

Mineralogical and Textural Changes of a Wild 2 Terminal Particle Pentlandite from Capture Heating in Aerogel. D. J. Joswiak, D. E. Brownlee and G. Matrajt, Department of Astronomy, 351580, University of Washington, Seattle, WA 98115, joswiak@astro.washington.edu.

Introduction: A primary goal of the Stardust (SD) mission was to return unmodified particles from comet Wild 2 to Earth. Thus far, a wide range of minerals and heated by-products of captured particles extracted from the aerogel tiles have been observed including silicates, sulfides, oxides, metals, glasses and minor carbonaceous matter [1,2]. The various SD particles have a large range of thermal stabilities and depending on their sizes and strengths, and other factors, will undergo variable modifications during capture heating, thus, to fully understand the nature of the grains that were derived from comet Wild 2 it is important to understand any heating effects that may have occurred from capture.

Using TEM techniques we studied the terminal particle (TP) from track 59. Analysis of this particle indicates that it has a bulk composition similar to the mineral pentlandite. Individual regions within the TP, however, are compositionally variable and show large Fe/Ni variations which are not consistent with a pentlandite composition. Texturally, the TP is composed of discrete subgrains or ‘islands’ of Fe-Ni-sulfides which are often separated by pure silica. Here we show that capture heating of the original particle, believed to be the mineral pentlandite, modified the grain into two high temperature Fe-Ni sulfides, an MSS phase with high Fe/Ni ratio and the high temperature Ni-rich sulfide heazlewoodite. This particle was particularly susceptible to thermal modification because of its small size of $\sim 2 \times 3 \mu\text{m}$ and the high thermal conductivity of pentlandites.

Techniques: Track 59 is a 0.35 mm long type A track [3] with an optically opaque terminal particle (TP) with sub-micron opaque debris along the track length. To prepare the sample for the TEM, the track was embedded in acrylic resin and flattened between glass slides [4]; the TP was then cut from the flattened track and microtome sections $< 100 \text{ nm}$ were produced using standard techniques.

TEM observations and EDX analyses were done with a Tecnai F20 STEM with attached EDAX Genesis Xray analysis system. Element maps were produced from 51,200 individual spectra that were collected from a $0.5 \mu\text{m} \times 0.6 \mu\text{m}$ region. To better understand the sulfide compositions, ROIs from irregular areas of differing composition were chosen and the pixels summed to produce quantitative spectra.

Petrography: A HAADF STEM image taken of a representative microtome section from the TP is shown in Figure 1a. The image shows that the TP is composed of rounded and disaggregated pieces (bright grains) cemented together by a SiO_2 matrix material (uniform gray areas) believed to have resulted from melting of aerogel. Many of these subgrains are rounded or spherical in shape suggesting melting; one are particularly evident along the periphery of

the grain. EDX analyses show that the subgrains are exclusively composed of Fe-Ni sulfides, many with a ‘bulk’ composition similar to pentlandite. Average Co contents are 1.0 atom %.

A conventional DF image and detailed Si, S, Fe and Ni element maps taken from the representative green rectangular region in Figure 1a are shown in Figures 1b – d. The DF image (Fig 1b) and the Si and S element map (Fig 1c) clearly delineate the sulfides from the silica matrix while the Fe, Ni and Si map (Fig 1d) indicates that Fe and Ni are heterogeneously distributed in the sulfide phases and form Fe-rich and Ni-rich regions, suggesting disequilibrium.

