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# **Synchrotron-based infrared microspectroscopy as a useful tool to study hydration states of meteorite constituents**

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**Abstract–**We present the results of the infrared (IR) microscopic study of the anomalous carbonaceous chondrites Dhofar (Dho) 225 and Dhofar 735 in comparison to typical CM2 chondrites Cold Bokkeveld, Murray, and Mighei. The Fourier transform infrared (FTIR) 2.5–14 µm reflectance measurements were performed on conventional polished sections using an infrared microscope with a synchrotron radiation source. We demonstrate that the synchrotron-based IR microspectroscopy is a useful, nondestructive tool for studying hydration states of meteorite constituents in situ. Our results show that the matrices of Dho 225 and Dho 735 are dehydrated compared to the matrices of typical CM2 chondrites. The spectra of the Dho 225 and Dho 735 matrices lack the 2.7–2.8 µm absorption feature present in the spectra of Cold Bokkeveld, Murray, and Mighei. Spectral signatures caused by Si-O vibrations in fine-grained, Fe-rich olivines dominate the 10  $\mu$ m spectral region in the spectra of Dho 225 and Dho 735 matrices, while the spectra of normal CM2 chondrites are dominated by spectral signatures due to Si-O vibrations in phyllosilicates. We did not detect any hydrated phases in the spectra of Dho 225 and Dho 735 polished sections. In addition, the near-infrared reflectance spectra of Dho 225 and Dho 735 bulk powders show spectral similarities to the Antarctic metamorphosed carbonaceous chondrites. We confirm the results of previous mineralogical, chemical, and isotopic studies indicating that the two meteorites from Oman are the first non-Antarctic metamorphosed carbonaceous chondrites.

## **INTRODUCTION**

The carbonaceous chondrite (CC) class consists of several groups with distinct bulk compositional and oxygen isotopic characteristics: CI, CM, CR clan, CV, CO, and CK (Rubin 1997; Bischoff 2001; Krot et al. 2002 and references therein). The CR clan includes CR chondrites, CH chondrites, and the metal-rich CB chondrites (Krot et al. 2002). Several CCs are ungrouped and need to be further investigated.

The mineralogic and petrologic properties of three CCs from Antarctica—Belgica (B-) 7904, Yamato (Y-) 82162, and Y-86720—indicate that they were thermally metamorphosed in their parent bodies, but their mineralogical and chemical characteristics correspond to those of CI1 or CM2 chondrites before metamorphism (Tomeoka et al. 1989a, 1989b, 1990; Akai 1990; Bischoff and Metzler 1991; Ikeda 1992). Several other Antarctic CCs with affinities to CM2 and CI1 chondrites—Y-86789, Y-793321, Y-86029, Asuka (A-) 881655, Wisconsin Range 91600, and Pecora Escarpment 91008—have been suggested to be metamorphosed (Zolensky et al. 2005), but the oxygen isotopic compositions of these six meteorites have not yet been determined. Clayton and Mayeda (1999) identified the main characteristics of metamorphosed carbonaceous chondrites (MCCs) as 1) similar oxygen isotopic compositions distinct from the CI1 and CM2 main groups, 2) low H<sub>2</sub>O content in bulk chemical compositions, and 3) infrared spectral characteristics of matrix phyllosilicates indicating dehydration.

Two unusual carbonaceous chondrites, Dhofar (Dho) 225

and Dho 735, were found in the desert of Oman (Ivanova et al. 2002, 2003). Similarly to the Antarctic MCCs, they are enriched in heavy oxygen and have low bulk water content compared to normal CM2 chondrites (Ivanova et al. 2002, 2003, 2005). Infrared studies indicating the dehydration of matrix phyllosilicates are needed to confirm that Dho 225 and Dho 735 are thermally metamorphosed (Clayton and Mayeda 1999).

