A NANOSCALE ANALYTICAL SCANNING TRANSMISSION ELECTRON MICROSCOPY STUDY OF THE PARIS METEORITE. K. L. Villalon[1,2,], K. K. Ohtaki[3], J. P. Bradley[3], H. A. Ishii[3], A. M. Davis[1,2,4], and T. Stephan[1,2]. [1]Department of the Geophysical Sciences, The University of Chicago, Chicago, IL, USA, [2]Chicago Center for Cosmochemistry, [3]Hawaiʻi Institute of Geophysics & Planetology, University of Hawaiʻi at Mānoa, Honolulu, HI, USA. [4]Enrico Fermi Institute, The University of Chicago, Chicago, IL, USA. E-mail: kvillalon@uchicago.edu

Introduction: Amorphous silicates with embedded nano-inclusions have been reported in the Paris CM chondrite [1]. They have chemical and morphological similarities to glass with embedded metal and sulfides (GEMS) found in interplanetary dust particles (IDPs) and micrometeorites believed to originate from comets. Using STEM nanodiffraction in combination with (conventional) TEM and STEM EDS, we have determined the mineralogy, crystallography and elemental compositions of the inclusions embedded in the GEMS-like objects of the Paris meteorite for comparison with those from *bona fide* GEMS. In a companion abstract [2], we compare the Fe oxidation states of the amorphous silicate material.

Paris is a breccia considered to be the least altered CM chondrite [3] but has evidence of heterogeneous aqueous alteration, containing both metal-rich lithologies with abundant anhydrous amorphous silicates as well as metal-poor lithologies with abundant phyllosilicates. GEMS-like material is abundant throughout Paris, particularly in the interchondrule matrix (ICM) of the least altered lithologies and fine-grained rims (FGRs) around chondrules [1]. If the GEMS-like material in primitive meteorites can be confirmed to be related to IDP GEMS, it may demonstrate the progression of silicates from the interstellar medium and/or early solar nebula to incorporation into a growing planetesimal and subsequent alteration. If the GEMS-like material in primitive meteorites is unrelated to IDP GEMS, it may represent a significant yet, until recently, unexplored class of objects.

We have also explored the differences between the fine-grained material from different regions of Paris: we sampled ICM material from both the highly altered, metal-poor lithologies as well as the less altered, metal-rich lithologies; and we also sampled the FGRs surrounding metal-rich chondrules. FGRs commonly enclose chondrules in carbonaceous chondrites, particularly CMs such as Paris. The origin of FGRs remains unclear. Both nebular [4, 5] and parent-body [6–9] origins have been proposed for FGRs. Some FGRs show distinct layers in backscattered electron imaging, usually an outer layer of dark, higher-porosity material and an inner layer of lighter, seemingly more compacted material [8]. Both the inner and outer layers of FGRs were sampled.

Methods: Nine electron-transparent lamellae were lifted out of section 2010-1 of the Paris meteorite and thinned using a TESCAN LYRA3 FIB-SEM at the University of Chicago; final thinning was done just before TEM analyses using a Helios NanoLab 660 FIB at the University of Hawaiʻi at Mānoa. Lamellae were collected from a range of petrographic settings with possibly different formation histories and varying degrees of aqueous alteration: two lamellae from highly altered ICM (metal-poor) regions; four from more pristine (metal-rich) ICM regions; two from the outer portions of FGRs surrounding metal-rich chondrules; and one from the inner portion of a FGR surrounding a metal-rich chondrule.

The sections were examined at 300 keV using a FEI 60–300 keV High-base Titan3 G2 (scanning) transmission electron microscope equipped with an EDAX Genesis 4000 Si(Li) solid-state X-ray energy-dispersive spectrometer at the University of Hawaiʻi at Mānoa. High spatial resolution EDS maps were acquired at 200 keV using the FEI TitanX 60-300 microscope at the Lawrence Berkeley National Laboratory. The sections were imaged using both conventional bright-field and HAADF modes. Elemental compositions were measured by EDS, while crystallographic information was acquired by electron diffraction: either nanodiffraction for nanoscale phases or SAED for larger phases. In some cases, high-magnification lattice-fringe images were also acquired. Diffraction spacings were calibrated *in-situ* against polycrystalline platinum and determined using ImageJ software [10] Crystal structure identifications were confirmed using simulated patterns generated with CrystalMaker (CrystalMaker Software Ltd.; www.crystalmaker.com).

Results: TEM imaging, EDS, and diffraction analyses indicate morphological, compositional, and mineralogical differences between the nanophase inclusions in IDP GEMS and Paris GEMS-like material. All Fe-rich nanoparticles in Paris have conspicuous rims that are either absent or minimal in IDPs (Fig. 1). Similar rimmed objects have been observed in other primitive meteorites [e.g., 11]. Rims are enriched in O and depleted in Fe compared to the interior of the inclusions. Rims do not appear to be thicker in samples from more altered regions.

