

GEMS IN CHONDRITIC METEORITES? K. K. Ohtaki¹, H. A. Ishii¹, J. P. Bradley¹, K. C. Bustillo², J. Ciston², K. L. Villalon³, D. E. Brownlee⁴, D. J. Joswiak⁴, T. Stephan³, A. M. Davis³. ¹Hawai'i Institute of Geophysics and Planetology, University of Hawai'i at Mānoa, Honolulu, HI, ²National Center for Electron Microscopy, Molecular Foundry, Lawrence Berkeley National Laboratory, Berkeley, CA, ³The University of Chicago, Chicago, IL, ⁴University of Washington, Seattle, WA. Email: kohtaki@hawaii.edu.

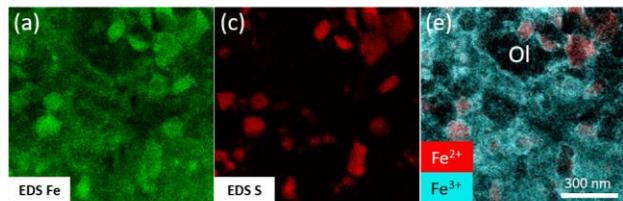
Introduction: GEMS (glass with embedded metal and sulfides) are among the most abundant silicates in anhydrous CP IDPs and ultracarbonaceous Antarctic micrometeorites (UCAMMs); both are believed to originate from small frozen bodies, including comets, which accreted at heliocentric distances beyond the giant planets. The properties of the most pristine GEMS reveal that they formed in extremely cold environments like the outer nebula, presolar molecular cloud, or interstellar medium [1, 2]. Whether GEMS were also incorporated into asteroids and meteorites has implications for grain transport and radial mixing in the solar nebula and the origin and state of preservation of matrices in chondrites. GEMS are composed predominantly of amorphous silicates (a-silicates). Prior studies of a-silicates in primitive chondrite matrices have speculated that they formed by rapid condensation in the hot solar nebula [3, 4]. We compared IDP GEMS with a-silicates in the fine-grained matrices of Acfer 094 (ungrouped CM-CO) and Paris (CM) chondrites by electron microscopy methods. Both meteorites are believed to have been minimally altered by parent body processing, and both contain “GEMS-like” material [5, 6].

Experimental: Electron-transparent sections of the fine-grained matrices of metal-rich regions of Paris (section 2010-7, Muséum National d'Histoire Naturelle in Paris) and Acfer 094 were harvested using conventional focused ion beam (FIB) methods and a new, hybrid ultramicrotomy-FIB method [7]. The elemental compositions were measured and mapped using multi-detector energy dispersive X-ray spectroscopy (EDS) (~0.7 sr) and monochromated electron energy loss spectroscopy (EELS). Fe oxidation state distributions, chemical shifts, and core-loss fine-structures were measured using EELS (~100 meV FWHM ZLP) over 0–3000 eV using a single electron discrimination CMOS camera.

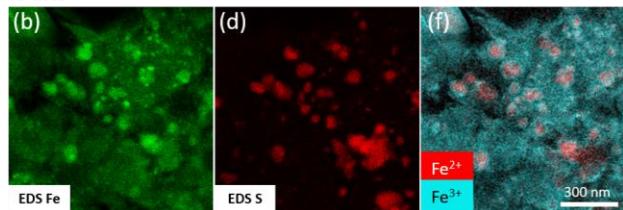
Results: EDS and EELS mapping reveal the spatial distribution of elements, their (mineral) hosts and, in the case of Fe, the distribution of oxidation states at the nanoscale (Fig. 1). In Acfer 094 and Paris, Fe is hosted mostly in Fe(Ni)-sulfides as Fe²⁺ and in the a-silicate matrix as Fe³⁺ (Fig. 1 a–f), as previously reported [8]. Fe⁰ metal grains (20–50 nm) are associated with Fe-sulfides (sometimes in silicate crystals) but not embedded in a-silicate matrix. In GEMS in IDPs, in contrast, Fe is hosted mostly in Fe²⁺-rich sulfides, and in Fe⁰Ni metal nano-inclusions as small as 1–2 nm in diameter (Figs. 1 g and h). Fe³⁺ is rare in pristine IDPs

and, when present, is in magnetite rims on sulfides and GEMS, formed during atmospheric entry. The Fe content of the a-silicate matrix in Acfer 094 and Paris varies between 20 and 50 at.%, and in GEMS in IDPs, it is 1–5 at.% (Fig. 2), consistent with prior work [9, 10]. Overall, the a-silicate in the chondrite matrices is Fe-rich, highly oxidized, hydrated, and relatively uniform in composition in the regions we examined.

Acfer 094



Paris



IDP LT29

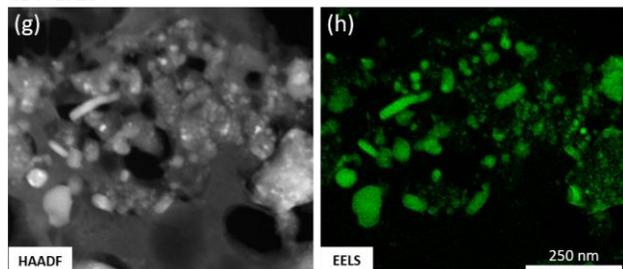


Figure 1: (a–d) EDS (Fe & S) and (e–f) EELS (Fe oxidation-state) maps of a-silicate matrix in Acfer 094 and Paris. Metallic Fe⁰ is absent in these regions, Fe²⁺ is concentrated in crystalline Fe-sulfides, and Fe³⁺ is distributed throughout the a-silicate matrices. Fe³⁺-rims are present on sulfide and olivine (Ol) grains. (g) HAADF image and (h) corresponding EELS Fe-L_{2,3} map of GEMS in IDP LT29 mixed with sulfide nanocrystals. Fe is in Fe-rich metal and sulfide nanocrystals, and the amorphous matrix of the GEMS is essentially Fe-free.