Synchrotron-based infrared (IR) microspectroscopy is a relatively new technique that allows the acquisition of IR spectra from extremely small samples. Due to a great improvement in lateral resolution (Dumas et al. 2000; Carr 2001), synchrotron IR microspectroscopy is an analytical tool of very high potential in different fields, including cellular biology, environmental sciences, geology, and mineralogy (e.g., Bantignies et al. 1998; Miller et al. 2000). The synchrotron radiation produced at various accelerator facilities provides a very bright source of radiation (including IR radiation) that can be used as a radiation source for IR microspectroscopy. The use of a synchrotron source instead of a conventional globar IR source significantly increases the signal-to-noise ratio and allows one to obtain diffractionlimited spatial resolution (Carr 2001). Synchrotron IR radiation does not damage a sample. Although some modern FTIR microscopes (e.g., the Bruker HYPERION series) also enable significant improvement of lateral resolution, in practice, such an improvement can only be achieved for materials of high optical and textural quality.

Synchrotron-based IR microspectroscopy has been successfully used to acquire infrared spectra of interplanetary dust particles and meteorite components (Raynal et al. 2000; Flynn et al. 2002, 2003, 2004; Keller et al. 2002; Quirico et al. 2003; Keller and Flynn 2003; Molster et al. 2003; Quirico and Bonal 2004; Matrajt et al. 2004, 2005). These measurements were performed in transmission mode, which requires either the use of an infrared transparent substrate or the preparation of an ultrathin section. Here we demonstrate the diagnostic potential of reflectance synchrotron-based IR microspectroscopy for nondestructive characterization of meteorite components in situ using conventional polished sections. In particular, our work focuses on the study of hydration states of matrices in new, metamorphosed carbonaceous chondrites Dho 225 and Dho 735. We also studied polished sections of the normal CM2 chondrites Mighei, Murray, and Cold Bokkeveld for comparison. In addition, we acquired reflectance spectra of bulk powders of the Dho 225 and Dho 735 in the range of  $0.3-50 \mu m$ .

It should be emphasized that IR characterization of hydration states of meteorite matrices without petrological, mineralogical, and geochemical studies is inconclusive regarding the hydration states of minerals and metamorphism on meteorite parent bodies (e.g., Clayton and Mayeda 1999; Quirico 2003; Bonal et al. 2006). IR spectroscopy can only be used as a complementary method. In particular, a conclusion regarding metamorphism of Dho 225 and Dho 735 is made based on detailed mineralogical, petrological (including SEM studies), and isotopic investigations. These results have been discussed by Ivanova et al. (2002, 2003, 2005) and will be summarized and published elsewhere. The lack of hydrated minerals in the matrices of Dho 225 and Dho 735 reported here only confirms the conclusions drawn from petrological, mineralogical, and geochemical studies of these meteorites.

#### **EXPERIMENTAL PROCEDURES**

The IRIS infrared beamline at the electron storage ring facility BESSY (Schade et al. 2002) is equipped with a Thermo Nicolet Continuum IR microscope coupled to a Nexus 870 FTIR spectrometer. We used an  $LN_2$ -cooled HgCdTe (MCT) detector, a KBr beam splitter, and a  $32\times$ Cassegrain objective with a numerical aperture of 0.65, which is equivalent to an opening angle of about 80°. The optical axis of the objective is normal to the sample surface. For reflectance measurements, half of the collimated entrance beam to the objective is blocked by a plane mirror that directs the reflected light to the detector. From this scheme, a biconical reflectance geometry with an angle of incidence of 20° and a cone opening angle of 40° can be estimated for our measurements.

This configuration is suitable for infrared microspectroscopy in the range of 1.4–14 µm. The spectral resolution applied was 8 cm<sup>−</sup>1. The instrument enables IR imagery and mapping, but we did not use this option in this study.

Some of our measurements were performed with an illuminating spot close to the diffraction limit. In this case, the focal depth is of the same order. This makes the confocal alignment very sensitive in all three directions. Since optical dispersive elements (beam splitters, windows, etc.) are always present in the beam path, the distance of the confocal arrangement becomes wavelength-dependent. To provide gold-plated surfaces for standard measurements and to minimize the effects on the spectra mentioned above, we deposited gold layers 1 mm wide and 100 nm thick directly onto the sample close to the areas of interest rather than using a separate reference standard.

