

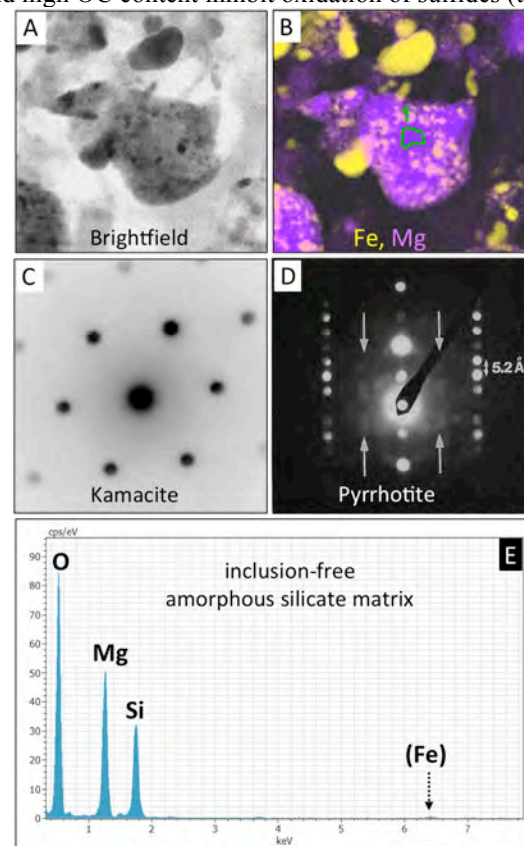
**PRISTINE GEMS, ALTERED GEMS, AND GEMS-LIKE MATERIAL.** H. A. Ishii<sup>1</sup>, K. K. Ohtaki<sup>1</sup>, J. P. Bradley<sup>1</sup>, D. J. Joswiak<sup>2</sup>, D. E. Brownlee<sup>2</sup> and K. C. Bustillo<sup>3</sup>, <sup>1</sup>Hawaii Institute of Geophysics & Planetology, University of Hawai'i at Mānoa, Honolulu, HI, USA, <sup>2</sup>Dept. of Astronomy, University of Washington, Seattle, WA, <sup>3</sup>Molecular Foundry, Lawrence Berkeley National Laboratory, Berkeley, CA. Email: hope.ishii@hawaii.edu.

**Introduction:** New evidence from electron, secondary ion and optical spectroscopies place the origin of GEMS and associated organic carbon (OC) in IDPs 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 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.

**Pristine GEMS:** Most are 0.1-0.5  $\mu\text{m}$  in diameter with  $\sim$ solar composition. They comprise three inorganic components: amorphous matrix, Fe,Ni-metal and Fe,Ni-sulfide nanocrystals; The Mg-silicate matrix is nearly Fe-free (<3 at.% Fe), metal is kamacite (bcc FeNi), and sulfides are low-Ni pyrrhotite (Fig. 1) [2,3,5-7]. Metal and sulfide nanocrystals are relatively uniformly distributed in the matrix, with metal grains smaller than sulfides, on average. GEMS are typically embedded in organic carbon (OC), and many also contain carbon throughout their interiors (Fig. 2).

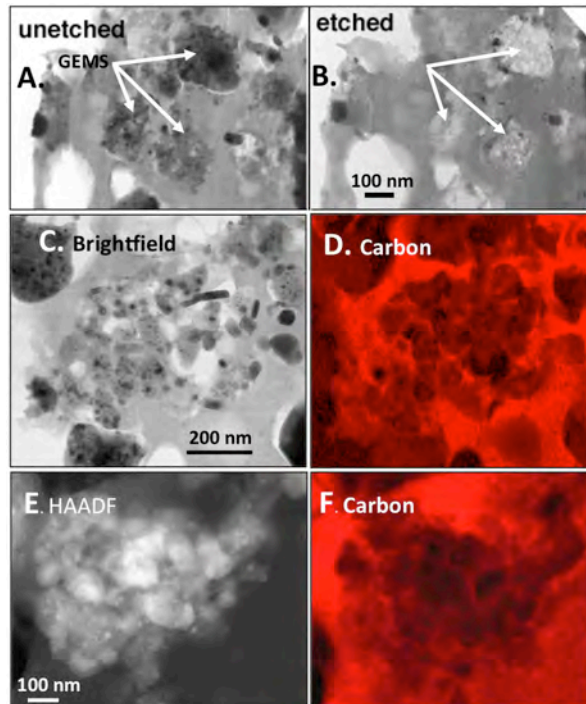
**Altered GEMS:** The average bulk GEMS composition is near solar, with element/Si (e/Si) ratios that are systematically depleted from solar ratios, i.e. Si is systematically enriched. (Individual GEMS can vary by as much as  $\sim 10\times$ .) Elevated Si in IDPs was viewed with suspicion as early as 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  $\sim 300^\circ\text{C}$  [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 GEMS or UCAMMs. Low porosity and high OC content inhibit oxidation of sulfides (to



**Figure 1: Inorganic components of GEMS.** (A) Brightfield 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 (green outline) shows that the amorphous silicate matrix is  $\sim$ Fe-free.

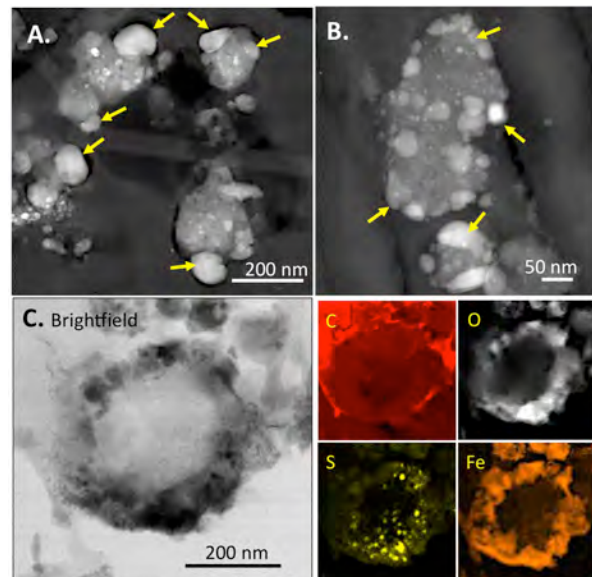
$\text{Fe}_3\text{O}_4$ ), but not migration of sulfides to the surfaces of GEMS. It is well established that IDPs collected in the stratosphere are contaminated to varying degree with silicone oil that also lowers e/Si ratios [e.g. 1,8,11], and even mild aqueous alteration of UCAMMs in snow and ice lowers element/Si ratios [12]. In general, significant  $\text{Fe}^{2+}$  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 2: Carbon in GEMS.** (A) GEMS before and (B) after HF etching to remove silicates revealing carbon residue (IDP W7207A-8D, [13]). (C) Brightfield 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 darkfield (HAADF) image of a section through the middle of a single GEMS grain in 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 *bone 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 3: Altered GEMS.** (A&B) Darkfield STEM images of altered GEMS decorated with thermally ripened sulfides (arrowed) in UCAMM0833-21(Cape Prudhomme). (C) Brightfield image and carbon, oxygen, sulfur and iron maps of a highly (thermally) altered, chemically segregated GEMS grain in the OC-rich clast L29 (from large cluster IDP U220GCA).

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