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Mineralogy and petrology of Stardust particles encased in the bulb of track 80: TEM investigation of the Wild 2 fine-grained material

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Abstract

We have characterized by transmission electron microscopy the mineralogy of samples extracted from the walls of the Stardust track 80. More than 500 fragments were studied using conventional imaging, electron diffraction and EDX microanalysis. Two categories of particles are distinguishable in equal proportions (wt%). The first one is comprised of relatively large crystalline grains ($\approx 1 \, \mu m$ on average), dominated by silicates (olivine and pyroxene). They display a wide range of compositions and microstructures comparable to those found in terminal particles. Minor phases including magnetite and apatite are also present. Their occurrence suggests that the Wild 2 material underwent aqueous alteration to some extent. The second type of particle, called GEMS-like material, is made of silica-rich glassy clumps embedding iron sulfide beads and vesicles. Their microstructure is characteristic of thermally modified particles that have suffered strong interaction with the silica aerogel during the hypervelocity impact. This melted material may form by shedding of melted and vaporized material, but given the shape of the impact track and high diversity of surviving mineral compositions, much of it originated from fine-grained aggregates that disaggregated during the collection. Chemical mapping at the nano-scale allowed the localization of individual components within the silica-rich glass. They are dominated by Mg-rich components with a size less than 300 nm. The average composition of this thermally modified material is close to the solar abundance for the major elements Fe, Mg and S. The finegrained material has probably not been chemically fractionated in the protoplanetary disk before its incorporation in comet Wild 2 unlike the sulfur depleted matrix of chondrites. From these two categories of particles, we deduce that Wild 2 is likely made of an assemblage of relatively large evolved grains (first category) cemented by a fine-grained material with primitive chemistry (second category). The pre-impact configuration of the incident material deduced from this study seems comparable to the matrix of the most primitive chondrites (3.0) or to chondritic porous interplanetary dust particles. Published by Elsevier Ltd.

1. INTRODUCTION

Characterization of mineralogy and petrology of cometary material is essential to support our understanding of dust components in the protoplanetary disk. Comet dust is believed to be unprocessed on the comet parent body; therefore, it must have preserved signatures of events that took place before accretion. Until recently, comets were only studied using distant observations and remote sensing spectroscopy. Studies of primitive interplanetary dust particles (IDPs) (e.g., Schramm et al., 1989) or micrometeorites (e.g., Duprat et al., 2010) of presumed cometary origin are also achievable but the material provenance is still under debate. Cometary material is now available for direct analysis since the Stardust mission (NASA) returned to Earth samples from the comet 81P/Wild 2 in January 2006.

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The cometary dust was collected within a tray composed of low-density silica aerogel cells (Brownlee et al., 2006). The particles impacted with a relative velocity close to 6.1 km s⁻ and caused complex deceleration tracks in the aerogel (Brownlee et al., 2006; Hörz et al., 2006; Zolensky et al., 2006). Tracks have different morphologies, from carrotshaped to bulbous cavities from which one or several slender tracks emanate (Hörz et al., 2006; Burchell et al., 2008). The cometary material is unevenly distributed along the tracks, as illustrated by synchrotron X-ray fluorescence (SXRF) studies of entire tracks (Flynn et al., 2006; Ishii et al., 2008a; Lanzirotti et al., 2008). This suggests that numbers of Wild 2 particles are made of poorly cohesive assemblages that have been broken and scattered during the impact into the aerogel. For carrot shaped tracks (type A) generated by cohesive single particles, ablation due to the friction with the aerogel also leads to matter deposition along the walls. The shape of the tracks is then linked to the structure, cohesion, minerals and any organics present in the particles (Hörz et al., 2006; Burchell et al., 2008; Kearsley et al., 2012). Terminal particles correspond to the best-studied Stardust material until now. They are made of coarse grains, including CAI-like or chondrule-like assemblages (Zolensky et al., 2006; Leroux et al., 2008a; Nakamura et al., 2008; Simon et al., 2008; Chi et al., 2009; Jacob et al., 2009a). With SXRF data taken from seven Stardust tracks, Lanzirotti et al. (2008) showed that the quantity of material (based on the iron mass) contained within the terminal particles is variable, from 10% to 80% depending on the track morphology. In most cases, track walls contain much more cometary material than terminal particles. Nevertheless, the mineralogical study of the incident particle fragments encased in track walls is rendered complex because of a strong interaction with the aerogel. TEM studies showed that the samples display a mixture of crystalline and amorphous phases (e.g., Zolensky et al., 2006; Leroux et al., 2008b). Crystalline grains mainly consist of silicates (olivine and pyroxene). The amorphous material shows clear evidences of thermal modification and strong intermixing with melted aerogel due to the capture process (Keller et al., 2006; Zolensky et al., 2006; Keller and Messenger, 2008; Ishii et al., 2008b; Leroux et al., 2008b, 2009; Rietmeijer et al., 2008; Stodolna et al., 2009; Velbel and Harvey, 2009).

Despite its abundance, the cometary material dispersed along the track walls has been studied little in comparison with terminal particles. In this work, we report results of a transmission electron microscopy (TEM) investigation of a piece of aerogel extracted from the wall of track 80. The samples have been prepared using a compression and acrylic embedding method (Matrajt and Brownlee, 2006). This sample preparation permits the study of many different fragments in each TEM slice. We describe the mineralogy of the observed assemblage and propose a comparison of the cometary dust with the matrix of primitive chondrites and interplanetary dust particles (IDPs).