We probed the meteorite matrices of low albedo with a spot size as small as  $15 \times 15 \mu m^2$  and  $20 \times 20 \mu m^2$ , thus avoiding the contribution of numerous sulfide, taenite, and tetrataenite grains to our measurements. Smaller footprints of  $10 \times 10$  µm<sup>2</sup> and  $5 \times 5$  µm<sup>2</sup> were applied to acquire IR reflectance spectra of the new Ca,Fe oxysulfide phase found in the Dho 225 meteorite (Ivanova et al. 2002). In several cases, we used the standard internal Globar source of the FTIR spectrometer to acquire reflectance spectra of larger areas of  $70 \times 70 \text{ }\mu\text{m}^2$ .

We acquired Vis-NIR reflectance spectra of bulk powders of Dho 225 and Dho 735 using the NASA-supported RELAB bidirectional spectrometer operating in the range of 0.3–2.6  $\mu$ m at  $i = 30^{\circ}$  and  $e = 0^{\circ}$  (Brown University) (Pieters and Hiroi 2004). The bidirectional reflectance spectra were measured relative to a halon standard. The FTIR reflectance spectra of the bulk samples were measured in the range of 2– 50  $\mu$ m at off-axis biconical geometry ( $i = e = 30^{\circ}$ ) using a Thermo Nexus 870 spectrometer equipped with multiple DTGS detectors and purged with dry air. The FTIR spectra were measured at 4 cm<sup>−</sup>1 resolution, relative to a rough gold standard, and merged with the bidirectional spectra at 2.4  $\mu$ m to obtain the composite spectra.

We collected the composite biconical  $(i = e = 20^{\circ})$ reflectance spectrum of the synthetic tochilinite powder using the IFS88 FTIR spectrometer at DLR (Berlin) equipped with a "Seagull" variable angle reflectance accessory. The measurements in the range of 0.5–16  $\mu$ m were performed in an atmosphere purged of  $H_2O$  and  $CO_2$ . A Si-diode detector was used from 0.5 to 1  $\mu$ m, an InSb detector from 0.9 to 5.4 µm, and an LN2-cooled MCT detector between 5 and  $16 \mu m$ . The measurements in the visible range were performed relative to a halon standard, while the infrared spectra were acquired relative to a gold-plated sandpaper standard. The sampling resolution was 4 cm<sup>-1</sup> between 1 and 16 µm and 8 cm<sup>−</sup>1 between 0.5 and 1 µm.

#### **RESULTS AND DISCUSSION**

### **The 3-Micron Spectral Region**

Fundamental stretching vibrations of O-H bonds and the first overtone of the H-O-H bending mode produce absorption bands between 2.5 and  $\sim$ 3  $\mu$ m in the spectra of minerals containing structural OH and/or interlayer/adsorbed  $H_2O$ (Eisenberg and Kauzmann 1969; Farmer 1974; Aines and Rossman 1984; Bishop et al. 1994). The O-H stretching vibrations of hydroxyl ions usually occur near 2.75 µm, the precise position of these features being affected by the cations to which the OH is bound by interlayer cations (if present), and by the configuration and charge distribution of the surrounding lattice (e.g., Farmer 1974). OH groups incorporated into a mineral lattice (structural OH) are very stable under heating, unlike physically adsorbed water, which is unstable in vacuum or can easily be removed from the mineral by mild heating. Some minerals (e.g., montmorillonites and hydrated salts) also contain chemically bound water, which is more stable under heating than physically adsorbed water. The spectra of minerals containing bound or adsorbed  $H_2O$  show a broad complex absorption feature at  $\sim$ 2.8–3 µm. In the case of bound water, cations to which the water molecules are bound affect the exact position of the water absorptions (e.g., Bishop et al. 1994). All this makes the 2.7–3 µm spectral region potentially diagnostic for spectroscopic detection of hydrated minerals in the matrices of primitive carbonaceous meteorites. It should be noted,

