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MICROSTRUCTURAL INDICATIONS FOR PROTOENSTATITE PRECURSOR OF COMETARY $MgSiO_3$ PYROXENE: A FURTHER HIGH-TEMPERATURE COMPONENT OF COMET WILD 2

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ABSTRACT

Microstructural studies by transmission electron microscope (TEM) techniques of a microtomed cometary enstatite (Mg/Si 0.858; Fe/Si 0.027; Ca/Si 0.01; Al/Si 0.009; Cr/Si 0.01) from Wild 2 sampled during NASA's *Stardust* mission were conducted. The enstatite is characterized by high stacking disorder parallel (100) which includes alternating clinoenstatite (CLEN) and orthoenstatite (OREN) lamellae and (100) twins. In addition a widespread occurrence of 4.5 Å wide half-planes parallel (100) are detected, which leads to 13.5 and 22.5 Å polytypes of the structure. These microstructural features are indicative of the direct transformation from a protoenstatite (PEN) precursor, which requires temperatures of more than 1275 K and rapid cooling (>10 K hr^{-1}). Our finding represents a further high-temperature component originally present in the cold icy region where comet Wild 2 was formed.

Subject headings: comets: general — comets: individual (Wild 2) — Kuiper Belt — Oort Cloud

1. INTRODUCTION

Comets are small bodies composed mainly of a mixture of ice and dust particles and were formed during accretion of the planetary system. Their reservoirs are the Kuiper Belt (30–55 AU) and the Oort Cloud (50,000 AU), which is the spherical cloud of comets representing the outer boundary of the solar system. The classical picture about the formation of short-period comets (e.g., comets Borrelly, Temple 1, Wild 2; A'Hearn 2006) is condensation of material beyond the frost line in the cold Kuiper Belt extending from the orbit of Neptune to 55 AU from the Sun. In contrast long-period comets condense much closer to the Sun and were ejected afterward out to the Oort Cloud. The so-called scattered disk (all trans-Neptunian objects) feeds the comets into the Oort Cloud and the Jupiter family (A'Hearn 2006) and therefore mixing of comet families occurs, making the classical picture more complex.

Wild 2 is a Jupiter family comet which was forced into its current orbit in 1974 by a close encounter with Jupiter and it is believed to have originated in the Kuiper Belt. The relatively close flyby of comet Wild 2, the successful dust capture in silica aerogel (Tsou et al. 2003), and the return of the sample to Earth by the *Stardust* mission provide information about the conditions during dust formation and the early solar system. Comets are made up of material relicts from the solar nebula after planet formation and have not (strongly) changed since, e.g., by thermal metamorphism or hydrous alteration. Therefore cometary material is believed to be the most pristine material in the solar system. As a remnant from the Kuiper Belt it is supposed to be composed of submicron to micron sized silicate and organic matter of presolar and/or nebula origin (Zolensky et al. 2006; Sandford et al. 2006; Rotundi et al. 2008).

Investigation on several tracks of the *Stardust* mission material (Zolensky et al. 2006; Brownlee et al. 2006; Flynn et al. 2006) have shown that contrary to all expectations most of the impacted mineral grains are high-temperature mineral phases like crystalline forsteritic olivine, crystalline low-calcium pyroxenes, and calcium-aluminum-rich inclusions (CAIs). For example, CAIs are believed to be formed in the solar nebula by high-temperature processes of precondensed material, including evaporation, condensation, and melting (Amelin et al. 2002 and references therein). These highly refractory mineral assemblages are built close to the proto-Sun and are the oldest materials in the solar system (4567.2 ± 0.6 Myr ago; Amelin et al. 2002). Grossman & Clark (1973) conclude that for example titaniferous pyroxenes and melilites in CAIs have their origin in condensation of solar nebula material and indicate temperatures of at least 1400 K. Concerning the crystalline high-temperature phases olivine and pyroxenes, Zolensky et al. (2006) propose that due to a wide compositional range it should require a large range of formation conditions, like different oxygen fugacities and varying temperatures. This also might lead to different locations of formation. At least, the *Stardust* results provide evidence for radial mixing at an early stage of cometary formation.