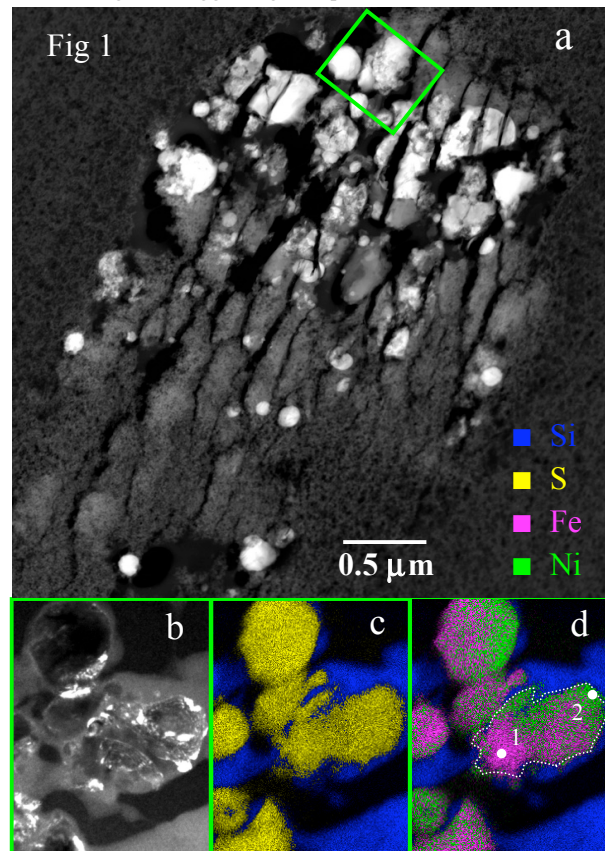


Figure 1: a) HAADF image of TP from Track 59 showing disaggregation of Fe-sulfide TP into smaller subgrains. Bright-colored grains are Fe-Ni sulfides of variable composition. Interstitial grey areas are silica glass. b) Dark-field image of portion of TP (green box in a) showing diffracting Fe-Ni sulfide grains admixed with silica (uniform interstitial gray areas). c) Si and S element map delineating Fe-Ni sulfide (yellow) from immiscible silica melt (blue). d) Fe, Ni and Si element map showing heterogeneous distribution of

Fe (purple) and Ni (green) in Fe-Ni sulfide. Numbers correlate to green triangles in Figure 2c.

Thermal metamorphism during capture: The presence of discrete Fe-Ni sulfide subgrains that form 'islands' within amorphous SiO₂ matrix indicates that severe fracturing and disaggregation of the impacting particle occurred during capture. The rounded Fe-Ni sulfide subgrains, particularly along the exterior, suggest melting which implies a minimum temperature of 862 °C, the melting point of pentlandite [5]. The heterogeneous distribution of Fe and Ni within the sulfides further suggests chemical disequilibrium which was enhanced by high thermal gradients [6].

The Fe-Ni(+Co)-S phase diagrams in Figure 2 show that the TP is composed of a mineralogically complex mixture of three Fe-Ni sulfides – pentlandite, MSS (monosulfide solid-solution) and heazlewoodite (Hz). Figure 2b indicates that the precursor grain (blue square) originating from comet Wild 2 was pentlandite. Frictional heating during capture raised the temperature above the stability of pentlandite (610 °C) converting portions of it to Fe-rich MSS (pyrrhotite) and Hz. This can be seen in Figure 2c by the red solid circles which are analyses taken from nm-scale regions within the element map area. These red circles span the Fe-Ni-S space from Fe-rich MSS to a region near Hz. A specific example is shown by the green triangles in the figure. These triangles show the compositions of the bulk grain (outlined in Figure 1d) and the Fe-rich and Ni-rich areas which are indicated by the white dots (Figure 1d). The data indicate that the original bulk composition is consistent with pentlandite which was converted to MSS and Hz during heating.

Figure 2c represents an intermediate state in which pentlandite is unstable. The final state of the TP is represented in Figure 2d which shows that pentlandite becomes stable with MSS and Hz ($T < 610$ °C). The positions of the red circles and green triangles, taken from nm-sized regions, show that the Fe-Ni-S grains are chemically complex. Many of these points – shown by the tie lines - fall in the two phase fields MSS+pentlandite or pentlandite+Hz. Presumably rapid cooling kinetically inhibited the full reconversion of MSS and Hz back to pentlandite leaving the sulfides in chemical disequilibrium.

