CRONSTEDTITE AND IRON SULFIDE MINERALOGY OF CM-TYPE CARBONACEOUS CHONDRITES FROM CRYOGENIC MÖSSBAUER SPECTRA

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Overview. Determinations of oxidation states and the crystal chemistry of iron-bearing minerals in CM meteorites by Mössbauer spectroscopy are complicated by thermally-induced electron hopping in cronstedtite and by ill-defined contributions from the hydrous iron sulphide phase believed to be tochilinite. Mössbauer spectral measurements at 30 K of several cronstedtite and tochilinite specimens have enabled modal proportions of these minerals, as well as Fe^{3+}/Fe^{2+} ratios, to be determined quantitatively for a suite of CM-type carbonaceous chondrites that included Murchison, Murray, Cold Bokkeveld, ALH 83100 and LEW 90500.

Background. The poorly-characterized phases (PCP) in CM carbonaceous chondrites consist of an intimate mixture of interstratified minerals comprising a hydrous iron sulfide believed to be related to tochilinite [1,2] and phyllosilicates dominated by the opaque, mixed-valence Fe^{2+}-Fe^{3+} serpentine mineral cronstedtite [3,4]. Although the matrix PCP's of several CM meteorites have been studied extensively, determinations of the chemical compositions, crystal chemistry and mineral proportions continue to pose acute difficulties, despite applications of high resolution electron microbeam techniques [3-5]. In a reconnoiter Mössbauer spectral study of suites of carbonaceous chondrites [6], we demonstrated that the oxidation states and modal mineralogy of iron could be determined quantitatively in the CI, CV, CO and CK meteorite-types. However, Mössbauer spectra of CM meteorites displayed unusual temperature variations that complicated analyses of iron in these carbonaceous chondrites. To better understand the crystal chemistry of iron in CM meteorites, detailed measurements of several terrestrial cronstedtite and tochilinite specimens were made, results of which are summarized here.

Tochilinite. The hydrous iron sulfide phase in CM meteorites having a formula approximating $Fe_{1.3}Ni_{0.1}SO_{1.4}$ [3-5] was identified as Fe-rich tochilinite [2]. The crystal structure of terrestrial tochilinite contains coherently stratified mackinawite (FeS) and brucite [$Mg(OH)_2$] sheets [1]. The mackinawite structure contains Fe^{2+} ions tetrahedrally coordinated to sulfur in layers if edge-shared [FeS_4] tetrahedra, while cations bound to OH^- ions occur in octahedral sites in brucite. In CM meteorites, some Fe^{2+} (+ Ni^{2+}) ions may also occur in the brucite layers of the tochilinite phase.

Mössbauer spectral measurements made on three terrestrial tochilinites at room temperature, 30 K and 4.2 K yielded a single peak, or closely-spaced doublet, located near 0.50-0.55 mm s^{-1} at 30 K. The isomer shift ($\delta \approx 0.55$ mm s^{-1}) of this peak differs from that of Fe^{2+} ions in sphalerite and wurtzite ($\delta \approx 0.65$-0.70 mm s^{-1}), the structures of which contain corner-shared [ZnS_4] tetrahedra.

Cronstedtite. Chemical compositions of jet-black platelets of cronstedtite indicate that in this serpentine-group mineral formulated as [$(Fe^{2+},Fe^{3+},Mg)_3(Si,Fe^{3+})_2O_5(OH)_4$], ferric iron is present in comparable amounts in both tetrahedral and octahedral coordinations. In octahedral sites located between layers of corner-shared [$(Si,Fe^{3+})O_4$] tetrahedra, each iron cation is coordinated to OH^- ions and non-bridging oxygens of the linked tetrahedra. The cis-[$FeO_2(OH)_4$] octahedra share edges with adjacent octahedra to form sheets parallel to the layers of corner-shared tetrahedra [7]. The close proximity of Fe^{2+} and Fe^{3+} ions in the octahedral sites causes thermally-induced electron delocalization to occur in cronstedtite so that this phyllosilicate is opaque and electrically conducting [8]. As a result, octahedral Fe^{2+} and Fe^{3+} ions cannot be distinguished in room-temperature Mössbauer spectra. When the temperature is lowered, however, electrons become localized on the Fe^{2+} ions so that ferrous and ferric cations become distinguishable in the Mössbauer spectra. At very low temperatures (<10 K), the onset of magnetic ordering occurs yielding very complex Mössbauer spectrum profiles. By measuring Mössbauer spectra of cronstedtites at 30 K, complications from electron delocalization and magnetic ordering are minimal so that site occupancies and relative proportions of Fe^{2+} and Fe^{3+} ions in cronstedites and CM meteorites may be determined accurately.

