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Letter

Igneous Ca-rich pyroxene in comet 81P/Wild 2

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Abstract

The Stardust spacecraft successfully returned dust from comet 81P/Wild 2 to Earth in January 2006. Preliminary examination of the samples showed abundant crystalline silicates comparable to those found in chondritic meteorites presumably formed in the asteroid belt. Here, we report results of a transmission electron microscopy (TEM) study of a pyroxene-bearing terminal particle, which contains lamellar intergrowths of pigeonite and diopside on the (001) plane. This microstructure is typical for an igneous process and formation by exsolution during cooling. Width and wavelength of the lamellae indicate a cooling rate within the range 10–100 °C/h, in close agreement with those of chondrules or lava from an asteroidal igneous rock. This observation shows that some Stardust material experienced periods of igneous processing similar to material found in the inner early solar system. This implies that igneous materials were common materials in a large region of the protoplanetary disk and were not restricted to the asteroid belt. Their presence in comet Wild 2 also supports the favored view of large radial mixing from the inner to the outer regions before the comet's accretion.
Keywords: Comet dust, electron microscopy, pyroxene, Stardust, phase transformation

Introduction

Samples returned from the Stardust mission show an unexpectedly high abundance of crystalline materials (Brownlee et al. 2006; Zolensky et al. 2006). Dust from comet Wild 2 therefore differs from anhydrous chondritic interplanetary dust particles (Ishii et al. 2008) that contain abundant amorphous materials, and from interstellar silicates, believed to be dominated by amorphous phases (Kemper et al. 2004). In this context, it is important to identify the process responsible for crystallization of the Stardust materials. Suggested crystallization mechanisms include thermal annealing of amorphous interstellar precursors, direct condensation in hot regions of the solar nebula, or crystallization from a melt during an igneous event such as those that result in chondrule formation or volcanic activity at a planetoid surface. Signatures of crystal formation are recorded in morphology, composition, and microstructure of crystals. Thus, their detailed study can provide better constraints for active processes that occurred in the early solar nebula and refine the understanding of the petrogenetic continuum between asteroids and comets.

Along with the high-temperature minerals, pyroxenes are of special interest because they are useful indicators for thermal and deformational events. In this paper, we use analytical transmission electron microscopy (ATEM) to study the microstructure of a Ca-rich pyroxene in one Wild 2 particle to provide information about its thermal history and the possible origin of the parent Stardust particle.

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Sample and analytical procedure

The studied Wild 2 sample is a terminal particle (grain 2) from track 69, labeled C2027,2,69,2,2 (Fig. 1). The sample, about 5 µm in diameter, was removed from aerogel, embedded in epoxy and sliced into ~70 nm thick sections with an ultramicrotome at the Johnson Space Center (NASA) (Zolensky et al. 2008). Sections were then transferred to amorphous C-supported Cu TEM grids. The ATEM study was performed using a Philips CM30 (LaB_6 filament) operating at 300 kV and a Tecnai G2-20 twin (LaB_6 filament) operating at 200 kV. Specimens were mounted on a Be low-background double-tilt holder. Microstructural analysis was carried out using conventional bright and dark field imaging. Chemical compositions were measured using energy dispersive X-ray spectroscopy (EDS) with a Thermo Noran Si-detector (CM30) and an EDAX Si(Li)-detector (Tecnai), both having ultrathin windows. For quantitative analyses, calculations of element concentrations and atomic ratios were carried out using calibrated *k*-factors and thin film matrix correction procedures. The absorption correction procedure was based on the principle of electroneutrality (Van Cappellen and Doukhan 1994). The *k*-factors for O and Mg were determined using quartz and forsterite standards by the parameter-less method of Van Cappellen (1990).

Results

The sample in this study does not demonstrate significant thermal alteration caused by the capture process, in contrast to several other Wild 2 particles (Zolensky et al. 2006; Leroux et al. 2008). Only a minor amount of melted material is found at the periphery in contact with compressed aerogel. The sample is dominated by orthopyroxene (enstatite) and minor Ca-rich clinopyroxene, both Fe-poor. Orthopyroxene contains a low density of crystal defects. A few dislocations and planar defects along the (100) plane are observed. The main feature of the diopside grain is an exsolution microstructure, consisting of continuous coherent (001) lamellae, ~7 nm in thickness, with wavelengths from 20 to 30 nm (Fig. 2a). The small thickness of the lamellae precluded the measurement of their individual compositions and only the average composition of the grain was obtained. Measured average compositions are $En_{95.8}Wo_{1.7}Fs_{2.5}$ for enstatite and $En_{71.4}Wo_{25.7}Fs_{2.9}$ for the Ca-rich component (see Table 1 for details). Selected area electron diffraction patterns (Figs. 2b–2c) confirm two distinct contributions, diopside with space group *C*2/*c* and pigeonite with space group $P2_1/c$. These two phases are distinguishable by their different monoclinic lattice angles and a slight difference in their lattice parameters in the 100* and 001* directions. Misfit dislocations are not present at the lamellae/host interface.