2. SAMPLES AND ANALYTICAL PROCEDURE

The sample used for the study came from the wall of track 80 (Fig. 1). Track size is about 4.5 mm in length



Fig. 1. Optical image showing the piece of Stardust track 80 bulb extracted for this study (Credit NASA).

and 2 mm in width. The track displays a very large bulbous cavity at the entrance and three terminal particles emanating out of the bottom of the bulb. According to the Stardust sample online catalog, their sizes are 7, 8 and 15 μ m. The track is classified as type B in morphology (Hörz et al., 2006) but is very close to type C. Samples from this track have been studied by Stodolna et al. (2009), Rietmeijer (2009a,b,c), de Gregorio et al. (2010, 2011) and Abreu et al. (2011). The terminal particles of this track have not been yet extracted, so their mineralogy in currently unknown.

In the present study, the sample corresponds to a full piece of wall from track 80 (Fig. 1) extracted at NASA JSC using the ultrasonic blade method (Ishii et al., 2005). Allocated TEM samples are designated C2092-3-80-0-53 and C2092-3-80-0-65. Each TEM grid contains two neighboring slices. They were prepared at the University of Washington using the acrylic embedding method (Matrajt and Brownlee, 2006). The preparation process consists of the following steps:

- The aerogel block is compressed between two glass slides.
- The compressed keystone is trimmed with a razor blade.
- The sample is embedded in a WELD-ON 40 acrylic resin and cured under high-pressure argon.
- Once the acrylic is cured, it can be trimmed and sliced with an ultramicrotome equipped with a diamond knife. The ultramicrotomed sections are deposited on TEM grids and washed with chloroform to dissolve the acrylic.

This method avoids the bias of optical selection of particles and preserves the aerogel medium in which Wild 2 particles are encased. Furthermore, it allows the study of numerous small fragments not visible under an optical microscope and thus not extractable. A high quantity of material in a single slice is preserved.

The samples were studied at the University of Lille (France) by analytical TEM using a Tecnai G2-20 twin (LaB₆ filament, 200 kV) and a Philips CM30 (LaB₆

filament, 300 kV) each equipped with an energy dispersive X-ray spectrometer (EDS). Grain microstructure was studied using bright- and dark-field imaging in conventional TEM mode and using bright and annular dark-field detectors in scanning (STEM) mode. The two microscopes are equipped with a precession module from the Nanomegas Company. Applying precession, the incident beam is scanned at a constant angle around the optic axis, in combination with a similar de-scan of the beam below the specimen (Vincent and Midgley, 1994). From a practical point of view, precession enables the collection of symmetrical diffraction patterns with intensities better related to the structure factors than in conventional diffraction mode. This is of great use for phase identification of small crystallites and reliable diffraction pattern indexing (Jacob et al., 2009b).

Chemical compositions were determined using Energy Dispersive Spectroscopy (EDS). The probe sizes ranged from 5 to 10 nm in STEM. For quantitative analyses, calculations of element concentrations and atomic ratios were carried out using calibrated k-factors and thin film matrix correction procedures. The k-factors for the major elements were determined using standard specimens according to the parameter-less method of Van Cappellen (1990). Elemental distributions were obtained by EDS X-ray intensity maps, using spectral imaging wherein each pixel of a spectrum image contains a full EDS spectrum (see Leroux et al., 2008b for details). The chemical composition of the crystalline grains was measured using an absorption correction based on electroneutrality (Van Cappellen and Doukhan, 1994). For crystalline silicates, elemental relative uncertainties are $\pm 3\%$ for major elements and $\pm 10\%$ for minor elements. For the silica-rich glassy clumps, the uncertainties associated with the elements Fe, Mg and S are estimated to ± 5 %.

3. RESULTS

3.1. General description

Each slice contains many fragments encased in the aerogel. The cometary material abundance and size is highly variable from place to place within the TEM samples. The regions near the wall display a large number of small fragments, typically below 1 μ m in diameter (Fig. 2a). Deeper in the aerogel, the number of fragments significantly decreases but their size is larger, about 2 μ m in average (Fig. 2b). The depth over which they are spread is about 200 μ m from the edge of the inside track wall. This should correspond to the maximum depth of implantation of fragments. The gradation in size shows that aerogel played a selective role. The very fine-grained material is stopped close to the boundary between the bulb cavity and the aerogel, and the larger components went deeper in the aerogel.

In both areas amorphous and crystalline fragments coexist but their relative proportion significantly differs. The small fragments found near the track wall are mainly amorphous (crystal/amorphous ~ 20%) while a large number of crystalline grains are present in the largest fragments found deeper in the aerogel (crystal/amorphous ~ 50–100%). The average crystal/amorphous ratio of the sample is about 50%.



3.2. Amorphous material

Approximately 400 amorphous fragments were studied. Their size is highly variable extending from tens of nanometers to 10 μ m with an average diameter about 1.6 μ m. These amorphous pockets scattered in the aerogel consist of a silica-rich glassy matrix embedded with a large number of small Fe–Ni–S inclusions and vesicles (Fig. 3). The size of the Fe–Ni–S beads extends from a few nanometers to one hundred of nanometers in rare cases. Their average abundance is variable from one fragment to another. Vesicles are usually bigger than metal beads but their number density is lower.

The average composition of the amorphous material is silica-rich. The other major elements are Mg, Fe and S. Some minor elements such as Al, Ca, Cr, Mn and Ni are also present in lower proportion (<0.5 at.%). In most case, their low concentration does not allow an accurate quantification. Measurements of the composition of 400 fragments are reported in a ternary Fe–Mg–S diagram (Fig. 4), as introduced by Leroux et al. (2009). The almost pure SiO₂ fragments, containing more than 99.5 mol% of silica, have been discarded. Compositions extend in a wide range between Mg, Fe and FeS endpoint compositions. Some fragments have end-members compositions of Mg,





Fig. 3. Bright-field TEM image showing a representative microstructure of the silica-rich glassy matrix of the amorphous particles. Fe–Ni–S beads are easily distinguishable in dark contrast and vesicles in bright. The shard-like aspect is due to sectioning by ultramicrotomy.