Thus, large-scale transport of rocky material must have occurred from the hot inner region of the solar nebula to the cold outer parts where comets formed (30 AU) before or during formation of comets. Models for these transport processes are already reported and vary from X-wind (Shu et al. 1997, 2001) to turbulent diffusion processes (Bockelée-Morvan et al. 2002). Here we present evidence for the former existence of the high-temperature $MgSiO_3$ polymorph protoenstatite (PEN; space group-SG: Pbnm) as a precursor for the formation of clino- (CLEN) and minor orthoenstatite (OREN).

Five well-characterized enstatite polymorphs are known. PEN is only stable at very high temperatures above about 1275 K and low pressures, whereas CLEN can exist in the C2/c structure at high temperatures (HT-CLEN, >1450 K) or high pressures (HP-CLEN, >6 GPa) and is stable at low temperatures and low pressures in the P21/c-modification (LTLP-CLEN). OREN (SG: Pbca) show a large stability field at moderate temperatures and pressures. The structure of enstatite was first determined by Warren & Modell (1930). The basic structural unit is SiO_3 chains parallel to the c-axis sharing oxygen of the SiO_4 tetraeder with neighboring chains. Larger cations (e.g., Mg, Fe^{2+}, Ca) are in octahedral coordination in respect to the oxygen on M(1) and M(2) sites. CLEN is formed by two alternating SiO_3 chains [Si(A), Si(B)]; OREN includes four chains [Si(A), Si(B), Si(A′), and Si(B′)] due to twinning of the CLEN structure along (100). Most natural enstatite crystals are a mixture of CLEN and OREN and therefore show 9 or 18 Å periodicities along [100]. Due to periodic repeats of stack-

TABLE 1
Characteristic Features of the Transformation from $MgSiO_3$ Polymorphs to Clinoenstatite (CLEN), Modified and Extended after Buseck & Iijima (1975)

Lamellae	CLEN Field Widths		4.5 Å Half-Planes	Twinning	APDs
	n9 Å	(n + 1)9 Å			
PEN	+	+	+	High	−
HT-CLEN	+	+	−	Absent[a]	+
HP-CLEN	+	+	−	Absent[a]	+
Martensic inversion from OREN[b]	+	−	−	Moderate to low	−
Static transformation from OREN	+	−	−	Moderate to low	−

[a] The transformation itself did not produce additional twinning of the structure.
[b] For homogeneous and inhomogeneous shear strain; shear plane along (010).

ing sequences a number of different polytypes are possible (e.g., Buseck & Iijima 1975; Iijima & Buseck 1975; Wang et al. 1993).

LTLP-CLEN can be formed by at least five transformation paths: (1–3) direct inversion from PEN, HT-CLEN, or HP-CLEN, (4) martensitic transformation (shearing) of OREN, and (5) slow static transformation from OREN. Buseck & Iijima (1975) described several differences between the various reaction paths and present a basic table with the most striking features. A modified and extended summary is given in Table 1.

Shearing (martensitic transformation) as a possible transformation mechanism between OREN and CLEN was first described by Turner et al. (1960). Martensitic transformation of OREN to CLEN always results in an even number of CLEN lamellae for each domain width, because a single OREN lamella will transform to a pair of CLEN lamellae. Moderate to low twinning favoring a single twin direction will occur in this case. The origin of CLEN due to inversion from PEN can lead to intense twinning and stacking disorder. It was proposed by Buseck & Iijima (1975) and later experimentally confirmed by Wang et al. (1993) that half-planes of only 4.5 Å width additionally occur. Compared to the other two transformation processes, twinning would not favor one specific orientation in this case. The absolute widths of stacked CLEN domains are related to the cooling rate whereas slow cooling favors larger packages of OREN lamellae (Buseck & Iijima 1975). Direct transformation from PEN, HT-CLEN, or HP-CLEN to LTLP-CLEN can only occur at high cooling rates of 10 K hr^{-1} (Brearley & Jones 1993).

The structural transformation from enstatite belonging to the C2/c space group (HT-CLEN and HP-CLEN) to the $P2_1/c$ modification (LTLP-CLEN) will lead to the formation of antiphase domains (APDs) due to the loss of a translational symmetry component (e.g., Bozhilov et al. 1999).

