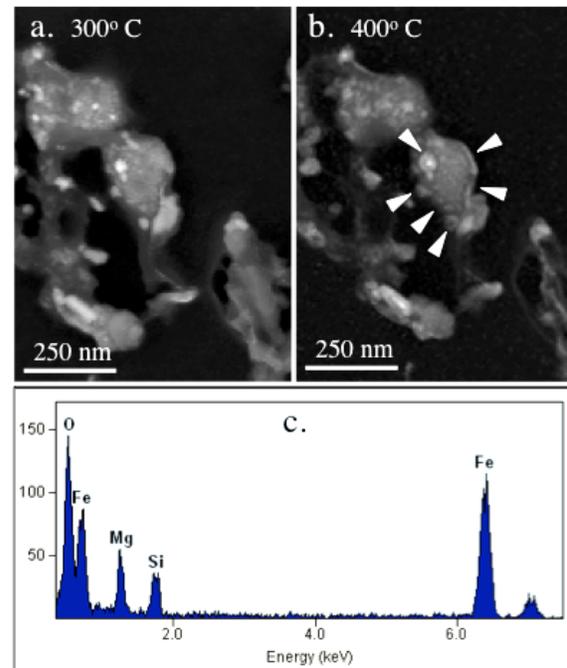


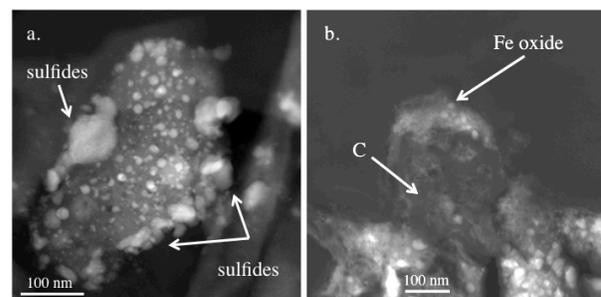
**IMPACT OF THE TERRESTRIAL ENVIRONMENT ON THE COMPOSITIONS OF GEMS.** J. P. Bradley<sup>1</sup>, H. A. Ishii<sup>1</sup>, P. Wozniakiewicz<sup>2</sup>, T. Noguchi<sup>3</sup>, C. Engrand<sup>4</sup>, D. E. Brownlee<sup>5</sup>. <sup>1</sup>University of Hawaii at Manoa, Hawaii Institute of Geophysics & Planetology <johnbrad@hawaii.edu>, Honolulu, HI 96822, USA. <sup>2</sup>Natural History Museum, London SW7 5BD, UK. <sup>3</sup>Ibaraki University, Ibaraki 310-8512, Japan. <sup>4</sup>CSNSM CNRS-Univ. Paris Sud, 91405 Orsay Campus, France. <sup>5</sup>University of Washington, Seattle, WA 98195, USA.

**Introduction:** GEMS are the most abundant silicates in chondritic porous (CP) interplanetary dust particles (IDPs). Based on their physical properties, size, shape, amorphous silicate matrix and superparamagnetic FeNi metal inclusions, Bradley [1] proposed that GEMS are surviving presolar interstellar (IS) amorphous silicates, leftovers from the presolar molecular cloud and a fundamental building block of the solar system. The major sources of IS amorphous silicates are AGB stars and supernovae (SNe), and O isotopic anomalies indicative of AGB and SNe constituents have been detected in several large GEMS [2]. Since the mineralogy and petrography of these anomalous GEMS are otherwise indistinguishable from those of the rest of the GEMS population, all GEMS may be presolar. The mineralogy and petrography of GEMS, i.e. metal and sulfides in amorphous silicate matrix, are relatively invariant yet bulk element abundances vary by an order of magnitude among GEMS [3]. Terrestrial alteration is a logical explanation for such a wide compositional range so we investigated the state of chemical preservation of GEMS. We performed heating experiments on GEMS to assess the impact of heating during atmospheric entry, and we compared the compositions of GEMS in IDPs collected in the stratosphere with GEMS in ultracarbonaceous Antarctic micrometeorites (UCAMMs) to assess the impact of aqueous alteration and contamination.

