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Raman identification of olivine grains in fine grained mineral assemblages fired into aerogel

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Abstract

NASA's Stardust mission returned from the comet 81P/Wild2 in 2006 and has yielded a plethora of research looking into the composition and attributes of the comet. The mission itself collected thousands of cometary dust particles as it flew through the coma of the comet at a relative speed of 6.1 km s^{-1} . This work focuses on one of the most abundant minerals in the solar system – olivine. Previous work has shown capture effects on this mineral in similar impacts to that experienced during the Stardust mission. However, the past work looked into effects on isolated mineral grains which would be a rare occurrence in the Solar System. A more accurate representation of this would be to investigate the capture effects on olivine as a constituent of an assemblage of minerals. Accordingly, here we used samples from the NWA 10256 CR2 carbonaceous chondrite meteorite. This natural sample contains fine grains of olivine, and brings additional issues when analysing the olivine due to limited homogeneity. Shifts in the Raman spectra for olivine, enstatite and hematite were observed after capture due to shock effects. However, this work suggests that olivine may well experience a different shock effect during capture when part of a mineral assemblage as distinct from that experienced by single grains.

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1. Introduction

NASA's Stardust mission [1] was a sample return mission to collect material from the coma of the Jupiter-Family Comet 81P/Wild2. The mission returned successfully in 2006, and it is estimated that it collected thousands of cometary dust particles, approximately 1 – 300 μm in size and totaling approximately 3×10^{-4} g in mass [1][2]. The dust particles were collected using aluminum foils and SiO_2 aerogel blocks as Stardust was passing the comet with a relative speed of 6.1 km s^{-1} [3]. Aerogel is a low density, highly porous medium which can capture small impacting grains relatively intact [2]. The aerogel used for the Stardust mission was transparent and had a density gradient of 5 mg cc^{-1} at the front face rising to 50 mg cc^{-1} at the rear. Aerogel is very useful as a capture material as it results in a low pressure impact spread along the length of a track formed as the projectile decelerates in the aerogel. The resulting captured grain at the end of the track is known as the terminal grain (see [4] for a review of the use of aerogel in dust capture in space). The process of capture in aerogel is thought to involve a low shock pressure of $\leq 300 \text{ MPa}$ [5], but it can heat the samples to over $1,000 \text{ }^\circ\text{C}$ for a brief period of a microsecond (see [6][7]). Furthermore, [7] has shown that $10 \mu\text{m}$ sized terminal grain particles remain unmelted and relatively unaltered after capture.

The mineral olivine ($(\text{Mg}^{+2}, \text{Fe}^{+2})_2\text{SiO}_4$), is a very abundant material found in the Solar System, including asteroids and comets. Its Raman spectra is easily recognised by a doublet at around 820 and 850 cm^{-1} , referred to as P1 and P2 respectively (Fig. 1). This doublet represents the internal stretching vibrational modes of the SiO_4 ionic group. The height of P1 and P2 are a function of the crystal orientation [8]. Additionally, it has been observed that the exact position of these peaks systematically varies with the olivine composition [9][10]. Olivine has two end-members forsterite (magnesium rich) and fayalite (iron rich). Therefore, the Fo content refers to the percentage of magnesium found in the olivine, i.e. Fo_{90} has a ratio of 90:10 of magnesium:iron.

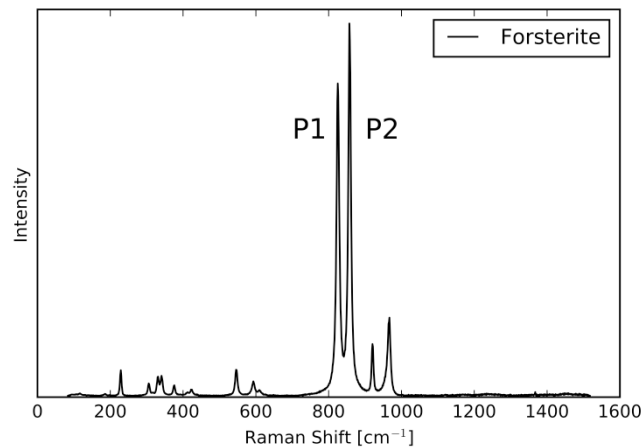


Fig. 1. Characteristic olivine spectra with doublet peaks P1 ($\sim 820 \text{ cm}^{-1}$) and P2 ($\sim 850 \text{ cm}^{-1}$). Sample from the RRUFF spectral database..