TABLE 2
EDX Measurements

Number	Mg/Si	Fe/Si	Ca/Si	Al/Si	Cr/Si
1	0.829	0.031	0.010	0.010	0.010
2	0.837	0.026	0.005	0.011	0.011
3	0.884	0.021	0.011	0.011	0.011
4	0.908	0.027	0.011	0.005	0.011
5	0.896	0.025	0.010	0.010	0.010
6	0.836	0.025	0.010	0.010	0.010
7	0.837	0.030	0.010	0.005	0.010
8	0.825	0.026	0.010	0.005	0.010
9	0.845	0.031	0.010	0.010	0.010
10	0.850	0.031	0.010	0.010	0.010
Mean	0.858	0.027	0.010	0.009	0.010
St. dev.	0.030	0.003	0.002	0.002	0.001

Notes.—EDX measurements along a traverse through the enstatite from the terminal particle of track 32 studied in this work; elemental ratios in at.%. The enstatite is characterized by low Fe contents and minor element concentrations of Ca, Al, and Cr.

2. EXPERIMENTAL

Two TEM grids from the terminal particle (TP) of track 32 (C2027,3,32,3,4 and C2027,3,32,3,8) were investigated using transmission electron microscopy. The samples were prepared by JPL (NASA), extracting the grains out of the aerogel and cutting them into 70 nm thick slices. The TEM slices were investigated using a 200 kV TEM (Phillips CM 200) at the Goethe University Frankfurt. We performed high-resolution imaging (HRTEM) in the bright-field (BF) mode and selected area electron diffraction (SAED) to identify crystal structures. Additional energy dispersive X-ray (EDX) analyses were also performed for determining the chemical composition, and d-spacings with respect to lattice fringe parameters were calculated from the SAED patterns and measured in the HRTEM micrographs.

3. RESULTS

The composition of the enstatite is measured along a traverse through the microtomed section of the particle. We found almost pure enstatite (Mg/Si = 0.858) with some minor element concentrations of Fe, Ca, Al, and Cr (Table 2).

In most of the studied areas, alternating CLEN and OREN with a dominance of CLEN lamellae were found (Fig. 1). The variable stacking sequence of the 9 Å CLEN and 18 Å OREN lamellae lead to a number of polytypes on a scale of less than 100 nm. CLEN fields showing odd and even numbers of lamellae were observed with no preference to one or the other. Field widths of 27 and 45 Å are shown in Figure 1, which corresponds to $(n + 1)9$ Å repeats ($n = 3, 5$), and also field widths of 54 and 90 Å are visible in the center of the image corresponding to $n9$ Å ($n = 6, 10$). The most striking feature of the micrograph is the occurrence of 13.5, 31.5, and 58.5 Å field widths, which cannot be explained by either the expression $(n + 1)9$ Å or $n9$ Å. Obviously, adding a 4.5 Å wide (100) half-plane of CLEN can explain these regions. Single occurrences of 4.5 Å lamellae can be found in the upper part of the image (Fig. 1).

SAED patterns of three different regions within the CLEN are shown for comparison in Figure 2. Nearly pure CLEN (9.1 Å) lamellae are present in the selected area of Figure 2a showing also some discrete spots of OREN; in Figure 2b OREN reflections (18.2 Å) are present. This is in good agreement with Figure 1, where only a few OREN lamellae can be seen in coexistence with CLEN. The chosen area for the SAED pattern in Figure 2c shows a high amount of stacking disorder including several 4.5 Å wide (100) half-planes. The intense disorder is also reflected in extra superstructure reflections between the