however, that matrix mineralogy of CM2 meteorites is very complex (see below), and therefore absorption features due to many individual hydrated and hydroxylated phases may overlap in this spectral range. The term "hydration state" in this paper is used in a qualitative sense. We demonstrate that the matrices of the new carbonaceous chondrites from Oman are poor in hydrated/hydroxylated phases compared to normal CM2 chondrites. The goals of our study include neither determination of OH/H<sub>2</sub>O ratios in the meteorite matrices nor identification of individual minerals causing OH/H<sub>2</sub>O-related absorptions in reflectance spectra of CM2 matrices.

We detected no signatures due to O-H vibrations (in structural OH and/or bound  $H_2O$ ) in the 2.5–3  $\mu$ m spectral range in the Dho 225 and Dho 735 matrices by synchrotronbased IR microspectroscopy. We carefully scanned all the surfaces of our polished sections using a mapping stage but detected no O-H signatures in the spectra of any constituents of the two meteorites. We are aware that the absence of O-H features in reflectance spectra of polished surfaces is not rigorous evidence for the absence of hydrated phases in the samples. A significant contribution from specular reflection could mask the O-H absorption features in the 2.5–3 µm spectral range. However, we detected relatively strong (15– 20%) O-H absorption bands in the matrix spectra of the main group CM2 chondrites Cold Bokkeveld, Murray, and Mighei (Fig. 1). The absorption features in the spectra of the latter meteorites are centered near 2.7–2.8 µm and therefore are related to O-H vibrations in structural OH in matrix phyllosilicates and hydrosulfides. In principle, the apparent lack of the O-H signatures in the spectra of Dho 225 and Dho 735 matrices could also be caused by a high abundance of opaque phases intimately intergrown with matrix-hydrated phases. Fine opaques are effective light absorbers, masking absorption bands of other minerals in reflectance spectra of mineral mixtures (Nash and Conel 1974; Clark 1983; Hapke 1993; Moroz and Arnold 1999). However, we have no evidence for a higher abundance (or finer grain sizes) of such opaques in the matrices of Dho 225 and Dho 735 than in the matrices of typical CM2 chondrites. Our results therefore suggest a lower content, if not the absence, of hydrated phases in the Dho 225 and Dho 735 matrices compared to those in normal CM2 chondrites (Fig. 1).

Dho 225 contains unusual inclusions, probably composed of a new phase, Ca,Fe oxysulfide (Ivanova et al. 2002). Its best-fit stoichiometry and low analytical total indicate a formula of  $Ca_{4.66}Fe^{2+}$ <sub>0.34</sub>Fe<sup>3+</sup><sub>6</sub>S<sub>5</sub>O<sub>9</sub> (Ivanova et al. 2002). Another possible formula is  $Ca_4Fe^{2+}{}_{5}S_4(OH)_4O_3$ (Ivanova et al. 2002) but the inclusions appear to lack OH, since they are stable under an electron beam. We have not detected absorption bands of structural OH at 2.7–2.8 µm in these grains. Given the presence of strong structural OH signatures in our reflectance spectra of tochilinite inclusions in Murray (Fig. 2), this result strongly suggests the absence of OH in the structure of the Ca,Fe oxysulfide.



Fig. 1. The average matrix reflectance spectra of Dho 225, Dho 735, and three normal CM2 chondrites in the spectral region of O-H stretching vibrations. Spot sizes are  $15 \times 15 \ \mu m^2$  and  $20 \times 20 \ \mu m^2$ .



Fig. 2. The O-H stretching feature in the infrared reflectance spectrum of tochilinite inclusion from CM2 chondrite Murray. Spot size is 15 ×  $15 \mu m^2$ .