Studies investigating the shock effects on olivine do exist. A permanent shift of the olivine doublet peaks for single grains fired onto both aluminium foil and aerogel at 6.1 km s^{-1} on comparison to the original un-shocked samples has been shown [11]. This effect was thought to be as a result of the strain on the olivine crystal lattice caused by the effect of the impact [11]. Furthermore, natural, homogeneous San Carlos olivine has been fired onto aluminium foils at a range of speeds ($1 - 6 \text{ km s}^{-1}$) [12]. This latter work showed that shifts in P1 and P2 only occurred at higher impact speeds ($> \sim 5 \text{ km s}^{-1}$) [12]. Furthermore, the direction of the shift was found to be twice the magnitude of previous work [11].

Singular grains of olivine would be a rare occurrence in space, so this paper investigates the shock effects on mineral assemblages being captured in aerogel. The work focuses particularly on the olivine content of the samples, but the capture effects on other minerals (enstatite and hematite) in the assemblages are also observed.

2. Method

2.1. Sample Material

The material used in this work was sampled from the NWA 10256 CR2 (carbonaceous) chondrite. Before shooting, the sample was analysed at the University of Leicester by SEM-EDX using a Phillips XL30 ESEM, both in thin section and in powdered form. The CR2 chondrite meteorite is 58% chondrules, with many greater than 1 mm in diameter. It is mostly composed of pyroxenes ($\text{En}_{89-98}\text{Wo}_{0-1}\text{Fs}_{1-10}$) and olivines (Fo_{91-99}) [13]. The chondrules are surrounded by a matrix of fayalitic olivines (Fo_{34-50}), Fe-sulfides, Fe-Ni-metals and Fe-oxides [13].

Material from the interior of the meteorite was ground into a powder with a grain size of 25 – 200 μm . In order to determine the compositions of the powders before firing, the University of Kent's Raman spectrometer was used. A 532 nm (green) laser was used to acquire the Raman spectra. This specific laser was chosen as it is similar to the laser to be used on ESA-Roskosmos' ExoMars rover [14]. The 532 nm laser was used at a low power to ensure there were no laser heating affects to the grains, as this is known to be a potential problem in the interpretation of Raman spectra, e.g. [15].

2.2. University of Kent's Two-Stage Light Gas Gun

The powdered meteorite was fired using the University of Kent's Two-Stage Light Gas Gun (LGG) (Fig. 2) [16]. The speed for each shot is selected by varying the pre-pressure of the light gas in the gun's first stage. Rifle powder is used to move a piston through the first stage, explosively compressing the light gas. This in turn ruptures a burst disc, allowing the gas to escape. The escaping gas propels a sabot containing the powdered sample down the range and onto the target. The launch tube is rifled to ensure sabot separation, meaning the sabot will not hit the target. The speed of each shot is determined by the use of two laser light curtains with a known spatial separation, resulting in a speed determination to better than $\pm 1\%$ [16]. Three shots were done, with speeds of 6.10, 6.20 and 6.28 km s^{-1} , i.e. comparable to the Stardust mission capture speeds.

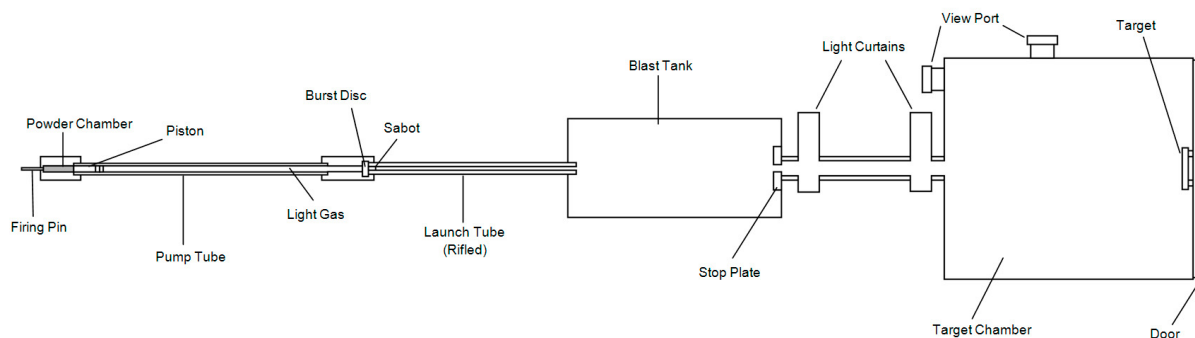


Fig. 2. Schematic of the University of Kent's Two-Stage Light Gas Gun. Overall length is about 5 m.

