

**ELECTRON ENERGY-LOSS SPECTROSCOPY (EELS) OF FE-BEARING SHEET SILICATES IN CM CHONDRITES.** Thomas J. Zega<sup>1</sup>, Laurence A. J. Garvie<sup>1</sup>, and Peter R. Buseck<sup>1,2</sup>, <sup>1</sup>Department of Geological Sciences and <sup>2</sup>Department of Chemistry and Biochemistry, Arizona State University, Tempe, AZ 85287 (tzega@asu.edu).

**Introduction:** The primitive character and hydrated mineralogy of the CM chondrites offers insight into some of the earliest reactions between solids and water. Such reactions profoundly affected the matrices and fine-grained rims (FGRs) [1-4], two of the most significant components of these meteorites [5]. We are using EELS combined with a transmission electron microscope (TEM) to investigate the compositions of Fe-bearing minerals, with emphasis on determining oxidation states and quantification of oxidation-state ratios.

Iron is among the most abundant elements in the solar system and it can occur naturally in three oxidation states: Fe<sup>0</sup>, Fe<sup>2+</sup>, and Fe<sup>3+</sup>. Determination of oxidation-state ratios is useful because they can be used to infer the redox conditions under which the minerals formed or were last equilibrated [6, 7]. We are particularly interested in understanding how the oxidation state of Fe was affected by the aqueous reactions of the CM chondrites.

**Analytical Methods:** Spectra were acquired using a Gatan 766 parallel electron energy-loss spectrometer attached to a Phillips 400 ST field-emission-gun TEM run at a 100 keV acceleration voltage. The TEM was operated in diffraction mode using cold-cathode emission, which provided an energy resolution of  $\leq 1$  eV as measured from the full width at half maximum of the zero-loss peak. The dark current and background were removed and the zero-loss peak was deconvoluted from each spectrum. Image and diffraction data were acquired with JEOL 2000FX and 4000EX TEMs. Samples were prepared using ion-milling methods [4] and by crushing.

**Results and Discussion:** Cronstedtite (Fig. 1a) and a chrysotile-like phase (Fig. 2a) are important hydrated minerals that occur in the FGRs and matrices of CM chondrites. Cronstedtite is a trioctahedral 1:1 phyllosilicate with ideal formula  $(\text{Fe}^{2+}_{3-x}\text{Fe}^{3+}_x)[\text{Si}_{2-x}\text{Fe}^{3+}_x\text{O}_5](\text{OH})_4$ , where  $0 < x < 1$  [8]. Its energy-loss spectra reveal a two-peaked Fe L<sub>3</sub> edge, indicating a mixture of Fe<sup>2+</sup> and Fe<sup>3+</sup> (Fig. 1b). Chrysotile, also a trioctahedral 1:1 sheet silicate, is ideally  $\text{Mg}_3\text{Si}_2\text{O}_5(\text{OH})_4$ , but Fe can substitute for Mg [9]. The Fe L<sub>3</sub> edge of the chrysotile-like phase in the CM chondrites exhibits a slight shoulder at  $\sim 707.5$  eV and a sharp peak at  $\sim 709.5$  eV, revealing that it contains both Fe<sup>2+</sup> and Fe<sup>3+</sup> (Fig. 2b).

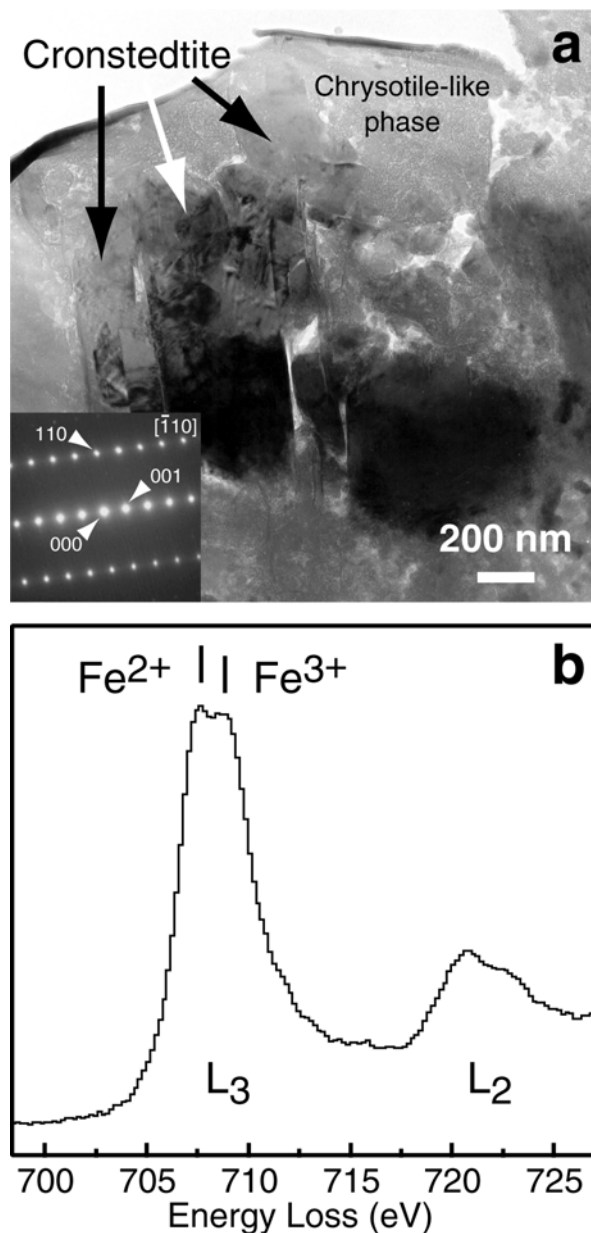


Fig. 1 (a) Cronstedtite laths from a FGR in the Cold Bokkeveld CM chondrite. The selected-area electron-diffraction pattern is from the grain in the center of the image (white arrow). (b) Energy-loss spectrum of cronstedtite reveals a split L<sub>3</sub> edge, indicating that it contains both Fe<sup>2+</sup> and Fe<sup>3+</sup>.

