

THE GLUE THAT HOLDS WORLDS TOGETHER: ABUNDANCE, ORIGIN & SIGNIFICANCE OF AMORPHOUS Fe,Mg SILICATE IN CARBONACEOUS CHONDRITES. K. T. Howard^{1,2}, J. Davidson³, C.M.O'D. Alexander³ and N. M. Abreu⁴. ¹Kingsborough Community College. ²American Museum of Natural History. ³Department of Terrestrial Magnetism, Carnegie Institute of Washington. ⁴Earth Science Program, Penn State DuBois. Email: khoward@amnh.org.

Introduction: X-ray and crystallographically amorphous Fe,Mg silicates, located in matrix, distinguish primitive chondrites from those that were significantly altered in asteroids and planets [1]. By understanding the origin of amorphous Fe,Mg silicates, we can explore the origin of matrix, the material that bound chondrules together to form planetesimals and we can contribute a mineralogical perspective on the chemical relationship between chondrules and matrix. Position sensitive detector X-ray diffraction (PSD-XRD) allows us to quantify the abundance of amorphous Fe,Mg silicates, transmission electron microscopy (TEM) provides us with images, structural constraints and compositional data. With PSD-XRD large sample volumes can be studied, enabling us to constrain how representative the TEM observations are. Amorphous Fe,Mg silicate appears to have been the main component of the pristine matrix. Abundance and compositional data indicate that after extraction of Mg-rich components to form chondrules, amorphous silicate quenched from the residual of a single, chondritic, reservoir.

Sample selection: Targeted for quantification of modal abundances were samples of carbonaceous chondrites (CCs) that TEM studies [e.g., 2,3,4] show contain amorphous silicates in their matrices, ALHA 77307 (CO), Acfer 094 (C2-ung) and Adelaide (C2-ung). We also report on an additional CR (MIL 090657) and 2 CO (MIL 090073, MIL 090010) samples from the Antarctic collection that we have determined are low petrographic types. These data are in addition to abundances determined for another set of COs [8] and CRs, including MET 00426 and QUE 99177 [5], which have been studied extensively by TEM [6,7].

Methods: Abundances of phases present in amounts >1 wt.% are determined by PSD-XRD, using a pattern fitting technique [5]. In addition to crystalline phases, we are able to quantify the total abundance of Fe-bearing X-ray amorphous material [5]. Modal determinations are for 100 mg aliquots of larger of powdered samples.

Results: The mineralogy of Acfer 094 is approximated as olivine (37 vol.%), pyroxene (31 vol.%), sulfides (3.1 vol.%), Fe,Ni-metal (1 vol.%) and Fe-bearing X-ray amorphous material (26 vol.%). ALHA 77307 is estimated to contain olivine (35 vol.%), py-

roxene (36 vol.%), sulfides (2.2 vol.%), Fe,Ni-metal (1.3 vol.%) and Fe-bearing X-ray amorphous material (16 vol.%). In Adelaide we resolve olivine (32 vol.%), pyroxene (45 vol.%), sulfides (4 vol.%), Fe,Ni-metal (<0.5 vol.%) and Fe-bearing X-ray amorphous material (16 vol.%). Olivine compositions are heterogeneous and range from Fo100-Fo40, the main population of olivine is forsterite (>Fo90). In Acfer 094 and ALHA 77307, there are roughly equal parts enstatite and clinoenstatite. In the new CR and CO samples studied here, the abundance of Fe-bearing amorphous material (11-23 vol.%) is similar to the CRs, QUE 99177 (15 vol.%) and MET 00426 (25 vol.%) [5] and also to the type 3.0 CO samples reported previously [8].

Identifying amorphous Fe-Mg-silicate. Amorphous materials in CCs are not restricted to Fe,Mg silicates, Fe-oxides, FeO(OH), \pm H₂O and sulfides can also be X-ray amorphous. In addition, the amorphous silicate is not a homogenous material. Extensive TEM studies of CR and CM matrix show that it is variably hydrated and contains nano-crystallites of many different phases, along with organics [6,7]. Even though we are careful to study interior chips from samples with low weathering grades, rusts may represent a component of the Fe-bearing amorphous material that we resolve, but petrography excludes its presence in amounts as large as 25 vol.%. Petrography and CC bulk and matrix compositions also exclude 25% of the bulk sample mineralogy from being amorphous sulfide. Therefore, we can be confident that the majority of amorphous material that we detect is Fe,Mg silicate.

Petrographic context. Chondrules also contain glassy, mesostasis material, most often its composition is similar to plagioclase [9]. With a maximum FeO content of a few percent [9], chondrule mesostasis will not contribute significantly to residual X-ray counts from fluorescence. This gives us confidence that the majority of amorphous Fe,Mg silicate that we detect by XRD is in matrix (including fine grained rims on chondrules), consistent with TEM [6]. If it is assumed that all of the detected amorphous Fe,Mg silicate is in matrix, the proportion of matrix that is amorphous Fe,Mg silicate is determined to range from 30-80 vol.%.

Discussion: Since first studied by TEM, matrix in the most primitive meteorite samples (e.g., Acfer 094) has been described as dominated by amorphous mate-

rials [2,3,6,7]. Quantifying the abundance of amorphous silicates magnifies the significance of the TEM observations and the need to explain this material.

