

## Ti Valence States in Al,Ti-rich Pyroxenes from Comet Particles: Anchoring Ti ELNES Spectra with Vanadium Thin-films

Dave Joswiak and Don Brownlee

Department of Astronomy, University of Washington, Seattle, WA USA 98195

Detailed investigations of particles captured from comet Wild 2 by the Stardust spacecraft and a giant cluster interplanetary dust particle (IDP) of probable cometary origin have shown that high temperature, moderately refractory materials are present in outer Solar System bodies where Kuiper Belt objects accreted [1,2]. Unraveling the physical and chemical processes of how these particles formed is vital toward understanding comets. The mineral pyroxene, a common phase in these refractory grains and believed to be a nebular condensation product, often contains significant amounts of the transition element Ti which can adopt different oxidation states, thus pyroxenes can provide evidence of redox conditions during formation of their host grains.

Refractory minerals in comet samples are typically micron to submicron in size and electron energy loss near-edge spectroscopy (ELNES) combined with transmission electron microscopy (TEM) is an effective technique to measure the valence states of Ti in the pyroxenes. With electron energy loss spectroscopy (EELS), this is possible because of the chemical shift that occurs in the Ti core-loss edges with oxidation number, typically 2 eV per oxidation state [3]. Interpretation of ELNES spectra, however, can be complex and difficulties are manifest in a least two ways. First, differences in the fine-structure of Ti core-loss spectra due to differences in coordination, octahedral volume, polyhedron distortions and site symmetries [3] complicate ELNES spectra comparisons. Secondly, instrument instabilities and local magnetic field perturbations induce energy drift in the EELS spectra during acquisition obscuring the absolute energy loss positions of ELNES spectra. It is this latter category that we address here with a technique that allows direct comparison between Ti ELNES spectra in both standards and examined pyroxenes.

The technique uses the element V to fix the Ti ELNES peaks on the energy loss axis. Because the V peaks have fixed energy positions and their core-loss edges occur above Ti (~58eV) they can be used to precisely position the Ti peaks whose energy positions vary with valence. This method removes the uncertainties due to energy drift during EELS spectrum acquisitions and anchors the Ti core-loss ELNES spectra on the energy-loss axis thus all measured spectra can be directly compared to one another. To implement the technique, a V-coated carbon film (V < 10 nm) on a separate TEM grid is placed directly below the TEM grid containing the pyroxene sample.

To estimate the Ti valence states in the pyroxenes we use the “white-line” method where Ti L<sub>2</sub>/L<sub>3</sub> core-loss ratios are measured and applied to a L<sub>2</sub>/L<sub>3</sub> vs Ti<sup>4+</sup>/(Ti<sup>4+</sup> + Ti<sup>3+</sup>) calibration curve established from Ti oxides with known oxidation states (Fig. 1). One eV-wide regions-of-interest (ROIs), chosen to maximize the L<sub>2</sub>/L<sub>3</sub> ratios from the Ti oxide standards, are used for the measurements. Because the local energy environments in the pyroxenes are different than those in the Ti oxide standards which were used to generate the calibration curve, the measured Ti<sup>4+</sup>/(Ti<sup>4+</sup> + Ti<sup>3+</sup>) ratios in the pyroxenes are considered semi-quantitative.

We have applied this technique to Ti-rich pyroxenes on  $<10\ \mu\text{m}$  particles from comet Wild 2 and an IDP of probable cometary origin (Fig. 2). In Fig. 3 detailed Ti ELNES spectra are compared to one another and are shown with the Ti oxide standards  $\text{TiO}_2$  (100%  $\text{Ti}^{4+}$ ) and  $\text{Ti}_2\text{O}_3$  (100%  $\text{Ti}^{3+}$ ). We measured  $\text{Ti}^{4+}/(\text{Ti}^{4+} + \text{Ti}^{3+})$  ratios of 0.39 and 0.55 in the comet Wild 2 sample and 0.27 – 0.89 in pyroxenes in the giant cluster IDP. The data indicate wide-ranging oxidation states in pyroxenes in refractory materials from comets. Because the pyroxene measurements were obtained from grains in close physical proximity to one another (within  $10\ \mu\text{m}$  particles), this suggests that refractory-rich materials in comets formed in the solar nebula in a region with significant spatial and/or temporal variations in oxygen abundance. Variable oxidation states in pyroxenes in refractory inclusions were obtained in some carbonaceous chondrite meteorites [5].