Notably, nanophase FeNi metal grains have yet to be identified within the amorphous silicate in Paris. Rare kamacite grains were identified that were clearly not embedded within the amorphous silicate domains. These metal grains were also much larger than those found in IDP GEMS. Some grains with EDS spectra suggestive of FeNi metal have diffraction patterns inconsistent with metal and, instead, are identified as carbides or oxides, demonstrating the problem with relying on EDS spectra alone in identifying nanoscale phases.

Sulfides are the most abundant nanoscale phase observed in Paris GEMS-like material. Sulfide compositions as measured by EDS are shown in Fig. 2. Using nanodiffraction, we confirmed crystallographically that the nanophase sulfides in Paris include pentlandite as well as both hexagonal and monoclinic pyrrhotite polytypes. Only hexagonal pyrrhotite has been found within and on the surfaces of GEMS [12]. The abundance of Ni-free or Ni-poor sulfides is higher in the least altered regions than in the more highly altered regions of Paris. In particular, Ni-free and Ni-poor sulfides are more abundant in FGRs than in ICM (Fig. 3). A Mann-Whitney U test [13, 14] confirms that the FGR and ICM nanosulfide populations are statistically different beyond 2σ. Pentlandite was found even in the least altered sections. Pentlandite is not found as inclusions within IDP GEMS and is usually considered to be evidence of hydration when present in IDPs [15].

Other phases identified in our Paris sections include the carbide haxonite, low-iron, Mn-enriched (LIME, MnO/FeO ≥1) silicates, an enstatite platelet, two forsterite whiskers, and numerous hollow carbon nanoglobules.

Conclusion: We have explored the chemistry and mineralogy of the nanophase inclusions embedded throughout the fine-grained amorphous silicate in Paris. Using nanodiffraction, we have not identified any metal inclusions embedded in the amorphous silicate matrix, but we have identified rare metal grains that reside outside of the amorphous silicate domains. In addition to the absence of metal grains, the GEMS-like material in Paris differs in morphology, composition, and mineralogy from GEMS from IDPs believed to derive from comets. It is unclear at this time whether these differences are due to alteration or whether they require independent origins. The presence of other phases commonly identified in IDPs, such as enstatite whiskers and platelets, LIME silicates, and carbon nanoglobules as well as isotopic measurements by other authors may support a genetic relationship between the GEMS-like material of Paris and those in IDPs, or these phases may be indicative of radial mixing in the solar nebula.

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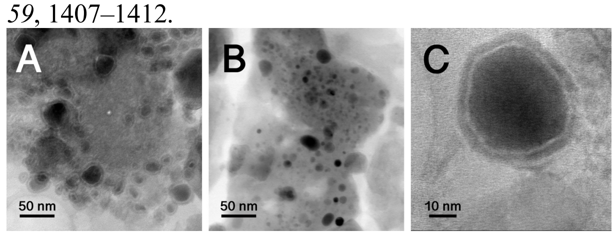

Figure 1: Bright-field images comparing (A) GEMS-like material in Paris and (B) GEMS from IDP U220GCA LT29. (C) A rimmed sulfide from Paris. Note that all the sulfides within amorphous silicate in Paris are rimmed and those in the IDP are not.

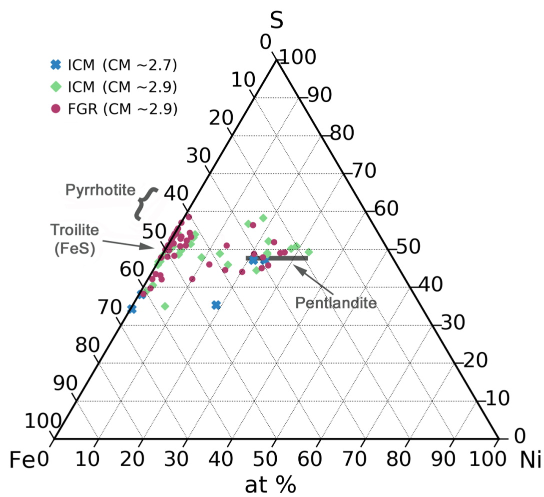

Figure 2: Compositions of nanophase sulfides in Paris obtained by EDS. All EDS measurements are likely skewed toward more Fe-rich compositions due to overlap of the surrounding Fe-bearing silicate groundmass.

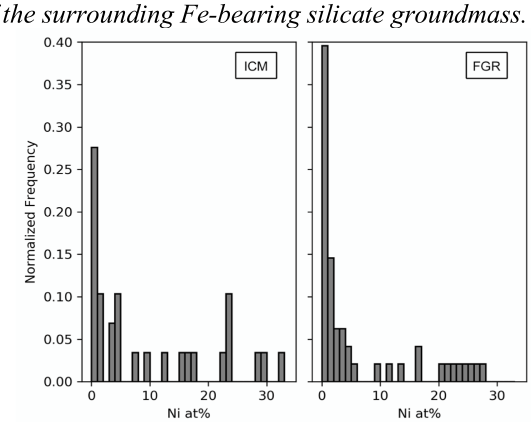

Figure 3: Normalized frequency of Ni concentrations in FGRs and ICM nanophase sulfides from metal-rich lithologies.