EXPERIMENTAL CONFIRMATION OF DEEP METASTABLE EUTECTIC VAPOR CONDENSATION IN ASTRONOMICAL ENVIRONMENTS AND THE SOLAR NEBULA. F. J. M. Rietmeijer¹, A. J. Brearley¹, and J. A. Nuth², ¹Department of Earth and Planetary Sciences, 1-University of New Mexico, MSC3-2040, Albuquerque, NM 87131-0001 USA, ²Astrochemistry Laboratory, Solar System Exploration Division, NASA Goddard Space Flight Center, Code 69, Greenbelt, Maryland 20771, USA.

Introduction: This work confirms our hypothesis that refractory grains will condense from a vapor phase. This conclusion is especially important for the formation of refractory materials in astrophysical environments and the solar nebula [1, 2]. It is a major step in establishing a simple, chemical kinetic model for nucleation, growth, and annealing of circumstellar oxide dust [3]. Our vapor phase condensation experiments found that the condensed matter (called smokes) are unique nanograin condensates with Deep Metastable Eutectic compositions (DME) as is illustrated in the hypothetical phase diagram A-B with two eutectics [Fig.1] [4]. DME nanograins are the defining phenomenon in these vapor phase condensation experiments.

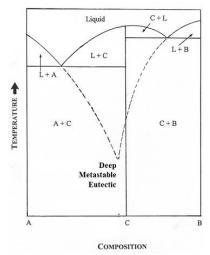


Fig. 1: When equilibrium phase boundaries (solid lines) are extended towards lower temperatures (dashed lines) they will intersect at the intermediate composition "AB." AB is the composition of a deep metastable eutectic compound. The hypothetical binary equilibrium phase diagram A-B showing the position of a deep metastable eutectic with composition "AB" defined at the intersect of metastable extensions of the liquidus surface (dashed lines) and located in between compositions of both eutectic points on the liquidus surface (solid lines).

Fe-Mg-(Ca-Al)-SiO-H vapors

These vapor phase condensation experiments systematically yielded nanograins, 10 to 15 nm in size, with X-Si-O (X: Mg, Fe, Al, Ca) DME compositions [5,

6, 7] [Table 1]. They also showed that the DME grains condensed in refractory Ca-SiO-H₂-O₂ vapors, *i.e.* Ca-Si-O and Ca-Fe-Si-O smokes [8], are much larger, and have more variable grain size ranges [Table 1]. Formation of these Ca-bearing smokes required longer quench times or higher temperatures than the (Mg,Fe-O) smokes.

Table 1: DME grain size and range of the smallest grain population in vapor phase condensed smokes.

System	Grain size (nm)	
	DME	Range
Mg-Si-O	~1	1 - 15
Fe-Si-O	~5	2 - 35
Al-Si-O	~7	7 - 12
Al-Fe-Si-O	5	5 - 30
Fe-Al-O	2	2 - 25
Ca-Si-O	20	20 - 60
Ca-Fe-Si-O	16	16 - 27

Fe-Mg-Al-O-H vapors

The primary condensates from these refractory smokes, *viz.* (*1*) Al-Mg-Ox, (2) Al-Fe-Oy and (3)Al-Mg-Fe-Oz, were pure amorphous Al-Mg and Al-Fe-aluminates. As expected, there were no mixed Fe-Mg-spinel as primary condensates even though FeO-MgO miscibility applies to this system [9].

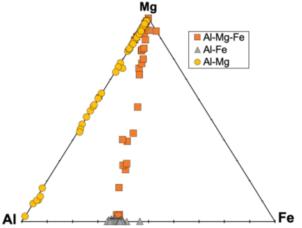


Fig 2. Ternary diagram of Al-Mg-Fe (at.% element) compositions of condensed smokes: (1) Al-Mg (yellow

circles), (2) Al-Fe (grey triangles), and (3) Al-Fe-Mg (orange squares).

The condensed nanograin compositions are presented in a ternary Mg-Al-Fe diagram, viz. Al-Mg (orange circles), (2) Al-Fe (grey triangles), and (3) Al-Fe-Mg (squares) (Fig. 2).