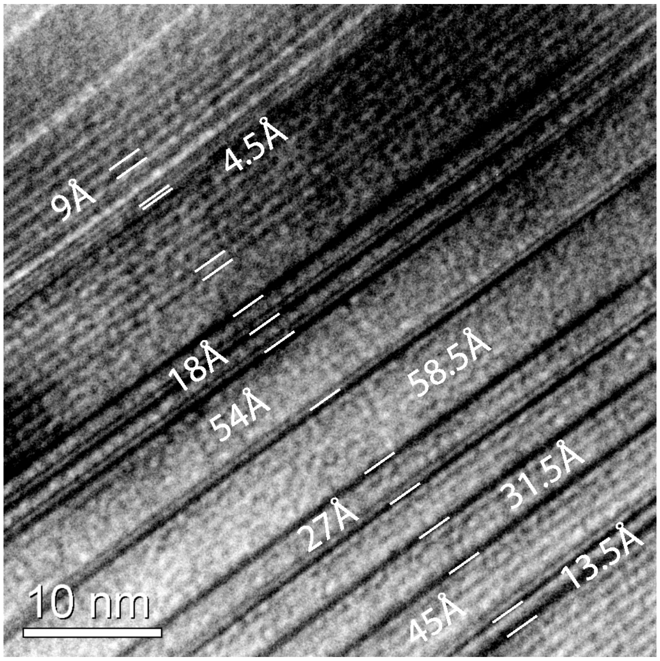

FIG. 1.—Bright-field TEM micrograph of lattice fringes of enstatite viewed perpendicular to [100]. Alternating chains of CLEN (9 Å) and OREN (18 Å) lamellae dominate the overall structure. Packages of CLEN lamellae show odd [$(n + 1)$9 Å] as well as even (n9 Å) repeats, which excludes an origin from martensitic transformation from precursor OREN.

first-order spots. A number of minor discrete spots occur which can be explained by variable sequences of 4.5 Å lamellae. The occurrence of a less intense streak between two extra spots representing d-values of 13.5 and 22.5 Å can be explained by a sequence of single and double layers of CLEN with an attached 4.5 Å half-plane. The streak between the two superstructure reflections is due to alternating 13.5 and 22.5 Å sequences.

In HRTEM mode the stacking sequence can be studied in greater detail. Figure 3 shows an HRTEM micrograph viewed parallel [$0\bar{1}2$]. A predominance of CLEN lamellae with d-spacings of 9.1 Å can be found. Again, stacking of CLEN lamellae with 4.5 Å half-planes occurs, resulting in 13.5 Å intervals. Single stacking faults can be observed which are similar to microstructures described in the experimental work of Wang et al. (1993).

Besides an overall present stacking disorder always containing 4.5 Å half-planes, we discovered lamellae in twin orientation parallel (100) which can be seen in Figure 4. The HRTEM image consists of CLEN lamellae and again chains containing cells of only 4.5 Å. Again, various stacking sequences are present. The combination of CLEN and 4.5 Å lamellae lead to values of 13.1–13.5 Å.

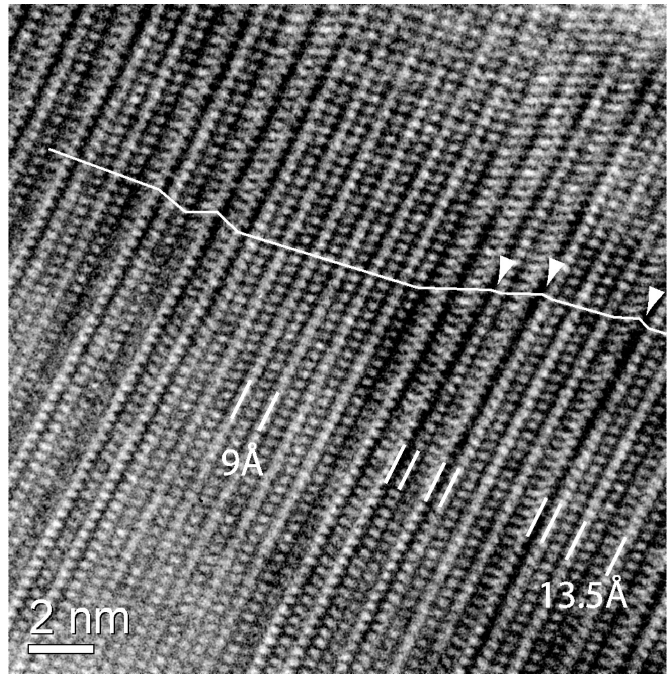

FIG. 3.—HRTEM micrograph of an enstatite region with high stacking disorder viewed parallel [$0\bar{1}2$]. Several 4.5 Å half-planes (marked by solid triangles) are visible which indicate transformation from precursor PEN (Wang et al. 1993; Buseck & Iijima 1975).