Mössbauer studies on terrestrial serpentines have revealed that  $\text{Fe}^{3+}$  can occur in the antigorite, chrysotile, and lizardite forms [10-12]. Chrysotile contains  $\text{Fe}^{2+}$  in octahedral sites and  $\text{Fe}^{3+}$  in both tetrahedrally and octahedrally coordinated sites [12].

Iron can undergo a change in oxidation state as a result of ion milling and irradiation by the electron beam [13]. Therefore, determinations of iron oxidation states with electron-beam methods must be made with care. Analyses of the chrysotile-like phase from crushed samples under low-dose conditions and short acquisition times reveal the presence of  $\text{Fe}^{3+}$ , suggesting that ferric iron was not artificially produced by ion milling or the electron beam. To our knowledge, this is the first report of another major  $\text{Fe}^{3+}$ -bearing sheet silicate in a CM chondrite.

TEM data from the Cold Bokkeveld CM chondrite suggest that chondritic cronstedtite reacted to form the chrysotile-like phase during aqueous alteration [4]. The EELS data provide additional insight into this reaction. The  $\text{Fe}^{3+}$  in the chrysotile-like phase may have been acquired from cronstedtite during the reaction or could have been directly oxidized. It is plausible that such processes occurred in other CM chondrites since cronstedtite altering to serpentine was also observed in the FGRs of ALH 81002 [3].

Chemical modeling studies on the CM chondrites have provided estimates of the conditions and minerals produced by aqueous alteration [14, 15]. Chrysotile is among the minerals reported by such models, but it is generally considered in its pure form without Fe. Our results suggest that future modeling studies might wish to consider these EELS data so as to provide more precise estimates on the minerals produced by aqueous alteration and the conditions under which they formed.

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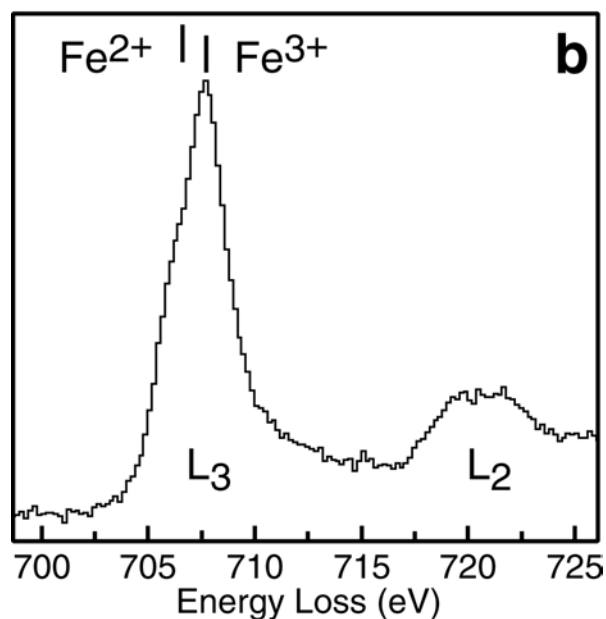
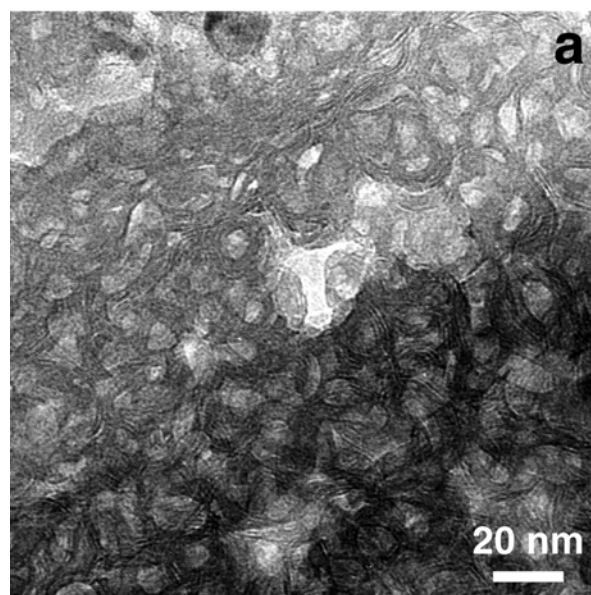


Fig. 2 (a) Grains of the chrysotile-like phase from a FGR in the Cold Bokkeveld CM chondrite. (b) The Fe  $L_3$  edge of the chrysotile-like phase exhibits a shoulder at  $\sim 707.5$  eV and a sharp peak at  $\sim 709.5$  eV, indicating that it contains both  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$ , respectively. Areas analyzed are approximately 40 nm in diameter.