Fig. 4. Compositions (at.%) of 400 amorphous fragments in a ternary Fe–Mg–S diagram from the wall of Satrdust track 80. Fragments with more than 99.5% of silica have been discarded. Some compositions are very close to the end-members Mg, Fe and FeS but most of them are scattered around the CI reference represented by the star (taken from Wasson and Kallemeyn, 1988). The disk represents the average composition taking into account the size and impregnation by SiO₂ of each particle. This average value is very close to CI.

Fe or FeS but most of them scatter around the CI value. The average composition of the 400 fragments, computed by taking each individual area compositions weighted in size, is very close to CI (Fig. 4). The cometary material percentage in the glassy matrix is low and highly variable from one fragment to another with a maximum frequency peak around 10 vol% and goes up to 30 vol% (Fig. 5). This fraction of cometary material was estimated by comparing the Si concentration to the other major elements Fe, Mg and S (see Stodolna et al., 2009 for details on this calculation).



Fig. 5. Frequency histogram of the percentage of cometary material in the silica-rich glassy clumps. Most of particles contain only 10 vol% of cometary material.

Taking into account the concentration of cometary material within each analyzed particle (Fig. 6a), it appears that the fragments with compositions close to the Mg, Fe and FeS end-members display a high concentration of cometary material compared to those close to the CI composition. Fig. 6b shows that smallest fragments are frequently found close to the pure Mg, Fe and FeS compositions. Particles close to the CI value are on average larger and more diluted by SiO₂. The composition distribution is thus quite different according to their sizes.

EDS X-ray intensity maps of large amorphous fragments evidence chemical heterogeneity (Fig. 7). Iron and sulfur are present mainly within the Fe–Ni–S metallic beads. Locally Mg-rich, Ca-rich and Al-rich areas are detected. They are not distinguishable in TEM bright field



Fig. 6. Compositions of the amorphous fragments taking into account their size and concentration in cometary material (a) the diameter of the disks is proportional to the concentration in cometary material in the fragments. The highest concentrations correspond to compositions close to Fe, Mg and FeS end-members, showing that the corresponding fragments were single-phased (b). Same data but now they are distributed into three separate diagrams for three different size ranges. Compositions close to the endpoints Mg, Fe and FeS characterize smaller particles while the biggest converge to the average CI composition.

imaging but only using chemical maps. The presence of these patches shows that mixing with the silica aerogel was not complete. Size and number of these Mg and/or Ca and/or Al-rich areas are variable in the fragments. Their diameter extends from some tens of nanometers to 1 μ m. The size distribution of these "shadow grains" (Leroux et al., 2008b) is represented in Fig. 8. These data come from 16 amorphous fragments with a diameter >1 μ m and represent 900 different Mg/Al/Ca hotspots on X-ray intensity maps. The size distribution is fit with a power law ($b \approx -3.2$; $R^2 \approx 0.997$). The surface ratio of "shadow grains"/silica matrix is about 0.1.

3.3. Crystalline material

About 120 crystalline fragments have been characterized. Two of them are shown in Fig. 9. The grain size ranges from some nanometers to 3.5 μ m in diameter with an average diameter close to 1.1 μ m. The dominant phases are olivine and low-Ca pyroxene. Iron oxides (magnetite) are also present, as well as other minor phases (titaniferrous oxide, spinel, brownmillerite, Ca-phosphates, cristobalite). They are usually rounded, crystalline in their center and often surrounded by an amorphous rim rich in SiO₂ (Fig. 9a). The proportions and compositions of crystalline phases found in the samples are summarized in Tables 1 and 2.

Crystalline grains are often found close to amorphous grains without any obvious relationship between them.

For instance, Fig. 2b shows a large olivine $(Fo_{69\pm2})$ located near an amorphous pocket with a ratio Mg/(Mg + Fe) close to 0.57 ± 0.05 . This suggests that the two populations are chemically unrelated and non-equilibrated.

3.3.1. Silicates

Olivine and pyroxene are the most abundant minerals. They represent a modal abundance about 85% of the crystalline material. The proportion of olivine and pyroxene grains is about 60-40% by volume, taking into account their apparent size on the TEM foils, and about 50-50% by number.

Olivine has an extremely wide composition range, from Fo_{40} to Fo_{100} . The Fe–Mg distribution is summarized in Fig. 10A in two-frequency diagrams as a function of the number of analyzed grains (Fig. 10Aa) or as a function of the grain surface area in thin section (Fig. 10Ab). Comparison of these two representations shows that the smallest grains contain more magnesium than the largest ones. Olivine also contains low content of minor oxides like MnO, Al_2O_3 , CaO and Cr_2O_3 with contents up to 0.7, 0.5, 0.8 and 1.8 wt%, respectively. In contrast with observations of Tomeoka et al. (2008) and Nakamura-Messenger et al. (2011) who identified a number of dislocations in glide configuration in olivine grains, the studied grains are free from microstructural defects.

Low Ca-pyroxene compositions are given in Fig. 10B and in Table 1. They range from En_{50} to En_{98} with a



Fig. 7. Bright-field STEM image and EDS elemental distribution for Si, Al, Mg, Ca, Fe and S of a glassy area. Fe and S are localized in the Fe–Ni–S beads. Mg, Al and Ca are found in more extended hot spots ("shadow grains" – some of them are arrowed).



