

**FORMATION AND PROCESSING OF AMORPHOUS SILICATES IN PRIMITIVE CARBONACEOUS CHONDRITES AND COMETARY DUST.** L. P. Keller and S. Messenger. Robert M. Walker Laboratory for Space Science, Code KR, ARES, NASA/JSC, Houston, TX 77058 ([Lindsay.P.Keller@nasa.gov](mailto:Lindsay.P.Keller@nasa.gov)).

**Introduction.** Chondritic-porous interplanetary dust particles (CP IDPs) exhibit strongly heterogeneous and unequilibrated mineralogy at sub- $\mu\text{m}$  scales, are enriched in carbon, nitrogen and volatile trace elements, and contain abundant presolar materials [1-4]. These observations suggest that CP IDPs have largely escaped the thermal processing and water-rock interactions that have severely modified or destroyed the original mineralogy of primitive meteorites. CP IDPs are believed to represent direct samples of the building blocks of the Solar System – a complex mixture of nebular and presolar materials largely unperturbed by secondary processing. The chemical and isotopic properties of CP IDPs and their atmospheric entry velocities are also consistent with cometary origins.

GEMS (glass with embedded metal and sulfides) grains are a major silicate component of CP IDPs. GEMS grains are  $< 0.5 \mu\text{m}$  in diameter objects that consist of numerous 10 to 50 nm-sized FeNi metal and Fe-Ni sulfide grains dispersed in a Mg-Si-Al-Fe amorphous silicate matrix [2, 5]. Based on their chemistry and isotopic compositions, most GEMS appear to be non-equilibrium condensates from the early solar nebula [2]. If GEMS grains are a common nebular product, then they should also be abundant in the matrices of the most physically primitive chondritic meteorites. Although amorphous silicates are common in the most primitive meteorites [6-9], their relationship to GEMS grains and the extent to which their compositions and microstructure have been affected by parent body processing (oxidation and aqueous alteration) is poorly constrained. Here we compare and contrast the chemical, microstructural and isotopic properties of amorphous silicates in primitive carbonaceous chondrites to GEMS grains in IDPs.

**Methods and Samples.** Matrix fragments of the ungrouped carbonaceous chondrite Acfer 094, and CR chondrites QUE 99177 and MET 00426 were embedded in epoxy and thin sections ( $\sim 70 \text{ nm}$  thick) were prepared by ultramicrotomy. We obtained quantitative chemical maps of the thin sections using energy-dispersive x-ray spectrum imaging with the JSC JEOL 2500 scanning-transmission electron microscope. Fe oxidation states were determined using electron energy-loss spectroscopy (EELS) with a Gatan Tridiem imaging filter. Additional matrix fragments were dried at  $70\text{C}$  for 24 h, crushed on diamond plates and infrared (IR) transmission spectra were obtained from 2.5-25  $\mu\text{m}$  using a Nicolet Continuum Fourier-transform IR microscope with HgCdTe detectors.

**Results and Discussion.** The mineralogy and petrography of the meteorite matrix samples we analyzed are broadly consistent with previous studies [7-9]. Common characteristics include: fine-grained ( $< 1 \mu\text{m}$ ) enstatite, forsterite, and diopside grains and sulfides (pyrrhotite and rare pentlandite) set in an amorphous silicate matrix. Rare polycrystalline aggregates occur in the matrix and resemble equilibrated aggregates in CP IDPs [10]. The amorphous silicate material occurs as 0.2-0.5  $\mu\text{m}$  nodules with minor inclusions of nanophase Fe-sulfides. Rare nanophase FeNi metal grains occur in Acfer 094 but are absent in QUE and MET. The average composition of these nodules is richer in O and Fe, and poorer in S compared to average GEMS grains (Table 1). The meteoritic amorphous silicate materials are relatively homogeneous and do not show the order-of-magnitude variation in Mg/Si and Fe/Si observed among GEMS grains (Figure 1). The meteorite amorphous silicates and GEMS grains are systematically depleted in Mg, Ca and S relative to solar. The Ca depletion in the meteoritic amorphous silicates is consistent with loss during aqueous activity on the parent body similar to the Ca depletions observed in other hydrated meteoritic materials. In contrast to GEMS grains, the meteoritic amorphous silicates are  $\sim$  solar with respect to Fe (bulk Acfer 094 has Fe/Si  $>$  solar). The higher Fe/Si and depleted S/Si ratios are consistent with parent body oxidation reactions. EELS measurements show that the Fe oxidation state in the meteorite amorphous silicates is a mixture of  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$ , with  $\text{Fe}^{3+}$  contents ranging from 50 to  $\sim 90\%$ . In contrast, EELS spectra from GEMS grains in IDPs show only  $\text{Fe}^0$  and  $\text{Fe}^{2+}$  [2]. Unlike most GEMS grains, all of the matrix nodules contain excess oxygen above that required for stoichiometry, which is consistent with substantial hydration of their silicate matrices. The OH/ $\text{H}_2\text{O}$  is not lost to the high vacuum of the TEM and so must be relatively tightly bound perhaps as structural OH.

Infrared transmission spectra of Acfer 094, QUE99177 and MET00426 matrix all show a strong 3  $\mu\text{m}$  O-H absorption feature that is consistent with gel-like hydrated silicates. High-resolution TEM images however, show a paucity of crystalline phyllosilicates in Acfer 094, while pockets of serpentine are common but heterogeneously distributed in the two CR chondrites. There are strong chemical and mineralogical similarities between the amorphous silicates in the meteorite matrix fragments and experimentally hydrated GEMS grains [11].