4. DISCUSSION

4.1. *Enstatite Formation*

The occurrences of 4.5 Å half-planes parallel (100) combined with a superstructure of a 13.5 and 22.5 Å repeats and (100) twins document the direct transformation of PEN to CLEN. Iijima & Buseck (1975) explained this kind of half-planes by (100) twinning in the a-b section. This theoretical aspect has been confirmed by experimental work by Wang et al. (1993) on the PEN-CLEN transformation which leads to new polytypes in the CLEN matrix with a periodicity of 13.5 and 22.5 Å. These new polytypes correspond to the width of CLEN

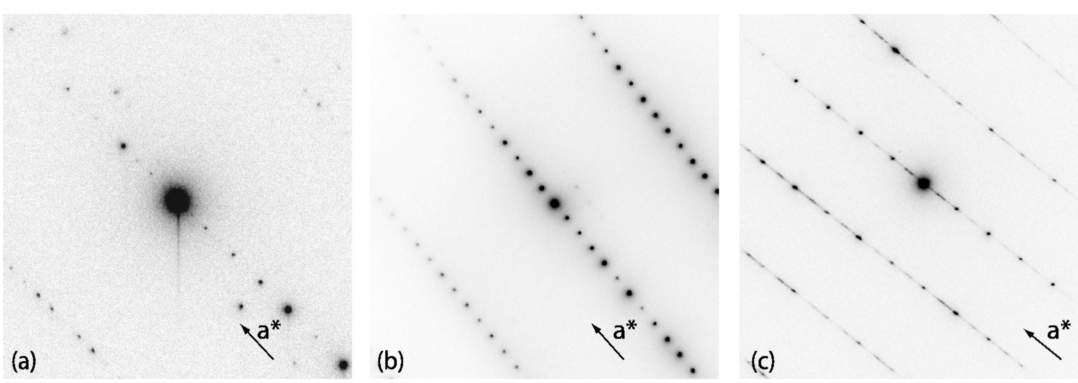

FIG. 2.—Selected area electron diffraction (SAED) pattern of several structurally diverse areas within the studied cometary enstatite. In (a) a nearly pure CLEN pattern with only some discrete OREN spots is recorded, (b) shows a region dominated by OREN, and (c) is related to a CLEN with pronounced stacking disorder. The respective SAED pattern (panel c) shows additional reflections along the a* direction corresponding to a 13.5 and 22.5 Å repeat and a streak between these spots which are due to variable stacking of these two polytypes.

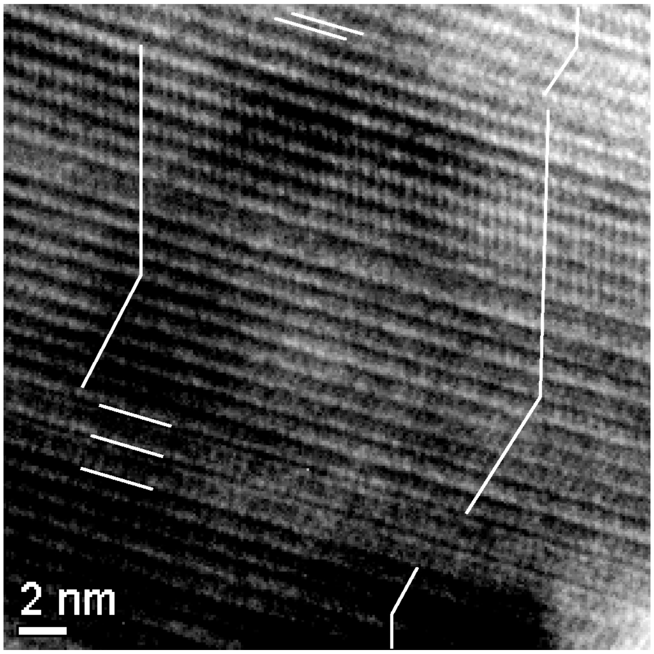

FIG. 4.—HRTEM micrograph of CLEN lamellae viewed parallel [01$\bar{1}$]. The change in orientation is due to twinning of enstatite parallel (100). Several 4.5 and 13.5 Å wide lamellae are indicated as well.