Tochilinite (coherently interstratified iron sulfide and magnesium iron hydroxide phase—ideally  $2Fe<sub>0.9</sub>S \times$  $1.67$ [(Mg,Fe)(OH)<sub>2</sub>]) is a major matrix component of CM2 chondrites (MacKinnon and Zolensky 1984; Zolensky et al. 1993). Tochilinite is also present as isolated inclusions in CM2 chondrites.

Figure 2 shows reflectance spectrum of a tochilinite inclusion from a polished section of the Murray meteorite. The OH signature is well pronounced, the unusual shape of the spectrum being due to the high contribution of specular reflectance. Although the presence of the OH signature is evident between 2.7 and 3 µm, the significant contribution of specular (surface) reflection makes it difficult to define its exact position. We also measured biconical 0.5–16 µm reflectance spectra of powdered (average grain size of a few micrometers) Fe, Mg to chilinite samples (Fe: Mg =  $4:1$ ) synthesized by Kozerenko et al. (2001). The composite spectrum of a synthetic tochilinite sample is shown in Figs. 3a and 3b. The fine tochilinite powder has very low reflectance, which is typical of sulfide phases (Hunt et al. 1971), and shows absorption features due to O-H vibrations in the 3 µm spectral region. Reflectance of the fine tochilinite powder in the 3 µm region is controlled mostly by volume scattering; absorption features are therefore seen as reflectance minima (Salisbury et al. 1981; Hapke 1993). We suggest that the two features at 2.7 and 2.78 µm (Fig. 3a) can



Fig. 3. The biconical reflectance spectrum of a synthetic tochilinite powder (a) in the region of O-H stretching vibrations, and (b) between 0.5 and  $16 \mu m$ .

be attributed to stretching vibrations of structural OH bound to Mg  $(2.7 \mu m)$  band) and Fe  $(2.78 \mu m)$  cations in the octahedral hydroxide layers of tochilinite (Ryskin 1974). The sharp 2.7 µm feature is absent in the spectra of tochilinite inclusion from Murray. If our assignment of this feature is correct, the lack of this band in the spectra of the Murray tochilinite is consistent with low Mg contents in tochilinites from the CM2 chondrites with the most Fe-rich matrices— Murray, Murchison, and Mighei (Zolensky 1987; Ivanova et al. 2005). Zolensky (1987) suggested that the more Mgrich matrices of some other CM2 meteorites may contain Mg-rich tochilinites. Indeed, Ivanova et al. (2005) report that a new "normal" CM2 chondrite, Dho 955, whose matrix phyllosilicates are enriched in Mg, is also characterized by a higher Mg/(Mg + Fe) ratio in tochilinite inclusions compared to other normal CM2 chondrites with available tochilinite analyses.

Spectral properties of tochilinites are discussed here in some detail, since their IR spectra have not yet been published. However, it should be noted that CM2 matrices contain many other minerals including hydrated/hydroxylated ones. Phyllosilicates within CM2 matrices include serpentinegroup minerals (chrysotile, lizardite, antigorite, cronstedtite, ferroan antigorite, greenalite, berthierine), saponite, clinochlore, talk, and, probably, chamosite. Associated with phyllosilicates are intergrowths of serpentine and tochilinite, as well as troilite, several hydroxide phases (brucite, goethite, and lepidocrocite) and rare grains of apatite and halides (Barber 1981, Rubin 1997, Brearley and Jones 1998). Fe-rich serpentine (cronstedtite) is the most abundant matrix component in "normal" CM2 meteorites. The spectral reflectance properties of Mg-rich and Fe-rich serpentinegroup minerals are discussed, e.g., by Calvin and King (1997).



Fig. 4. The infrared reflectance spectrum of a carbonate inclusion from Cold Bokkeveld CM2 chondrite. Spot size is  $50 \times 50 \mu m^2$ .



Fig. 5. The infrared reflectance spectra of isolated olivine grains from Dho 225, Dho 735, Murray, and Cold Bokkeveld. Spot size is  $20 \times$ 20  $\mu$ m<sup>2</sup> (Dho 225, Dho 735, and Cold Bokkeveld) and 15  $\times$  15  $\mu$ m<sup>2</sup> (Murray).

