

**TEM-EELS MEASUREMENTS OF TITANIUM OXIDATION STATE IN HIBONITES.** Mattia Giannini<sup>1</sup>, T. Boffa Ballaran<sup>1</sup>, F. Langenhorst<sup>2</sup>, A. Bischoff<sup>3</sup>. <sup>1</sup>Bayerisches Geoinstitut, Universität Bayreuth, D-95447 Bayreuth, Mattia.Giannini@uni-bayreuth.de; <sup>2</sup>Institut für Geowissenschaften, Universität Jena, D-07749 Jena; <sup>3</sup>Institut für Planetologie, Universität Münster, D-48149 Münster.

**Introduction:** Chondritic meteorites are representative samples of primordial matter in the solar system. They contain different materials (i.e. Fe-Ni alloys, sulfides, chondrules, amoeboid olivine aggregates and Calcium-Aluminum-rich Inclusions (CAIs) embedded into a fine-grained matrix) formed at different times, temperatures, and places in the solar nebula and accreted together to form parent bodies. CAIs yield the oldest measured ages of any solar system material [1], thus they are believed to be the first condensates of the solar nebula. They consist mainly of melilite, spinels, perovskite, hibonite, grossite, diopside, metal and anorthite. Although corundum ( $\text{Al}_2\text{O}_3$ ) is predicted to be the first major oxidic phase to condensate from a hot solar gas, it is found rarely in Calcium-Aluminum-rich Inclusions; instead the most Al-rich phase found in CAIs is hibonite (nominally  $\text{CaAl}_{12}\text{O}_{19}$ ) [2]. However, grossite ( $\text{CaAl}_4\text{O}_7$ ) is a very abundant Ca-aluminate in CAIs from CH chondrites like Acfer 182 [3].

Hibonite belongs to the magnetoplumbite group minerals: it has the ideal formula  $\text{CaAl}_{12}\text{O}_{19}$  and crystallizes in space group  $P6_3/mmc$ . Al ions are distributed over five different sites: three with octahedral, one with tetrahedral and one with bipyramidal coordination. Substitution of different cations can occur on these sites, thus, the mineral hibonite usually contains significant amounts of Ti, Mg, Fe, Si and V. Among these cations, Ti is of particular interest, because its oxidation state in hibonite has been qualitatively related to the oxygen fugacity ( $f\text{O}_2$ ) at which hibonite has formed and evolved in the solar nebula [4, 5]. However, in order to correlate the  $\text{Ti}^{3+}/\text{Ti}^{4+}$  ratio to the  $f\text{O}_2$  conditions, a calibration of such ratio as a function of oxygen fugacity, temperature and composition is necessary. This study addresses the question whether the oxidation state of Ti is a measure of oxygen fugacity in the solar nebula. Therefore, we have measured the oxidation state of Ti in meteoritic samples by means of Energy Electron Loss Spectroscopy (EELS) and compared it to the  $\text{Ti}^{3+}/\text{Ti}^{4+}$  ratio of samples with similar composition synthesized at different temperatures and oxygen fugacities.

**Experimental methods:** We have analyzed three CAIs within two petrographic thin sections of chondrites Acfer 182 (CH; PL01036, Fig. 1, [6]) and one of Dar al Gani (DaG) 203 (CO3; PL96274) with a JEOL JXA-8200 electron microprobe (EMPA). From each CAI we have chosen one grain of hibonite and

prepared it for TEM analysis using a FEI Quanta 3D Field Emission Gun (FEG) Focused Ion Beam (FIB).

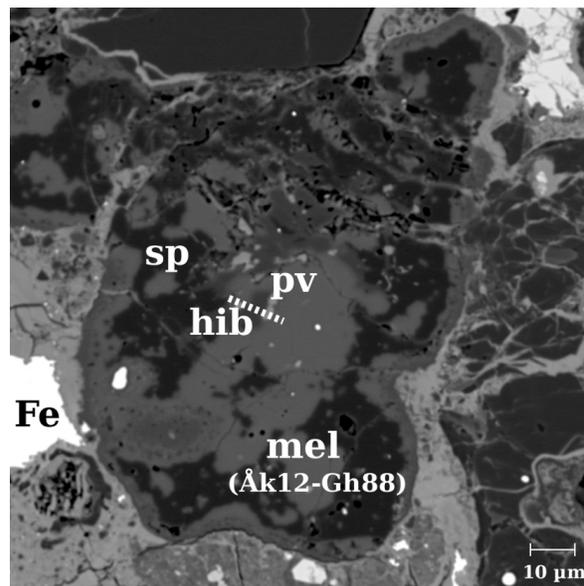


Figure 1: SEM-BSE image of a CAI from Acfer 182 Chondrite. sp = spinel, pv = perovskite, hib = hibonite, mel = melilite, dashed line = chosen area for FIB preparation.