Fig. 8. Size distribution of the Mg–Al–Ca hot spots extracted from 16 amorphous particles (frequency as a function of the radius (log₁₀–log₁₀)). This distribution fit with a power law ($R^2 \approx 0.997$) and $b \approx -3.2$.

pronounced peak at En_{98} . As with olivine, the larger grains are more ferroan. Pyroxenes also include low content of minor oxides as MnO, Al_2O_3 , CaO and Cr_2O_3 with contents up to 1.1, 1.1, 0.7 and 1.9 wt%, respectively. The dominant microstructure of the Fe-rich grains consists of a monoclinic phase containing a high density of lamellae parallel to the (100) planes (Fig. 11). The lamellae width ranges from 5 to 50 nm. The selected area diffraction pattern (SAED) pattern consists of the superimposition of two monoclinic patterns $(P2_1/c)$ related by a mirror plane along (100) typical of twinned domains. Jacob et al. (2009a) already reported this twinned microstructure in Stardust terminal particles. The Fe-poor grains are orthoenstatite with space group *Pbca*. They contain (100) planar clinoenstatite lamellae (space group $P2_1/c$). Schmitz and Brenker (2008), Tomeoka et al. (2008) and Jacob et al. (2009a) have also previously reported a similar microstructure within terminal particles.

3.3.2. Magnetite

About 10% of the crystalline fragments are iron oxides. They are single crystals and their size extends from 100 nm to 1.8 μ m in diameter. Crystals are usually found in close association with other Wild 2 material. Chemical composition and SAED patterns reveal pure magnetite grains (Table 1) with homogenous composition. The grains have very low minor element contents (<0.2 wt% for Al₂O₃, MgO and MnO). They are rounded and display a dense SiO₂-rich amorphous rim, as observed for olivine and pyroxene (Fig. 12 and Table 1). The grains are free of microstructural defects.

3.3.3. Minor crystalline phases

About 5% of the crystalline material is made of minor phases. They have been identified by EDS and SAED. A Ti and Fe bearing oxide grain with a diameter close to 500 nm was found (Fig. 9b). Micro-analysis reveals bulk Ti concentration close to 11 at.%. The diffraction patterns consist of the superposition of a trigonal phase corresponding to ilmenite and a cubic phase corresponding to



Fig. 9. TEM bright-field images of two crystals and their associated diffraction pattern. The grain at the left is olivine (Fo₆₅), diffraction pattern in the zone axis [010]. Note the presence of a thick amorphous rim due to the high temperature stage of the collection. The grain at the right (b) is a titanium and iron bearing oxide grain with a bulk titanium concentration close to 11 at.%. The diffraction pattern consists of the superimposition of a trigonal phase corresponding to ilmenite (zone axis [241]) and a cubic phase corresponding to ulvöspinel (zone axis pattern [51–3]).

Table 1	
Representative elemental compositions (at.%) of the studied silicates.	. The compositions of the surrounding amorphous rims are also reporte

		0	Si	Mg	Fe	Al	Ca
Olivine							
Particle 1 (Fig. 2b)	Crystal	57.9	13.3	12.0	13.3	0.80	0.46
	Amorphous rim	63.9	19.8	7.64	1.68	3.41	0.27
Particle 2	Crystal	57.3	14.6	26.7	1.43	0.02	0.02
	Amorphous rim	66.1	32.3	0.03	1.20	0.21	0.05
Particle 3	Crystal	56.8	13.6	27.3	2.33	0.03	0.02
	Amorphous rim	65.4	25.7	4.28	0.76	3.71	0.17
Particle 4	Crystal	57,0	14.0	22.7	6.10	0.00	0.00
Particle 5	Crystal	57.2	14.1	22.1	5.90	0.00	0.00
Particle 6	Crystal	57.3	14.5	26.7	1.30	0.00	0.00
Pyroxenes							
Particle 1	Crystal	59.7	18.8	5.60	5.62	1.03	0.32
	Amorphous rim	65.4	30.6	0.84	2.59	0.54	0.02
Particle 2	Crystal	60.1	18.2	16.9	0.40	1.20	0.46
	Amorphous rim	65.4	25.9	2.89	1.33	1.01	0.28
Particle 3	Crystal	60.7	20.0	17.3	0.60	0.30	0.42
	Amorphous rim	63.3	24.5	9.58	0.56	0.72	0.34

ulvöspinel. The microstructure is made of lamellar defects. Unfortunately the grain was too thick and in inadequate orientation to be completely characterized. Nevertheless, a thinner area allowed deduction of the planar association of the ulvöspinel/magnetite with the ilmenite/hematite lamellae. Several grains of brownmillerite Ca₂(Fe,Al)₂O₅ grains have also been identified in one area of the sample, suggesting that they could originate from a larger grain that have been broken during the impact into the aerogel. Some are melted and mixed with aerogel while others are still crystalline with diameters extending to a micron. Two grains with chemistry and diffraction signatures compatible with F-apatite have also been found. A small crystalline grain containing Al and Cr with a spinel structure and an Al-Ca rich pyroxene are also present in these samples. Two small cristobalite grains have been characterized. One is in close association with a pyroxene grain. They

contain amorphous areas probably due to the high temperature stage of the collection or to the electron irradiation within the microscope since this phase is very beam-sensitive. Compositions of these minor crystalline phases are given in Table 2.

4. DISCUSSION

4.1. Fragmentation of the incident particle

Our TEM study of a piece of wall from track 80 reveals that the incident cometary particle was strongly fragmented during the hypervelocity impact. A very high number of sub-micrometer-sized fragments are found encased in the aerogel. The configuration suggests that the initial material was poorly cohesive and was disaggregated during the collection. As a function of the distance from the wall, the

Table 2
Representative elemental compositions (at.%) of minor phases of the studied sample. For some of them SiO ₂ is present due to the proximity of
melted aerogel around them. The number of grains and their modal proportions by volume are also reported.

