

(S)TEM Characterization on the Refractory Minerals from Comet 81P/Wild-2. M. Chi^{1,2}, Hope Ishi², Zurong Dai², S. Simon⁴, N. D. Browning^{1,3} and J. P. Bradley², ¹Institute of Geophysics and Planetary Physics, Lawrence Livermore National Laboratory, Livermore, CA, ²Department of Chemical Engineering and Materials Science, University of California, Davis, CA, ³Institute of Geophysics and Planetary Physics, ⁴Materials Science and Technology Division, Lawrence Livermore National Laboratory, Livermore, CA, ⁵Department of Geophysical Sciences, University of Chicago, Chicago, IL

Introduction: The Stardust spacecraft collected a sample of the Kuiper belt comet 81P/Wild-2 in aerogel and returned it to Earth January 15, 2006. Since comet 81P/Wild-2 is believed to have formed at the outer fringes of the solar nebula, the returned samples were expected to be mostly material indigenous to the outer solar system, perhaps dominated by interstellar grains inherited from the parent presolar interstellar molecular cloud. However, an accumulating body of evidence indicates that Wild-2 contains materials like those found in chondritic meteorites that formed close to the early Sun [1, 2].

TEM studies indicate that the 81P/Wild-2 sample is heterogeneous at the nanometer scale. It contains Ca- Al- rich minerals that are found in CAI's, including a Ti-rich pyroxene (fassaite), gehlenite, diopside, spinel and V-bearing osbornite [3, 4] (Fig. 1). This suite of minerals is attracting special attention because it potentially provides a direct link to CAIs in chondritic meteorites. CAI's in meteorites are believed to have formed in the inner solar system close to the sun. The question we address is whether the refractory minerals in the 81P/Wild 2 CAI "Inti" are part of the same population as those in found meteorites. Towards this end we have measured the valence state of Ti in fassaite in "Inti" and compared it with the valence state of Ti in fassaite in a CAI from Allende. The valence of Ti provides information about oxygen fugacity and the redox environment of formation [3,4]. We have also investigated TiN-TiO solid solution in osbornite inclusions in Inti. Since coexisting TiO and TiN are stable within CAI's only at high temperature and high C/O ratio TiN/TiO can further constrain the conditions of formation [5].

Experimental: Scanning Transmission Electron Microscopy (STEM) combined with both Energy Dispersive X-ray spectroscopy (EDX) and High-resolution Electron Energy Loss Spectroscopy (HREELS) have been applied to investigate the compositions and crystal structures of osbornite and Ti-pyroxene in the returned sample. The combination of these microscopy techniques allows us to determine the valence states of the elements of interest as well as the crystallographic sites for those valence states. It should be noted that STEM is particularly well-suited for characterizing small mineral grains such as those present in the Stardust samples because it can achieve simultaneous imaging and chemical analysis at high spatial resolution.

In this case, the chemical analysis can be precisely associated with local microstructures, and the oxidation state of transition metal elements can be studied by investigating their core-loss spectra. The microscope used in this work is a Tecnai F20 G2 UT (S)TEM microscope equipped with an EDAX Si(Li) solid state energy-dispersive x-ray detector and a Tri-diem Gatan Imaging Filter HREELS spectrometer. All EELS spectra were recorded with a collection angle of 5.6 mrad and a dispersion of 0.1 eV/channel with 2048 channels. The EELS energy resolution we used is 0.7 eV with 3 seconds acquisition and the spatial resolution is ~0.16 nm. The energy shift of each spectrum was calibrated by a reference zero loss peak taken immediately after each core-loss edge.

Results: Ti-L edges from the Inti Ti-pyroxene, compared with those from LaTiO₃ and SrTiO₃, reveals the coexistence of Ti³⁺ and Ti⁴⁺ in the pyroxene (Fig. 2). The EELS spectra from the Inti Ti-pyroxene has been further compared with those from Allende meteorite. The TEM specimens from Allende were purposely taken from a pyroxene at different locations with various Ti³⁺/Ti⁴⁺ ratios, which were measured by microprobe. It is revealed that the fine structure of Ti-L edges from Inti Ti-pyroxene are very close to the spectrum from a region of the Allende pyroxene with a Ti³⁺/Ti⁴⁺ ratio of 2.15±1.1. This error bar presents the uncertainty of FIB locating for the TEM sample preparation and the local variety of the oxidation states of Ti according to electronprobe measurements. To further evaluate this result, we have studied the Ti³⁺/Ti⁴⁺ ratio by considering the linear combination of Ti-L edges from LaAlO₃ and SrTiO₃ as references, since the coordination of V in these materials are the same as those in Fassaite. Our result shows that the fine structure of L-edges from Inti-fassaite is very comparable to a 2:1 combination of Ti³⁺/Ti⁴⁺. Such high Ti³⁺ content in the Inti Ti-pyroxene implicates a highly reducing formation environment.

