

EVIDENCE FOR HOT CHEMISTRY UNDER REDUCED CONDITIONS IN THE THERMALLY MODIFIED STARDUST SAMPLES. H. Leroux¹, F. J. M. Rietmeijer², D. Jacob¹ and M. Roskosz¹. ¹ Laboratoire de Structure et Propriétés de l'Etat Solide - UMR CNRS 8008, Université des Sciences et Technologies de Lille, 59655 Villeneuve d'Ascq, France, hugues.leroux@univ-lille1.fr. ² Department of Earth and Planetary Sciences, University of New Mexico, MSC03-2040, Albuquerque, NM 87131, USA.

Introduction: The Stardust mission brought to Earth samples from the comet 81P/Wild 2. The hyper-velocity impacts created deceleration tracks in the aerogel, along which the cometary material is unevenly distributed in various proportions [1-3]. The material dispersion along the tracks suggests weakly bounded material that mechanically disaggregated during the impact into aerogel. Several Stardust samples show evidence for thermal-induced modifications [1, 4-5]. Their typical microstructure consists of a dense silica-rich glassy matrix containing widespread beads of nanoscale Fe-Ni-S phases. This microstructure gives clear evidence for melting of the cometary dust and mixing with molten aerogel. Mixing was spatially limited and heterogeneous as shown by the presence of “dust-rich” submicron patches dispersed in molten aerogel [4]. In addition to melting, chemical reactions were established to occur in the high temperature melt as demonstrated by the presence of iron-silicides in some samples [5]. The objective of the present study is to discuss the chemical reactions which may have occurred in the thermally modified samples during the high temperature regime. We propose also a new petrological groundwork based on Fe-Mg-S ternary diagrams.

Samples and experimental procedures: The five TEM (transmission electron microscope) ultramicrotomed samples used for this study were extracted from several track walls. Details about extraction, manipulation and preparation for TEM by ultramicrotomy can be found in [1]. Results have been obtained at the University of Lille (France) using a TEM Philips CM30 (300 keV) and a TEM FEI Tecnai G2-20 twin, both equipped with Energy Dispersive X-ray Spectroscopy (EDX) (see [4] for a full description of the analytical procedure).

Results: The dominant microstructure of the thermally modified samples is the presence of Fe-Ni-S nanophases within a SiO₂-rich glassy matrix (Fig. 1). The glassy matrix contains also Mg, Al or Ca as for the most abundant ones. Their distribution is highly variable from place to place. They are mainly present as “dust-rich” patches in the melted aerogel matrix. Figure 2 shows an elemental distribution for Mg and Fe for an entire TEM slice. The correlation between Mg and Fe is relatively good.

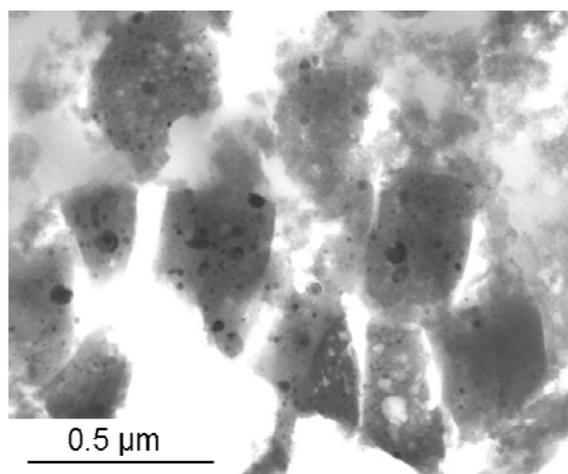


Figure 1: Bright field TEM image of sample C2054,0,35,52,3. The typical microstructure of the thermally modified samples consists of a silica-rich glassy matrix embedding nanoscale Fe-Ni-S phases.

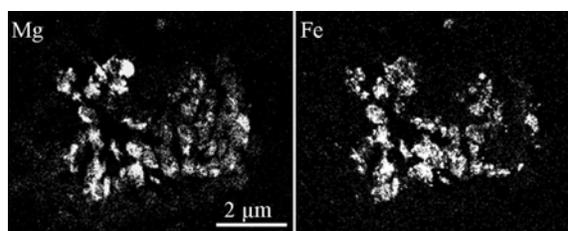


Figure 2: EDS intensity maps for Mg and Fe for an entire ultramicrotomed slice. Note the relatively good correlation between Mg and Fe.

The average composition of the five samples studied are close to the CI-composition, within an interval lower than 15% for the major elements (Al, Mg, S, Ca, Cr, Mn, Fe, Ni). Figure 3 shows these compositions in the Fe-Mg-S ternary diagram. For bulk analysis, the analysed surfaces of microtomed slices is high, typically several μm^2 . It is interesting to establish how the composition evolves on the ternary Fe-Mg-S diagram when the analysed surface is reduced. One representative diagram is given on figure 4. This figure shows the average composition and sub-areas $0.3 \times 0.3 \mu\text{m}^2$ in size taken randomly. The corresponding data scatter from around the average bulk composition, along a line which joins approximately the Mg-corner to an average composition of the Fe-S join. The data scatter

along this line increases when the analysed surface is decreasing (not shown). The figure 4 also shows compositions associated with Mg-rich areas in silica matrix in between Fe-Ni-S inclusions. It is remarkable that these areas have a very low Fe concentration while S is still present in significant relative proportion for most samples, typically with a S/Mg ratio of about 0.03. All samples studied display similar trends although it was not possible to measure for each of them an accurate composition of the dust-rich areas between the Fe-Ni-S phases because of their widespread distribution and small size. These measurements strongly suggest that the silica-rich glassy matrix which includes the Fe-Ni-S nano-phases is FeO-poor.