## **The 10-Micron Spectral Region**

The strongest diagnostic features of minerals composing the stony meteorites are present in the spectral region around 10 µm. For example, silicates show fundamental vibration absorption features between 8 and 12 µm due to strong asymmetric stretching of Si-O bonds (Farmer 1974). Carbonates show a strong band near 6–7 µm due to asymmetric C-O stretching vibrations and a weaker band near 11.5 µm due to bending modes (Vincent and Hunt 1968; Farmer 1974).

Absorption coefficients at the band centers are so high that reflectance is controlled solely by surface scattering, which produces reflectance maxima rather than minima in reflectance spectra of smooth surfaces and powders (Vincent and Hunt 1968). These reflectance maxima (so-called Reststrahlen bands) are of certain diagnostic potential, although their shapes and intensities are strongly affected by grain size, crystal orientation, and degree of crystallinity (Lyon 1964; Vincent and Hunt 1968; Salisbury et al. 1991).

Reflectance minima called Christiansen features (Conel 1969) occur just prior to each fundamental vibration band, where the refractive index approaches that of the medium (air), resulting in a minimum of backscattering. Christiansen features in reflectance spectra are very useful for characterization of mineral composition, since the



Fig. 6. The infrared reflectance spectra of olivine and pyroxene grains from Murray CM2 chondrite. Spot size is  $15 \times 15 \mu m^2$ .



Fig. 7. The infrared reflectance spectra of fine-grained olivines from olivine aggregates and chondrules in the Murray and Dho 225 meteorites (spot size is  $70 \times 70 \mu m^2$ ) compared to the average spectra of the Dho 225 and Dho 735 matrices.

wavelength positions of these features do not vary as a function of grain size, crystal orientation, or crystallinity (Conel et al. 1969; Salisbury et al. 1991; Cooper et al. 2002). Figure 4 shows the Reststrahlen bands and Christiansen features in the spectrum of a calcite inclusion from CM2 chondrite Cold Bokkeveld.

Olivines in CM2 chondrites are found in amoeboid aggregates, chondrules, and as isolated grains in the matrices (Fuchs et al. 1973; Grossman and Olsen 1974). In Fig. 5, reflectance spectra of several isolated olivine grains from the polished sections of the Murray, Cold Bokkeveld, Dho 225, and Dho 735 meteorites are shown. The spectra exhibit significant variations. Figure 5 demonstrates that the shapes,

widths, and relative contrasts of individual Si-O Reststrahlen bands are strongly affected by crystal orientation. Nevertheless, the wavelength positions of Christiansen features (9.1–9.2  $\mu$ m) and a weak band near 12  $\mu$ m present in all spectra allow one to unambiguously identify these grains with olivines. As the fundamental vibration bands shift to a longer wavelength with increasing depolymerization of the silicate structure, the wavelength of the Christiansen feature shifts accordingly (Conel 1969; Salisbury and Walter 1989). This makes the Christiansen feature a good compositional indicator. For example, the Christiansen features located between 8.9 and 9.4 µm enable one to distinguish olivine spectra from pyroxene spectra showing the Christiansen



Fig. 8. The average matrix spectra of Dho 225, Dho 735, and normal CM2 chondrites in the spectral region dominated by Si-O stretching features. Spot sizes are  $15 \times 15 \mu m^2$  and  $20 \times 20 \mu m^2$ .

features at shorter wavelengths (Fig. 6). Furthermore, the spectra of low-Ca pyroxenes show an additional Reststrahlen band near 14 µm (Fig. 6) which is absent in the spectra of olivines and is shifted to longer wavelengths in the spectra of high-Ca pyroxenes.

