**TIME, TEMPERATURES AND PRESSURE INDICATED BY METASTABLE IRON-SULFIDE NANO-PHASES IN MELTED STARDUST AEROGEL.**

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**Introduction:** FeS sulfides are present in comet 81P/Wild 2 but most FeS and FeNiS compositions appear to define a continuous range from "FeS" to metal due to heating on collection [1] that appears to be independent of grain size. No data exist yet to allow a definitive conclusion and there are hints that the range is discontinuous [2,3]. Among the grains extracted from deceleration tracks are globules (up to ~20 microns) of melted aerogel contaminated with Wild 2 debris [4] that contain silicate minerals (>500nm), FeNiS nanophases (a few nanometers up to ~80nm), and Fe-silicide spheres (60-180nm) [2-4].

I present evidence for discrete metastable sub-sulfur FeS compositions that in zoned Ni-free FeS nanophases dispersed in melted aerogel globules constrain *temperature, time and pressure* conditions during Wild 2 debris deceleration in silica-rich aerogel.

**Ni-free FeS nanophases**: For the data discussed here from the allocations CF3,0,2,1,6; CF17,1,5; C2004,1,44,4,3 and C2054,0,35,24,1, I used the 200 keV JEOL 2010 HRTEM that was equipped with a LINK ISIS energy dispersive spectrometer at UNM.

Once-melted nanophases smaller than 5-10nm are chemically homogeneous. When larger, they typically have a core-mantle texture. The cores are spherical but traces of crystal faces exist. The rim is commonly (sub)spherical in sharp contact with the core. Rims can be asymmetric, *e.g.* oval-shaped and 'wing-like'. Other rims form highly irregular tails, *e.g.* 'comet-like' [examples in 2,3]. *The non-spherical rim textures suggest that "nanophase melt droplets" moved through hot (melted) aerogel. There is no evidence for mixing of these nanophases and silica aerogel.*

**Discrete sub-S FeS compositions**: The average FeS nanophase compositions found in melted aerogel are compared to pyrrhotite and sub-sulfur FeS compositions in chondritic interplanetary dust particle L2011A9 (Table 1; Figure 1).

**Table 1**: Average sulfur (wt %) contents of the FeS nanophases in melted aerogel (the bulk composition in brackets was calculated) and FeS compounds in IDP2011A9 that is a highly thermally processed matrix-rich IDP (**Figure 2**).

| IDP L2011A9 | Wild 2; in melted aerogel globules | |
|---|---|---|
| 38.5 | 38 (fragment) | |
| 34.5 | | 33±3 (rim) |
| 20 | [21] | |
| | | 9±2 (core) |

The Wild 2 compositions are a ~80nm pyrrhotite fragment (38wt% S), bulk of zoned FeS nanophases and their cores and rims. In silica-rich aerogel globules the sub-S FeS compositions form well-defined groups, *incl.* deep metastable eutectic (DME) compositions, shown in a modified Fe-S phase diagram (Figure 1).
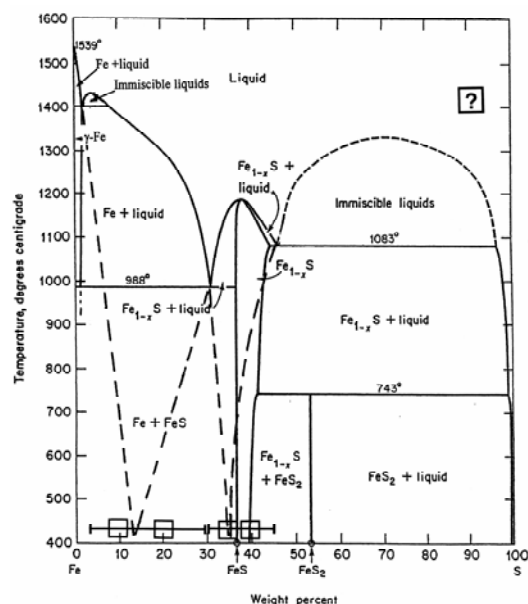


**Figure 1**: Two deep metastable eutectic compositions (dashed lines) between 30-45wt% S and second between 2-30wt% S in the modified Fe-S phase diagram reproduced from [2], and the compositional groups in melted aerogel and the IDP listed in Table 1 (open squares).
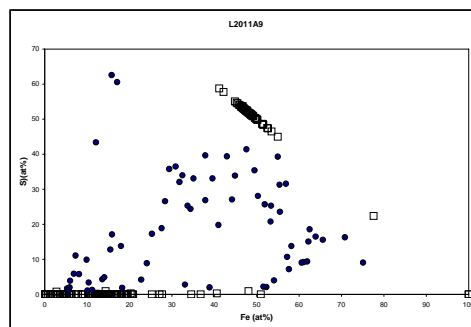


**Figure 2**: Fe vs. S (atomic%) of constituents in matrix-rich IDP L2011A9. It is a mixture of Mg,Fe-silicates and sulfides, incl. thermally modified pyrrhotite, a rare low-S FeS compound, and sulfur 'hot spots' in amorphous silica-rich matrix. The dots are ferromagnesiosilica PC compositions [5].

The FeS compositions (Figure 1) match pyrrhotite and one of DME compositions instead. This same fea-

ture is found in an intensely heated aggregate IDP and FeS nanophases from thermally modified, probably chondritic [2], grains from the weakly constructed nanometer-scale aggregate grains in comet Wild 2 [1] that resembled ferromagnesiosilica PCs [4].

