

Nanometer-scale measurements of iron oxidation states of cronstedtite from primitive meteorites

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ABSTRACT

We report the first nanometer-scale measurements of the iron (III) to total iron ($\text{Fe}^{3+}/\Sigma\text{Fe}$) ratios from primitive meteorites. These ratios from the matrices and fine-grained rims (FGRs) of the Murchison, Murray, and Cold Bokkeveld CM chondrites fall within a tight range, from 0.45 to 0.54 (± 0.02). The measurements were made using electron energy-loss spectroscopy (EELS) on cronstedtite, which is a product of aqueous alteration early in the history of the solar system. The results indicate that the alteration of these meteorites, which display a broad range of alteration intensity, occurred under similar redox conditions and, further, that alteration likely occurred in situ on asteroidal bodies rather than in the solar nebula.

INTRODUCTION

The CM carbonaceous chondrites are among the most primitive materials from the solar system, providing insights into its physical and chemical evolution. Aqueous alteration profoundly affected these meteorites early in their history (Zolensky and McSween 1988), and considerable effort has been devoted to deciphering its complex mineralogic signatures. The products of this alteration are ubiquitous in the matrices and fine-grained rims (FGRs) of CM chondrites (Barber 1981; Brearley 1995; Buseck and Hua 1993; Lauretta et al. 2000; McSween 1979; Zega and Buseck 2003; Zolensky et al. 1993). However, information on alteration conditions is sparse, and the environments in which it occurred remain a topic of controversy. For example, petrologic studies provide evidence for parent-body alteration at low temperatures (Bunch and Chang 1980; Hanowski and Brearley 2001; Hua et al. 2002; Zolensky et al. 1993) that O-isotope measurements suggest are $<25^\circ\text{C}$ (Clayton and Mayeda 1999). In contrast, alteration prior to parent-body formation also has been proposed, e.g., on precursor planetesimals or in a high density nebular gas (Bischoff 1998; Metzler et al. 1992), and in icy regions of the solar nebula by shock-induced hydration of anhydrous minerals (Ciesla et al. 2003).

The matrix and FGR components of CM chondrites contain fine-grained, intimately mixed phases at the nanometer scale (Brearley 1995; Lauretta et al. 2000; Tomeoka and Buseck 1985; Zega and Buseck 2003). Inferring the conditions of alteration by thermodynamic calculations is challenging because data for many of the phases are unknown, although computer simulations, which assume thermodynamic equilibrium, suggest that aqueous alteration occurred at low redox potentials (Zolensky et al. 1989). Determining the redox state through

direct measurements would improve our understanding of alteration conditions in the early solar system, but the problem is difficult because of the small grain sizes of the minerals.

Conventional analytical methods such as electron microprobe, X-ray diffraction, and infrared and Mössbauer spectroscopies preclude in situ analysis of individual nanometer-sized grains because they average the signals from various mineral phases and therefore risk homogenizing important spatial information. These problems can be overcome using electron energy-loss spectroscopy (EELS) combined with a transmission electron microscope (TEM).

Minerals that contain elements with mixed oxidation states can provide information on the redox conditions under which they formed or were last equilibrated. Thus, Ti^{3+} to Ti^{4+} ratios were used to determine the oxygen fugacity (f_{O_2}) recorded by Ca- and Al-rich inclusions (CAIs) in the Murchison CM chondrite (Beckett et al. 1988), and the f_{O_2} of the Martian mantle was determined from Fe^{2+} and Fe^{3+} ratios in Martian meteorites (Herd et al. 2001).

Cronstedtite is a trioctahedral 1:1 phyllosilicate with idealized formula $(\text{Fe}_{3-x}^{2+}\text{Fe}_x^{3+})[\text{Si}_{2-x}\text{Fe}_x^{3+}\text{O}_5](\text{OH})_4$, where $0 < x < 1$ (Hybler et al. 2000). Terrestrial cronstedtite occurs in banded iron-formations and in veins that also contain low-temperature hydrothermal sulfides (Fron del 1962; Gole 1982), and exhibits $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratios from 0.15 to 0.57 (Burns and Fisher 1991; Gole 1982; Hybler et al. 2002; Mackenzie and Berezowski 1981). In meteorites, cronstedtite occurs in the matrices and FGRs of CM chondrites and is a product of aqueous alteration (Browning et al. 1996; Lauretta et al. 2000; Müller et al. 1979; Tomeoka and Buseck 1985; Zega and Buseck 2003; Zolensky and McSween 1988). Here we report the first nanometer-scale measurements of the oxidation state of cronstedtite from the matrices and FGRs of CM chondrites through in situ analyses of $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratios using EELS with a TEM.

