Magnetite or Hematite? The Iron-Oxides Returned by Stardust. N. J. Foster[1,2], M. J. Burchell[1], J. A. Creighton[1] & M. J. Cole[1] & The United Kingdom Stardust Consortium. [1]Centre for Astrophysics and Planetary Science, School of Physical Science, Univ. of Kent, Canterbury, Kent, CT2 7NH, United Kingdom. [2]nf40@kent.ac.uk

Introduction: With NASA's Stardust mission [1] returning to Earth and the first set of results being published by the preliminary examination teams (PETs), the samples have now been passed to other members of the community. As part of the UK Stardust Consortium, we have so far received several samples for analysis. The two samples examined, a section of C2044,0,41 and a terminal grain pressed in gold foil, C2005,2,121,2,0, have both shown strong Raman signals. Wopenka *et a*l. [2] have shown hematite Raman signals in thin microtone sections of the Stardust grains. However, the origin of this hematite is unclear. It has been shown [3] that magnetite is prone to oxidation from heating, thus changing to hematite. The heating effect associated with capture in aerogel is more then high enough to induce this change.

Background: During capture in aerogel particles experience flash heating for a few microseconds at temperatures high enough to melt the aerogel (i.e. greater then 1600 ºC) which can be clearly seen on captured particles as a molten wrap around the outside of the particle [4]. Alteration of olivine has been shown due to the capture process in aerogel [5] where a decrease in wavenumber of the two strongest peaks associated with olivine at ≈ 820 & 850 cm^{-1} was observed. As mentioned magnetite is very prone to alteration by heating, this occurs at temperatures of greater then 240 ºC [3]. When heated to excess of 240 ºC the strong Raman band around 660 cm^{-1} starts to be lost in intensity in comparison to the hematite signal that starts to emerge. The spectral intensity of the hematite is dominated by the peaks at ≈ 226, 293 & 410 cm^{-1}.

Method: In addition to the analysis of Stardust samples, laboratory analogues were produced for comparison to Stardust samples. These used powdered samples of hematite and magnetite with a typical grain size of 10 - 20 µm (the same size as observed grain size in the Stardust samples). Samples of powdered magnetite were supplied by the Natural History Museum, London, from a source catalogued by the British Museum. Samples of hematite came from within our laboratory. Grains of the two minerals were fired separately using the University of Kent's two stage light gas gun at the at speeds of typically 6.1 km s^{-1} (the Stardust cometary encounter speed). The targets were blocks of aerogel of density ≈ 30 kg m^{-3}. These blocks were not Stardust grade aerogels which had a density gradient from the front face of 5 kg m^{-3}, rising to 50 kg m^{-3} at the rear face. Instead, these blocks are of an intermediate density between these two extremes. Several grains were captured by the aerogel during each shot.

Raman Analysis: This was performed at the Univ. of Kent with a Jobin Yvon microRaman module (HR640) attached to an Olympus microscope (BX40). The illuminating laser line was at 632.8 nm (HeNe) capable of delivering power in a range between 0.8 – 10 mW. The spectrograph had a 1200 gr/mm grating. Data were taken on a liquid nitrogen cooled CCD. For raw (unshot) grains the sample exposure times were typically 10x30 secs (x100 Mag.). For grains measured in-situ after capture in aerogel, the exposure times were typically 10x30 sec (x50 Mag.).

Temperature values were calculated using the ratio between Stoke and anti-Stoke intensities on the peaks in the -700 – -150 & 150 – 700 cm^{-1} range using carbon tetrachloride (CCl_4) as a reference response for the spectrometer. Equation 1, which is based on the Boltzmann distribution of modes between energy level, is used to find the temperatures.

$$\frac{I_{Stoke}}{I_{anti-Stoke}} = \left(\frac{\nu_{HeNe} - \nu_R}{\nu_{HeNe} + \nu_R}\right)^4 e^{+\frac{hc\nu_R}{kT}} \quad \textbf{Eq. (1)}$$

The laser power was controlled using neutral density filters, enabling us to alter the laser power from 0.8 mW – 10 mW in varying steps. Each grain analysed started at 0.8 mW of laser power and then increased powers up to 10 mW. Stoke and anti-Stoke measurements were recorded for all samples.