Discussion

The composition and the exsolution microstructure of the Ca-rich Wild 2 grain are hardly compatible with a formation by condensation or annealing from an amorphous precursor. While exceedingly rapid vapor condensation or rapid decompression (from impact) can result in immiscible glasses (Zolensky and Koeberl 1991), it is difficult to conceive of a situation leading from this to a pyroxene exsolution texture, or vapor condensation scenario that would lead directly to such an exsolution structure (G. Lofgren, personal communication). The microstructure

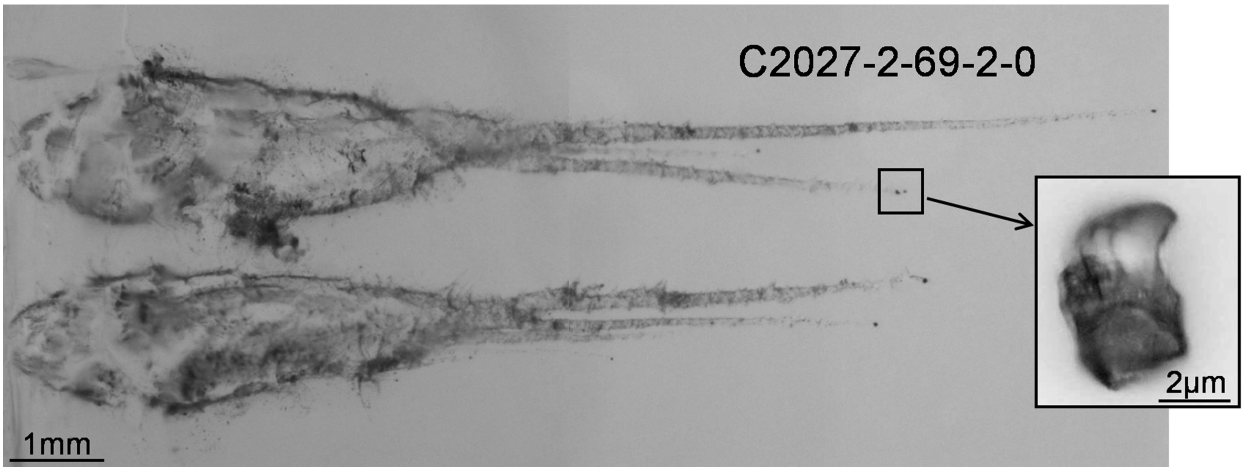

Figure 1. Optical micrograph of tracks 32 and 69. Impacting comet dust particles created tracks with various morphologies. Both of these tracks have a bulbous entry region (left side) and are terminated by several carrot-like sub-tracks (right side). The studied grain comes from one of the track termini of track 69. The grain particle has been extracted and prepared for TEM by ultramicrotomy at NASA-JSC.