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SAMPLES AND METHODS

We examined six thin sections of the Murchison, Murray, and Cold Bokkeveld CM chondrites using reflected- and transmitted-light optical microscopy and scanning electron microscopy. These meteorites were chosen because they experienced varied degrees of alteration (Browning et al. 1996) and brecciation (Metzler et al. 1992) prior to their arrival on Earth. Over 50 FGRs and matrix areas of interest were identified, and 10 that showed no appreciable sign of brecciation were chosen for detailed examination. Samples were prepared by mounting a Cu-ring onto areas of interest in a petrographic thin section. The ring with the sample attached was removed from the thin section and thinned to electron transparency using a Gatan precision ion-polishing system (PIPS) and Model 600 Dual Ion Mill cooled with liquid nitrogen. Analyses were made on grains away from the amorphous edge to avoid areas that may have sustained damage during ion milling. We also examined a terrestrial cronstedtite (KH-11) from Kutná Hora (Bohemia, Czech Republic), which was prepared by gentle disaggregation and dispersion onto a lacey carbon TEM grid with methanol. Image and diffraction data were acquired using a 200 keV JEOL 2000FX TEM and a 400 keV JEOL 4000EX TEM.

Spectra were acquired using a Gatan 766 parallel electron energy-loss spectrometer attached to a Phillips 400 ST field-emission-gun TEM operated at a 100 keV acceleration voltage. The TEM was operated in diffraction mode using cold-cathode emission, which provided an energy resolution of ≤ 1 eV as measured from the full width at half maximum height of the zero-loss peak (ZLP). Spectra were acquired from regions measuring 20 to 100 nm in diameter using 3 to 4 s acquisition times and 16 and 11 mrad convergence and collection semiangles, respectively. Spectral processing included subtraction of the dark current, alignment and summation of offset spectra to reduce channel-to-channel gain variations, background subtraction of the form $AE^{-\alpha}$ (Egerton 1996), deconvolution of the ZLP to remove the effects of its asymmetry on the core-loss edge, and subtraction of the continuum intensity beneath the $Fe\ L_{2,3}$ edge using a straight line from 708 to 730 eV. For a more detailed explanation of these procedures, see Garvie and Buseck (1998, 1999) and Garvie et al. (1994).

The $Fe^{3+}/\Sigma Fe$ ratio was quantified using the two-peaked L_3 edge because it exhibits well-defined multiplet structure that is indicative of oxidation state. Spectra were quantified using a multiple, linear, least-squares fitting method with fayalite (Fe_2SiO_4) as the model Fe^{2+} end-member and a mixed aegirite/hematite/leucite (synthetic leucite containing only $^{54}Fe^{3+}$) $L_{2,3}$ spectrum representing the Fe^{3+} end-member. The Fe^{3+} composite spectrum permitted optimal fitting because it accommodated variations in the fine structure that arise from differences in coordination environment.

RESULTS AND DISCUSSION

Cronstedtite was identified in the TEM by its characteristic lath-like morphology, diffraction contrast, selected-area electron-diffraction (SAED) patterns, and energy dispersive X-ray spectrum (Zega and Buseck 2003). Crystals range in size from 20 to 500 nm (Fig. 1).

EELS spectra of Fe^{2+} - or Fe^{3+} -bearing minerals exhibit distinct $L_{2,3}$ edge shapes and chemical shifts, whereas minerals containing both Fe^{2+} and Fe^{3+} exhibit two-peaked L_3 edges that are intermediate in shape between the two single-valence end-members (Garvie et al. 1994). The changes in relative heights of the L_3 peaks qualitatively reflect changes in the $Fe^{3+}/\Sigma Fe$ ratio (Garvie and Buseck 1998; van Aken and Liebscher 2002). All EELS spectra of terrestrial and meteoritic cronstedtite exhibit a two-peaked $Fe\ L_3$ edge indicative of a mixture of Fe^{2+} and Fe^{3+} (Fig. 2). The spectral shapes of cronstedtite from the different meteorites are similar, with minor variations in the relative peak intensities of Fe^{3+} and Fe^{2+} (Fig. 3). Our measurements indicate that the $Fe^{3+}/\Sigma Fe$ ratios from the matrix of a given CM chondrite are similar to those from its FGRs (Table 1). The values also exhibit a significant degree of overlap from the least-altered (Murchison) to most-altered (Cold Bokkeveld) of these CM chondrites (Table 1). As the CM chondrites do not exhibit significant evidence of heating after alteration, we as-