The target material used to capture the fired sample was aerogel with a density gradient of 25 mg cm^{-3} at the front face and rising to 55 mg cm^{-3} at the rear. The blocks were 30 mm thick. Due to the transparent nature of aerogel, the Raman spectra of the terminal grains can be obtained without extraction from the aerogel [17]. The track lengths were measured using a microscope.

3. Results and Discussion

3.1. Raman Characterisation

Before shooting, the powdered meteorite was characterised using the Raman spectrometer and the 532 nm (green) laser, obtaining 120 separate spectra. This suggested that as expected, the sample consisted of predominantly olivine and enstatite. However, we also found some hematite. To assure correct identification, comparative spectra from the RRUFF online database [18] was used, which has a complete set of high quality spectra data from well characterised materials. In Fig. 3 we show example spectra for each mineral.

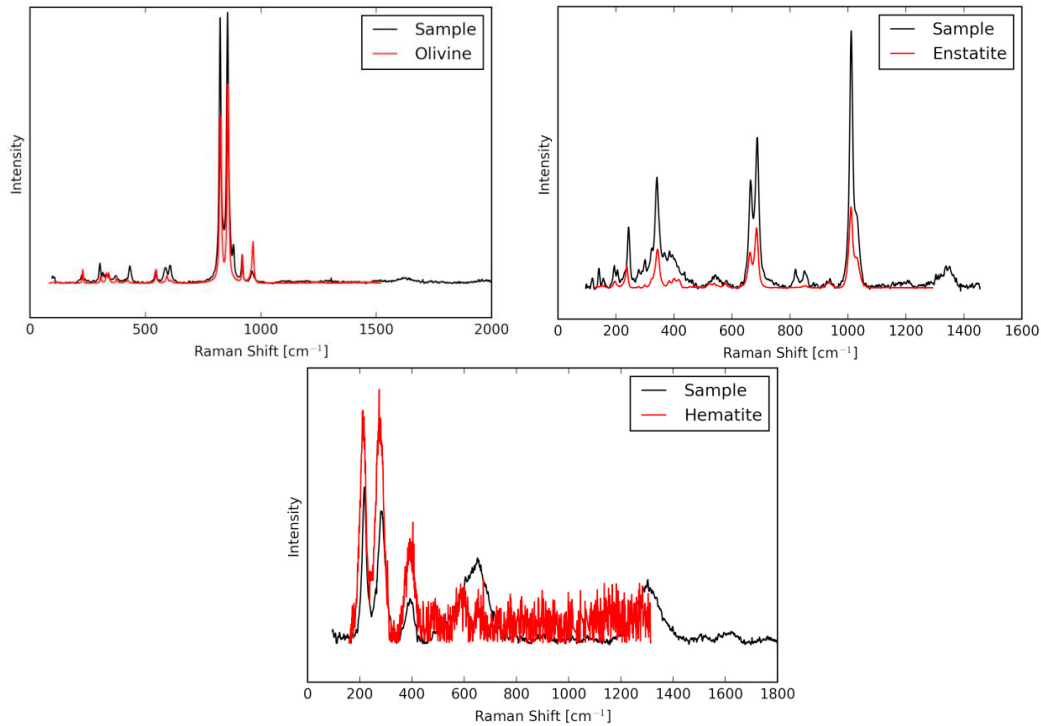


Fig.3. Example spectra (black) of each mineral from the CR2 meteorite with accompanying comparison spectra (red).