lamellae (9.1 Å) and additional 4.5 Å half-planes. They propose that each stacking sequence of 4.5, 9.1, and 18.2 Å structural units should be possible. The absence of APDs and the presence of packages of odd repeats of 9 Å lamellae exclude the direct conversion from HT-CLEN or OREN, respectively. Buseck & Iijima (1975) propose that the formation of field widths with $(n + 1)9$ Å sequences is energetically less favored than the $n9$ Å and they therefore interpret the formation of LTLP-CLEN in that case as a high-temperature process due to inversion of PEN. The PEN-to-CLEN transition takes places at temperatures around 1275 K and is therefore a further high-temperature indicator found in comet Wild 2. According to clino- to orthoenstatite reversal experiments of Brearley & Jones (1993) our finding indicates cooling rates on the order of 10 K hr^{-1} at about 1275 K. Thus, another high-temperature indicator which in addition requires fast cooling (10 K hr^{-1}) could be identified beside the refractory inclusions (CAIs) and crystalline mineral phases reported by Zolensky et al. (2006).

4.2. *Comet Formation and Mixing in the Protoplanetary Disk*

Concerning the formation of the comet Wild 2, the presence of an additional high-temperature mineral phase in cometary matter further strengthens the conclusion that comets are not formed in isolation in the solar system, requiring at least some mass transport. Highly refractory and other high-temperature mineral phases found in cold icy and dusty objects indicate large-scale radial mixing in the protoplanetary disk with a large amount of mass transport from the inner part of the solar nebula to the outer parts. Due to the formation temperature of CAIs between 1400 and 2000 K and a minimum temperature of 1275 K for PEN, several components originate from very close to the proto-Sun. Mixing processes must occur over distances to at least 30 AU (A'Hearn 2006) where short-period comets were formed in the Kuiper Belt and these minerals were implanted.

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REFERENCES

A'Hearn, M. F. A. 2006, Science, 314, 1708
Amelin, Y., Krot, A. N., Hutcheon, I. D., & Ulyanov, A. A. 2002, Science, 297, 1678
Bockelée-Morvan, D., Gautier, D., Hersant, F., Huré, J.-M., & Robert, F. 2002, A&A, 384, 1107
Bozhilov, K. N., Green, H. W., II, & Dobrzhinetskaya, L. 1999, Science, 284, 128
Brearley, A. J., & Jones, R. H. 1993, Lunar Planet. Sci. Conf., 24, 185
Brownlee, D., et al. 2006, Science, 314, 1711
Buseck, P. R., & Iijima, S. 1975, Am. Mineral., 60, 771
Flynn, G. J., et al. 2006, Science, 314, 1731
Grossman, L., & Clark, S. P., Jr. 1973, Geochim. Cosmochim. Acta, 37, 635
Iijima, S., & Buseck, P. R. 1975, Am. Mineral., 60, 758
Rotundi, A. 2008, Meteoritics Planet. Sci., 43(1/2), 1
Sandford, S. A., et al. 2006, Science, 314, 1720
Shu, F. H., Shang, H., Glassgold, A. E., & Lee, T. 1997, Science, 277, 1475
Shu, F. H., Shang, H., Gounelle, M., Glassgold, A. E., & Lee, T. 2001, ApJ, 548, 1029
Tsou, P., Brownlee, D. E., Sandford, S. A., Hörz, F., & Zolensky, M. E. 2003, J. Geophys. Res., 108, E10, doi: 10.1029/2003JE002109
Turner, F. J., Heard, H., & Griggs, D. T. 1960, XXI Int. Geol. Congress (Copenhagen), 18, 339
Wang, Y. G., Yu, Y. D., Ye, H. Q., & Huang, W. K. 1993, J. Material Science, 28, 4037
Warren, B. E., & Modell, I. 1930, Z. Kristallogr., 75, 1
Zolensky, M. E., et al. 2006, Science, 314, 1735