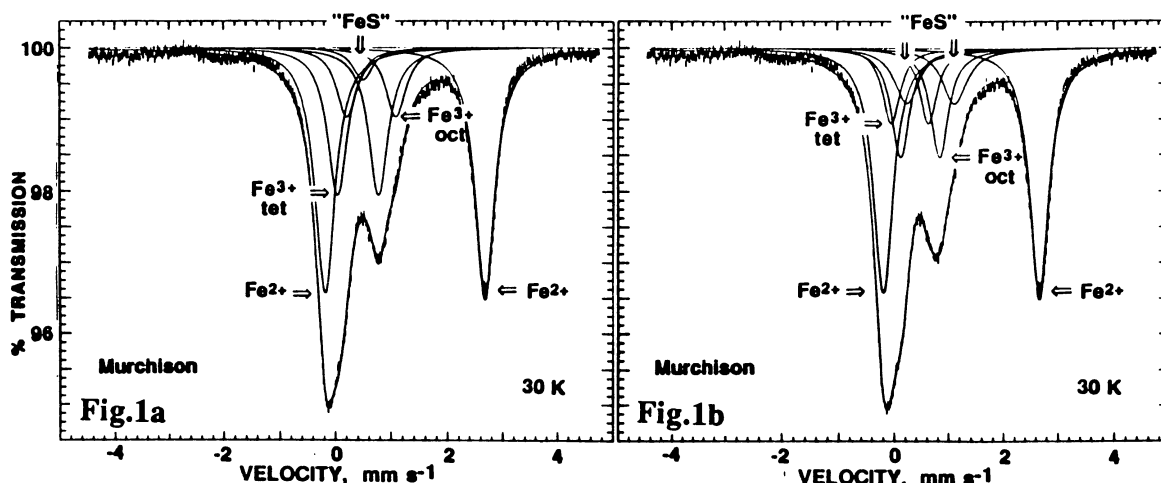## MINERALOGY OF CM-TYPE METEORITES: Fisher, D. S. and Burns, R. G.

Figure 1. Mössbauer spectrum of the Murchison meteorite at 30 K. (a) 7 peak fit; (b) 8 peak fit.

Five cronstedtites assembled for this investigations included a Mg^{2+}-rich cronstedtite from Pribram, Czechoslovakia that also was used in the crystal structure determination [7]. The chemical composition determined by our microprobe and Mössbauer spectral analyses yielded the chemical formula

$$(Mg_{0.58}Mn_{0.14}Fe^{2+}_{1.43}Fe^{3+}_{0.87})_{3.02}(Si_{1.32}Fe^{3+}_{0.66})_{1.98}O_5(OH)_4],$$
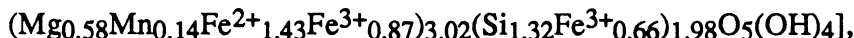
which closely resembles formulae of cronstedtites identified in carbonaceous chondrites [3]. Curve-fitting of the 30 K Mössbauer spectra of the cronstedtites to three doublets provided peak locations for octahedral Fe^{2+}, octahedral Fe^{3+} and tetrahedral Fe^{3+} ions. These three-doublet fits guided the curve-fitting models for resolving the Mössbauer spectra of CM-type meteorites.

Carbonaceous Chondrites. Specimens of ALH 83100, LEW 90500, Murchison, Murray and Cold Bokkeveld were used in the Mössbauer spectral measurements. In the course of the investigation, LEW 90500 was confirmed to be a CM-type carbonaceous chondrite. Two different curve-fitting models were used to resolve the Mössbauer spectrum profile of each meteorite. They are shown for the 30 K spectrum of Murchison in figure 1. The first approach incorporated a seven-peak fit (fig.1a), which consisted of one Fe^{2+} doublet and two Fe^{3+} doublets (to accomodate the iron cations in cronstedtite) and a single peak at ≈ 0.55 mm s^{-1} (to represent tochilinite). However, the isomer shift ($\delta \approx 0.45$ and 0.65 mm s^{-1}) and quadrupole splitting ($\Delta \approx 0.75$ and 0.85 mm s^{-1}) parameters of the doublets assigned to ferric iron in all of the CM meteorite spectra, as well as their relative intensities, failed to match the parameters for octahedral Fe^{3+} ($\delta \approx 0.50$ mm s^{-1}; $\Delta \approx 0.65$ mm s^{-1}) and tetrahedral Fe^{3+} ($\delta \approx 0.30$ mm s^{-1}; $\Delta \approx 0.50$ mm s^{-1}) ions in the cronstedtites.

In the second approach, eight peaks were fitted to the spectra of the CM meteorites (fig.1b). The ferric peak intensities and Mössbauer parameters for the tetrahedral Fe^{3+} ($\delta \approx 0.30$ mm s^{-1}; $\Delta \approx 0.60$ mm s^{-1}) and octahedral Fe^{3+} ($\delta \approx 0.50$ mm s^{-1}; $\Delta \approx 0.70$ mm s^{-1}) ions in the meteorites now more closely matched those for the cronstedtites. The fourth doublet attributed to iron chemically bound to sulfur yielded isomer shift parameters ($\delta \approx 0.68$ mm s^{-1}) comparable to those measured for tetrahedrally coordinated Fe^{2+} ions in iron-bearing sphalerites and wurtzites. The coordination environment of iron in the [FeS4] tetrahedra of the "FeS" phase of CM meteorites apparently differs from that of iron in terrestrial tochilinites, perhaps reflecting different distortions of the [FeS4] tetrahedra and next-nearest neighbor interactions with surrounding cations.

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