The existence of osbornite inclusions has been established using high resolution TEM and nanodiffraction (Fig. 3a-c). Most osbornite particles contain V in solid solution substituting Ti. Additionally, it is also possible that O is substituting some of the N in the TiN lattice. Since the osbornite nanocrystals are embedded in (O-rich) silicates, establishing the presence of TiO

in solid solution is non-trivial. An O post-edge image (Fig. 3d) shows that contrast from the osbornite inclusions is similar to that from the surrounding matrix, which indicates the *possible* presence of O in Ti(V)N inclusions, since one should expect a darker contrast of the inclusion relative to the silicate matrix if the inclusion is free of O. The presence of O in some of the (V-free) osbornite inclusions is further supported by examination of the detailed fine structures of the O-K, Ti-L and N-K edges. Unfortunately, it has so far not been possible to rigorously establish the presence of O in TiN by EELS due to the complexity of the core-edge fine structures, possibly influenced by both V and O. However, the presence of TiN itself indicates a high temperature (probably >1300K) and a high C/O ratio (>0.85) of their formation environment.

Discussion: The oxidation states of Ti in the Inti pyroxene imply a low oxygen fugacity in the formation environment of the refractory minerals in comet P81/Wild-2. Since the oxygen fugacity of the environment can be estimated by the oxidation state of Ti, by considering the thermodynamic reactions of Ti-pyroxene with other CAI's [4], a comparable oxidation state of Inti-pyroxene with that of Allende meteorite indicates a similar oxygen fugacity of their formation environments. This means Inti Ti-pyroxene should also have formed in an environment similar to some Allende CAI's [4].

The similarity between the chemical and isotopic compositions of Inti and those of CAI's in meteorites suggests that the refractory minerals in comet Wild-2 also formed under similar conditions. On the other hand, the high C/O ratio suggested by the presence of TiN and the possibility of TiO-TiN solid solution indicates that the Inti osbornites originate from the region very close to the proto-sun, since theoretical calculations show that this high C/O ratio (>0.85) actually only exist at a region with a radial distance shorter than 0.3 AU. [6]. Although the osbornite inclusions may not have formed in the same region or at the same time as the host refractory mineral matrix, the high formation temperature of these refractory minerals suggests that they originated at a similar heliocentric distance. Hence, these refractory minerals must have formed in the inner solar nebula region close to the proto-sun and then were transported outwards to the region of comet accretion.

Conclusion: We have performed a (S)TEM study of Ti-pyroxene (Fassaite) and osbornite inclusions in the refractory minerals within the CAI "Inti" from comet P81/Wild-2. The Ti^{3+}/Ti^{4+} ratio in the Fassaite revealed by EELS is comparable to that of CAI's in some meteorites. Combining this result with the similar chemical and isotopic compositions of Inti with

those of CAI's from meteorites, suggests a common inner-solar origin. The possible existence of TiN and TiO suggests that the Inti osbornite crystals must have formed very close to the proto-sun, indicating large-scale radial transport in the solar nebula. Our results suggest that it is unlikely that Inti originated outside of the the solar system.

References: [1] Brownlee, D., Tsou, P. et al. (2006) *Science* 314(5806): 1711-1716. [2] Zolensky, M. E., Zega, T. J. et al. (2006) *Science* 314(5806): 1735-1739. [3] Beckett, J. R. and Grossman, L. (1986) *LPS XVII*, 36-37. [4] Grossman, L., Beckett, J. R. et al. (2007). *Oxygen in Earliest Solar System Materials and Processes*. [5] Ebel, D. (2006). *Meteorites and Early Solar System 2*, Univ. of Arizona, D. Ebel Press, Tucson, AZ, 2006: pp. 253-278. [6] Dyl, K. A., J. I. Simon, et al. (2005) *LPS XVI*.

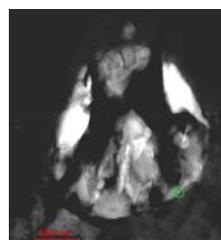


Figure 1: STEM (HAADF) image with refractory minerals in the returned samples from comet Wild-2. a osbornite inclusion is observed in this specimen as circled in this image.

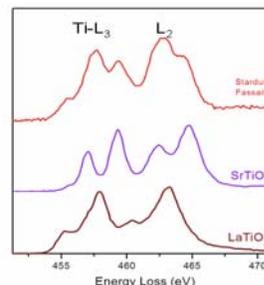


Figure 2: An EELS spectrum from stardust fassaite is compared with those from $SrTi(4+)O_3$ and $LaTi(3+)O_3$. The comparison of their fine structures reveals the coexistence of Ti^{4+} and Ti^{3+} in stardust Fassaite.

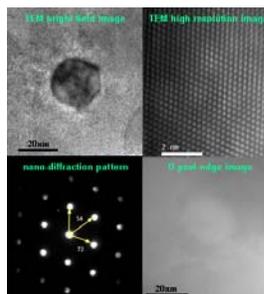


Figure 3: TEM high resolution image, nanodiffraction and O-post image establish the presence of TiN and the possible solid solution of O in TiN.