

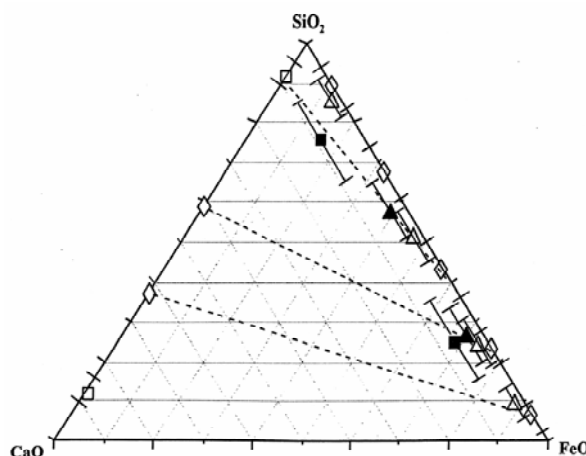
**REFRACTORY DEEP METASTABLE EUTECTIC VAPOR PHASE CONDENSATES EVOLVE TO AMORPHOUS, BUT NOT QUITE, EQUILIBRIUM MINERALS.** Frans J. M. Rietmeijer<sup>1</sup>, Aurora Pun<sup>1</sup>, Joseph A. Nuth III<sup>2</sup> and Yuki Kimura<sup>3</sup>, <sup>1</sup>Department of Earth and Planetary Sciences, MSC03-2040, 1-University of New Mexico, Albuquerque, NM 87131-0001, USA, <sup>2</sup>Astrochemistry Laboratory, Solar System Exploration Division, Code 691, NASA Goddard Space Flight Center, Greenbelt, MD 20771, USA, <sup>3</sup>Laboratory for Nano-Structure Science, Department of Physics, Ritsumeikan University, 1-1-1 Nojihigashi, Kusatsu-shi, Shiga, 525-8577, Japan.

**What's the problem?:** Solar nebula condensation is traditionally described as an equilibrium process that produces discrete well-ordered solids with a stoichiometric composition. Their nature and relative appearances (sequential or not) is a function of pressure, temperature, C/O ratios and activities of the condensing gas phase species of stoichiometric mineral compositions. Variants exist on the nature of the condensing species such as simple metal-oxides. It is likely that there were kinetic factors that would effectuate non-equilibrium condensation as an important, if not dominant, process. De [1] introduced the notion of non-equilibrium nebula condensation that leads to the formation of solids with the properties of dissipative structures wherein extreme disorder becomes a new (metastable) state of matter. This particular condensation behavior systematically occurs in our vapor phase condensation experiments and leads to the formation of nanometer amorphous solids with a deep metastable eutectic (DME) composition [2,3]. Non-equilibrium processes should not exclude the possibility of forming well-ordered stoichiometric solids (minerals) but probably through intermediate 'amorphous minerals'. There must be pathways for non-equilibrium compounds to evolve to solids that are identical to the predicted equilibrium solar nebula condensates. The meteorite record is inconclusive on specifics of solar nebula condensation but some of the predicted equilibrium mineral condensates are amazingly prolific around many young stars [4], in aggregate IDPs [5,6] and in comet Wild 2 [7,8]. *Yet, we don't know whether they formed as equilibrium phases or whether they evolved from non-equilibrium condensates.*

**'Amorphous silicates':** We submitted that post-condensation chemical dust evolution involves the aggregation of condensates with DME compositions to form larger grains with compositions in between the DME end-members of a mixing line. Likely compositions will be found at intersections of two or more mixing lines. This mixing of DME compounds can be exclusive. For example, mixing in the MgO-FeO-SiO<sub>2</sub> system is limited to FeO-poor, slightly silica-rich, ferromagnesian silicate grains [2,6]. It can be inclusive, e.g. mixing of DME condensates ultimately produced 'huge' (~400nm) amorphous 'FeAlSiO' compounds with a stoichiometric Fe-cordierite composition [9],

i.e. a chemically complex 'amorphous silicate'. Mixing lines occur between DME compositions on opposite sides of a ternary diagram. They were postulated to bring systematic order in the observed ternary grain composition distributions.

**Here we report the first observational evidence for a mixing process of DME condensates** produced using the Condensation Flow Apparatus (CFA) and characterized by high-resolution TEM and energy dispersive spectroscopy analyses [2,3,9] (Figure 1).