The average O isotopic compositions of GEMS grains have recently been shown to be close to terrestrial composition ( $\delta^{17}\text{O} = -16.1 \pm 25\text{‰}$ ,  $\delta^{18}\text{O} = -2.3 \pm 8\text{‰}$ ;  $2\sigma$ ) [2]. In situ ion microprobe analyses of Acfer 094 matrix also cluster around terrestrial [12] as do the whole rock data for the CR 3.0 chondrites [13]. Overall, the oxygen isotopic compositions of most (>90%) GEMS grains and amorphous silicate material in primitive meteorites suggest they formed from the same isotopic reservoir in the inner Solar System. Brearley [6] suggested that the amorphous silicates in ALH 77307 matrix were non-equilibrium condensates that formed prior to accretion. Similarly, others have also proposed a non-equilibrium condensation origin for the amorphous silicates in the CR 3.0 chondrites [8] and for GEMS in IDPs [2]. Bradley [14] suggested that GEMS grains were preserved interstellar amorphous silicates, but the majority of GEMS grains and the amorphous silicates in primitive meteoritic materials analyzed here have markedly different chemical and isotopic properties than those inferred for average interstellar silicate grains [2].

The large range in circumstellar silicate abundances among CP IDPs (300 to > 10,000 ppm) is attributed to pre-accretional thermal processing in the early solar nebula [15]. Presolar silicates are less abundant in the primitive carbonaceous chondrites (~100-200 ppm) than IDPs, likely because of parent body aqueous processing.

**Conclusions.** The precursors of the amorphous silicates in the matrices of Acfer 094, QUE 99177 and MET 00426 were likely GEMS-like grains whose Fe metal was oxidized and silicate matrices were hydrated during parent body processing. The amount of aqueous activity was sufficient to homogenize the silicate compositions and leach Ca and S, but not to produce abundant phyllosilicates. The aqueous processing is also likely to have destroyed some presolar silicates. As with the cometary amorphous silicates, the meteoritic amorphous silicates are chemically distinct from interstellar dust grains.

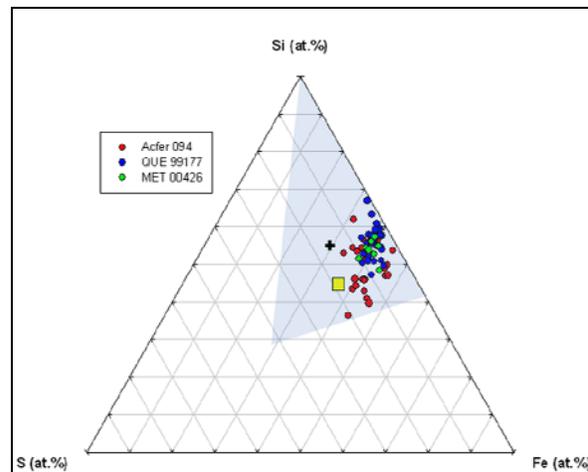
**References.** [1] Keller, L. P. and Messenger, S. (2005) *ASPC Series* 341, 657. [2] Keller, L. P. and Messenger, S. (2011) *GCA* 75, 5336. [3] Floss, C. *et al.* (2002) *GCA* 70, 2371. [4] Nguyen, A. *et al.* (2007) *LPSC XXXVIII*, #2332. [5] Bradley, J. P. (1994) *GCA* 58, 2133. [6] Brearley, A. J. (1993) *GCA* 57, 1521. [7] Greshake, A. (1997) *GCA* 61, 437. [8] Abreu, N. and Brearley, A. J. (2010) *GCA* 74, 1146. [9] Keller, L. P. *et al.* (2009) *MAPS* 44, #5371. [10] Keller, L. P. and Messenger, S. (2009) *LPSC XV*, #2121. [11] Nakamura-Messenger, K. *et al.* (2011) *MAPS* 46, 843. [12] Sakamoto, N. *et al.* (2007) *Science* 317, 231. [13]

Schrader, D. S. *et al.* (2011) *GCA* 75, 308. [14] Bradley, J. P. (1994) *Science* 265, 925. [15] Messenger, S. *et al.* (2009) *MAPS* 44, #5357. [16] Lodders, K. and Palme, H. (2009) *MAPS* 44, #5154.

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**TABLE 1.** Chemical composition (element/Si in at.%) of GEMS grains [2] and amorphous silicates in primitive chondrite matrices compared to Solar abundances [16]. (MET=MET 00426, Acfer=Acfer 094 and QUE=QUE 99177.

<i>El/Si</i> (at.%)	<i>O</i>	<i>Mg</i>	<i>Al</i>	<i>S</i>	<i>Ca</i>	<i>Fe</i>	<i>Ni</i>
GEMS	3.30	0.67	0.07	0.30	0.04	0.56	0.03
MET	4.10	0.43	0.07	0.12	0.01	0.75	0.04
Acfer	4.99	0.48	0.07	0.15	0.05	0.98	0.05
QUE	4.39	0.53	0.06	0.08	0.01	0.85	0.05
Solar		1.03	0.09	0.42	0.06	0.85	0.05



**Figure 1.** Chemical compositions of amorphous silicates in the matrices of Acfer 094, QUE 99177 and MET 00426. The shaded region is the compositional field for GEMS grains in IDPs with the average indicated (+) [2]. The yellow square is the solar composition.