Summary. A ~3 um solid pentlandite (track 59) originating from comet Wild 2 impacted into aerogel and was fractured and disaggregated during deceleration. The grain was heated to high temperatures variably causing melting and breakdown of the pentlandite to Fe-rich MSS and heazlewoodite. Rapid cooling apparently quenched these phases in nm-scale regions which now exist in chemical disequilibrium. The Fe-Ni sulfides are in sharp contact with immiscible silica melt which was produced from the aerogel during heating. Unlike larger pentlandite grains observed in other SD tracks which show little thermal modification, the TP from track 59 was severely modified because of its smaller size. It represents an intermediate state between the

larger ~> 5 um sulfides and the ubiquitous nm-sized Fe sulfide/metal beads that are present with melt in most tracks..

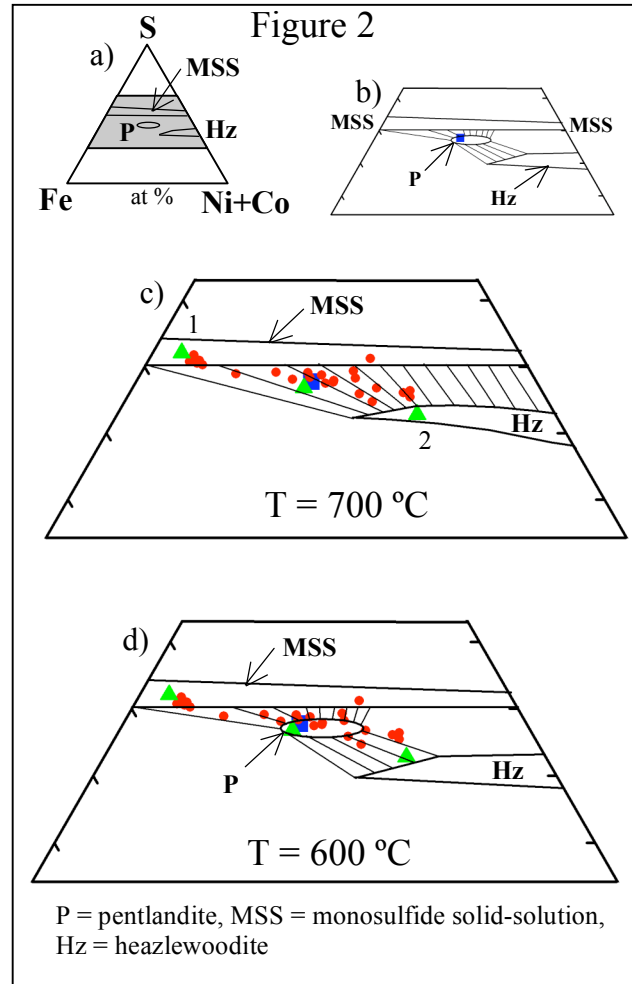


Figure 2. a) Fe-Ni(+Co)-S ternary diagram showing the relevant phases discussed in this study. MSS = monosulfide solid-solution, P = pentlandite, Hz = heazlewoodite. Figures b – d from the central shaded region. b) Blue square, representing the bulk composition within the white dotted line in Figure 1d. The blue square plots in the pentlandite field showing that the original grain from comet Wild 2 was pentlandite. c) EDX analyses from element map region plotted on 700 °C isothermal section showing that nm-scale regions in original pentlandite converted to MSS and Hz. Numbers refer to green triangles and correlate with Figure 1d. d) Final state of Fe-Ni-S terminal particle showing that sulfides consist of mixtures of pentlandite, MSS and Hz. Phase diagrams from [7].

References: [1] Zolensky M. et al. (2006) *Science* 314: 1735-1739. [2] Joswiak D. J. et al. (2007), *METSOC* 42, 5256. [3] Burchell M. J. et al. (2008), *MAPS*, 23 – 40. [4] Matrajt G. and Brownlee, D. E. (2006) *MAPS*, 41, 1715-1720. [5] Kullerud, G. (1963) *Canad. Miner.* 353-366. [6] Noguchi et al. (2007) *MAPS* 42, 357-372. [7] Waldner P. and Pelton, A. D. (2004) *Metal. Mater. Trans.*, 35B, 897-907.