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

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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). The classical picture about the formation of short-period comets (e.g. Comets Borrelly, Temple 1, Wild 2; [1]) 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.

Here we present evidence for the former existence of the high temperature $MgSiO_3$ polymorph protoenstatite (PEN) 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 ca. 1275K and low pressures. CLEN can exist in the C2/c structure at high temperatures (HT-CLEN, >1450K) or high pressures (HP-CLEN, >6GPa) and is stable at low temperatures and low pressures in the P21/c-modification (LTLP-CLEN). OREN (Pbca) show a large stability field at moderate temperatures and pressures. Most natural enstatite crystals are a mixture of CLEN and OREN and therefore show 9Å or 18Å periodicities along [100]. Due to periodic repeats of stacking sequences a number of different polytypes are possible (e.g. [2], [3], [4]).

LTLP-CLEN can be formed by at least five transformation paths. [2] described several differences between those various reaction paths and present a basic table with the most striking features (Table 1).

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 (see also [5]).

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 9Å CLEN and 18Å OREN lamellae lead to a number of polytypes on a scale 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 27Å and 45Å are shown in Figure 1 which corresponds to *(n+1)*9Å repeat (n=3, 5) and also field widths of 54Å and 90Å are visible in the center of the image corresponding to *n*9Å (n=6, 10). The most striking feature of the micrograph is the occurrence of 13.5Å, 31.5Å, 58.5Å field widths which cannot be explained by either the expression *(n+1)*9Å or by *n*9Å. Obviously adding a 4.5Å wide (100) half plane of CLEN can explain these regions. Single occurrences of 4.5Å lamellae can be found in the upper part of the image (Fig. 1). SAED pattern of three different regions within the CLEN are shown for comparison in Figure 2. Nearly pure CLEN (9.1Å) lamellae are present in the selected area of Figure 2a showing also some discrete spots of OREN, in Figure 2b OREN reflections (18.2Å) 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 4.5Å wide (100) half planes. The intense disorder is also reflected in extra superstructure reflections between the first order spots. A number of minor discrete spots occur which can be explained by variable sequences of 4.5Å lamellae. The occurrence of a less intense streak between two extra spots representing d-values of 13.5Å and 22.5Å can be explained by a sequence of single and double layer of CLEN with an attached 4.5Å half plane. The streaks between the two super structure reflections are due to alternating 13.5Å and 22.5Å sequences [5].

Conclusion: The occurrences of 4.5Å half planes parallel (100) combined with a superstructure of a 13.5Å and 22.5Å repeats and (100) twins document the direct transformation of PEN to CLEN. [3] explained this kind of half planes by (100) twinning in the *a-b* section. This theoretical aspect has been confirmed by experimental work by [4] on the PEN-CLEN transformation which leads to new polytypes in the CLEN matrix with a periodicity of 13.5Å and 22.5Å. These new polytypes correspond to the width of CLEN lamellae (9.1Å) and additional 4.5Å half planes. The absence of anti-phase domains (ADPs) and the presence of packages of odd repeats of 9Å lamellae exclude the direct conversion from HT-CLEN or OREN, respectively. The PEN to CLEN transition takes places at temperatures around 1275K and is therefore a further high temperature indicator found in comet Wild 2. According to clino- to orthoenstatite reversal experiments of [6] our finding indicates cooling rates on the order of 10 K/hr at ca. 1275 K.

Table 1: Characteristic features of the transformation from $MgSiO_3$ polymorphs to clinoenstatite (CLEN) (modified and extended after [2]).

	CLEN field widths				
	n 9Å	*(n+1)* 9Å	4.5Å half planes	Twinning	ADPs
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 didn't produce additional twinning of the structure.

[b] For homogeneous and inhomogeneous shear strain; shear plane along (010).

Concerning the formation of the comet Wild 2, the presence of an additional high temperature mineral phase in cometary matter further strengthen 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 SN to the outer parts.