**Results: Atmospheric entry heating:** Magnetite rims are known to form on the surfaces of GEMS during atmospheric entry. To determine the temperature of rim formation, we identified a CP IDP (U220A19) without rimmed GEMS and pulse heated it in air from 100° to 500°C in 100°C increments. Below 300°C, visible changes were minimal, but between 300 and 400°C, Fe-sulfides began to sublime/melt in some GEMS, migrate to surfaces and react with terrestrial oxygen forming magnetite (Figs. 1a & b). Sulfides on surfaces of GEMS (e.g. Fig. 2a) have been interpreted as evidence of gas-phase sulfidization in the solar nebula [2]. However, our experiments reveal that the sulfide decoration occurs during atmospheric entry. Some magnetite rim compositions exhibit elevated Mg (Fig. 1c) indicating that, like S and Fe, Mg is mobile during atmospheric entry. Our experiments show that GEMS can become thermally unstable in air at temperatures as low as 300°C. Since most CP IDPs >15 µm diameter are heated above 300°C during atmospheric entry, GEMS that have *not* been chemically and isotopically modified by heating are probably rare.



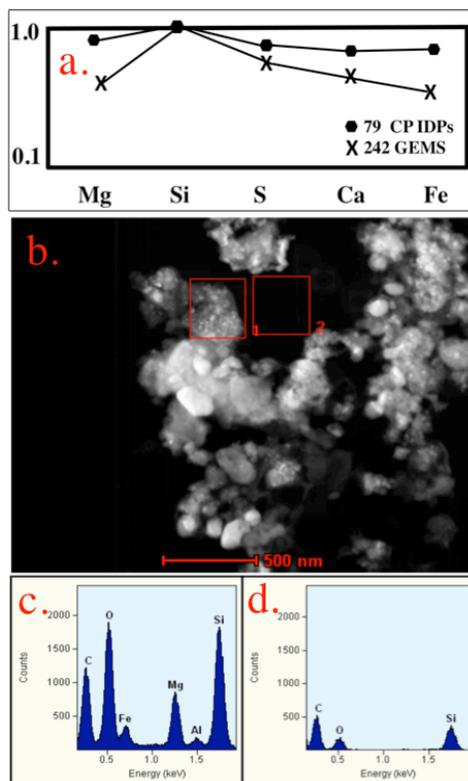
**Figure 1:** (a) Darkfield image of GEMS in CP IDP U220A19 at 300°C and (b) at 400°C. Arrows show FeS-Fe<sub>3</sub>O<sub>4</sub> rims migrated to the GEMS' surface between 300 and 400°C. (c) EDX spectrum from Fe<sub>3</sub>O<sub>4</sub> rim on GEMS in CP IDP U220GCA. Highly elevated Mg in the rim, relative to the bulk GEMS, underscores Mg volatility and mobility when GEMS are heated during atmospheric entry.



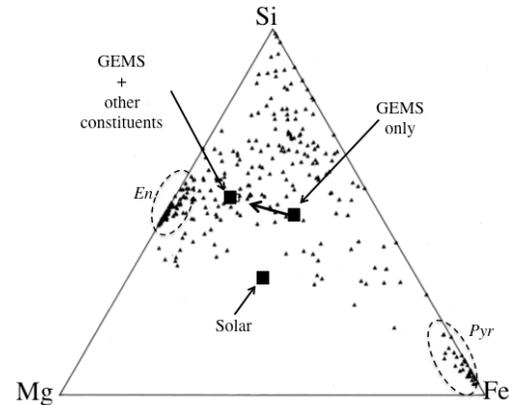
**Figure 2:** Terrestrially altered GEMS in UCAMMs. (a) Fe-sulfide surface decoration of GEMS likely resulting from heating during atmospheric entry (UCAMM0833-21), (b) GEMS with only Fe-oxide(s) and carbonaceous material ("c") remaining. Mg-silicate matrix and Fe sulfides were presumably removed by leaching during residence in Antarctic snow, ice or water (UCAMM D051B84).