Discussion: GEMS-like a-silicates are common in meteoritic materials [3–5, 11–13]. However, despite superficial similarities in composition and texture, GEMS are different: They contain FeNi metal and FeNi sulfide nanocrystals in amorphous Mg-silicate matrix that are embedded in and/or co-accreted with organic carbon. In

this study, we observe fundamentally different a-silicates in Acfer 094 and Paris.

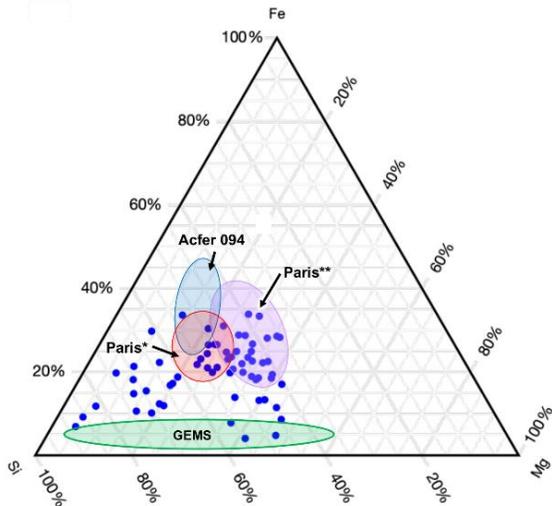


Figure 2: Fe-Si-Mg ternary diagram (at%) of the a-silicate composition in Acfer 094 matrix, Paris matrix, and GEMS. Paris*=this study, Paris**=[5]. Blue dots indicate the bulk compositions of GEMS from different regions in IDP thin sections. Shaded regions show compositions of a-silicates only.

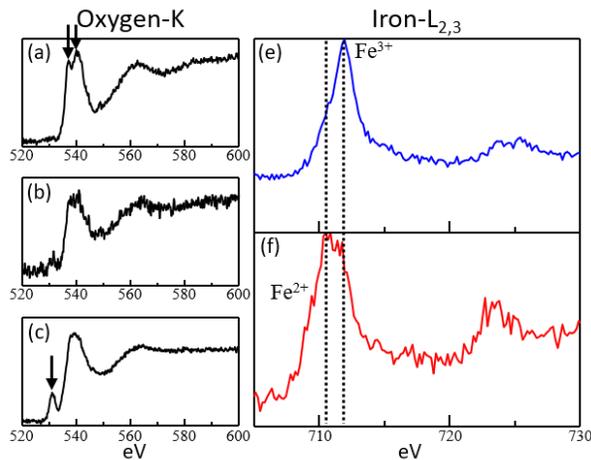


Figure 3: Monochromated EELS core scattering edges (100 meV energy resolution). (a–c) O–K edges in Acfer 094 from (a) anhydrous crystalline Mg-rich silicate, (b) amorphized surface of the crystalline silicate, (c) a-silicate matrix. Fe–L_{2,3} edges from (e) a-silicate matrix, (f) Fe-sulfide crystalline inclusion in the matrix.

We find that the meteorite matrices are heterogeneous on the micrometer-scale and altered by parent body secondary (aqueous) alteration even in metal-rich regions. Imaging and mapping show crystalline silicates, sulfides, and other minerals partially altered *in situ* on the parent body. For example, Fe³⁺-rims on sulfide and silicate grains are consistent with *in situ*

oxidation resulting in mobilization of Fe into the surrounding a-silicate matrix (Figs. 1, 3). We suggest alteration may produce much of the Fe-Mg-bearing a-silicate groundmass in limited-water conditions. To date, we find no evidence for GEMS or other primary a-silicate in either meteorite. Conversely, in CP IDPs, we find no evidence of aqueous alteration of crystalline silicates, i.e., GEMS are primary accretional aggregates. GEMS in IDPs have highly reduced chemistry, whereas the meteorite matrices are oxidized with very low Fe⁰ and high Fe³⁺ abundances. Furthermore, the a-silicates in GEMS are highly Fe-depleted (Fig. 2) consistent with previous measurements [9, 10], whereas in Acfer 094 and Paris, they are very Fe⁽³⁺⁾-rich. Another key difference is nanophase (5–20 nm) FeNi metal in a-silicate matrix, ubiquitous in GEMS in IDPs and nearly absent in the meteorite matrices. Larger FeNi-rich grains are common in the meteorite matrices, but most are (hydr)oxides and carbides. FeNi grains, some with sizes similar to those in GEMS, are also present, but preliminary evidence suggests that they may have originated as inclusions in crystalline sulfides that were subsequently released into the matrices during aqueous alteration, a key distinction from GEMS, where metal and sulfides are decoupled.

Conclusions: Although GEMS are viable precursors of GEMS-like material in the fine-grained matrices in Acfer 094 and Paris, and condensation mechanisms of formation have also been proposed [e.g. 3, 4], we have yet to observe definitive evidence of either. However, given the micrometer-scale heterogeneity of the matrices, future studies may still reveal evidence of inherited GEMS in meteorites. We suggest that an alternative mechanism needs further investigation, that is, *in-situ* formation of GEMS-like a-silicates from crystalline sulfides and silicates during secondary alteration in limited-water conditions on the meteorite parent bodies. At least some GEMS-like material in least-altered regions of both meteorites studied here appears to be unrelated to GEMS.

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