

CONSTRAINING THE EFFECTS OF CAPTURE-HEATING ON CHEMISTRY AND STRUCTURE OF COMETARY SULPHIDES UNDER STARDUST ENCOUNTER CONDITIONS. P. J. Wozniakiewicz^{1, 2}, A.T. Kearsley¹, M. J. Burchell³, P. A. Bland², H. A. Ishii⁴, Z. R. Dai⁴, N. Teslich⁴, G. Collins², J. P. Bradley⁴, S. Russell¹, M. J. Cole³, M. Lee⁵. ¹Impacts & Astromaterials Research Centre (IARC), Dept. of Mineralogy, Natural History Museum (NHM), London SW7 5BD, UK. E-mail: p.wozniakiewicz@nhm.ac.uk. ²IARC, Dept. Earth Sci. & Eng., Imperial College London, South Kensington Campus, London SW11 2AZ, UK. ³School Phys. Sci., University of Kent, Canterbury, Kent CT2 7NH, UK. ⁴Inst. of Geophys. & Planetary Phys, Lawrence Livermore National Laboratories (LLNL), Livermore CA94550. ⁵Dept. Geographical & Earth Sci., University of Glasgow, Glasgow G12 8QQ, U.K.

Introduction: Return of the Stardust cargo and the ensuing Preliminary Examination (PE) revealed successful capture of many particles in both aerogel and Al foil [1]. Whilst originally primarily intended as a means of securing the aerogel, the value of the foils as an informative collection medium was quickly realised [2]. Fully exploiting this unique material requires an understanding of the impact process occurring on these foils; and in particular, whether one can distinguish the most important minerals expected within cometary materials, and establish how they may have been modified during capture.

Our preliminary work aimed to determine whether scanning electron microscopy (SEM) and energy dispersive X-ray microanalysis (EDX) analyses of crater residues from laboratory experiments would be helpful in understanding initial projectile composition [3-6]. Analyses of projectiles were compared against those of the resulting residues. A range of magnesium silicates (including olivine compositions from Mg-rich forsterite to Fe-rich fayalite) and two iron sulphides, pyrrhotite and pentlandite, were investigated. Both classes of minerals have been identified as important components of Stardust materials [7]. The magnesium silicates remained identifiable, albeit with an increase in Mg to Si ratio, largely attributable to the analysis technique. Residues from the sulphide minerals exhibit variable loss in S relative to Fe and Ni (Figure 1), as also inferred from analyses taken from aerogel-trapped particles in Stardust [7], suggesting that low S is due to capture, and is not necessarily an indication of original diverse non-stoichiometric composition. Fully understanding this process required an investigation of both the chemical and structural alteration occurring at sub- μm resolution, using transmission electron microscopy (TEM). Both the original projectile and resulting residue have been analysed by TEM and compared to determine how the impactor has been modified. Here we present the results of these analyses.

Experimental methodology: For the SEM EDX studies [3-6], a series of light gas gun shots were conducted at the University of Kent, firing minerals into Stardust foils. Powdered sulphides, pyrrhotite and pentlandite, were prepared from grains carefully ex-

tracted from terrestrial ore minerals. The powders were fired as single component buckshots [8] and it is these same shot foils that form the basis for this investigation.

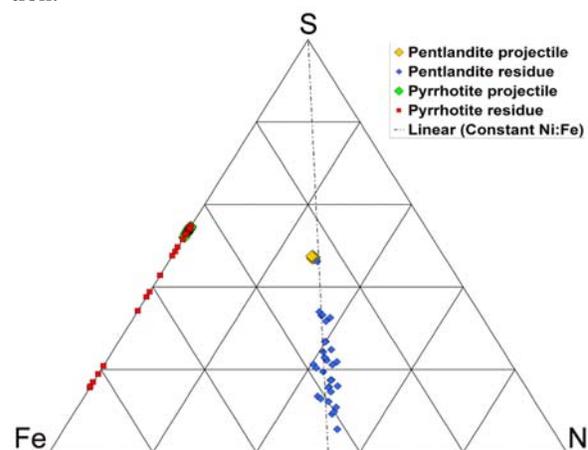


Figure 1: Ternary diagram displaying S, Fe and Ni atomic% data from SEM EDX analyses of iron sulphide projectile residues in Al foil [reported in 6].