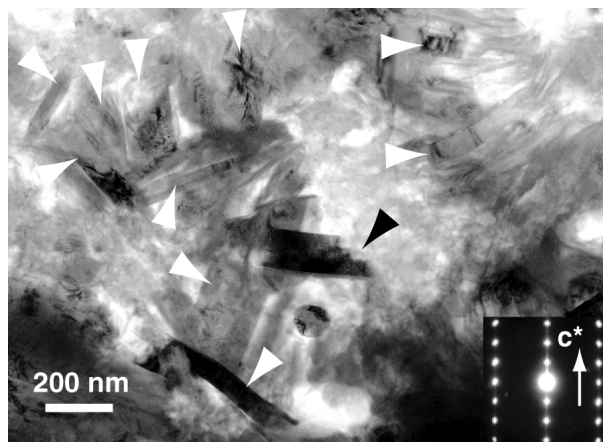


FIGURE 1. TEM image of cronstedtite laths (white arrowheads) from the matrix of the Murchison CM chondrite. The grains exhibit various degrees of diffraction contrast because of differences in their orientations. The SAED pattern (inset) from the grain in the center of the image (black arrowhead) reveals ~ 0.7 and 0.27 nm periodicities, consistent with the d -spacings in $[001]$ and $[110]$ directions, respectively, of cronstedtite $1T$ (Hybler et al. 2000).

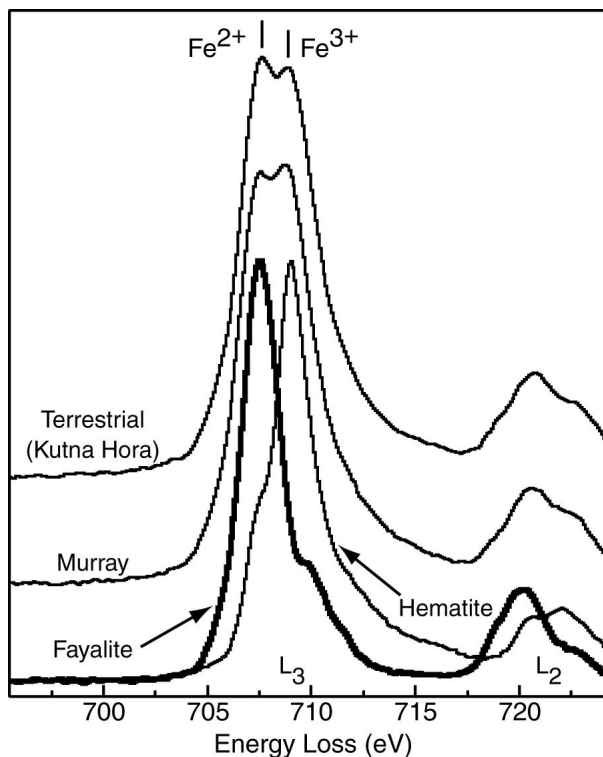


FIGURE 2. Anatomy of the $Fe\ L_{2,3}$ core-loss edge. Iron in different oxidation states has distinct core-loss edge shapes. Fayalite (Fe_2SiO_4) and hematite (Fe_2O_3) spectra are shown below those of terrestrial (Kutna Hora, Czech Republic) and meteoritic (Murray CM chondrite) cronstedtite, illustrating the distinct $Fe\ L_{2,3}$ edge shapes and chemical shifts of Fe^{2+} - and Fe^{3+} -bearing minerals, respectively. Energy-loss spectra from cronstedtite exhibit a double $Fe\ L_{2,3}$ edge, indicating the presence of Fe^{2+} and Fe^{3+} (cf., the fayalite and hematite spectra). The Fe^{2+} and $Fe^{3+}\ L_3$ white-line maxima are separated by approximately 1.6 eV.