When pyrrhotite was the dominant sulfide in these pre-impact Wild 2 grains and deep metastable eutectic FeS compositions are preferred, then the release of significant amounts of sulfur, or high-S FeS, compounds (melt or vapor) was inevitable. This material will be dispersed in aerogel.
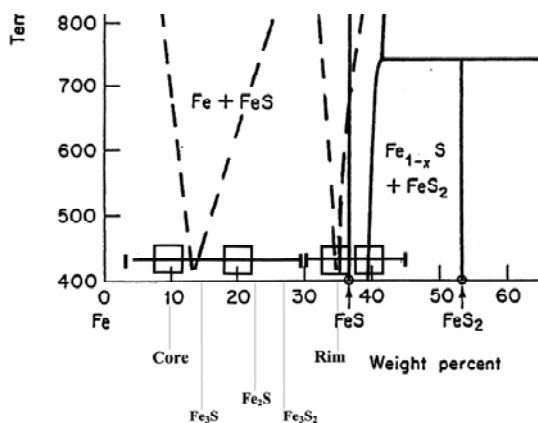


**Figure 3**: Section of the modified Fe-S phase diagram (see Fig. 1) showing the average core and rim compositions in zoned FeS nanophases dispersed in melted silica-rich aerogel globules. Also shown are the high-pressure (equilibrium) iron-sulfur compounds, $Fe_3S_2$ (14-18 GPa), $Fe_2S$ and $Fe_3S$ (>21 GPa) between 950 and $1400^oC$ [6].

The calculated bulk composition of *nanophase melt-droplets* at 21wt% S is a DME composition that resembles those of several high-pressure sulfide compounds (Figure 3). It suggests that this particular composition might have formed in response to pressure when *nanophase melt-droplets* moved at hypervelocity speed through hot aerogel. No firm conclusions yet can be drawn but it appears that pressure should be considered as a physical parameter to explain observed FeS nanophase compositions.

**Time-temperature relationships**: The FeS nanophase zoning in DME core and rim compositions (Figure 3) is a post-melting feature but it is unclear whether it formed when the precursor was still a homogenous melt or in the solid state at lower temperatures. Wagner developed mathematical models describing the behavior of interfaces in response to isothermal diffusion [7]. I selected the model whereby the rim develops moves inwards from the grain boundary [7; fig. 1-22]. These calculations are possible because the bulk, core and rim compositions are systematically constrained (Figure 3). The displacement of the inter-

face that corresponds to the rim width, 7 to 27nm, is calculated as a function of time (μsec). Iron and S diffusion coefficients for sub-S FeS compositions are unavailable; I used values for stoichiometric pyrrhotite at 277 and $697^oC$ and sulfide melt at $1180^oC$ [8, figs. 10 & 18] assuming identical diffusion coefficients in the core and rim.
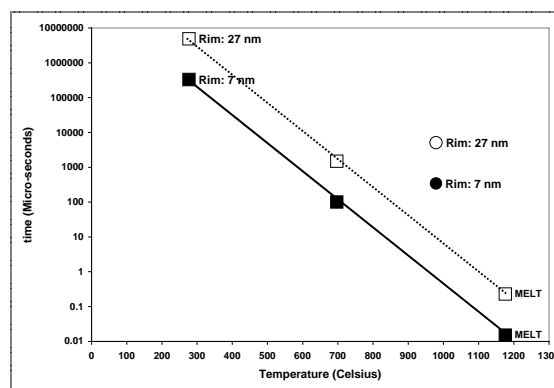


Figure 4: time (**μ-seconds**) to establish the rim on zoned FeS nanophases vs. temperature in the MELT and solid state for Iron diffusion (solid & open squares) and one value when sulfur is the diffusing species (dot & open circle).

**Conclusions**: Rapid heating produced pressure-stabilized *nanophase melt-droplets* moving at hypervelocity speed in hot aerogel. Zoning when developed in the melt phase was established in less than a microsecond. The irregular tails seem to support this scenario. If one, probably correctly, assumes that sulfur diffusion was a rate-controlling parameter in the solid state, zoning was established in ~0.5 to ~10 **milliseconds** (700-$1000^oC$. The core-rim texture is consistent with these lower temperatures when at rest in a silica-rich glass matrix. The DME compositions suggest high quenching rates of the FeS nanophases in silica-rich melt produced at <$1400^oC$; the observation do not require, but not exclude, higher temperatures. Models of aerogel behavior should account for the physical conditions recorded in captured Wild 2 grains.

**References:** [1] Zolensky M. E. et al. (2006*) Science, 314*, 1735-1939. [2] Leroux H. et al. (2007) *Meteoritics & Planet. Sci., in press*. [3] Rietmeijer F. J. M. (2007) *Meteoritics & Planet. Sci., in press*. [4] Rietmeijer F. J. M. (2007) *LPS XXXIII,* Abstract #1082. [5] Rietmeijer F. J. M. (2002) *Chemie Erde, 62*, 1-45. [6] Fei Y. et al. (2000) *Am. Mineral., 85*, 1830-1833. [7] Jost W. (1952) in Phys. Chemistry (Hutchison E., ed.), 68-75. Acad. Press Inc. NY. [8] Condit R. H. et al. (1974) *Oxidation Metals, 8*, 409-455.