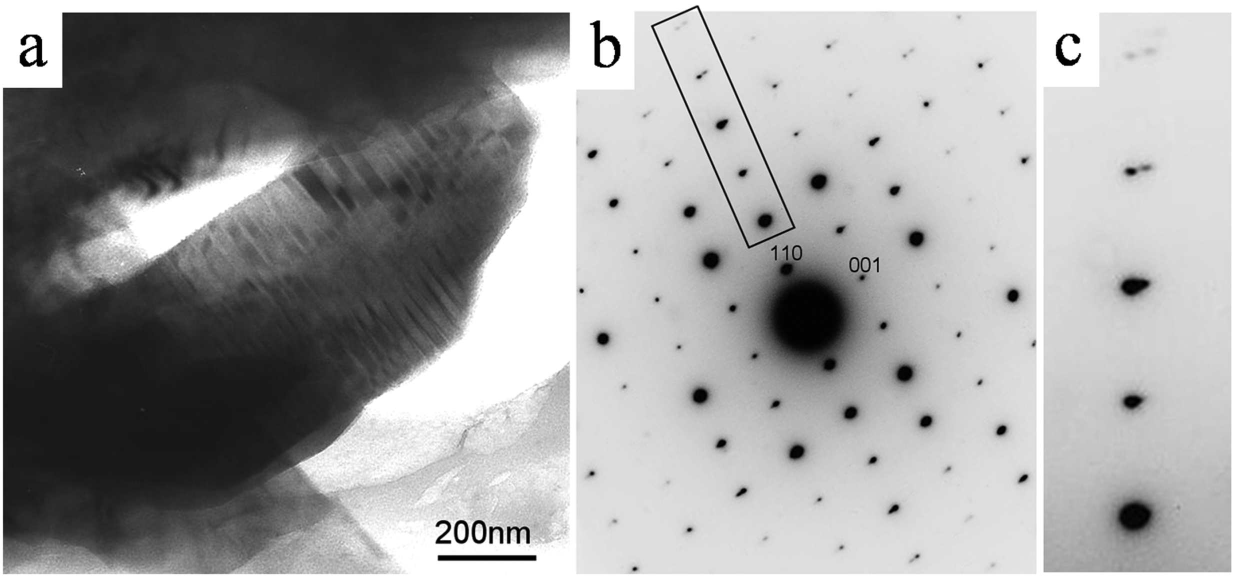

Figure 2. (**a**) TEM bright field image of the Ca-rich grain showing exsolution lamellae in (001). (**b**) SAED pattern, zone axis [$\bar{1}$10]. The spots show splitting along the [110]* direction, as better seen on the enlargement on **c**. This splitting is due to an alternation of Ca-rich and Ca-poor clinopyroxene corresponding to a $\Delta\beta$ of about 3° in the [100]* direction.

TABLE 1. EDS composition for the pyroxene particle from track 69 (normalized to 60 at% oxygen)

O	Si	Mg	Ca	Al	Ti	Cr	Mn	Fe
				Enstatite				
60.0	19.6	19.0	0.33	0.28	0.01	0.27	0.10	0.50
–	(0.1)	(0.1)	(0.04)	(0.04)	(0.01)	(0.02)	(0.03)	(0.04)
				Diopside				
60.00	18.6	13.6	4.9	1.4	0.16	0.40	0.24	0.56
–	(0.1)	(0.6)	(0.5)	(0.3)	(0.02)	(0.03)	(0.03)	(0.09)

Note: Estimated standard deviations are given in parentheses.

is fully consistent with crystallization from a FeO-poor melt, pyroxene-like in composition. According to the $Mg_2Si_2O_6$-$CaMgSi_2O_6$ binary phase diagram (Fig. 3[1], see also Carlson 1988), the primary crystallization leads to the formation of orthoenstatite and diopside. The bulk composition of the diopside grain includes approximately 32 mol% of $CaSiO_3$, indicating a temperature of crystallization of 1400 °C. During subsequent cooling, the solubility of enstatite decreases rapidly in Ca-rich compositions while it only slightly increases in the Mg-rich endmember. The primary diopside crystals thus enter a two-phase field, namely pigeonite + diopside. During subsequent cooling, pigeonite is exsolved in the form of coherent lamellae in the (001) plane in a diopside matrix that becomes enriched in Ca. This formation mechanism has been explained as a spinodal-decomposition-like process or coherent nucleation and growth, followed by coarsening (e.g., McCallister and Yund 1977; Grove 1982; Jantzen 1984). In contrast, the adjacent enstatite grains, because of the relatively constant Ca solubility within the range of temperature 1200–1400 °C, do not present an exsolution microstructure on cooling.

Exsolution formation and coarsening in pyroxene is controlled by diffusion, which is a time and temperature-dependent process. The widths of exsolution lamellae can be used to estimate the cooling rate of terrestrial and extraterrestrial rocks (e.g., Champness and Lorimer 1971; Takeda et al. 1975; Lally et al. 1975; Grove 1982; Schwartz and McCallum 2005; Weinbruch and Müller 1995; Weinbruch et al. 2001; Watanabe et al. 1985; McCallister and Nord 1981; Leroux et al. 2004). The development of (001) lamellae first requires an incubation period for the spinodal process or coherent nucleation to be completed, followed by the coarsening process. Lamellae coarsening have been calibrated with isothermal annealing or continuous cooling experiments (Grove 1982; Weinbruch et al. 2001), including experiments at compositions close to those found in this Wild 2 sample (McCallister 1978; Weinbruch et al. 2003, 2006). Coarsening in isothermal growth experiments is described by an empirical equation $\lambda^n(t) - \lambda_0^n = k\,(t - t_0)$, where k and n are empirical constants, λ_0 the average initial wavelength at t_0, $\lambda(t)$ is the wavelength at time t. The exponent factor n is close to 3, indicating a volume diffusion controlled process (Weinbruch et al. 2003). For continuous cooling, the cooling rate can be estimated with a time-temperature transformation (TTT) diagram constructed with isothermal growths (Fig. 4[1], see also Weinbruch et al. 1995). The average wavelength observed in the Wild 2 sample is 25 nm. When plotted in the TTT diagram, this value yields a cooling rate in the range 10–100 °C/h, within the temperature interval 1350–1200 °C. At lower temperature, the diffusion is too slow to account for coarsening. The main coarsening process occurred at $T > 1200$ °C.

