

CONSTRAINTS ON THE COSMOCHEMICAL SIGNIFICANCE OF ELEMENT/SI RATIOS AND OXYGEN ISOTOPIC COMPOSITIONS OF GEMS FROM IDPs COLLECTED IN SILICONE OIL. J. P. Bradley, P. Wozniakiewicz, H. A. Ishii. Institute of Geophysics & Planetary Physics, Lawrence Livermore National Laboratory, 7000 East Avenue, Livermore, CA 94550 USA.

Introduction: GEMS (Glass with Embedded Metal and Sulfides) are found in high abundance in chondritic porous interplanetary dust particles (CP IDPs) collected in the stratosphere by impact into silicone oil. The source of GEMS prior to incorporation into IDPs and their small outer solar system parent bodies has intrigued researchers for decades. Clues to their origin and mechanisms of formation include isotopic and elemental compositions, the latter typically reported relative to Si [1-5]. It has been proposed that GEMS are surviving presolar interstellar amorphous silicates [3], and non-solar oxygen isotopic anomalies have been detected in 6 GEMS [1,2,6,7]. An alternative proposition, predicated on element/Si ratios, is that most GEMS formed in the solar system [8]. GEMS average bulk chemical composition shows systematic major element/Si depletions that are, it is argued, complementary to the crystalline components also contained in CP IDPs [4,8]: Since the average bulk composition of CP IDPs is ~solar (CI), all CP IDP components are likely of solar system origin [8,9]. Here we show that there are apparent element depletions when CP IDP and GEMS compositions are reported as element/Si ratios, but these depletions are absent when reported as element/Mg or element/Fe ratios. Instead, major element abundances in CP IDPs and GEMS typically cluster within $\pm 40\%$ of solar (CI) composition with a significant *excess* of only one major element, Si. Residual silicone-oil in which IDPs are collected is implicated in these Si excesses. Impact on oxygen isotope measurements of GEMS is considered.

Methods: We used analytical scanning transmission electron microscopy (STEM) and energy-dispersive x-ray spectroscopy (EDX) to measure and compare bulk compositions of GEMS in ultramicrotomed thin sections of 5 CP IDPs and in 2 CP IDPs dispersed on thin-carbon TEM support films. The relative abundances of Mg, Si, S, Ca and Fe were quantified using a Cliff-Lorimer thin-film correction procedure (typically to within 5-10% relative error) using k-factors calibrated against thin-film mineral standards.

Results and Discussion: Figure 1a compares average major element/Si ratios, relative to CI, in 90 CP IDPs [10] and 186 GEMS [8,11] from the literature. Although the mean element/Si abundance ratios for the CP IDPs plot close to CI values, they appear systematically depleted: Mg/Si by ~6% S/Si ~10%, Ca/Si ~15% and Fe/Si ~25%. A similar and more pronounced element/Si depletion pattern is evident in the population of GEMS. Their mean element/Si abun-

dance ratios appear depleted by ~40% for Mg, S and Fe and ~20% for Ca. Element/Mg and element/Fe ratios are plotted in Figures 1b and 1c. In both cases, Si is present in GEMS at levels significantly above CI. Synchrotron x-ray fluorescence measurements on 5 CP IDPs, also using Fe as the ratio element, find no systematic depletion or enrichment in the major, minor and trace elements for $Z=16$ (S) and above [12].

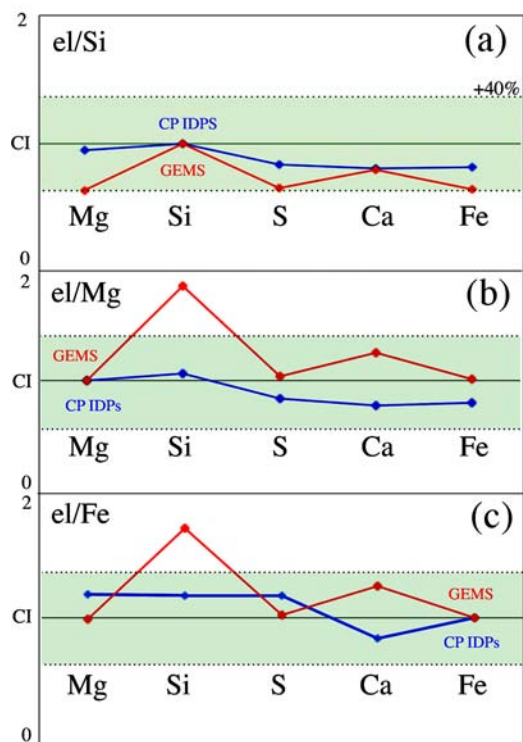


Figure 1: Elemental abundances given relative to a ratio element and to CI in 90 CP IDPs [10] (blue) and 186 GEMS (red) [8,11]: (a) element/Si, (b) element/Mg and (c) element/Fe. (Note linear vertical scale where prior work has been presented on a logarithmic scale, i.e. [12].)