Mg/Si and the origin of amorphous Fe,Mg silicate. In Fig. 1, amorphous Fe,Mg silicate defines a trend connecting the Mg/Si composition of average bulk chondrules with that of average matrix, the average matrix Mg/Si composition being approximately equal to that of average amorphous silicate. If Mg-rich components in chondrules are first to crystallize, extracting Mg from the bulk reservoir, the composition of the residual would evolve along a path towards Mg-depletion (i.e., fayalite), as the trend defined by the amorphous Fe,Mg silicate compositions does.

Chemical relationship to chondrules. Amorphous silicates have sub-chondritic Mg/Si ratios. In Fig. 1, a linear mixing line has been constructed between average chondrules (super-chondritic Mg/Si) and average amorphous silicate. Addition of 25-30 wt.% amorphous Fe,Mg silicate (\leq the upper limit of the amounts detected), to the bulk chondrule compositions [10], gives a chondritic bulk Mg/Si ratio, but at higher absolute Mg and Si abundances than measured for bulk CR and CO samples [10]. However, these bulk chondrule data are only for silicates and the bulk rock data includes Fe from metal and sulfide in matrix [10]. Therefore, only the Mg/Si ratio can be used to explore evidence for a genetic relationship [10].

The Mg/Si ratios suggest that amorphous silicates formed in the nebula by the same type of heating event that formed chondrules. This interpretation appears contrary to available O-isotopic data from pristine CR matrix [11], but we are not suggesting that all matrix materials are by-products of chondrule formation. Matrix is a mixture of materials from different origins, including phases (i.e., organics, presolar grains) that did not undergo the kind of high-temperature processing that formed chondrules. The conclusion that pristine CR matrix is a distinct component, formed separately from chondrules [11], is based on one of three bulk matrix analyses for QUE 99177 plotting outside the field of type I chondrules. In light of the diverse origins of matrix, the fact that not all matrix O-isotope analyses are collinear with type I chondrules is not surprising and does not necessarily place constraints on the origins of individual matrix components.

Secondary processing of amorphous silicates. Amorphous Fe,Mg silicate was initially assumed to be highly reactive to water [6]. However, TEM shows that amorphous silicate still exists in the matrices of highly altered samples, including the CM2 samples Y 791198 [12] and Paris [13] and the CR1 GRO 95577 (this study). This may be explained by experiments showing that high Fe content \neq high reactivity [14]. Structurally

bound OH may also stabilize the material in the presence of fluid [7]. In the event of its hydration, amorphous Fe,Mg silicate is predicted to form Fe-serpentine [6]. CM2 chondrites contain ~ 35 vol.% Fe-serpentine, this could be produced by hydration of ~ 20 vol.% amorphous silicate (assuming a 40% increase in volume results from hydration). Thermal metamorphism of amorphous Fe,Mg silicate can form ferrous olivine [15]. Thermally metamorphosed samples, e.g., CVs, contain between 14-28 vol.% ferrous olivine ($< \text{Fo}_{60}$) [16]. These values agree closely with the bulk abundance of amorphous Fe,Mg silicate in pristine samples. Overlapping Mg/Si ratios in all of these phases mean that speculated alteration pathways would preserve the primary sub-chondritic Mg/Si ratio of amorphous silicate, provided that mobilization of Mg and Si was limited [c.f., 17].

Conclusion: Abundant amorphous Fe,Mg silicate is not a just feature of anomalous primitive meteorites [1], it is a signature of type 3.0 matrix. At the onset of CC accretion, amorphous Fe,Mg silicates must have dominated the fine-grained material. Therefore, we must not only ask what nebular processes formed mafic chondrule phenocrysts, but also under what nebular conditions crystal growth was inhibited.

References: [1] Nuth J. A. et al. (2005) *Chondrites and the Protoplanetary Disk*, 675–700. [2] Greshake A. (1997) *GCA* 61, 437–452. [3] Brearley A. J. (1993) *GCA* 57, 1521–1550. [4] Brearley A. J. (1991) *LPS* 22nd, p. 133. [5] Howard K. T. et al. (2015) *GCA* 149, 206–222. [6] Abreu N. M & Brearley A. J. (2010) *GCA* 74, 1146–1171. [7] Le Guillou C. & Brearley A. J. (2014) *GCA* 131, 344–367. [8] Howard K. T. et al. (2014) *LPS* 45th Abstract #1830. [9] Kurahashi E. et al. (2008) *GCA* 72, 3865–3882. [10] Hezel D. C. & Palme H. (2010) *EPSL* 294, 85–93. [11] Schrader D. et al. (2014) *EPSL* 407, 48–60. [12] Chizmadia L. J. & Brearley A. J. (2008) *GCA* 72, 602–625. [13] Hewins R. H. et al. (2014) *GCA* 124, 190–222. [14] Chizmadia L. J. et al. (2006) *LPS* 37th, Abstract #2187. [15] Huss G. R. et al. (2006) *MESS* 2, 567–586. [16] Howard K. T. et al. (2010) *GCA* 74, 5084–5097. [17] Bland P. A. et al. (2005) *PNAS* 102, 13755–13760.