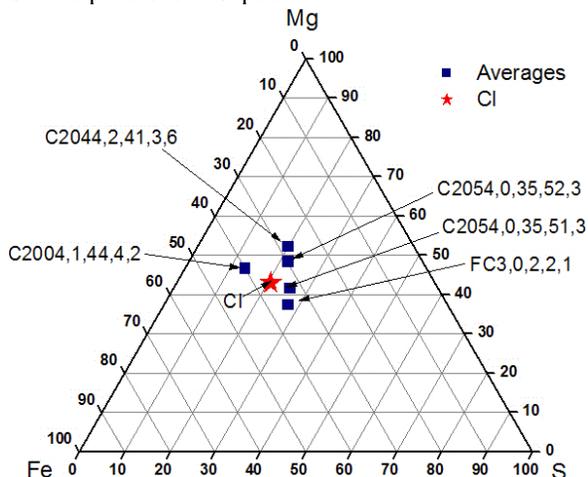


Figure 3: Average composition of the five thermally modified samples in the Fe-Mg-S ternary diagram.

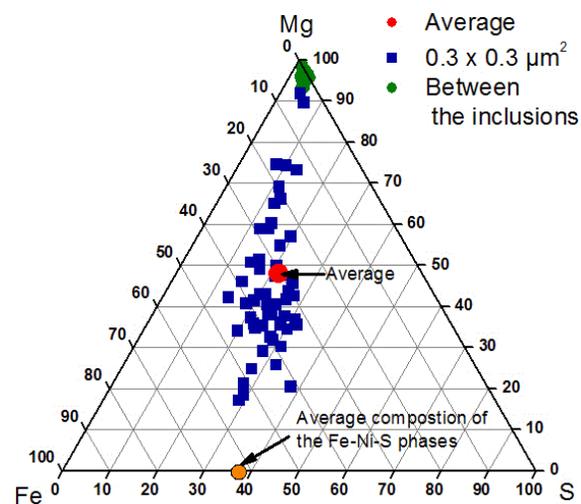


Figure 4: Evolution of the composition of one thermally modified sample (C2054,0,35,52,3) when the analysed domains is progressively decreased.

Discussion: These thermally modified samples display evidence for melting and partial mixing of Wild 2 dust grains with molten aerogel. Their average composition is close to CI, including S which does not appear to be depleted [4]. In the Fe-Mg-S ternary diagrams, the local compositions of areas within molten silica-rich grains extracted from the tracks walls are scattered along a mixing line between Mg and the average composition of the Fe-Ni-S nanophases. This particular composition distribution suggests that the silica-rich glassy matrix is FeO free. However the incoming silicates grains are probably not FeO-free, as suggested by number of survived crystalline silicates trapped in aerogel [1,4]. This low FeO concentration suggests a low oxygen fugacity during the high temperature capture event into aerogel. Chemical reaction with carbon components originally present in the incoming particles might have induced the following reaction:



According to the Gibbs free energy change for the reduction-oxidation reactions versus the temperature, this reaction occurs for $T > 700^\circ\text{C}$. The actual temperature is clearly higher in the thermally modified Stardust samples since the initial cometary material and aerogel has been melted [4]. The Fe-rich nanophases distributed in the glassy matrix are thus secondary products, due to a reduction process of FeO bearing silicates at high temperature. The core-shell structure (metallic core + iron-sulfide mantle) of the Fe-Ni-S phases [4] is likely due to a corrosion process due to sulfur redistribution at high temperature. The presence of S in the glassy matrix is also indicative for S redistribution and very low oxygen fugacity. The exchange reaction between MgO and gaseous sulfur species implies a redox reaction and would occur at $T > 1800^\circ\text{C}$ according to the thermodynamic database.

Summary: The thermally modified samples display evidence for chemical reactions at high temperature. The Fe-Ni-S phases within the glassy matrix are likely resulting from a reduction reaction in presence of carbonaceous material. The widespread presence of sulfur in the rim of the Fe-Ni-S nano-phases is likely the result of S redistribution and corrosion of the first stage Fe-Ni precipitates due to reduction of ferromagnesian silicates.

References: [1] Zolensky M. E. et al. (2006) *Science*, 314, 1735-1739. [2] Hörz F. et al. (2006) *Science*, 314, 1716-1719 [3] Flynn G. J. et al. (2006) *Science*, 314, 1731-1735. [4] Leroux H. et al. (2008) *Meteoritics & Planet. Sci.*, in press. [5] Rietmeijer F. J. M. et al. (2007) *Meteoritics & Planet. Sci.*, in press.

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