Overall of the 120 spectra, approximately 47% were olivine, 46% were enstatite and 7% were hematite. The Fo content of each olivine spectra was determined using Eq. 3 in [9]. This split the olivines into three Fo groups – Fo₄₃₋₅₇ (7%), Fo₇₀₋₈₂ (29%) and Fo₈₈₋₉₉ (64%), see Fig. 4. The comparative spectra for hematite (RRUFF ID: R070240) has a measured chemistry of $(\text{Fe}^{3+}_{1.97}\text{Al}_{0.02}\text{Mn}^{3+}_{0.01})\text{O}_3$ and was confirmed as hematite by X-ray diffraction and chemical analysis [18]. This sample was collected from the Moshgai, Gobi Desert in Mongolia [18]. The broadness of the spectral peaks in this reference spectrum is due to the sample being poorly crystalline. Hence, the hematite grains in the meteorite sample are also poorly crystalline.

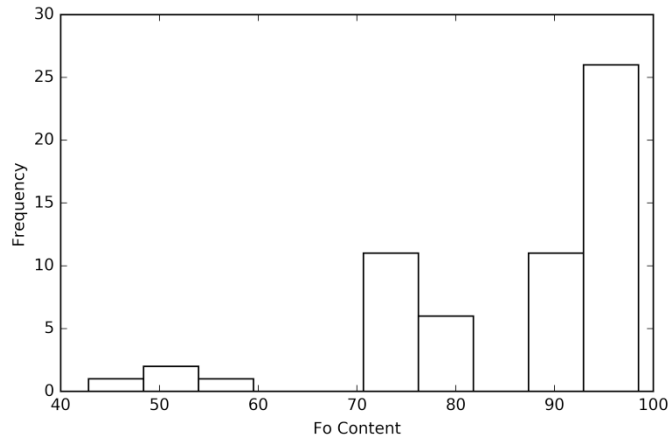


Fig.4. Fo content for the pre-shot characterised olivine samples. This shows the sample splits into three groups – Fo₄₃₋₅₇, Fo₇₀₋₈₂ and Fo₈₈₋₉₉.

3.2. Olivine Capture

In the three shots there were 52 observable grains. Fig. 5 is an image of a track and terminal grain. Typically, between 15 – 20 particles were captured per shot with a broad variation in track lengths (0.82 – 21.3 mm) and terminal grain sizes (diameter 6.28 – 74.4 μm). There was one grain which passed through the aerogel block and into the back plate.



Fig.5. Image of terminal grain and capture track. The grain entered the block of aerogel at the right side of the image. An arrow indicates the terminal grain.

Raman spectroscopy was performed on these captured grains in situ. There were significant issues in acquiring strong spectra due to significant fluorescing (producing stray backgrounds), and, the depth of the locations within the aerogel block meaning they could not be focused upon easily. Overall, six terminal grains produced olivine spectra. Of these grains, five terminal grains were found in one shot and one in another. Fig. 6 is plot of the six terminal grain’s Fo content determined using the P1 and P2 peak positions [9]. The red, black and blue lines in Fig. 6 represent the boundaries of the determined Fo groups discussed in the previous section. There appears to be three spectra that have an Fo content outside the characterised groups (Spectrum 3, 5 and 6, circled in Fig. 6). This suggests that these spectra have been altered upon capture in the aerogel. As previous work has shown that capture in aerogel results in a shift to a lower wavenumber for both peaks P1 and P2 [11], we deduce that Spectrum 3 has been shifted down from the Fo₈₈₋₉₉ group and Spectra 5 and 6 down from the Fo₇₀₋₈₂ group. These alterations in the Fo content are as a result of the capture process, which involves shock and heating effects. It is of course possible that other spectra have been shifted, e.g. Spectrum 1, but they cannot be positively demonstrated.