References: [1] A'Hearn M.F.A. (2006) *Science, 314,* 1708. [2] Buseck P.R. and Iijima S. (1975) *Am. Mineral., 60*, 771. [3] Iijima S. and Buseck P.R. (1975) *Am. Mineral., 60*, 758. [4] Wang Y.G., Yu Y.D., Ye H.Q. and Huang, W.K. (1993) *J. Material Science, 28*, 4037. [5] Schmitz S. and Brenker F. (2008) *ApJL, 681*, L105. [6] Brearley A.J. and Jones R.H. (1993) *LPS XXIV*, 185.

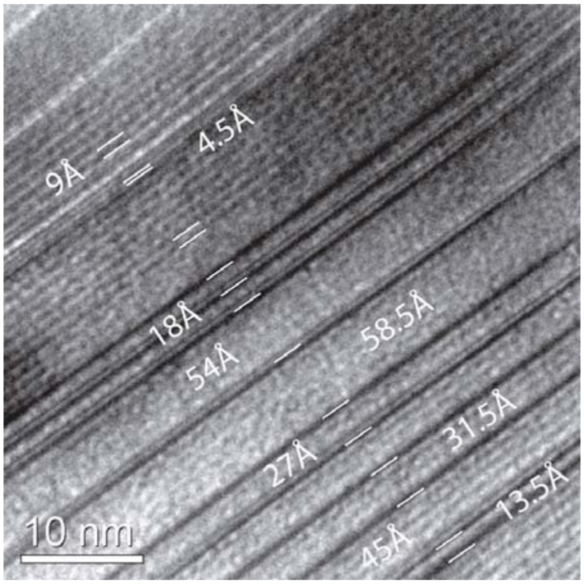

Figure 1: Bright field TEM-micrograph of lattice fringes of enstatite viewed perpendicular to [100]. Alternating chains of CLEN (9Å) and OREN (18Å) lamellae dominate the overall structure. Packages of CLEN lamellae show odd (*(n+1)*9Å) as well as even (*n*9Å) repeats, which excludes an origin from martensitic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

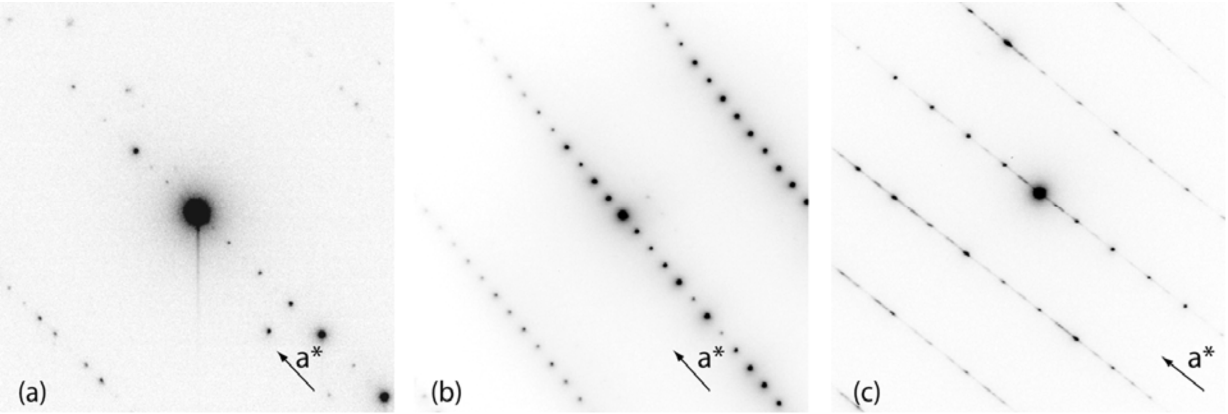

Figure 2: Selected area electron diffraction (SAED) pattern of several structurally diverse areas. In a) a nearly pure CLEN pattern with only some discrete OREN spots is recorded, b) shows a region dominated by OREN and c) is related to a CLEN with pronounced stacking disorder. The respective SAED pattern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