Phase	No. of grains	Modal proportion	0	Si	Mg	Fe	S	Ni	Ca	Al	Ti	Cr	Mn	Р	F
Magnetite	11	9.57	50.16	0.34	0	49.39	0	0	0	0	0	0.11	0	_	_
			49.86	0.08	0.01	49.82	0	_	0	_	0.23	_	_	_	_
Magnetite rim			56.63	12.03	0.12	30.42	0.56	_	0.04	0.12	0	0.08	0	_	_
Titanium oxide	1	0.74	56.67	2.75	_	30.17	_	_	_	0.32	10.19	_	_	_	_
Brownmillerite	6	0.16	56.02	6.74	1.18	8.29	0.15	_	17.64	9.98	_	_	_	_	_
Fluorapatite	2	0.13	56.99	0.28	_	_	_	_	24.95	_	_	_	_	13.48	4.3
Chromiferrous spinelle	1	0.04	56.95	11.63	9.63	1.38	0.21	0.01	0.43	15.73	0.05	3.82	0.16	-	-
Âluminum rich pyroxene	1	1.1	64.19	22.32	2.1	0.17	0.01	00	1	11.18	0	0.02	0.01	-	-

nature and size of the fragment differ. Close to the wall, the fragments are small and dominated by amorphous materials. Some of these materials are likely the result of melting and ablation of larger particles in the aggregate. Deeper in the aerogel, the fragments are bigger and a significant number of crystalline phases was detected. This configuration shows that the aerogel played the role of a filter, with the coarser grains penetrating deeper the aerogel similarly to terminal particles of tracks made of coarse and dense grains (Zolensky et al., 2006; Tomeoka et al., 2008). Actually the deceleration tracks contain three levels of segregation: the very small grains stopped close to the track walls within the bulb, the dense micron-sized particles penetrated into the aerogel track walls along a distance of hundreds of micrometers, and the coarse dense grains (typically on the order of 10 µm) stopped at the end of the tracks after traveling millimeters. Studying samples coming from the bulbous regions is thus a good opportunity to study the finegrained material of Wild 2 that may be the most primitive. The preparation method used in this study has concentrated the fragments and thus allowed the characterization of a large number of them in a limited number of TEM slices (500 different fragments have been studied).

Unfortunately the fine-grained material was heavily modified due to extreme thermal conditions of the collection. Amorphous fragments are the consequence of this event (see below). The relative proportion of crystalline versus amorphous material was calculated near the border of the wall and deeper in the aerogel. For amorphous fragments, we subtracted the contribution of aerogel because they are strongly enriched in SiO₂, as explained in the results section. Near the wall, the percentage of crystalline fragments is about 30%. This percentage is much higher deeper in the aerogel and reach 85%. The average value for the sample is close to 50%. This result is in good agreement with µXANES studies of Westphal et al. (2009) who found a crystalline/amorphous ratio (two sided, 2σ) on 194 particles originating from 11 tracks although that study included only Fe-bearing grains. These percentages correspond to samples recovered after the collection and it is important to note that some fragments were heated and melted during the impact. The crystalline to amorphous ratio of Wild 2 was therefore higher than the values deduced from this study. Experimental shots of silicates in aerogel at 6.1 km s⁻¹ demonstrated that a significant part of crystalline silicate are melted and mixed with melted aerogel during the high temperature stage of the collection (Stodolna et al., 2012). Thus 0.5 must be considered as the minimum crystalline/amorphous ratio for the particle before its collection.

Crystalline silicates have been detected in several long period comets (Wooden et al., 2004) and in some Jupiterfamily comets (Kelley et al., 2008). The crystallinity seems to be quite variable among the studied objects: however, it is difficult to constrain crystallinity from infrared observations. For example the mass fraction of crystalline silicates varies between 12.5% (Min et al., 2005) and 88% (Wooden et al., 1999) for the coma of the Hale–Bopp comet as a function of the grain size and the porosity parameter chosen for data reduction. Also Tempel 1 comet shows a crystalline fraction between 35% (Harker et al., 2005) and less than 1% (Sugita et al., 2005). Lisse et al. (2006) report a crystalline fraction about 72% for olivine and more than 90% for pyroxene in Temple 1 Deep Impact ejecta (average 81%). Nevertheless some comets seem strongly deficient in crystalline silicates like C/2006 P1 McNaught (Kelley et al., 2007), while others seem to have high crystalline silicate fractions, for example up to $\sim 70\%$ for C/2001 Q4 (Wooden et al., 2004). Despite the thermal modification due to the collection, the determination of the crystalline fraction of this Stardust sample seems in accordance with a high degree of crystallinity for Wild 2.

4.2. Thermally modified material

The thermally modified material studied here is quite similar to that already described in detail by Leroux et al. (2008b, 2009). It originates from the interaction of the cometary material with the shock-heated aerogel. The temperature reached was high enough to induce melting of the particle fragments and part of aerogel. Both components were melted and mixed together. The rapid cooling and silica impregnation of the fused grains prevented crystallization during cooling. Iron sulfides were thermally decomposed and scattered within molten aerogel as Fe–S beads (Ishii et al., 2008b; Leroux et al., 2009). For the silicates, the intermixing with melted aerogel was not complete (Leroux et al., 2008b, 2009). Some remnants are still preserved as "shadow



Fig. 10. Fe–Mg distribution in olivine (A) and pyroxene (B). Data represents (a) the number of analyses (b) the average grain area (μm^2) of the analyzed grains. The frequency versus the composition of the silicates shows most of the grains are Mg-rich. The average grain area versus the composition shows the small grains are mainly Mg-rich and large grains contain more iron in both silicates. The two silicates present a very wide range of composition typical of a non-equilibrated material.

grains" within the silica-rich glassy matrix. In any case the distribution of the elements within the glassy matrix suggests that the cometary material included ultrafine-grained components (Zolensky et al., 2006; Leroux et al., 2009; Stodolna et al., 2009; Rietmeijer, 2009b). Here we use our data from a large number of grains to attempt a reconstruction of the initial fine-grained material and to deduce some properties.