**Aqueous alteration:** Recently discovered ultracarbonaceous Antarctic micrometeorites (UCAMMs) provide a valuable new source of GEMS-rich meteoritic material [4-6]. In the most well-preserved UCAMMs from fresh snow (e.g. Fig. 2a), GEMS compositions measured to date, although similar to those in CP IDPs, do not exhibit the order-of-magnitude variations observed in CP IDPs collected in the stratosphere, in part because UCAMMs are not exposed to silicone oil (Si-oil). In other UCAMMs, GEMS that were exposed on outer surfaces have been aqueously leached (Fig. 2b).

**Contamination:** CP IDPs collected in the stratosphere in Si-oil retain contamination, even after thorough washing, that manifests as a systematic depletion of CP IDP bulk element/Si ratios below solar (CI) ratios (Fig. 3a). Schramm et al [7] estimate that up to 10 wt.% or more of the Si in CP IDPs may be due to Si-oil contamination. Si-oil is preferentially sequestered in the carbonaceous components and nanoporous GEMS, suppressing GEMS' element/Si depletions even further below solar ratios (Fig 3b-d [8]).



**Figure 3:** (a) Element/Si ratios in CP IDPs [7] and GEMS [9] normalized to solar (CI) abundances. Both bulk CP IDP and GEMS compositions are systematically depleted from solar element/Si due in part to silicone oil contamination. (b) Darkfield image of a thin section of giant cluster CP IDP U220GCA. (c) EDX spectrum from GEMS (red box 1) (d) Spectrum from Si-oil contaminated C support substrate (red box 2).



**Figure 4:** Mg-Fe-Si ternary plot (relative at.%) of 239 point count EDX analyses from a thin section of CP IDP W7027H14 [10]. Black squares indicate average compositions. GEMS average is enriched in Si relative to solar composition. In this CP IDP, inclusion of other components drives bulk composition closer to solar in Mg/Si and further from solar in Fe/Si.

**Lack of compositional complementarity:** It has been argued that elemental compositions establish that most GEMS formed in the solar system [2]. The foundation of this argument is *compositional complementarity*, i.e. CP IDPs have ~solar bulk compositions and, thus, all CP IDP components, including GEMS, formed from the same solar-composition reservoir. This argument incorrectly assumes no contamination or alteration. We note that CP IDP compositions relative to Si and solar (CI) abundances have historically been reported on log-scale plots, but CP IDPs are only within a factor of 2–3x solar. Relative to the other (crystalline) components, GEMS are collectively underdense and, although they tend to dominate the volume, the other components tend to dominate the mass and bulk compositions. On average, the non-GEMS components of CP IDPs (predominantly enstatite (En) and pyrrhotite (Pyr)) are solar in composition; They are not super-solar in *complement* to sub-solar GEMS. (Solar composition lies between En and Pyr in Fig 4 [10].) Instead, GEMS tend to draw the average composition of CP IDPs slightly sub-solar (Fig 3a). In most IDPs, there is no *compositional complementarity* relationship between GEMS and the other components.

**References:** [1] Bradley J. P. (1994) *Science*, 90, 1151–1154. [2] Keller L. P. and Messenger S. (2011) *GCA* 75, 5336–5365. [3] Bradley J. P. (2013) *GCA* 107 336–340. [4] Duprat J. et al. (2010) *Science* 328, 742–745. [5] Dobrica E. et al. (2012) *GCA* 76, 68–82. [6] Noguchi T. et al. (2013) *LPS XLIV*, Abstract #1380. [7] Schramm L. S. et al. (1989) *Meteoritics* 24, 99–112. [8] Bradley J. P. et al. (2011) *LPS XLII*, Abstract 1320. [9] Ishii H. A. et al. (2008) *Science* 319, 447–450. [10] Bradley J. P. et al. (1989) *EPSL* 93, 1–11.