a GEMS-rich sub-clast in an OC-rich clast, L29, from giant cluster IDP U220GCA. (E) High-angle annular dark field (HAADF) image of a section through the middle of a single GEMS grain in IDP U217B19 and (F) corresponding EDX carbon map showing organic rims on subgrains within the GEMS grain (from [1]).

## GEMS-like Material

There are multiple reports of GEMS and/or "GEMS-like" material in CC matrices and in impact tracks in Stardust aerogel [e.g. 14-17]. While the grains identified exhibit compositional and textural similarities to actual GEMS, the reported textures and compositions are not unique. As Figures 1 and 2 illustrate, confirmation of *bona fide* GEMS is to be found at the nanoscale, specifically by establishing that the grains under investigation contain (organic) carbon in variable proportions, pyrrhotite and kamacite as nanoparticles, and low-Fe, Mg-silicate as the amorphous matrix. It is possible, perhaps even likely, that some grains in primitive CC matrices are parent-body-altered GEMS. In depth knowledge of the nanoscale characteristics of pristine and altered GEMS is necessary in comparing and contrasting GEMS look-alikes in other meteoritic materials [e.g. 15].

**Figure 4: GEMS-like material in Stardust.** Comparison of GEMS in a CP IDP and GEMS-like material in Stardust returned samples and in a laboratory impact of FeS into silica aerogel at 6 km/s [from 16]. Bright field images of (top row) metal-sulfide inclusions and (bottom row) similarities in textures.



**Figure 5: GEMS-like material in Paris meteorite matrix.** Dark field images of GEMS-like material in Paris matrix with ~solar bulk composition display subtle differences from GEMS in IDPs. (Work in progress) →

References: [1] Ishii H. A. et al. (2018) *Proc. Nat. Acad. Sci.* 115, 6608-6613. [2] Bradley J. P. (1994) *Geochim. Cosmochim. Acta* 58, et al. (1999) *LPSC* 30, Abstract 2031. [6] Bradley J. P. (2014) in *Treatise of Geochemistry*, 1, pp. 287-308. [7] Groat T. K. et al. (2018) *G. & Brownlee D. E.* (1991) *Icarus* 89, 26-43. [11] Bradley J. P. (2013) *Geochim. Cosmochim. Acta* 107, 336-340. [12] Yabuta H. et al. *Planet. Sci.* 38, 305-322. [15] Leroux H. et al. (2015) *Geochim. Cosmochim. Acta* 170, 247-265. [16] DeGregorio B. et al. (2017) *Mete-*



2123-2134. [3] Dobrica E. et al. (2012) *Geochim. Cosmochim. Acta* 76, 68-82. [4] Ishii H. A. (2019) *Meteorit. Planet. Sci.* 54, 202-219. [5] Brownlee D. E. *LPSC* 49, Abstract 2083. [8] Fraundorf P. (1981) *Geochim. Cosmochim. Acta* 45, 915-943. [9] Bradley J.P. et al. (2014) *LPSC* 45, Abstract 1178. [10] Love S. (2017) *Geochim. Cosmochim. Acta* 214, 172-190. [13] Brownlee D. E. et al. (2000) *LPSC* 31, Abstract 1921. [14] Zolensky M. E. et al. (2003) *Meteorit. orit. Planet. Sci.* 52, A65. [17] Gainsforth Z. et al. (2018) arXiv:1807.00063. [16] Ishii H. A. et al. (2008) *Science* 319, 447-450.

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Background image: GEMS and crystals in UCAMM 0835B13. T. Noguchi