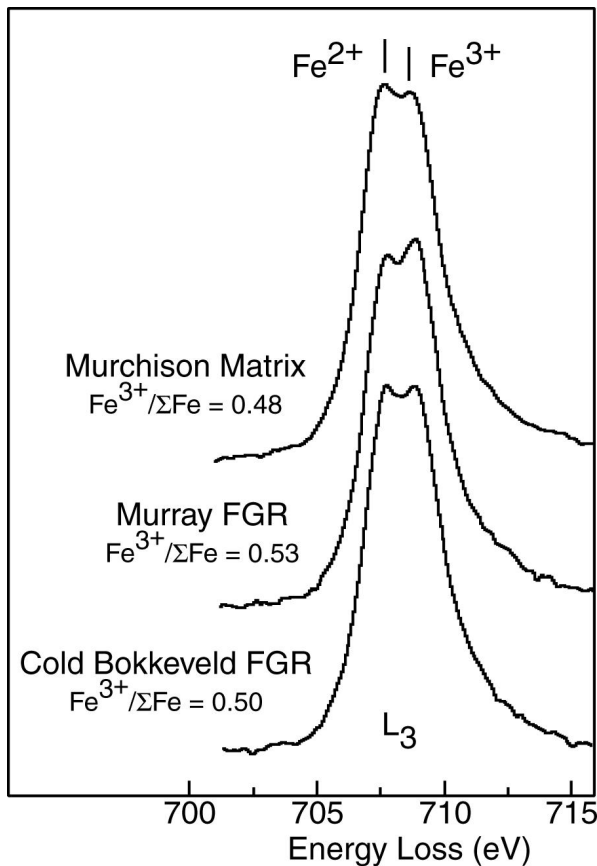


FIGURE 3. Representative EELS spectra of cronstedtites from CM chondrites. The meteorite and component (matrix or FGR) from which each spectrum was acquired are shown to the left of each spectrum above the L_3 edge.

TABLE 1. $Fe^{3+}/\Sigma Fe$ ratios as determined by EELS

Component	Murchison (68)*	Murray (47)	Cold Bokkeveld (44)
FGR	0.53 0.45	0.53 0.48	0.50 0.47
Matrix	0.51 0.48	0.51 0.48	0.54 0.48

*Number of spectra used to quantify the $Fe^{3+}/\Sigma Fe$ ratios are indicated in parentheses. High and low values for each component are indicated by the upper and lower rows, respectively. Most analyses were made on separate grains. However, some grains contain thin areas that are large enough to permit multiple measurements, and in such cases analyses were made on separate areas of individual grains. The estimated error of these measurements is ± 0.02 .

sume that the $Fe^{3+}/\Sigma Fe$ ratios record the conditions at the time cronstedtite formed and serve as a proxy for f_{O_2} .

It is widely accepted that aqueous alteration was important in the evolution of the CM chondrites (Zolensky and McSween 1988), but textural and mineralogical data from some chondrules and FGRs have been interpreted as indicating alteration prior to accretion (Lauretta et al. 2000) in either a high-density nebular gas (subnebula) or a precursor planetesimal (Bischoff 1998; Metzler et al. 1992). However, observations from primitive type-3 chondritic meteorites reveal that the nebular f_{O_2} varied by several orders of magnitude above and below that of a

solar gas (Krot et al. 2000). In contrast, the narrow range of the $Fe^{3+}/\Sigma Fe$ ratios that we observe suggest that the f_{O_2} of the environment in which hydration occurred was nearly constant, consistent with in situ alteration on a parent body.

The EELS data show no correlation among degree of alteration, brecciation, and redox state for the CM chondrites studied; intensely altered and moderately brecciated CM chondrites such as Cold Bokkeveld (Browning et al. 1996; Metzler et al. 1992) experienced aqueous alteration under similar values of f_{O_2} as that of mildly to moderately altered and intensely brecciated CMs such as Murchison and Murray. Although matrix may have been derived through impact-induced brecciation of dust-coated components in a parent-body environment (Metzler et al. 1992), it experienced alteration under f_{O_2} conditions similar to the FGRs. This similarity implies that the unequilibrated mineralogy observed in some FGRs (Lauretta et al. 2000; Metzler et al. 1992) reflects heterogeneities in the extent of parent-body alteration rather than the accretion of hydrous material from multiple reservoirs.

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