Polycrystalline hibonites were synthesized with compositions corresponding to the studied meteoritic hibonites, using a typical ceramic method. Pellets of the corresponding oxide mixtures were heated at  $1430\text{ }^\circ\text{C}$  for about 12 hours in air or under controlled oxygen fugacity in a gas mixing furnace using a  $\text{CO}/\text{CO}_2$  flux. Thin sections of less than  $30\text{ }\mu\text{m}$  of such pellets were subsequently thinned down to less than  $100\text{ nm}$  using a Gatan DuoMill 600 argon ion milling machine.

The valence state of Ti in both meteoritic and synthetic hibonites was measured by means of EELS using a  $200\text{ keV}$  Philips CM20 scanning Transmission Electron Microscope (TEM), equipped with a Gatan PEELS 666 parallel electron spectrometer. The calibration technique used is based on the spectral features and intensities of the  $L_{3,2}$  white lines of Ti. The advantage of this technique is that the  $\text{Ti}^{3+}/\text{Ti}^{4+}$  ratio can be determined directly with high lateral resolution at the nano-scale [7].

**Results: Meteoritic samples.** Hibonite grains from the three CAIs contain significant amounts of Ti and Mg ranging from 0.8 to 6.1 wt% and from 0.5 to 5.4 wt% respectively. Subordinate amounts of Si, Fe

and V were also detected. The chemical formulae of the three selected hibonite grains are the following:  $\text{Ca}_{1.06}\text{Al}_{10.29}\text{Ti}_{0.86}\text{Mg}_{0.77}\text{Fe}_{0.01}\text{Si}_{0.03}\text{O}_{19}$  for Acfer 182-2,  $\text{Ca}_{1.03}\text{Al}_{10.58}\text{Ti}_{0.69}\text{Mg}_{0.68}\text{Fe}_{0.01}\text{Si}_{0.04}\text{V}_{0.02}\text{O}_{19}$  for DaG 203-1 and  $\text{Ca}_{1.04}\text{Al}_{11.43}\text{Ti}_{0.28}\text{Mg}_{0.24}\text{Fe}_{0.03}\text{Si}_{0.01}\text{V}_{0.01}\text{O}_{19}$  for Acfer 182-3.

The EELS measurements for the chosen hibonite grains as well as the  $\text{Ti}^{3+}/\text{Ti}^{4+}$  ratios obtained are shown in Fig. 2.

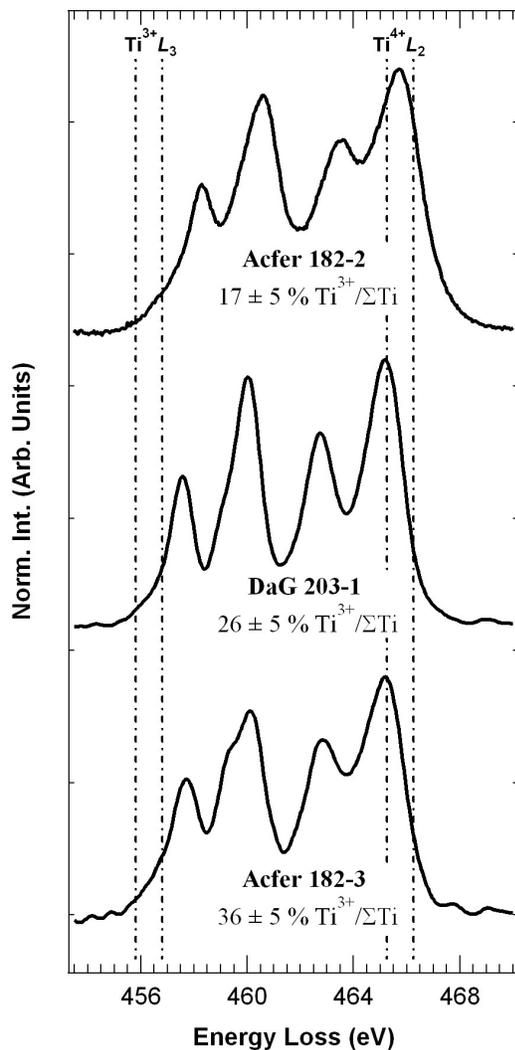


Figure 2: Energy Electron Loss Spectra of the three selected hibonite grains. The dashed lines indicate the integration windows for  $\text{Ti}-L_{3,2}$  edges.