The smokes are mostly open aggregates of tangled chains of numerous individual nanograins. Most nanograins in these smokes are probably amorphous. The Al-Mg and Al-Fe condensate grains are mostly ~10 nm in size but (mixed?) Fe-Mg-Al grains are somewhat larger [9].

Al-Mg smoke

The MgO-Al₂O₃ phase diagram has two eutectics to allow for a DME composition at ~50 at.% within the intermediate grain cluster along the Al-Mg join (Fig. 2, circles). The MgO-Al₂O₃ (wt.%) phase diagram [10] with two eutectic points at 50 wt.% and ~90 wt.%, meets the condition for a DME at ~70 wt.% (Fig. 3). Coincidentally it "overlaps" the MgAl₂O₄ (i.e. spinel) composition, i.e. this condensate is amorphous MgAl₂O₄ spinel. The elongated cluster of high-Mg condensates (Fig. 3) are amorphous MgO_x nanograins. A similar cluster of amorphous eutectic Al₂O₃ nanograins with compositions close to corundum is also present.

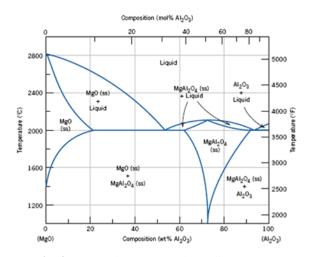


Fig. 3: MgO-Al₂O₃ (wt%) phase diagram [10].

Al-Fe smoke

The Al-Fe nanograin compositions form an elongated cluster with a single outlier [Fig. 2]. The FeO-Al₂O₃ phase diagram (Fig.4) has two eutectic points with the possibility of a DME that is close to the FeAl₂O₄ composition. These nanograins are most likely amorphous hercynite.

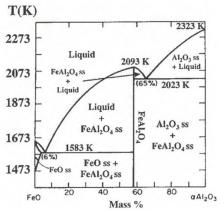


Fig. 4: FeO-Al₂O₃ phase diagram[11]

Al-Fe-Mg smoke

These amorphous MgO-(FeO.Al₂O₃) grains (Fig. 2), when in crystalline form would be immiscible but there is no known mineral matching this composition.

Conclusions: These experiments demonstrate that amorphous, metastable nanophase Al-Mg-Fe condensates could form from a gas phase due to rapid quenching in the solar nebula. Our work confirms that under these highly disequilibrium conditions, the metastable condensates have compositions consistent with deep metastable eutectics based on binary phase diagrams.

References: [1] Nuth J. A. and Donn B. (1982) Astrophys. J., 257, L103-L105. [2] Nuth J. A. and Ferguson F. (1993) Ceramic Trans., 30, 23-34. [3] Rietmeijer F. J. M. et al. (2019) 50th Lunar planetary Science Conference, #1530, Lunar and Planetary Institute, Houston [4] Rietmeijer F. J. M. and Nuth III J. A. (2000) Trans. Amer. Geophys. Union, EOS, 81(36), 409 + 414-415. [5] Rietmeijer F. J. M. and Nuth III J. A. (2015) Laboratory Astrochemistry, Schlemmer S., Giessen T., Mutschke H. and Jäger C. (Eds), Wiley-VCH Verlag GmbH & Co. KGaA, 455-466. [6] Rietmeijer F. J. M. and Karner J. M. (1999) J. Chem. Phys. 110, 4554-4558. [7] Rietmeijer F. J. M. et al. (2008) *Icarus* 195, 493-503. [8] Nuth III J. A. et al. (2000) J. Geophys. Res., 105(A5), 10,387-10,396. [9] Rietmeijer F. J. M. et al. (2020) 51st Lunar and Planetary Science Conference, #1313, Lunar and Planetary Institute, Houston [10] Hallstedt B. (1992) J. Am. Ceramic Soc. 75, 1502-1505; modified Fundamentals of Materials Science and Engineering; https://media.cheggcdn.com/study/00e/00e8bc9a-9d63-4859-826a-6fdd73cc5a30/11191-12-39IOP1.png. [11] Maitre A. M. et al. (2002) Phys. Chem. Chem.

Phys. 4, 3887-3893.

Acknowledgments: This work was supported by grant NNH16ZDA001N-APRA