Compositions of amorphous fragments in the Fe–Mg–S ternary diagram (Fig. 4) extend in the triangular Mg–Fe–FeS composition field but most of the data are very close to the CI value. Fragments having a composition close to the endpoints Mg, Fe and FeS should have magnesium-rich silicates (like forsterite or enstatite), Fe-metal or Fe oxides and iron sulfides, respectively, as precursors. Fig. 6a and b also shows that they are the smallest (typically < 300 nm) fragments, with the lowest dilution ratio into the aerogel. In contrast, the fragments close to the CI composition are

usually larger (>300 nm) and more diluted into the silica aerogel. The cometary material concentration is lower for these larger fragments because the impregnation is easy into the inter-grain spaces, in particular if the assemblage is disaggregated into the molten aerogel. This amorphous material likely originates from several small loosely bound individual components (various proportions of silicates, Fe-metal or Fe-oxides, Fe-sulfides) that have been melted and mixed with aerogel. This set of 400 fragments shows a gradation from the individual grains (small and rich in cometary material with a mineral like composition) to the aggregates (large and diluted by SiO₂, with compositions which reveal a mixture of several phases in various proportions). The average CI composition reveals the signature of unprocessed material.

EDX elemental mapping is a good method to estimate the nature and size of the grains that could constitute the



Fig. 11. TEM bright-field imaging and associated SAED diffraction of a (100) mirror plane-twinning defect on a clinopyroxene grain $En_{74}Wo_2Fs_{24}$. The zone axis is [013].



Fig. 12. TEM bright field image and associated SAED diffraction in the [1-1-1] zone axis of a magnetite grain. An amorphous rim due to high temperature interaction with aerogel during the collection is observed.

aggregate trapped in the melted aerogel (Fig. 7). For silicates, they appear as Mg, Al or Ca-rich patches. Leroux et al. (2009) call them "shadow grains" because they are not observable by standard imaging (TEM and STEM) but they are distinguishable using elemental maps. The mixing with the aerogel was incomplete during the collection due to an immiscibility gap between the composition of the melted grains and the SiO₂ liquid (see Leroux et al., 2008b; Roskosz et al., 2008 for details). A significant number of "shadow grains" contain metal and sulfides beads.

Their microstructure closely resembles GEMS (glass with embedded metal and sulfides), as described by Brownlee et al. (2006) and Keller et al. (2006). They were named "relict GEMS" by Keller and Messenger (2008). GEMS are spheroids ~ 0.1 to 0.5 µm in diameter composed of amorphous Mg-rich silicates containing nanometer-sized inclusions of low-Ni metal and low-Ni iron sulfides (Bradley, 1994). They are present in abundance in chondritic porous IDPs, and some have been shown to have isotope anomalies indicating they are surviving grains from the interstellar medium (Bradley, 1994; Messenger et al., 2003; Floss et al., 2006: Keller and Messenger, 2011). In the Stardust aerogel, compositions of the GEMS-like objects are variable but scattered around the CI value. The vast majority of them belong to the GEMS composition field determined by Keller and Messenger (2011) (Fig. 13). However, their enrichment in silica shows that the material experienced melting and mixing with aerogel, which makes difficult their unambiguous identification. The thermally modified fragments of track 80 could originate from GEMS grains, just as they could come from an assemblage of small aggregates composed of silicate and sulfide submicron-sized crystals. In Fig. 13, some GEMS-like objects have compositions close to the Mg, Fe and FeS endpoints. Their corresponding precursors likely derive respectively from Mg-silicates, Febearing minerals (Fe-silicates, metal or magnetite) and iron-sulfide. Laboratory light gas gun shots of pyrrhotite particles into aerogel also showed the formation of microstructures consisting of sulfide-metal beads in Mg-free silicate glass (Ishii et al., 2008a,b). This experimental work demonstrated that the interaction between particles containing sulfide grains and aerogel could lead to the formation of GEMS-like objects.

4.3. Crystalline material

Crystalline grains represent 50% of the cometary material in the sample. This percentage was probably higher in the particle before impact because many of the fine grains (typically lower than 1 μ m) have been melted during impact in aerogel. The grain size of crystals is highly variable as well as their chemical composition, as evidenced by the large variability of the Fe–Mg distribution in silicates. The relative abundance is about 85% for crystalline silicates (olivine and pyroxene), 10% for magnetite with the rest being minor phases like fluorapatite, brownmillerite and titanium oxide. This diversity indicates that the assemblage of grains in the particle that created track 80 is not chemically equilibrated.