The spectra of the  $70 \times 70 \text{ }\mu\text{m}^2$  areas composed of finegrained olivines from amoeboid aggregates and chondrules (Fig. 7) show that the decrease in grain size (i.e., random crystal orientation) significantly affects relative intensities of individual Reststrahlen bands. For example, the features located at wavelengths shorter than 10.6 µm lose their contrasts compared to features at longer wavelengths. In addition, with decreasing grain size, the band centered near 11.4 µm becomes more prominent compared to other Reststrahlen bands related to Si-O stretching vibrations in olivine crystals. The peak at  $11.2-11.5$  µm is the strongest absorption band in the absorption spectra of olivines (Lehmann et al. 1961; Jäger et al. 1998; Koike et al. 2003). The spectra of Dho 225 and Dho 735 matrices (Fig. 7) are clearly dominated by fine-grained olivines. The overall shapes of the matrix spectra (Fig. 7) strongly resemble the shapes of olivine absorption spectra (e.g., Koike et al. 2003).

The individual Si-O stretching vibration bands and Christiansen features in the infrared spectra of olivines shift to longer wavelengths with decreasing content of the forsterite (Fo) component  $(Mg/[Mg + Fe])$  in olivine (Lehmann et al. 1961; Jäger et al. 1998; Koike et al. 2003). This makes it possible to obtain a rough estimate of the Fo content based on the infrared spectra. Comparison of individual band positions in the spectra of the Dho 225 and Dho 735 matrices with the data from the ASTER online spectral library (Salisbury et al. 1994; http:// speclib.jpl.nasa.gov) and the data of Koike et al. (2003) gives

an Fo content of  $Fo_{30}$ – $Fo_{50}$ . This result is in good agreement with the average chemical composition of the Dho 225 and Dho 735 matrices, which corresponds to the olivine composition of Fo<sub>45</sub>.

Figure 8 shows the average spectra of the Dho 225 and Dho 735 matrices compared to the average matrix spectra of typical CM2 chondrites Cold Bokkeveld, Murray, and Mighei. The matrix spectra of the nonmetamorphosed CM2 chondrites (Fig. 8) display an unstructured Reststrahlen band centered near  $\sim$ 10  $\mu$ m and attributable to Si-O stretching in the mixtures of disordered Fe-rich and Mg-rich phyllosilicates (Brindley and Zussman 1959; Stubican and Roy 1961; Calvin and King 1997). This result is in agreement with the data of Quirico and Bonal (2004) who reported IR absorption spectra of the matrices of several typical CM2 chondrites including Murray and Cold Bokkeveld. The broadness and lack of structure of the 10 µm features in the matrix spectra of Murray, Mighei, and Murchison suggest poor crystallinity of phyllosilicates, but may also result from overlapping Si-O absorptions of various phyllosilicates composing the matrices of CM chondrites.

Unlike the matrices of normal CM2 chondrites, the matrix spectra of Dho 225 and Dho 735 are clearly dominated by fine-grained crystalline olivine as discussed above, although traces of phyllosilicates cannot be ruled out.

Thus, the 10  $\mu$ m spectral region provides clear evidence for the dehydrated state of the Dho 225 and Dho 735 matrices compared to the matrices of nonmetamorphosed CM2 chondrites.

Such a dramatic difference between nonmetamorphosed and metamorphosed CM chondrites in this spectral region is not evident in the reflectance spectra of their bulk powders (Fig. 9). Spectral signatures of olivine dominate the spectra



Fig. 9. The biconical reflectance spectra of Dho 225 (particle size <125 µm) and Dho 735 (particle size <150 µm) bulk powders compared to the spectra of normal CM2 chondrites Murchison and Murray (from the ASTER spectral library; particle size <75 µm).



