

A RAMAN STUDY OF CARBONATES AND ORGANIC CONTENTS IN FIVE CM CHONDRITES. Q. H. S. Chan¹, M. E. Zolensky¹, R. J. Bodnar², C. Farley², and J. C. H. Cheung³. ¹NASA Johnson Space Center, Houston, TX, USA. E-mail: hschan@nasa.gov. ²Department of Geosciences, Virginia Tech, Blacksburg, VA 24061, USA. ³Met Office, Exeter, UK.

Introduction: Carbonates comprise the second most abundant class of carbon-bearing phases in carbonaceous chondrites after organic matter (~2 wt.%), followed by other C-bearing phases such as diamond, silicon carbide, and graphite [1]. Therefore, understanding the abundances of carbonates and the associated organic matter provide critical insight into the genesis of major carbonaceous components in chondritic materials. Carbonates in CM chondrites mostly occur as calcite (of varying composition) and dolomite [2-4].

Properly performed, Raman spectroscopy provides a non-destructive technique for characterizing meteorite mineralogy and organic chemistry. It is sensitive to many carbonaceous phases, allows the differentiation of organic from inorganic materials, and the interpretation of their spatial distribution. Here, with the use of Raman spectroscopy, we determine the structure of the insoluble organic matter (IOM) in the matrix and carbonate phases in five CM chondrites: Jbilet Winselwan, Murchison, Nogoya, Santa Cruz, and Wisconsin Range (WIS) 91600, and interpret the relative timing of carbonate precipitation and the extent of the associated alteration events.

Samples and Analytical Techniques: We studied five CM chondrites - Jbilet Winselwan (hereafter, Jbilet) (CM2.3, a find from the Western Sahara, 2013), Murchison (CM2.5, a fall from Australia, 1969), Nogoya (CM2.2, a fall from Argentina, 1879), Santa Cruz (CM2, a fall from Mexico, 1939), and WIS 91600 (CM-an, a find from Antarctica, 1991). WIS 91600 was provided by the Meteorite Working Group (MWG) and the JSC Meteorite Curator. The remaining samples were provided by meteorite collectors. We prepared polished thin sections of the meteorite samples with isopropanol, and then identified carbonates in each sample with an optical microscope. Standard carbonates aragonite (CaCO₃), calcite (CaCO₃), dolomite (CaMg(CO₃)₂) and siderite (FeCO₃) were provided by M. Zolensky and R. Morris (NASA JSC).

The samples were analyzed using a Jobin-Yvon Horiba LabRam HR (800 mm) Raman microprobe at the Department of Geosciences, Virginia Tech. The excitation wavelength was 514.53 nm (green) provided by Modu-Laser Stellar Pro-L 514 nm, 100 Mw solid-state laser operated at 50 mW at the source). The Raman probe spatial resolution at the analyzed spot was 1.14 μm at the 40x magnification. Three accumulated spectra were collected from each analytical spot to identify and discard spurious signals, such as those from cosmic rays. Wavelength calibration against a silicon wafer sample was checked daily

prior to sample analyses. Custom software written in the Python programming language [5] was used to fit the Raman data using Lorentzian profiles and applying a linear baseline correction in order to determine the peak center positions (ω) and full width half-maximum (FWHM, Γ) of each Raman band..

Results and Discussion: We compared the ~1100 cm⁻¹ band positions of the CM carbonates to the dolomite and calcite standards (Table 1), and concluded that most selected carbonates identified in this study are calcite, except for a single dolomite grain in Nogoya (Grain 5). This does not preclude the presence of other carbonate phases in the CMs. The ν_1 positions of the CM calcites are 2–3 cm⁻¹ higher than pure calcites, which suggests that they contain significant impurity cations. The cations in the Ca-carbonates are mainly Fe, and occasionally Mn and Mg in CMs [2, 3], and Sr in CIs [6].

Table 1. Peak center locations and the corresponding assignments of the carbonate bands of the CM2 samples, calcite and dolomite standards.^a

Jbilet	Murchison	Nogoya (Gr 5)	SantaCruz	WIS 91600	Calcite	Dolomite
158 ± 0.1	157 ± 0.5	177 ± 0.3	157 ± 0.1	^b	156	176
285 ± 0.3	283 ± 0.8	300 ± 0.6	284 ± 0.3	284 ± 1.1	282	299
716 ± 0.3	715 ± 0.1	726 ± 1.1	715 ± 0.4	^b	712	724
1090 ± 0.4	1089 ± 0.5	1100 ± 0.3	1089 ± 0.2	1090 ± 1.6	1087	1097

^aUncertainties are 1 σ standard deviation of the mean.