4.3.1. Silicates

Compositions of olivine and pyroxene extend within the wide ranges Fo_{40-100} and En_{50-98} , respectively. These Fe-Mg distributions are comparable to the 85 olivine and 84 pyroxene grains from 26 terminal particles reported by Zolensky et al. (2008). Crystalline silicate grains in track 80 are thus very heterogeneous in composition despite originating from a single track, while Zolensky et al. (2008) reported the composition of silicates from 26 different tracks. The initial Wild 2 particle that formed track 80 therefore



Fig. 13. Composition of the 400 amorphous fragments of the studied sample in the ternary Fe–Mg–S diagram, compared to the composition field of GEMS in IDPs (Keller and Messenger, 2011). The disk represents the weighted average composition (taking into account the size and impregnation by SiO_2 of each particle). The star represents the CI composition.

contains minerals that are not equilibrated. This is consistent with the model of cometary particles that consist of an aggregate formed by components from different origins (e.g., Hanner and Bradley, 2003). The diversity seems due to a very efficient mixing in the protoplanetary disk maybe more extensive than proposed in current models (Shu et al., 1996; Gail, 2001; Bockelée-Morvan et al., 2002; Boss, 2008; Vinković, 2009). This result is in accordance with the conclusion of Ogliore et al. (2009) who compares the crystalline fraction of Wild 2 as a function of radius from the sun with that calculated from different silicate grains mass accretion rates (Gail, 2001) and the efficiency of turbulent radial mixing models (Bockelée-Morvan et al., 2002).

The ratio of olivine/pyroxene deduced from the observation is about 1.5. Nevertheless this value is certainly overestimated for an extrapolation to the Wild 2 particles. Indeed the melting temperature of pyroxene is typically 300 °C lower than olivine. Pyroxene is thus preferentially melted during the high temperature stage of the impact (Stodolna et al., 2012), and therefore the original olivine/pyroxene ratio before the collection was likely ≤ 1.5 . This result is consistent with the one obtained by Leroux et al. (2010) that used residues of crater foils to obtain a value close to 1. Except for the CR chondrites, this value close to 1 (Weisberg et al., 1993) is inconsistent with carbonaceous chondrites which usually contain much more olivine than pyroxene.

The majority of olivine and pyroxene is magnesium-rich. Again, this could be the consequence of collection into aerogel: the melting point of magnesium rich silicates is higher than the iron rich ones. For instance, the melting point of forsterite is 1900 °C but only 1200 °C for fayalite. Iron rich silicates have been preferentially melted and mixed with aerogel to form amorphous patches enriched in SiO₂. The comparison of the two diagrams in the Fig. 10 shows than iron-rich olivines are bigger than the magnesium-rich, which is in accordance with this

interpretation. The small Fe-rich silicates were likely fully consumed in the melted aerogel.

4.3.2. Evidence for aqueous alteration signatures

Lisse et al. (2006, 2007) reported the presence of alteration products (phyllosilicates and carbonates) on the comet Tempel 1 based on Spitzer Space Observatory data. To date, evidence for aqueous alteration products in Wild 2 samples is still limited (see discussion in Zolensky et al., 2008). Recently, Foster et al. (2008), Matrajt et al. (2008) and Bridges et al. (2010) have reported the presence of magnetite. Berger et al. (2011) reported the occurrence of low temperature sulfide mineral assemblages and they suggest aqueous activity in Wild 2. In our study, several iron oxide grains (magnetite) have been identified. They represent approximately 10% of the total crystalline material. The silica-rich glassy rim around them (Fig. 12) shows that these grains interacted with aerogel at high temperature, which is typical of Wild 2 grains in Stardust samples. These grains of magnetite are not contaminants. All the magnetite grains studied are single crystals and have a rounded shape. Although rounded shapes may result from ablation during collection, we interpret this configuration to be the result of the disaggregation of a magnetite framboid during the collection. Magnetite framboids are typically found in CI carbonaceous chondrites and originated from aqueous alteration of the parent body (Kerridge, 1970; Kerridge et al., 1979). Berger et al. (2011) reported some similarity between CI chondrites and Wild 2 grains. Fluorapatite is also a phase found in matrix of carbonaceous chondrites that were subjected to alteration processes (Brearley and Jones, 1998). It can also be formed by thermal metamorphism or during cooling and differentiation of magma. Here, the coexistence of this phase with magnetite suggests a formation process by aqueous alteration. The case of brownmillerite is probably more complex. So far, this phase is not reported as a constituent of extraterrestrial minerals. In terrestrial context, brownmillerite is the consequence of high-temperature contact metamorphism and forms by reaction between silicates and Ca-carbonates (e.g., Sharygin et al., 2008). The first stage thus requires the formation of carbonates by aqueous alteration which can later react with silicates to form brownmillerite at high temperature.

The presence of magnetite, brownmillerite and fluorapatite in Wild 2 suggests that some cometary material experienced aqueous alteration. Berger et al. (2011) suggest the formation of pockets of liquid due to a soft heating from low velocity collisions, which could occur throughout the comet's lifetime, or short-lived radionuclides on comet Wild 2. In the aqueous altered chondrites magnetite is often associated with phyllosilicates (Brearley and Jones, 1998). Nevertheless there is still no evidence for phyllosilicates in the Wild 2 material (Zolensky et al., 2006, 2008). It appears that they could have been completely melted or decomposed during the high temperature stage of the collection. Their low decomposition temperature, typically 800 °C (Akai, 1992), associated with a small size (<200 nm in matrix of primitive chondrites for example) can explain their apparent absence in the Stardust samples (if present on Wild 2). Noguchi et al. (2007) showed the formation of an amorphous rim with a thickness close to $0.5-1 \,\mu\text{m}$ around serpentine grains shot into aerogel with the Stardust collection conditions. Phyllosilicates grains smaller than $0.5-1 \,\mu\text{m}$ are thus expected to be melted on impact.

4.4. Comparison with CP IDPs and matrix of primitive chondrites

Fig. 14 shows the average composition of the crystalline material, of the thermally modified material and the average bulk composition of the samples for the major elements (Fe, Mg and S). This average bulk composition is calculated by weighting the compositions by the volume fractions of the two categories of fragments (amorphous and crystalline). The thermally modified material is very close to the CI composition. In contrast, the crystalline material is particularly poor in sulfur because no large iron sulfides grains were identified. The sulfur-bearing phases are present embedded as nanophases in the silica-rich glassy matrix. The total average composition falls in the chondrite field (Fig. 14). We have not detected in our samples a clear demonstration for the presence of fragments of chondrules, although large crystalline grains of olivine and pyroxene may have this origin. We studied only a portion of track wall of Track 80, and the terminal particles, yet to be analyzed, are still potential chondrule fragments.