Results: Raman data was recorded from two Stardust grains (see Introduction); these are shown in Figure 1, the upper spectra from the terminal grain, and the lower spectra from section the of C2044,0,41. Upon initial inspection both of these spectra appear to be hematite due to the very strong peaks associated with hematite at ≈ 226 & 293 cm^{-1}. However, upon closer inspection and comparison of spectra taken from raw samples of magnetite and hematite (Figure 2 upper spectra magnetite, lower spectra hematite) it can be seen that in the Stardust sample a peak at ≈ 660 cm^{-1} is also present, indicating magnetite not hematite, thus demonstrating that the samples return by Stardust are not pure hematite. Shots carried out using the hematite as a projectile exhibit a Raman spectrum the matching that of unshot hematite, without the magnetite feature at ≈ 660 cm^{-1}. When grains of magnetite were heated in the laboratory their Raman spectra changed to resemble a spectra very similar to that of the spectra found in the terminal grain and track section. Figure 3 shows a sample of the heated magnetite, again although very similar to that of hematite it also displays the magnetite peak at ≈ 660 cm^{-1} thus demonstrating that there are still magnetite features present, although the mineralogy has been altered. The temperatures of the Stardust grains were measured during analysis. The particle in C2044,0,41 had a mean value of 209 ºC calculated from the bands at ≈ 226 & 293 cm^{-1}, below that of the temperature shown to change the signal shown in [3]. A lower laser power (and thus temperature) was used on the terminal grain. Thus in both cases the temperature during analysis was below that shown previously [3] to cause alteration.

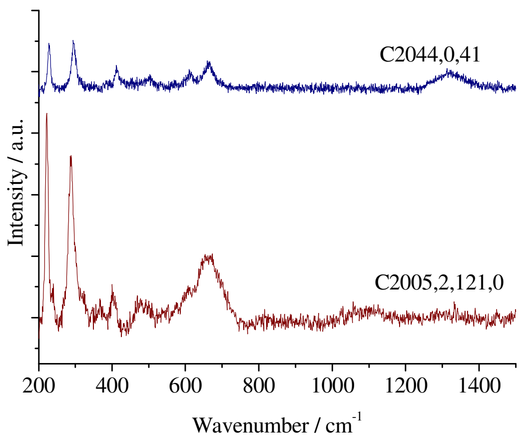

Figure 1. Raman data from C2044,0,41 (upper spectra) and from section of track C2005,2,121,0 (lower spectra).

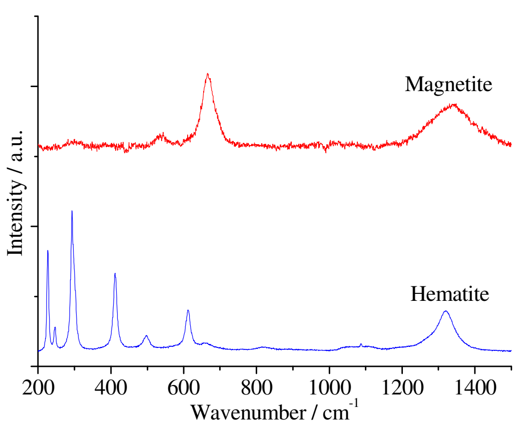

Figure 2. Raman data taken from mineral samples. Upper spectra magnetite, lower spectra hematite.

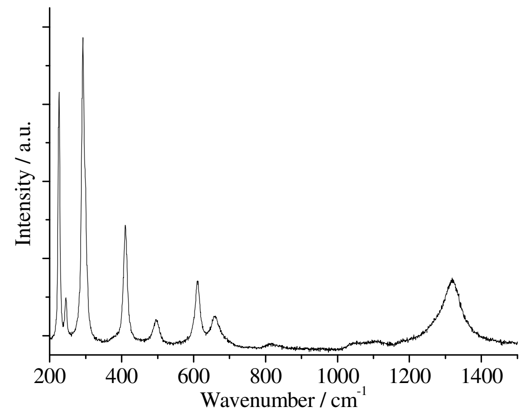

Figure 3. Raman spectra of a sample of magnetite heated by laser to show alteration.

Conclusion: The Stardust grain samples analysed at Kent have both shown strong Raman signals. Both of these samples display a hematite Raman signal, but with a peak more normally associated with magnetite at ≈ 660 cm^{-1}.

It is known that heating can alter the oxidation state of magnetite, resulting in a hematite spectrum similar to that shown in the two Stardust samples [3]. The maximum temperatures during analysis here remained lower then that of the temperature which has been found to cause this oxidation effect (240 ºC). By deliberately heating raw grains of magnetite in the laboratory we can obtain Raman spectra similar to those of Stardust. It has previously been demonstrated that the capture process in aerogel can change Raman spectra [5] and effect the mineralogy of captured particles [4], suggesting elevated temperatures of > 1600 ºC, and giving reason to think that alteration during capture of these Stardust samples may have occurred.

References: [1] Brownlee D. E. et al. (2006) *Science 314*, 1711-1716. [2] Wopenka B. et al. (2007) *Meteoritics & Planet. Sci., 42,* 5048. [3] de Faria D.L.A et al. (1997) *J. Raman Spectrosc. 28,* 873 – 878. [4] Noguchi T. et al. (2007) *Meteoritics & Planet. Sci., 42,* 357 – 372. [5] Foster N.J. et al. (2007) *Meteoritics & Planet. Sci., 42,* 5186.

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