It has long been recognized that IDPs collected in the stratosphere retain significant polymerized silicone oil [10,13,14]. In a study of five chondritic IDPs using ToF-SIMS, all were found to be contaminated throughout, even after aggressive solvent extractions, such that silicone oil is the *only* species detectable on their outer surfaces [14]. We explored the effect of silicone oil on the compositions of several CP IDPs collected during the early era of ER2 flights out of NASA-Ames and dispersed on TEM carbon support substrates. Isolated silicone oil droplet residues in the dispersions contain minor P (Fig. 2a). Using P as a tracer, we are able to estimate the silicone oil content of GEMS and correct

the measured element/Si ratios (Figs. 2 & 3). Unfortunately, P cannot be used as a tracer for silicone oil in all IDPs since it is not detected in all residues.

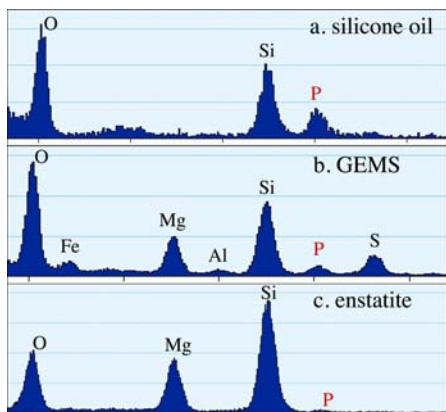


Figure 2: Representative EDX spectra from (a) silicone oil, (b) GEMS grain & (c) enstatite crystal in a dispersion of CP IDP u2-12a 34A on a continuous thin-film carbon substrate.

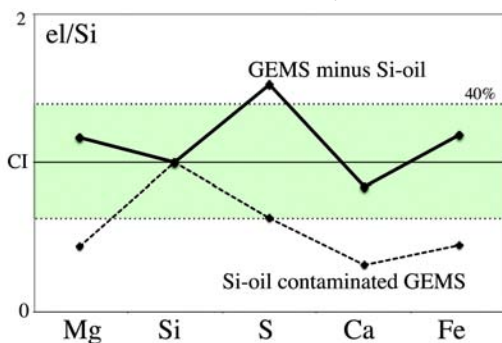


Figure 3: Mean element/Si ratios for 25 GEMS in CP IDP U211B6 before and after subtraction of Si from residual silicone oil. Linear vertical scale plot.

The impact of residual - and permanent - silicone oil contamination on the bulk compositions of IDPs and GEMS is shown in Figure 1. Relative to Si, all elements appear to be systematically depleted from CI abundances (Fig. 1a & 3), but relative to Mg and Fe, the systematic depletions disappear and only one element, Si, is enriched (Fig. 1b & c). Excess Si is especially pronounced in GEMS (e.g. Fig. 2b) because they are embedded in and may contain amorphous carbonaceous material known to preferentially sequester silicone oil [10,13]. The somewhat porous amorphous silicate matrices of GEMS may also adsorb silicone oil.

Silicone oil contamination provides not only excess Si atoms but also excess O atoms in its siloxane backbone. Based upon the subtraction of excess Si from oil contamination (Fig. 3), >30% of the O atoms in the GEMS in CP IDP U211B6 are from silicone oil residue. Such contamination clearly would have a normalizing effect on oxygen isotope measurements. With a geometric mean diameter of ~210 nm, the majority of GEMS are too small for statistically definitive isotope measurements, even using nanoSIMS that requires

grains ≥ 250 nm [15]. In the 6 GEMS in which oxygen isotope anomalies have been identified, the mean diameter is more than twice that of the population mean.

Summary and Implications: Silicone oil contamination from collection of IDPs is preferentially associated with GEMS in CP IDPs. The cosmochemical significance of systematic element/Si depletions observed in the GEMS population needs to be reassessed in the context of contamination. Element/Mg and element/Fe ratios indicate that the GEMS and CP IDP populations are, on average, a close match to solar abundances for most major, minor and trace elements [12,16], although real, sometimes relict-grain driven, deviations from CI abundances do occur among individual GEMS, e.g. Mg/Si ~1.8X CI [3]. The significance of the normal (solar) O isotopic compositions of most GEMS also requires reassessment because silicone oil dilutes any anomalies present in already frequently-too-small grains. Recently discovered GEMS in carbon-rich micrometeorites [17,18] have never been exposed to silicone oil, although aqueous alteration in Antarctic snow and ice may also alter element/Si ratios [19]. We recently proposed a program of “clean” IDP collection at sea level in the mid-Pacific. Elemental and isotopic compositions from GEMS collected without silicone oil may provide more reliable measures of these key characteristics for determining the origin of GEMS.

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