Fig. 10. The bidirectional Vis-NIR spectra of Dho 225 and Dho 735 bulk powders. Particle sizes are <125 µm (Dho 225) and <150 µm (Dho 735).

of all CM2 chondrites in this spectral region. IR reflectance spectra of loose mineral powders show smooth reflectance maxima called "transparency features" (Salisbury et al. 1991). In the spectra of bulk powdered CM2 chondrites, the transparency features are observed between 12 and 14 µm (Fig. 9), which is consistent with fine-grained olivine (Mustard and Hays 1997). The Reststrahlen region is dominated by olivine Si-O stretching near 11.2–11.5 µm. The olivine band  $(11.9-12 \mu m)$  in the spectra of loose powders is seen as a reflectance minimum just prior the transparency feature (Fig. 9). Although the bulk powdered CM2 chondrite materials are composed of both hydrated and anhydrous minerals, the hydrated phases are poorly crystalline and

extremely fine-grained compared to the anhydrous minerals. Infrared reflectance spectra of mineral powders are strongly affected by particle size variation; in particular, Reststrahlen bands lose their contrasts with decreasing particle size (Lyon 1964; Salisbury and Wald 1992). Therefore, the spectral contribution of the fine-grained CM2 matrix phyllosilicates is low in the Reststrahlen region compared to the coarsegrained anhydrous silicates (mostly olivine). The spectral dominance of olivine in the mid-IR spectra of the bulk CM2 chondrite powders has previously been reported by Calvin and King (1997). However, the spectra of the normal CM2 chondrites Murray and Murchison (Fig. 9) lack the weak reflectance minimum near 10.5 µm that is typical of olivine. The absence of this feature is probably related to the overlapping Reststrahlen bands of phyllosilicates. The 10.5 µm feature is weak but detectable in the spectra of Dho 225 and Dho 735 bulk powders, as well as in the spectra of the Antarctic MCCs Y-82162 and Y-86720 acquired by Hiroi et al. (1996). The feature is also evident in the spectra of CM2 meteorite Murchison heated to ≥700 °C by Hiroi et al. (1996).

# **Reflectance Spectra of Dho 225 and Dho 735 Bulk Powders in the Vis-NIR Range**

Figure 10 shows the Vis-NIR reflectance spectra of powdered Dho 225 and Dho 735 samples. The spectra have flat near-infrared slopes and are featureless, except for the UV-falloff typical of carbonaceous chondrites (Johnson and Fanale 1973). The reflectance spectra of the Antarctic metamorphosed carbonaceous chondrites B-7904, Y-82162, and Y-86720 are also characterized by the flat NIR spectral slopes (Hiroi 1993, 1994), while the reflectance spectra of normal CM2 chondrites have positive (reddish) spectral slopes in the NIR (Johnson and Fanale 1973; Moroz and Pieters 1991). Typical CM2 chondrites usually show a weak absorption band near 0.7  $\mu$ m due to Fe<sup>2+</sup>→Fe<sup>3+</sup> charge transfer transitions in hydrated silicates (Johnson and Fanale 1973; Gaffey and McCord 1979). This feature is absent in reflectance spectra of the Antarctic metamorphosed carbonaceous chondrites (Hiroi 1993; 1994), Dho 225, and Dho 735 (Fig. 5). The flat spectral curves and the lack of the 0.7 µm absorption band may be due to dehydration of serpentine (Hiroi et al. 1994, 1996) and/or carbonization of organic components induced by thermal metamorphism (Moroz 2005).

Thus, the shapes of the Vis-NIR reflectance spectra of powdered Dho 225 and Dho 735 are in good agreement with other observations indicating that the two carbonaceous chondrites from Oman are thermally metamorphosed.

## **CONCLUSIONS**

Our results confirm that the matrices of Dho 225 and Dho 735 are dehydrated compared to normal CM2 chondrites. Along with chemical, mineralogical, and isotopic studies, this indicates that the two new meteorites from Oman are the first non-Antarctic metamorphosed carbonaceous chondrites. Synchrotron-based IR reflectance microspectroscopy is a nondestructive tool to study the hydration states of meteorite phases. Information from the 3 µm and 10 µm spectral regions should be combined to draw conclusions regarding hydration states of CC matrices, the spectral region where Si-O stretching vibrations occur being particularly useful. Spectral similarities between the bulk powders of the Dho 225, Dho 735, and the Antarctic MCCs in the near-infrared region is an additional indication for similarities in the thermal evolution of these carbonaceous chondrites.

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