

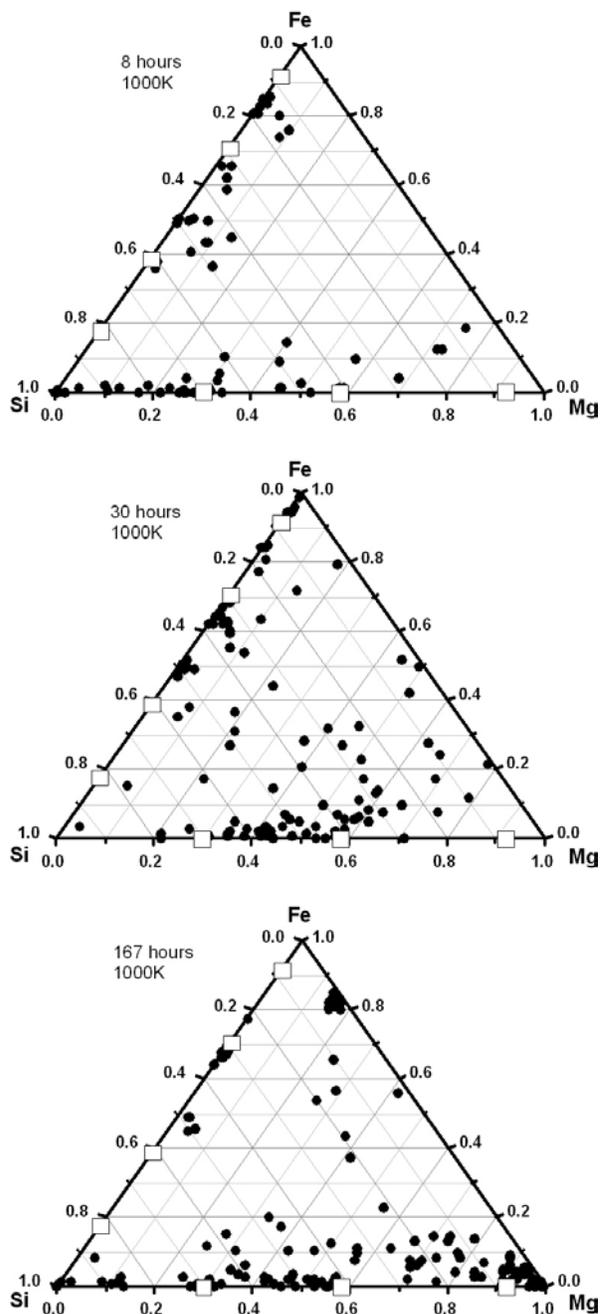
**MAKING AMORPHOUS FERROMAGNESIOSILICA AND METASTABLE MAGNESIOFERRITE AND FAYALITE.** Frans J. M. Rietmeijer<sup>1</sup>, A. Pun<sup>1</sup> and J. A. Nuth<sup>2</sup>, <sup>1</sup>Dept of Earth and Planetary Sciences, MSC3-2040, University of New Mexico, Albuquerque, NM 87131-0001, USA (fransjmr@unm.edu), <sup>2</sup>Astrochemistry Laboratory, Solar System Exploration Division, Code 691, NASA Goddard Space Flight Center, Greenbelt, MD 20771, USA.

**Introduction:** Vapor phase condensation in dynamic environments, *e.g.* a turbulent solar nebula, is not without kinetic effects. Laboratory experiments showed that amorphous Mg,Fe-silicates cannot be formed by vapor phase condensation under non-equilibrium conditions. Still, crystalline Mg,Fe-olivine and Mg,Fe-pyroxene could equilibrate from amorphous precursors. When vapor phase condensation is a dominant process, the formation of amorphous Mg,Fe-silicates will require coagulation of condensed deep metastable eutectic (DME) nanograins during a continuous process of chemical evolution that include:

- (1) Mixing and coagulation of amorphous DME magnesiosilica and ferrosilica condensates that will yield amorphous low-Fe [ $\text{Fe}/(\text{Fe}+\text{Mg}) = 0-0.35$ ] ferromagnesiosilica grains [1], and
- (2) (continued) Mixing and coagulation of these amorphous low-Fe ferromagnesiosilica grains and high-Fe DME condensate nanograins. The resulting ferromagnesiosilica grains will have  $\text{Mg}/(\text{Mg}+\text{Fe}) < 0.65$  [2,3],
- (3) Post-condensation mixing and coagulation of condensed DME and chemically evolved amorphous magnesiosilica nanograins and iron or Fe-oxide nanograins that allows formation of Mg,Fe-oxides [1,3].

Condensation of Mg-Fe-SiO<sub>2</sub>-H<sub>2</sub>-O<sub>2</sub> vapors also produced pure SiO<sub>2</sub> and very low-silica, MDE magnesiosilica and ferrosilica nanograins [3]. The compositions of the latter are very close to eutectic periclase and Fe-oxide compositions in the MgO-SiO<sub>2</sub> and SiO<sub>2</sub>-Fe-oxide systems. This condensation process cannot produce Mg,Fe-oxides.

**Annealing experiments:** In these thermal annealing experiments at 1000K samples of condensed magnesiosilica smokes with trace amounts of an iron-oxide were heated for 8, 30 and 167 hours [4] (Fig 1a-c). At 8h the amorphous DME magnesiosilica and iron oxide grains had reacted with SiO<sub>2</sub>. Very few DME magnesiosilica grains survived. Newly formed Fe-rich ferrosilica grains coagulated and reacted with magnesiosilica grains. This process continued at 30 and 167h. After 30 hours mixed Mg,Fe-oxide grains appeared. Most grains remained amorphous but a small fraction that had obtained a stoichiometric mineral composition equilibrated and formed fine-grained olivine, tridymite and maghémite and at 167h a cluster of magnesioferrite single-crystal nanocrystals had formed (Table 1). The grain sizes increased with annealing times.



