GEMS REVEALED: SPECTRUM IMAGING OF AGGREGATE GRAINS IN INTERPLANETARY DUST.
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Introduction. Anhydrous interplanetary dust particles (IDPs) of cometary origin contain abundant materials that formed in the early solar nebula. These materials were transported outward and subsequently mixed with molecular cloud materials and presolar grains in the region where comets accreted [1]. GEMS (glass with embedded metal and sulfides) grains are a major component of these primitive anhydrous IDPs, along with crystalline Mg-rich silicates, Fe-Ni sulfides, carbonaceous material, and other trace phases. Some GEMS grains (~5\%) are demonstrably presolar based on their oxygen isotopic compositions [2]. However, most GEMS grains are isotopically solar and have bulk chemical compositions that are incompatible with inferred compositions of interstellar dust, suggesting a solar system origin [3]. An alternative hypothesis is that GEMS grains represent highly irradiated interstellar grains whose oxygen isotopic compositions were homogenized through processing in the interstellar medium (ISM) [4].

We have obtained the first quantitative X-ray maps (spectrum images) showing the distribution of major and minor elements in individual GEMS grains. Nanometer-scale chemical maps provide critical data required to evaluate the differing models regarding the origin of GEMS grains.

Methods and Samples. We used a JEOL 2500SE 200 keV field-emission scanning-transmission electron microscope (STEM) equipped with a JEOL thin window energy-dispersive X-ray (EDX) spectrometer to obtain spectrum images of GEMS in ultramicrotome thin sections of IDPs L2011B10, L2036C4 and U2073A5B. Solar flare tracks are present in each of these IDPs, and B10 contains isotopically anomalous presolar silicates associated with molecular cloud material [5]. Spectrum images contain a high count-rate EDX spectrum in each pixel, enabling the determination of quantitative element abundances in addition to displaying the spatial distribution of major and minor elements. Spectrum images of ~30 GEMS grains were acquired by rastering a 4 nm incident probe whose dwell time was minimized to avoid beam damage and element diffusion during mapping. Successive image layers of each GEMS grain were acquired and combined in order to achieve ~5\% counting statistics for major.

Results. Spectrum imaging of individual GEMS grains reveals that many are compositionally heterogeneous at the <50 nm scale, and that this chemical heterogeneity manifests itself in different ways. Many GEMS grains that appear as single objects in bright-field TEM images are shown to be porous aggregates of even smaller distinct grains in the spectrum images (Figure 1). The population of subgrains exhibits large intragrain variations in Mg/Si and other elemental ratios. The most common subgrain compositions are 1) amorphous silica-rich, sulfur-poor grains with embedded FeNi metal grains, and 2) single crystal Fe-Ni sulfide grains (Figure 2). Less common are amorphous Mg-silicate (Mg/Si at. <1) and Ca-rich (diopside normative) domains. Compositional heterogeneities are also observed in less porous GEMS grains but the domains are not as clearly defined suggesting that these GEMS may have undergone limited thermal annealing. Rare GEMS grains are observed that have a layered structure consisting of chemically distinct, continuous layers ~20nm thick. GEMS grains with discontinuous layers are also observed. We have yet to observe a GEMS grain with a crystalline core, although we have observed rare GEMS-like coatings on enstatite platelets.

The FeNi sulfide grains in GEMS are generally not embedded within the volume of individual GEMS grains, but occur preferentially on their peripheries. The sulfide grains have variable Fe/Ni ratios and occur as 50-100 nm single crystals with a range of morphologies, from euhedral grains to spherical grains that appear to have accreted as molten droplets. Sulfur-poor GEMS contain nanophase (5-10 nm) taenite with Fe:Ni approaching 50:50, the taenite grains are far from equilibrium with the coexisting nanophase kamacite grains. It is probable that the taenite formed as a result of reaction of earlier formed kamacite, but the processing is unlikely to have occurred in their present petrographic setting. Rare nanophase chromium-rich grains associated with Fe (either as metal or possibly chromite) occur as inclusions within GEMS. Zn-rich sulfides are occasionally observed in association with GEMS grains.

Discussion. The bulk chemical compositions of GEMS grains are inconsistent with the inferred compositions of ISM silicates based on spectroscopic studies [3]. Furthermore, the GEMS grains and crystalline components in IDPs have complementary elemental compositions that, taken together, nearly match solar composition. This relationship suggests that GEMS grains are also condensates (non-equilibrium) from a solar gas that had earlier (at higher temperatures) fractionally condensed crystalline silicates and metal [3].

Most of the GEMS grains studied here exhibit strongly heterogeneous chemical compositions that are at odds with uniform chemical gradients expected from...
ion-mixing effects associated with extensive irradiation. We suggest that the observed nano-scale chemical heterogeneities reflect the primary formation conditions of GEMS through the accretion of compositionally distinct condensate subgrains. We observe a continuum of GEMS morphologies from porous to solid GEMS to equilibrated (crystalline) aggregates [6] that may in fact reflect a sequence of preaccretional thermal annealing at subsolidus temperatures (below the thermal stability limit of pyrrhotite).

**Conclusions.** We conclude that most GEMS grains are aggregates (nano-rocks) composed of even smaller subgrains with diverse compositions that accreted in the early solar nebula. The subgrain compositions are dominated by two major components, silica-rich and FeS-rich grains that likely formed as late stage non-equilibrium condensates. The bulk compositions of GEMS grains can be explained largely by variable mixtures of these two subgrain compositions. The observed compositional heterogeneity in GEMS is unlikely to have resulted from extensive radiation processing, which would tend to homogenize their elemental distributions via ion-mixing [e.g. 7].

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![Figure 1. A brightfield STEM image of a cluster of GEMS in IDP L2011B10 (top) and the corresponding Mg+Si distribution map extracted from the EDX spectrum image (bottom). The white arrows indicate the numerous compositionally distinct subgrains that comprise the GEMS aggregate grain.](image1)

![Figure 2. Ternary plot of measured Fe, Si, and S atomic abundances in GEMS subgrains showing the silica-rich (blue) and FeS-rich (red) subgrain compositions. The dashed line defines a field that encompasses previous bulk GEMS grains analyses [3, 8].](image2)