The thermally modified grains are likely derived from Wild 2 fine-grained aggregates. Since their composition is close to CI, it is interesting to compare the studied track 80 samples with chondritic porous IDPs. These IDPs are aggregates composed of weakly cohesive components that consist mainly of fine-grained amorphous grains, frequently called GEMS, micrometer-scale silicates (mainly olivine and pyroxene) and Fe,Ni sulfides (see details in Bradley, 1994; Rietmeijer, 1998, 2002). This aggregate configuration is in good agreement with our observations. Indeed, our Stardust samples contain both unmelted micrometer-sized silicates grains and a material much finer that was melted in the aerogel during the high temperature stage of the impact. It is not possible to go further in the comparison because the thermal event has obliterated the original microstructure. However the chemical composition of melted grains is close to CI, and is therefore compatible with the ultrafine-grained component of IDPs. Similar conclusions were drawn recently by Rietmeijer (2009b).

Actually the studied material seems to have properties comparable to some matrix of primitive chondrites like MET00426, QUE99117 (CR3.0 – Abreu and Brearley, 2010), ALH A77307 (CO3.0 – Brearley, 1993), Acfer 094 (ungrouped – Greshake, 1997; Keller et al., 2009), Adelaide (ungrouped – Brearley, 1991; Greshake et al., 2004), Kakangari (K – Brearley, 1989). These matrices are usually composed of amorphous material mixed together with small crystals (<500 nm). The amorphous material is heterogeneous at the submicron scale, depleted in sulfur and magnesium and enriched in iron and silicon. The typical size of the amorphous areas in the matrices is about 1–10 μ m (Brearley, 1993). This size is in accordance with our previous calculations (Stodolna et al., 2009) where we deduced the initial size of thermally modified fragments from the incident particle of



Fig. 14. Average composition of the fine-grained material of track 80, bulk composition and composition of matrices of carbonaceous chondrites (McSween and Richardson, 1977) and amorphous material in the matrix of the primitive meteorite ALH A77307 (Brearley, 1993). The star represents the CI composition. The average composition of the studied sample matches the composition of the matrix of the primitive meteorites. The CI composition of the thermally modified material is richer in sulfur than the fine-grained components of the chondrite matrices.

track 80 before its melting and mixing with aerogel (<10 μ m). The size of crystals present in amorphous pockets of chondrite matrices corresponds to the typical size of the "shadow grains" from Wild 2 (<200–300 nm). Concerning the surviving silicate crystals, their composition (Fo_{40–100} and En_{50–98}), the ratio olivine/pyroxene (1 < *X* < 1.5), their microstructure (olivine free of defects and ortho/clino lamellae in the pyroxenes (Fig. 11)) and the presence of magnetite (diameter < 10 μ m) are other parameters that match with this family of material and particularly with ALH A77307. The presence of very small sulfides (100–300 nm) and the low amount of phyllosilicates (0.3–1 μ m in size) in this primitive CO chondrite can also explain their absence in the Stardust samples due to the extreme collection conditions.

The major difference is the concentration of sulfur which is greater in the thermally modified samples than in the different constituents of the matrices of the meteorites (Fig. 14). In fact, it may originally have been even greater due to loss of volatile sulfur during the extreme capture event (Flynn et al., 2006). There is no evidence of a sulfur rich component on this family of material even in the amorphous areas (Brearley, 1991, 1993). Sulfur has possibly been mobilized in the parent bodies of primitive meteorites to precipitate in the form of large sulfides, leaving the fine matrix depleted in this element. If this interpretation is correct, the Stardust track 80 material did not experienced S mobilization which is observed in the inter chondrule fine-grained matrix of type 3.0 chondrites, in agreement with what may be expected from dust accreted in a very cold region of the protosolar nebulae.

5. CONCLUSION

We have characterized the mineralogy of grains trapped in the walls of the Stardust track 80 cavity. The aerogel has acted as a filter separating the fine-grained material and the larger (micron-sized) crystalline grains. The fine-grained material suffered from extreme thermal processing due to the collection into the aerogel. It now consists of silica-rich glassy clumps scattered in the aerogel. Even if the finegrained material has been melted and mixed with the silica aerogel, relevant information can be deduced from its bulk composition or locally by elemental mapping at the nanoscale. The glassy areas have a CI average composition and contain sub-micron sized silicate components likely originated from fine-grained precursor. The original size of the sub-grain could have been modified during the interaction with the aerogel. Crystalline grains are predominantly well-preserved silicates that display a wide range of compositions typical of a non-equilibrated assemblage. Some phases, magnetite, apatite and brownmillerite are new evidence of material present in Wild 2 that likely formed by aqueous alteration. Nevertheless it is difficult to state more precisely where this aqueous alteration has occurred (prior to the accretion on Wild 2 or on the comet). We deduce that the Wild 2 particle that created track 80 was initially made of a refractory material including large crystalline silicates (possibly chondrules fragments) and altered phases stuck together by a fine-grained material with a primitive chemistry. The assemblage shows numerous similarities with chondritic porous IDPs and matrices of the most primitive chondrites. Compared with the primitive matrices of chondrites, the major difference is higher sulfur content in the Wild 2 finegrained material, maybe because this material escaped sulfur depletion due to larger heliocentric distances relative to the material that formed the matrices of chondrites.

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