^bThe intensity is too low for accurate determination of the peak center position

Organo-carbonate associations. The high Raman spatial resolution (~1 μm) and large carbonate grain sizes (28–318 μm) allowed accurate analyses of the carbonate grains without interference from surrounding phases. Typical first-order D bands at ~1350–1380 cm⁻¹ and G band at ~1580–1590 cm⁻¹ were detected in ~25% of the analyzed carbonate grains in the meteorite samples, indicating the presence of amorphous carbon in the carbonates (Figure 1, top). This suggests that carbonates not only provide sources of carbon from their carbonate frameworks, but also trap and preserve organic carbon present in the mineralizing fluids. However, while the D and G bands were observable in the matrix of Murchison, its carbonate crystals are apparently devoid of organic matter at levels detectable by Raman (Figure 1, bottom). In fact, it is more common for carbonates to not contain Raman-active organic matter, as opposed to CM meteorite matrix which in our experience always shows D and G Raman bands. While the Raman peak parameters of the CM samples

conform to the IOM of primitive chondrites, they also exhibit well-defined trends and are distinguishable between carbonates and matrix (Figure 2). Carbonates generally have narrower band widths (Γ_D , Γ_G), lower D band locations (ω_D), I_D/I_G ratios, but higher G band locations (ω_G).

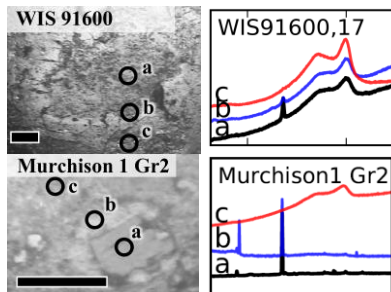


Figure 1. Raman spot locations and associated Raman spectra (500–2000 cm^{-1} region). Scale bar is 40 μm .

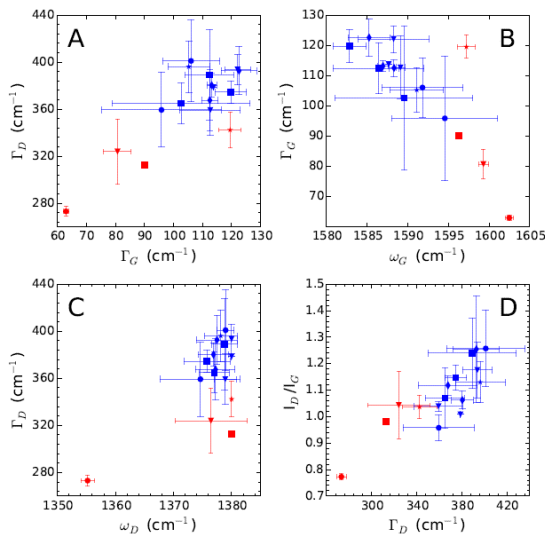


Figure 2. Comparison between different Raman peak parameters of selected spectra of the CM chondrites. Blue markers – matrix; Red markers – carbonates.

OM maturity and the estimated PMT. Visual examination of the overall shapes of the Raman spectra shows that the CM samples have experienced low peak metamorphic temperatures (PMT), which are equivalent to terrestrial metamorphic facies from lower greenschist grade ($\sim 200^\circ\text{C}$) to upper greenschist grade ($\sim 330^\circ\text{C}$) [7]. The wide Γ_D and Γ_G are indicative of highly disordered carbonaceous materials. However, this does not provide any information regarding weaker, possibly transient, thermal events such as flash-heating or impact [8]. Estimated PMTs (276–355 $^\circ\text{C}$) were calculated for the meteorite matrix with the band widths Γ_D using the geothermometer given by Busemann et al. [9]. Jbilet calcite has experienced the lowest PMT among the analyzed CMs. The spectra of Jbilet Grain 2 show well defined shapes with

prominent D1–D4 bands, permitting a more accurate five-Lorentzian profiles peak-fitting procedure. We applied the geothermometer derived by Kouketsu et al. [10] to estimate PMT ranging from 150–400 $^\circ\text{C}$, and obtained a PMT of $194 \pm 4^\circ\text{C}$ for the Jbilet calcite.

The organic compositions of the analyzed carbonates in the CM samples show notable variations. All the analyzed carbonate grains (calcite) observed in Murchison samples lacked typical Raman OM features. Calcite grains in Nogoya were also barren of organics, but the dolomite grain (Grain 5) contains organic material that is distinctive from the organics observed in Nogoya matrix. Jbilet and Santa Cruz are hosts to a mixture of carbonate grains that are with and without organics. Our Raman observations support the view that carbonates in the CM meteorite were produced at different regimes, perhaps with an evolving fluid composition. This situation might explain the wide range of estimated Mn-Cr ages of carbonates in carbonaceous chondrites [e.g., 11, 12].

Conclusions: We used Raman spectroscopy to study the organo-carbonate relationships in five CM chondrites. The estimated PMTs of the meteorite matrix range from 276–355 $^\circ\text{C}$, but were only $\sim 250^\circ\text{C}$ for the carbonates. For unmetamorphosed CMs, these temperatures are in excess of those indicated by matrix mineralogy [13]. Our study suggests that (1) the carbonates were formed at a later stage as compared to the bulk matrix, (2) the parent bodies of the CM samples have experienced at least two different regimes of metamorphism, and (3) the carbonates might not have formed under equilibrium conditions from a single fluid.

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