IRON VALENCE STATE DISTRIBUTION AT THE NANO-SCALE IN COMET WILD2 MATERIAL FROM THE STARDUST MISSION — A COORDINATED TEM / STEM EDX / STXM STUDY J. Stodolna[1], A. Butterworth[1], H. Leroux[2], Z. Gainsforth[1], T. Tyliszczak[3], D. Jacob[2] and A. J. Westphal[1]; [1]Space Sciences Laboratory, University of Berkeley, California, USA, [2]Unité Matériaux et Transformations, Université Lille1, 59655 Villeneuve d'Ascq, France, [3]Advanced Light Source, Lawrence Berkeley National Laboratory, MS 6-2100, Berkeley, CA 94720, USA. j.stodolna@ssl.berkeley.edu.

Introduction: The cometary dust from 81P/Wild2 was collected in a tray of low-density silica aerogel cells during the NASA Stardust mission [1]. The expected fine-grained material from a body stored in cold regions since the formation of the solar system is present but its characterisation is complex because of the strong interaction with the aerogel during deceleration, which resulted in the formation of altered material by melting, mixing and cooling processes [2-3]. This material is called "GEMS-like" material [4] because of its microstructure, made of amorphous material embedded with Fe-Ni-S beads that characterize GEMS in CP IDPs. Because of its composition close to CI [2], it is believed to originate from the most primitive component of Wild2. It is important to understand the chemical modification that happened during the collection to elucidate its nature.

Some large crystalline oxidized phases like magnetite, hematite and cubanite are reported [5-7]. They could be evidence for aqueous alteration on the comet or on a previous parent body. Nevertheless, possible oxidation processes may have modified the initial mineralogy of cometary grains during or after their collection.

Here we present the results of a nanoscale study of the iron valence state of Stardust samples using a synchrotron-based Scanning Transmission X-ray Microscopy (STXM). The goal is to determine if oxidation or reduction processes modified the mineralogy during the collection, the sample preparation, or the storage of the samples. We also characterize the iron valence state distribution of the GEMS-like material and combine the results with microstructure and Mg and Fe elemental distributions measured by Transmission Electron Microscopy (TEM) to better understand the chemical modifications during capture versus the primary nature of the fine-grained material.

Samples and experimental procedures: We studied six samples. Five of them are GEMS-like fragments from the track C2092,3,80 "Tule". All of them are in the same microtome slice on the same TEM grid. The sixth sample is a terminal particle from track C2052,2,74 called "Callie". The microstructure and chemical composition information were acquired by TEM. The iron XANES spectrum acquisitions were done by STXM at the ALS beamline 11.0.2. The scanning microscope focuses the synchrotron beam to a ~20 nm spot. The energy resolution is better than 0.1eV. The present work was done at the Fe L3 edge

(~700 eV). We developed a MATLAB program to construct iron valence state distribution maps.

Collection, sample preparation or storage effect on the oxidation state: The terminal particle "Callie" consists mainly of well-preserved olivines (Fo_{63}). There is a typical amorphous silica-rich fusion crust around the core due to the interaction of the particle with surrounding aerogel during the collection. Compositions of the crystal and the amorphous components indicate that the amorphous material originates from the olivine that has been partially melted and mixed with aerogel during the collection. The Fe-XANES spectra of these two areas (crystalline and amorphous) both have the Fe^{2+} signature (Fig. 1 for the amorphous part). This shows that neither oxidation nor reduction occurred here during the collection, the sample preparation, or the storage of this particle, even in its amorphous component.
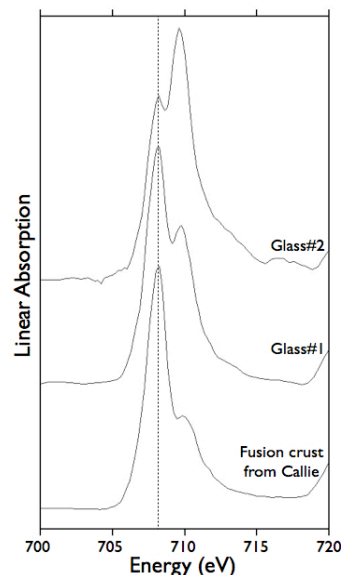

Fig.1: *Fe-L XANES spectra of two standard glasses Glass#1 that contain 90-95% of Fe^{2+}(the complement is Fe^{3+}) and Glass#2 that contain 50-60% of Fe^{3+} (the complement is Fe^{2+}) and of amorphous material from the fusion crust of Callie at the Fe L_3 edge. The dashed line represents the positions of the Fe L_3 maxima for Fe^{2+} in glass at 708.2 eV. The maximum energy is the same for the glass#1 and the amorphous material, showing the fusion crust of Callie contains mainly Fe^{2+}.*

The iron valence state maps of the five GEMS-like samples show a heterogeneous distribution. The samples are composed of a mixture of Fe^{2+}, Fe^{3+}, Fe^0 and Fe sulfides (Fig. 2). Two samples are mainly composed of Fe^{2+}, two of Fe^{3+}, and the last of an equal mixture of both. Since the entire range of Fe^0 to Fe^{3+} is present, it is not likely that oxidation or reduction were very significant as it would have eliminated either the Fe^0 or the Fe^{3+} component depending on whether it was an oxidizing or reducing environment. These results associated with standard free energies calculations of formation of oxide and reduction reaction show the Fe^{3+} and the Fe^0 are not formed by redox reactions during or after the collection.