The diopside-enstatite phase assemblage, the composition and the exsolution microstructure of the Ca-rich component show that the studied Wild 2 particle experienced an igneous (melting) episode. Before discussing an indigenous origin, it is necessary to know if the capture of the particle in silica aerogel could be responsible for this igneous microstructure. The capture of particles in aerogel has been demonstrated to induce local melting due to the hypervelocity impact at 6.2 km/s in the silica aerogel collectors (Zolensky et al. 2006; Leroux et al. 2008). The melted material has been quenched as a glass mixed with silica glass coming from melted silica aerogel. This easily recognized microstructure is not observed in our sample, except at the periphery of the grain. The cooling rate we deduced in the present study appears to be much lower than the one deduced from the thermal regime associated to the capture (Roskosz et al. 2008), showing that the formation of an exsolution microstructure in pyroxene during the capture is unrealistic. The igneous microstructure is thus indigenous to this particular Wild 2 material itself.

Several causes can be invoked for melt formation in the solar system. They include chondrule formation, volcanic activity at asteroid or planetoid surfaces, and impact melting. Exsolution microstructure in impact melt rocks has never been observed, probably because most material experienced rapid cooling after shock heating. Exsolution in pyroxene occurs frequently in igneous rocks originated from lava of differentiated asteroids or planets with associated cooling rates usually lower that the one we extracted from the Wild 2 Ca-rich particle (e.g., Takeda et al. 1975; Leroux et al. 2004; Schwartz and McCallum 2005). If the Wild 2 particle originated from such an igneous environment, it might be located at the upper part of the lava flow. Exsolution lamellae in Ca-rich pyroxene were also found in an almost Fe-free clinopyroxene in granular olivine-pyroxene chondrules from the Allende CV3 chondrite for which the wavelength of the exsolution lamellae is within the range 25–33 nm (Weinbruch and Müller 1995). This microstructure (and the associated cooling rate) is quite comparable to the one of the studied Ca-rich pyroxene grain and suggests that the studied Wild 2 particle could originate from a fragmented chondrule. Igneous textures or potential chondrule-bearing minerals have been identified in other Wild 2 particles (Zolensky et al. 2006; Joswiak et al. 2007; Nakamura et al. 2008) and suggest that chondrule-like objects are found not only in meteorites but also in bodies assembled at large distances from the inner region of the solar system.

A significant fraction of dust is crystalline in the circumstellar disks of Herbig Ae/Be and T Tauri stars (Waelkens et al. 1996; Van Boekel et al. 2004) and in cometary trails (Crovisier et al.

[1] Deposit item AM-08-058, Figures 3 and 4 (binary phase diagram and a time-temperature transformation diagram). Deposit items are available two ways: For a paper copy contact the Business Office of the Mineralogical Society of America (see inside front cover of recent issue) for price information. For an electronic copy visit the MSA web site at http://www.minsocam.org, go to the American Mineralogist Contents, find the table of contents for the specific volume/issue wanted, and then click on the deposit link there.

1997; Wooden 2002). The Stardust sample return of comet Wild 2 provides the unique opportunity to study extraterrestrial material coming from a location other than the asteroid belt, and thus to discuss the ubiquitous occurrence of crystalline silicates in the protoplanetary disk. Diopside-pigeonite exsolution microstructure in a Wild 2 particle demonstrates that igneous material is present, with comparable characteristics to the chondrules from primitive meteorites (Weinbruch and Müller 1995). The occurrence of igneous signatures in comet Wild 2, together with the discovery of calcium-aluminum inclusions (CAIs) (Brownlee et al. 2008), suggest that minerals formed in the inner region of the solar nebula were redistributed by a radial transport mechanism in the protoplanetary disk into the region of comet formation (Brownlee et al. 2006; Zolensky et al. 2006). Alternatively, it could indicate that igneous episodes were not restricted to the inner region and could have occurred at various distances in the protoplanetary disk, including beyond Jupiter. The recent report of a collisionally fragmented large Kuiper Belt object (Brown et al. 2007) demonstrates that fragments of geologically evolved outer solar system bodies were available for incorporation into later-formed comet nuclei.

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