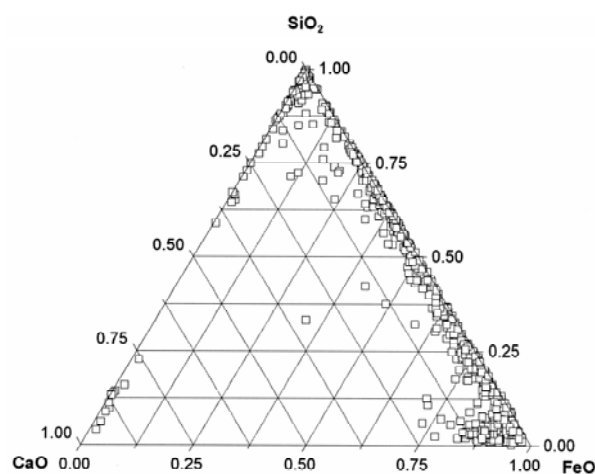


**Figure 1:** CaFeSiO mixing lines (dashed) in the CaO-FeO-SiO<sub>2</sub> (pseudo) ternary diagram between the observed CaSiO DME and FeSiO DME compositions (open diamonds; open squares only single data) that include the low-silica CaFeSiO grain populations #2 (open triangles) and #3 (solid triangles) and both high-CaO CaSiO population #4 (solid squares). Error bars are the one-std. deviation range. These DMEs match the previously determined ferrosilica [10] and calcisilica [3] DME compositions. Properly, the Fe-oxide should be listed as 'FeO' in recognition that condensation and autoannealing occurred at high ferrous/ferric iron ratios.

**Autoannealing:** Conceptually we define two regimes in a condensation experiment: nucleation/growth & autoannealing of grains settling through the vapor and settled on the collector inside the CFA. Autoannealing allows condensate growth with concomitant deviations from DME compositions. It is an integral part of the condensation experiment occurring during dissipation of thermal energy from the solids and vapor, including heat of condensation, while cooling to the collector temperature. This unavoidable ex-

perimental artifact when using the same CFA for all our experiments is mostly constrained by the difference between the vapor and collector temperatures. The difference is larger for refractory vapors than in the previous Mg-Fe-SiO-H<sub>2</sub>-O<sub>2</sub> vapor phase condensation experiments. Thus, CaSiO condensate grains are on-average larger (~60nm), and are more evolved chemically, than those from Mg-Fe-SiO-H<sub>2</sub>-O<sub>2</sub> vapors (~25nm). These unavoidable modifications can be exploited to trace the earliest chemical evolution.

**Refractory vapor condensation:** We report new data for a Ca-Fe-SiO-H<sub>2</sub>-O<sub>2</sub> vapor phase condensation experiment. The average of all analyzed grains, SiO<sub>2</sub> = 46 wt%, FeO = 50 wt% and CaO = 4 wt%, represents the bulk smoke composition and is a proxy of these oxide abundances in the vapor. This bulk composition resembles the Orgueil meteorite for these oxides.



**Figure 2:** The CaO-FeO-SiO<sub>2</sub> (pseudo) ternary diagram showing the compositions of 733 individual condensate grains that include both DME and evolved grain compositions. A cluster in the FeO corner includes a calciowüstite DME condensate (*in prep.*). Evolved CaSiO and FeSiO grain populations exist between DME populations.

Individual grain compositions are concentrated on the FeO-SiO<sub>2</sub> join between zero and 5-wt% CaO (Figure 2). These compositions include four groups, and each group has two or more different populations identified by their mean compositions (Figure 1):

- (1) CaO-free grains (335 grains), 5 populations of DME condensates,
- (2)  $1.5 \leq \text{CaO} < 3$  (80 grains), 4 populations,
- (3)  $3 < \text{CaO} \leq 5$  (27 grains), 2 populations, and
- (4) 6 and 9-wt% CaO, 15 grains equally distributed between two populations.

When ternary-oxide compositions evolved along mixing lines between DME compositions that could cross to either one of the binary joins, the shifts in the

SiO<sub>2</sub>/FeO ratios from groups 1 to 4 show how CaFe-SiO grains evolved between FeSiO and CaSiO condensates (Figure 1). Starting at the FeSiO DME condensate compositions FeO = 56 and 76-wt%, the mean compositions of groups #2, #3 and #4 are on a straight line that, according to the prediction, should intersect the CaO-SiO<sub>2</sub> join at the CaSiO DME compositions of CaO = 8 and 41-wt% CaO, respectively (Figure 1). It is indeed the case! A mixing line between the ferrosilica and calciosilica DMEs at 93-wt% FeO and 63-wt% CaO, albeit less constrained, is also as predicted.

**Discussion:** As expected, the low-CaO bulk content means a much lower abundance of pure CaSiO grains than FeSiO condensates but scarcity of CaSiO condensates also reflects their assimilation in evolving low-Ca FeSiO grains. There are no mixing lines between intermediate FeSiO and CaSiO grain populations reflecting the limited extent of autoannealing in this condensation experiment [*in prep.*].

**Conclusions:** The concept that ternary condensate grain compositions evolve along mixing lines between DME condensates is proven correct. Intersections of mixing lines will be favorable ternary compositions that will include ‘*amorphous silicates*’. In the (pseudo) ternary CaO-‘FeO’-SiO<sub>2</sub> system they will be amorphous compounds such as stoichiometric hedenbergite, CaFeSi<sub>2</sub>O<sub>6</sub>, or kirschsteinite, CaFeSiO<sub>4</sub>, compositions (the grain below the center of Fig. 2 is consistent with this olivine). Both silicates occur in CV meteorites wherein their origins, e.g. nebular or parent body processing, are uncertain [11,12].

Such minerals existing as ‘*amorphous silicate*’ precursors in meteorites, IDPs and in comet Wild 2 would not necessarily imply thermodynamic stability during their formation.

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