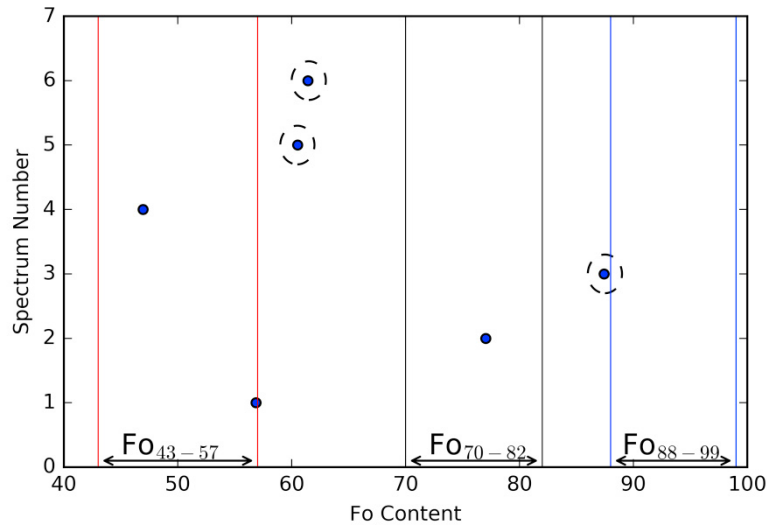


Fig. 6. The Fo content for each olivine spectra captured in aerogel. The two red lines refer to the boundaries of the FO_{43-57} group, the black for the FO_{70-82} group and the blue for the FO_{88-99} group. Circled are the three spectra which lay outside these three groups.

In order to ascertain an estimate of the peak shift for Spectra 3, 5 and 6 (circled in Fig. 6) we assume that they are shifted from the mean Fo content peak position of the pre-shot spectra in the bands to their immediate right in Fig. 6. This suggests a downward peak shift for Spectra 3, 5 and 6 of 1.21 , 1.56 and 1.48 cm^{-1} for P1 and 1.81 , 3.40 and 3.21 cm^{-1} for P2. Comparing the results from this work to past work we see a shift in the same direction but with a lower magnitude. This may well be an effect of the olivine being a constituent of the mineral assemblage or the small size of the sub-grains.

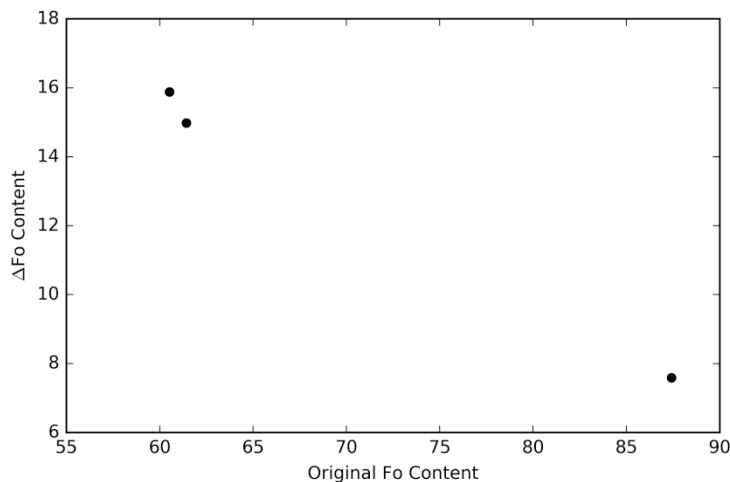


Fig.7. Magnitude of the difference in Fo content from the measured captured grain to the mean Fo content of the Fo group vs. captured grain Fo content.

In Fig. 7 we show the magnitude of the change in measured Fo content vs. the original Fo content. It would suggest that the lower original Fo content has a greater difference. This is as a result of the P2 peak experiencing a greater shift. This suggests that the shock is causing the peaks to move closer together. This agrees with the separation in the peak position corresponding to the different Fo content (see Fig. 9 in [11]). Furthermore, it has

been shown that San Carlos olivine (Fo_{92}) can experience up to 10 cm^{-1} in shift, to the left corresponding to ΔFo of approximately 25, when captured in aerogel [11]. This shift is greater than that experienced by the Fo_{88-99} olivines in this work. This could be due to the olivines being a constituent of the mineral assemblage.

3.3. Other Minerals

In Fig. 8 we show the Raman spectra of the other minerals found in the terminal grains. The enstatite was identified by comparing the peak positions to that of a reference sample from the RRUFF database (RRUFF ID: R070641). Interestingly, it would appear that some of the spectra experienced far greater capture alterations than the other minerals. This appears to be in contradiction with past work [19] which suggests enstatite experiences less alteration as a result of capture. It appears that along with a possible peak shift the peaks have widened indicating a break-down of crystallinity, both due to shock and/or heat effects. An additional reason for the broadening of the enstatite peaks could be due to the surface being partially melted and therefore the spectra are suggesting some glassification of the mineral surface.