**Figure 1a-c [top to bottom]:** Individual grain analyses (el%) [dots] in thermally annealed samples of mixed condensed magnesiosilica smokes and FeO grains (option 3) at 1000K for 8 (1a), 30 (1b) and 167 (1c) hours. Squares denote deep metastable eutectic compositions. All smoke samples contained silica. Some smokes contained only few MgO nanograins.

**Table 1: Minerals formed in annealed mixtures of magnesian silicas and Fe-oxide grains at 1000K for 8, 30 and 167 hours; nd: not detected because of sample heterogeneity, which is not unusual [5]**

8h	30h	16h
Forsterite	Forsterite	Forsterite
Tridymite	Tridymite	Tridymite
	Fayalite	Fayalite
nd	Maghémite	nd
nd?	nd	Periclase
	(Mg,Fe)oxide	Magnesian ferrite

There is no evidence for ferrosilite ( $\text{FeSiO}_3$ ). Magnesian ferrite,  $\text{MgFe}_2\text{O}_4$ , has  $\text{Fe}/(\text{Fe}+\text{Mg}) = 70$ .

**Discussion:** The compositions of amorphous ferromagnesian silicas grains that evolved chemically from magnesian silica and ferrosilica vapor phase condensates (options 1 & 2) will be different from those that evolved by option 3. Only option 3 would allow early nucleation of pure fayalite (no evidence was found for ferrosilite) and magnesian ferrite. Chemical evolution of nanograins condensed from Mg-Fe-SiO-H<sub>2</sub>-O<sub>2</sub> vapors cannot yield Mg,Fe-oxides [1,2]. These experiments were conducted to confirm qualitatively the notion of nanograin mixing and coagulation, which they did. The small grain sizes suggest that surface free energies still support the metastable existence of these crystalline solids, though small solids are unstable to growth through coagulation.

The process did not reach its logical end with the formation of a homogeneous amorphous ferromagnesian silica grains matching those (>90 nm) in chondritic aggregate IDPs. The transformation of dust agglomerates to zero-porosity amorphous grains is unknown but the metastable dust would facilitate the process. The calculated average composition (at%) of all grains is very close to their CI value (Table 2).

**Table 2: Comparison of the calculated average composition of the data in Fig. 1 and the solar composition**

	Calculated	CI
Si	41	33.6
Mg	38	36.1
Fe	21	30.3

**Implications for Comet P/Halley:** The bulk composition of its nanometer dust fraction is slightly more Si-rich than CI [6]. A small but significant fraction of its grains had low-Si (Mg,Fe) compositions [6] that could be periclase (or brucite) [7] and Fe (metal or oxide) grains [6]. The annealed samples (30 and 167h) included periclase and maghémite nanograins (Table 1) in a “bulk sample” with a slightly Si-rich CI

composition. The similarities suggest that the comet Halley nanograins are coagulated mixtures of condensed nanometer magnesian silica and Fe-metal and/or Fe-oxide grains. The low-Si, (Mg,Fe) grain compositions in the comet did not include magnesian ferrite from a reaction between periclase and maghémite. This reaction occurs at 600 °C [8] and could not occur in the icy nucleus. Nanocrystalline magnesian ferrite occurred in CM-like IDP L201103 [9]. The annealing experiments suggest that this spinel might be metastable which could facilitate its formation in a hydrous CM parent body environment.

**Implications for Fayalite:** Fayalite formed after 30h annealing at 1000K by reacting maghémite with condensed silica in the right stoichiometric proportions in the samples. Equilibrium solar nebula models for fayalite-rich olivine (Fa = 60-90) formation are not viable but kinetic models with high  $f\text{O}_2$  values due to dust enrichments of 50 to 500 times greater than the solar dust/gas ratio might work [10] but it is not clear condensation would produce pure fayalite. The annealing experiments suggest that (metastable) fayalite might form during parent body alteration.

**Conclusions:** In an ongoing effort to study the formation of the most common amorphous and crystalline astronomical silicates, we conducted a few simple non-equilibrium thermal-annealing experiments. In these experiments magnesian silica condensates reacted with pure Fe-oxide grains to magnesian ferrite that compositionally match Fe<sub>2</sub>O-nanograins, which in comet Halley may be magnesian wustite. Either way, neither are primary condensates. The annealing experiments confirmed that the formation of amorphous ferromagnesian silicates requires a combination of vapor phase condensation and post-condensation coagulation with chemical evolution of increasingly larger grains.

**References:** [1] Rietmeijer F. J. M. (2000) *Chemie der Erde*, 62, 1-45. [2] Rietmeijer F. J. M. (1998) *Rev. Mineral.*, 36 (J. J. Papike, ed.), 2, 1-95. [3] Nuth III, J. A. et al. (2000) *JGR.*, 105(A5), 10,387-10,396. [4] Fu G. and Rietmeijer F. J. M. (1994) *LPS XXV*, 493-494. [5] Rietmeijer F. J. M. et al. (2002) *PCCP*, 4, 546-551. [6] Jessberger E. K. et al. (1988) *Nature*, 332, 691-695. [7] Fomenkova M. N. et al. (1992) *Science*, 258, 266-269. [8] Azhari A. et al. (2010) *Mat. Chem. Phys.*, 124, 658-663. [9] Rietmeijer F. J. M. (1996) *Meteoritics & Planet. Sci.*, 32, 278-288. [10] Rubin A.E. et al. (1988) *MESS* (Kerridge J. F. & Matthews M. S., eds), 488-511, Univ Arizona Press. FJMR was supported by Cosmochemistry grant NNX10AK28G (PI; J.A. Nuth)