Therefore, if redox reactions occurred during or after the collection of the Wild-2 samples, the reaction was incomplete and was at most a minor modification of the initial material.

Precursor material: The spatial and spectral resolutions of the STXM data allows us to see clearly different areas inside each sample (Fig.2). This enables comparison of the chemical distribution of Mg and Fe from EDX maps with the valence state of iron. Four different chemical areas are clearly distinguishable on the EDX maps and correspond to areas of well-defined Fe valence state. We tentatively identify the precursors:

- (1) Mg-rich areas without Fe-S beads and Fe^{2+} signature. These should originate from Mg-rich phases, probably crystalline, as precursors (like silicates).
- (2) Areas with low-Mg content and Fe-S beads with a Fe^0+FeS signature. These seem to be the result from the decomposition of pristine iron sulfides [2,3].
- (3) Mg-rich + Fe^{2+} matrix + FeS beads. These could have GEMS as precursor. In GEMS in IDPs, the matrix around the beads is made of Fe^{2+} [8]. The presence of iron sulfides, the chemical composition and the typical size (hundreds nanometers in diameter) are also in accordance with GEMS. A very fine-grained aggregate (diameter less than 200nm) of small Mg-rich and sulfide grains could also be at the origin of these areas.
- (4) Areas with a low concentration of Fe and Mg and Fe-S beads. Two of four such areas show a Fe^{2+} signature and the other two show a Fe^{3+} signature. The precursor could be a silica-rich amorphous material containing small sulfides as observed in the matrices of primitive chondrites. The Fe^{3+} areas could have aqueously altered minerals as precursors. Such phases have been recently detected in some other Stardust samples [5-7].

Conclusions: This study shows that neither oxidation nor reduction was a complete redox reaction during or after collection into aerogel. Many observations of oxidized material have been reported in the Stardust samples [5-7]. The present study shows they are probably formed prior the collection.

Furthermore TEM/EDX/STXM correlation studies give information about the precursor mineralogy. Relics of Mg-rich phases like silicates, iron sulfides, amorphous matrix and possibly GEMS or very fine-grained aggregate are identified.
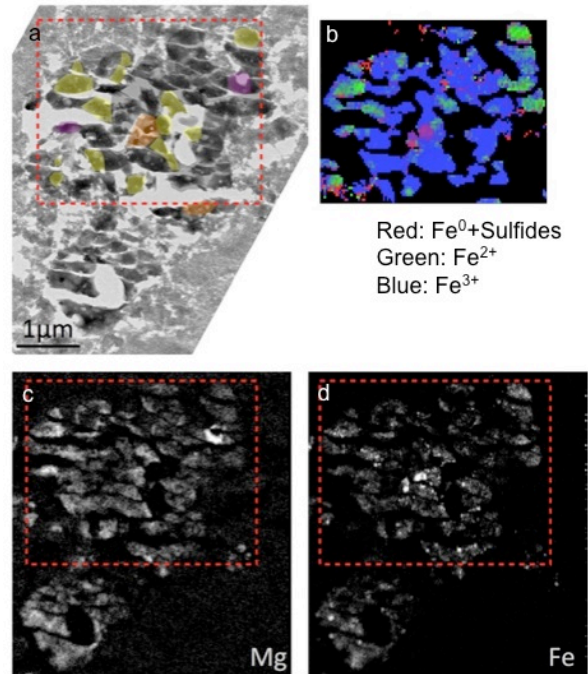

Red: Fe^0+Sulfides
Green: Fe^{2+}
Blue: Fe^{3+}

Fig2: *Amorphous material from track 80: (a) TEM bright field image, (b) iron valence state map and elemental maps from EDX data of (c) Mg and (d) Fe. Four chemically distinct areas are highlighted. They show a strong correlation with the iron valence state distribution: (1) Mg-rich areas without Fe-S beads (highlighted in purple on the BF-TEM image) correspond to Fe^{2+} (2) Areas with Fe-S beads and no Mg (highlighted in orange on the BF-TEM image) correspond to Fe^0 and FeS. (3) Mg-rich areas with Fe-S beads (highlighted in yellow on the BF-TEM image) correspond to Fe^{2+} in the matrix and Fe^0+FeS in the beads, (4) areas with low Mg and Fe (highlighted in grey on the BF-TEM image) correspond to Fe^{3+}. Some samples present Fe^{2+} instead of Fe^{3+} in these areas.*

References: [1] Brownlee D. E. et al. (2006) *Science*, *314*, 1711-1716; [2] Leroux H. et al. (2008) *Meteorit. & planet. Sci.*, *43*, 97-120; [3] Ishii H. et al. (2008) *Science 319*, 447-450; [4] Zolensky M. E. et al. (2006) *Science 314*, 1735-1739; [5] Berger E. et al. (2011) *Geochim. Cosmochim. Acta*, *75*, 3501-3513; [6] Bridges J. et al. (2010) *Meteorit. Planet. Sci.* 45,55-72. [7] Stodolna J. et al. (2010) *LPSC 41st* abstract #1657; [8] Keller L. & Messenger S. (2011) *Geochim. Cosmochim. Acta*, *75*, 5336-5365.