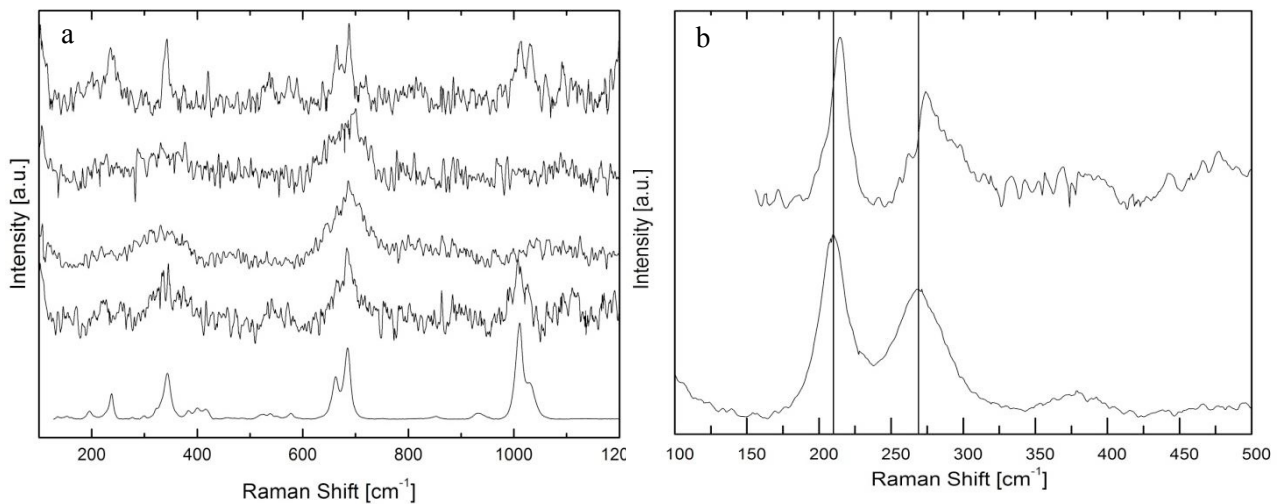


Fig. 8. (a) Top four spectra are of possible enstatite captured grains with the bottom being a reference enstatite spectrum. (b) Top spectrum is hematite that has been captured in aerogel, the bottom is a hematite spectrum from the pre-shot meteorite.

We also observe one spectra of hematite (Fig. 8b). The proportion in which we find olivine:enstatite:hematite (6:4:1) are within statistics comparative with those in the raw sample (47:46:7). In Fig. 8b there appears to be a peak shift of approximately $+4 \text{ cm}^{-1}$ due to shock and heating effects upon capture. Unlike the olivine in this work the shift is to higher wavenumbers. Previous experiments firing $10 \mu\text{m}$ grains of hematite into aerogel at 6 km s^{-1} showed a downward shift in the Raman spectra, as opposed to an upward shift here [20]. Similar shifts and broadening has been reported previously when magnetite and their product hematite samples are heated e.g., see [21].

4. Conclusions

A carbonaceous chondrite (CR2) meteorite was fired into aerogel at speeds between 6.1 and 6.3 km s^{-1} in order to investigate the capture effects on olivine as a constituent of a mineral assemblage, and act as an analog for the Stardust cometary collection. We can detect three examples of shifted olivine spectra. An estimate of the shift for the peaks P1 and P2 for the three spectra are 1.21 , 1.56 and 1.48 cm^{-1} and 1.81 , 3.40 and 3.21 cm^{-1} , both to lower wavenumbers, respectively. However, the magnitude of these shifts are not in full agreement with past work [11]. The magnitude is lower than previous work [11] which could be as a result of being a constituent of a mineral assemblage, meaning that it could be due to the shock wave propagating differently through the inhomogeneous

material. This would affect the olivine differently in comparison to when it is a singular grain. Given that the position of P1 and P2 are used to determine the relative Mg/Fe content of the olivine, these results indicate that there may be uncertainties in the Mg/Fe content of the olivines found by Stardust if identified by Raman spectroscopy. We also identified other minerals (enstatite and hematite), and see changes to their spectra as well.

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