Electron Energy Loss Spectroscopy Measurements of Titanium Valence States in Refractory Nodule Pyroxenes from a Likely Cometary IDP

D.J. Joswiak[1], D.E. Brownlee[1], H.A. Ishii[2] and S.R. Sutton[3]
[1]Univ. of Washington, Dept. of Astronomy, Seattle, WA, [2]Hawai'i Inst. of Geophysics and Planet., Univ. of Hawaiʻi at Mānoa, [3]Dept. of the Geoph. Sci., Univ. of Chicago, Chicago IL

Introduction: Mineralogical and bulk chemical composition studies of refractory materials from comet Wild 2 and a giant cluster IDP (believed to have a cometary origin) have shown that the most refractory-rich grains that are commonly observed in primitive chondrites (i.e. Type A CAIs, spinel-hibonite inclusions, corundum) are absent or underrepresented [1]. In comet samples, observed refractory particles include AOAs, Al-rich chondrules and Type C CAI equivalent grains. To further investigate refractory grains in comets we are studying the titanium oxidation states in fassaites to probe oxidation conditions in which they may have formed and compare with equivalent materials in chondrites. A Ti valence calibration curve utilizing EELS standards whose Ti is octahedrally coordinated should provide reasonable estimates of the $Ti^{3+}/(Ti^{3+} + Ti^{4+})$ ratios in the comet fassaites [1]. Here we provide preliminary results of Ti valence measurements from fassaites in nodules from a ~12 µm particle that was present in a large cluster IDP.

Methods: P6-14 is a transparent particle extracted from an anhydrous cluster IDP composed of thousands of particles whose properties are consistent with derivation from a comet [2]. Ultrathin microtome sections were examined with a Gatan electron energy loss spectrometer attached to a Tecnai 200 keV STEM with EDX capability. The EELs spectra were collected in diffraction mode around the Ti $L_{3,2}$ edges with an energy dispersion of 0.1 eV/channel and ZLP resolution of ~0.9 eV. To position the Ti peaks precisely on the energy-loss axis all EELS spectra were collected simultaneously with vanadium $L_{3,2}$ peaks which have fixed energy positions [1]. Titanium “white-line” intensity ratios resulting from 2p to 3d orbital transitions in octahedrally-coordinated Ti were measured using newly applied standards including fassaite from a Type B2 CAI from Allende [3], titanite and a synthetic $NaTi^{3+}Si_2O_6$ grain.

Results and Discussion: IDP P6-14 is a porous particle consisting of an aggregate of 1-5 µm concentric spinel+anorthite(An_{96-98})+diopside/fassaite(TiO_2 = 0.0 – 22.0 wt%) nodules with fine-grained matrix. Rims of enstatite ($En_{99.5}$) and rare forsterite ($Fo_{99.8}$) enclose the nodules. Ti EELs spectra were collected from fassaites on two ~2-4 µm nodules spaced ~4 µm apart in the particle. $Ti^{3+}/(Ti^{3+} + Ti^{4+})$ ratios ranging from 0.17 – 0.79 were measured indicating formation of the nodules in widely varying oxidation conditions from oxidizing to highly reducing. The similar nodule sizes, their moderately refractory minerals and concentric monomineralic layers are consistent with a nebular condensation origin from a spatially restricted nebular region. Taken together, we interpret these properties as evidence that the refractory nodules in IDP P6-14 are products from an environment(s) in the solar nebula with significant variations in f_{O2}, similar to some Type C CAIs [4] and a single fassaite grain from an Allende Type B1 inclusion [5].

References: [1] Joswiak D. J. and Brownlee D. E. (2015) LPSC abst. 2252. [2] Pepin et al. (2015) LPSC abst. 1705. [3] Chi M. et al. (2009) *GCA* 73: 7150-7161. [4] Krot et al. (2007) *GCA* 71: 4342-4364. [5] Simon S. et al. *GCA* 71: 3098-3118.