#### References:

- [1] S. Simon et al. (2008) *Meteoritics and Planetary Science* 43: 1861-1877.
- [2] D. J. Joswiak and D. E. Brownlee (2014) 45<sup>th</sup> Lunar and Planet. Sci. Conf., abstract #2282.
- [3] E. Stoyanov, F. Langenhorst and G. Steinle-Neumann (2007) *Amer. Mineral.* 92: 577-586.
- [4] H. Tan, J. Verbreeck, A. Abakumov and G. Van Tendeloo (2012) *Ultramicro.* 116: 24-33.
- [5] K. A. Dyl, J. I. Simon and E. D. Young (2011) *Geochim. et Cosmochim. Acta* 75: 937-949.

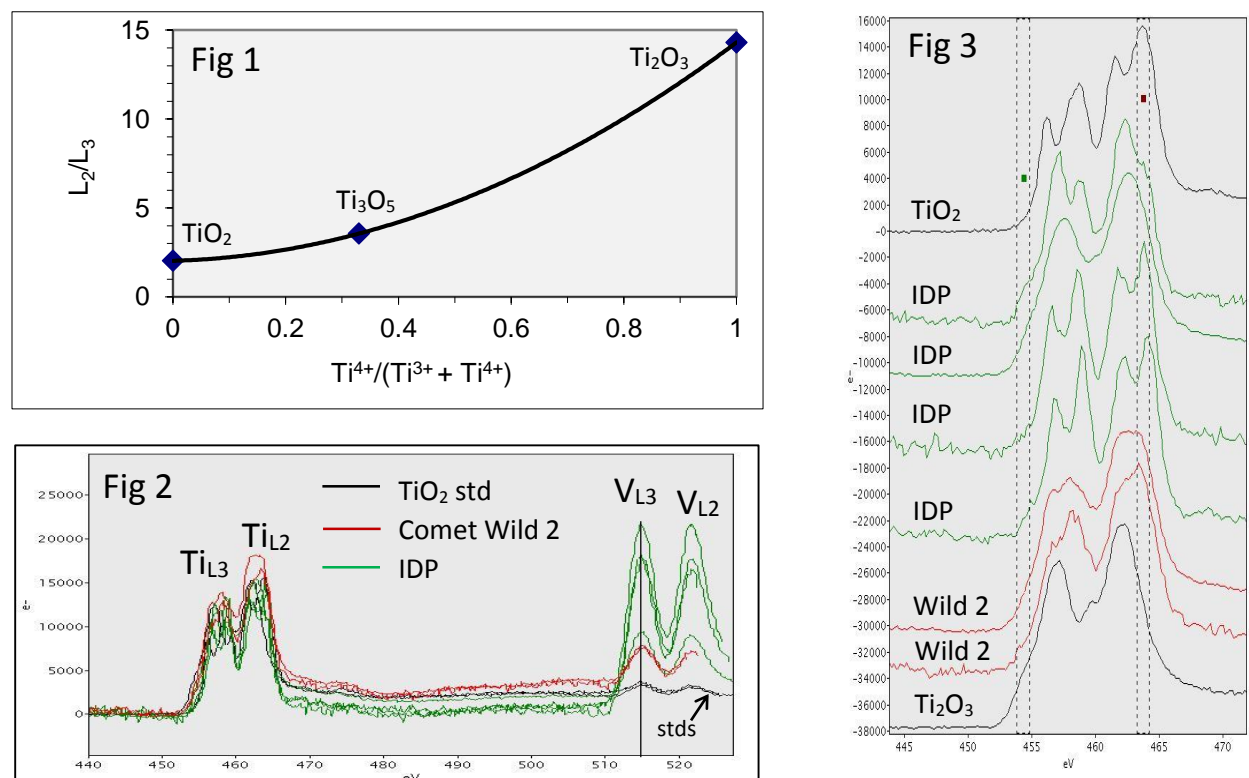


Fig. 1) “White-line” calibration curve used to estimate  $\text{Ti}^{4+}/(\text{Ti}^{4+} + \text{Ti}^{3+})$  ratios in pyroxenes in comet samples. Fig. 2) Cometary pyroxene and Ti oxide (standards) spectra showing both Ti and V peaks. Vertical line shows  $\text{V}_{L3}$  peak anchored to 514.4 eV. Fig. 3) Ti ELNES spectra of cometary pyroxenes (green, red) and Ti oxide standards (black). ROIs shown with dotted lines.