The Focused Ion Beam (FIB) was used to prepare sections for analysis by TEM. The FIB process for creating TEM sections is greatly complicated by non-flat sample geometry (e.g. deep craters). Indeed, the deepest regions of our craters, where the majority of residue resides, remain inaccessible to FIB lift-out. For this reason a section of foil was mounted vertically within a resin block. This block was then polished down until the cross section of a suitable (>50 μm diameter) crater was exposed on the surface. Projectile material was prepared in similar resin blocks.

The TEM sections were created using the FEI Nova600 NanoLab dual-beam FIB microscope at Lawrence Livermore National Laboratories (LLNL). They were then imaged and analysed using the 200kV FEI Technai20 G2 FEG monochromated scanning transmission electron microscope (STEM), also at LLNL. EDX analyses and diffraction patterns were collected for both the projectile and residue samples, and X-ray maps were created for areas of interest in the residues.

Comparison demonstrated how the impactor had changed.

Results and Discussion: TEM sections were successfully extracted from the projectile and residue of both sulphides. The projectiles were confirmed as pure and crystalline examples of pyrrhotite and pentlandite. High angle annular dark field (HAADF) STEM images of each residue immediately show that the effects of impact are complex (Figure 2 is from a pentlandite shot).

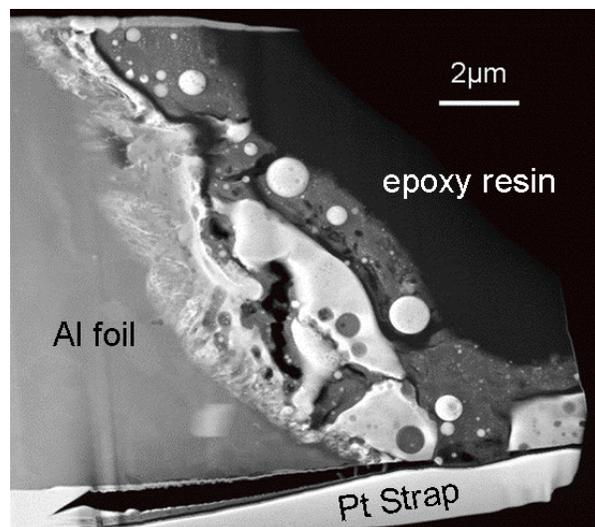


Figure 2: STEM image of pentlandite residue section.

The pentlandite residue section (Figure 2) displays no clear boundary between residue and Al target. Instead, the impactor appears to have diffused itself into the Al. There are multiple components to the residue all exhibiting various degrees of sulphur loss. Of particular interest are crystalline spheres and blocks of FeNiAl alloy; with crystals up to $\sim 2\mu\text{m}$ in size and in some case containing spheres of sulphur. Clearly melting has occurred, with mixing of target and impactor and separation of some phases, followed by recrystallisation, all in a very short period of time (see calculations below). The pentlandite composition and structure are completely destroyed.

The pyrrhotite residue is much better preserved, with the majority of the residue maintaining both a pyrrhotite composition and pyrrhotite diffraction pattern, if a little damaged compared to that of the original projectile. There are however some signs of melting; as with pentlandite, we see spheres of FeAl alloy with varying amounts of S, and again some elemental sulphur droplets.

These results explain previous EDX data for sulphides [5,6], with residues of both minerals showing clear evidence of melting and (some) recrystallisation

of material. For the pyrrhotite impact an estimate of peak pressure can be obtained by means of the graphical method outlined in [9] and available Hugoniot data of [10] and [11]. Post-shock temperature and time taken to return to room temperature can then be estimated by using the equations of [12] and data of [13,14]. These give a peak pressure of $\sim 84\text{GPa}$ and a post-shock temperature of $\sim 2500\text{K}$ decaying to room temperature in $\sim 10^{-4}\text{s}$. Crystal growth to a few μm therefore occurred within a very short time, implying crystals of this size can form readily from such a quenched melt. Conditions for the pentlandite impact are expected to be the same (although lack of Hugoniot and thermodynamic data for pentlandite prevents us from performing the same calculations). The difference in the extent of modification exhibited by these two iron sulphides could be due to their different melting temperatures [15,16].

Conclusions: It is clear the variable S levels exhibited by residues of sulphides are due to loss through capture-heating. We anticipate that other chalcophile volatiles will also be lost during capture. The different extent of alteration exhibited by the two iron sulphides suggests that some minerals experience more alteration than others and that the task of deciphering original chemistry from some residues may not be an easy one. Finally, we have also observed the crystallisation of new phases over surprisingly short timescales.

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