**Synthetic samples.** The chemical formulae (measured with EMPA) of the synthetic analogues (SA) for the studied hibonite grains are:  $\text{Ca}_{0.99}\text{Al}_{10.54}\text{Ti}_{0.79}\text{Mg}_{0.69}\text{O}_{19}$  for Acfer 182-2SA;  $\text{Ca}_{1.03}\text{Al}_{10.39}\text{Ti}_{0.85}\text{Mg}_{0.75}\text{O}_{19}$  for DaG 203-1SA and  $\text{Ca}_{1.04}\text{Al}_{11.40}\text{Ti}_{0.37}\text{Mg}_{0.19}\text{O}_{19}$  for Acfer 182-3SA. Their  $\text{Ti}^{3+}/\text{Ti}^{4+}$  ratios obtained from the EELS measurements are reported in the following Table.

Sample	Synthetic conditions	$\text{Ti}^{3+}/\Sigma\text{Ti}$
	$[-\log_{10}(f\text{O}_2)]$	[%]
Acfer 182-2SA	Air	$20 \pm 5$
	11	$18 \pm 5$
DaG 203-1SA	Air	$14 \pm 5$
	11	$18 \pm 5$
Acfer 182-3SA	Air	$20 \pm 5$
	11	$31 \pm 5$

**Discussion and Conclusions:** Measurements of both meteoritic and synthetic samples indicate the clear presence of  $\text{Ti}^{3+}$ . However, in the case of the synthetic analogues of Acfer 182-2 and DaG 203-1 the  $\text{Ti}^{3+}$  content appear to be independent of the oxygen fugacities at least down to a  $-\log_{10}(f\text{O}_2) = 11$ . In the case of Acfer 182-3 (which has a smaller Ti concentration with respect to Acfer 182-2 and DaG 203-1) we observe that the content of  $\text{Ti}^{3+}$  in the meteoritic sample is closer to that obtained for its SA equilibrated at  $-\log_{10}(f\text{O}_2) = 11$ . Moreover, this composition has a clear dependence on the oxygen fugacity as there is a significant difference on  $\text{Ti}^{3+}/\Sigma\text{Ti}$  for the two SA synthesized at different  $f\text{O}_2$  conditions.

These data indicate that the  $\text{Ti}^{3+}$  content in hibonites depends not only on the redox conditions at which they formed and evolved but also on their crystal chemistry. Even at very oxidizing conditions the substitution mechanism  $\text{Mg}^{2+} + \text{Ti}^{4+} = 2\text{Al}^{3+}$  is not unique and some  $\text{Ti}^{3+} = \text{Al}^{3+}$  substitution takes place. However, a large Mg content seems to be correlated to a large amount of  $\text{Ti}^{4+}$ , via the coupled substitution even at very reducing conditions. It appears therefore that only hibonites with low Mg, Ti content (i.e. 1-3 %) can record the oxygen fugacity of their formation / evolution. More experiments are under way in order to verify this hypothesis as well as to clarify the effect of temperature on the  $\text{Ti}^{3+}/\text{Ti}^{4+}$  ratios.

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**References:** [1] Meibom A. *et al.* (2007) *Astroph. J.*, 656, L33-L36. [2] Grossman L. (1972) *GCA*, 86, 597-619. [3] Weber D. and Bischoff A. (1994) *GCA*, 58, 3855-3877. [4] Beckett J. R. *et al.* (1988) *GCA*, 52, 1479-1495. [5] Ihinger P. D. *et al.* (1986) *EPSL*, 78, 67-79. [6] Bischoff A. *et al.*, (1993) *GCA*, 57, 2631-2648. [7] Stoyanov E. *et al.* (2007) *Am. Min.*, 92, 577-586.