

Understanding the organo-carbonate associations in carbonaceous chondrites with the use of micro-Raman analysis

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Abstract

Carbonates can potentially provide sites for organic materials to accrue and develop into complex macromolecules. This study examines the organics associated with carbonates in carbonaceous chondrites using μ -Raman imaging.

1. Introduction

Carbonaceous chondrites are primitive meteorites that contain a large variety of carbon- and nitrogen-bearing compounds, which have been widely investigated for life's origins in past decades. While <5 wt% of bulk meteorite is carbon-bearing materials, including organic matter (~2 wt%), carbonate, diamond, silicon carbide, and graphite, carbonates only make up <0.2 wt% [8, 9]. Meteoritic carbonates are thought to be formed on primitive parent bodies through aqueous alteration [5]. Aqueous processing also synthesizes organic molecules and results in molecular asymmetry that depicts life on Earth [4]. Organo-carbonate associations in aqueous setting allow the adsorption of organic matter onto carbonate mineral surfaces, which make carbonate an effective medium for the accumulation and concentration of organic matter, including carboxylic acids, amino acids, fatty acid etc. [2, 10-12]. Properly performed Raman spectroscopy provides a non-destructive technique for characterizing meteorites. It is sensitive to carbon phases, and allows the differentiation of organic and inorganic materials as well as the interpretation of their spatial distribution.

2. Samples

We prepared polished thin sections of five CM2s: Jbilet Winselwan (hereafter, Jbilet) (Find, Western Sahara, 2013), Murchison (Fall, Australia, 1969), Nogoya (Fall, Argentina, 1879), Santa Cruz (Fall, Mexico, 1939), and Wisconsin Range (WIS) 91600

(Find, Antarctica, 1991). We identified carbonates in each meteorite sample with an optical microscope.

3. Methods

Raman analyses were performed at the Department of Geosciences, Virginia Tech. with a Jobin-Yvon Horiba LabRam HR μ -Raman spectrometer, equipped with a Modu-Laser Stellar Pro-L Argon laser (514 nm) (laser spot diameter was ~1 μ m). Wavelength calibration was checked daily prior to sample analyses against a silicon wafer sample. The peaks were determined by simultaneous peak fitting to six pure Lorentzian profiles (one calcite, one G and four D bands, see Figure 1) and linear baseline correction accomplished using a custom software written in the Python programming language.

4. Results

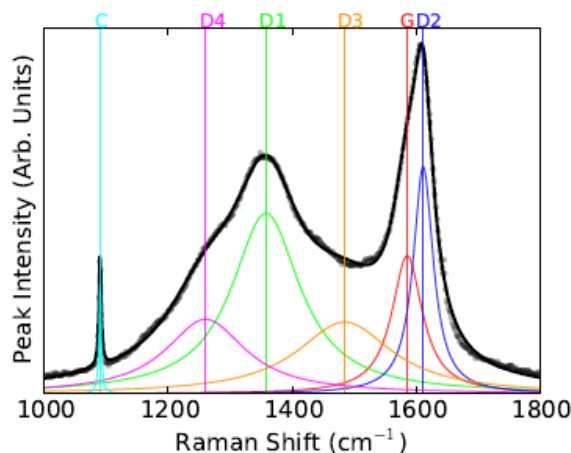


Figure 1: Peak-fitting result with pure Lorentzian profiles showing the first-order region (1000 to 1800 cm^{-1}) of Jbilet. (●): Background-corrected data. Black solid line: Peak-fitting result. C: calcite; G:

graphite band; D1-D4: disordered (defect-activated) bands.

Representative Raman spectra of the carbonates in CM2 meteorite samples are shown in Figure 2. Carbonates were identified with optical examination and confirmed by the distinctive Raman band in the $\sim 1100\text{ cm}^{-1}$ region which corresponds to the symmetric stretch mode of the $(\text{CO}_3)^{2-}$ anion [3]. The typical first-order D bands at $\sim 1350\text{ cm}^{-1}$ and G band at $\sim 1580\text{ cm}^{-1}$ were detected in the carbonates in Jbilet, Nogoya and WIS 91600. On the contrary, while carbon peaks are observable in the matrixes of Murchison and Santa Cruz, the carbonate crystals are clearly devoid of organic matter. Linear Raman analysis from the center of a $>40\text{ }\mu\text{m}$ carbonate grain extending into the fine-grained matrix also shows that the center of carbonate is deprived of organic matter, while the D and G bands can be observed at and beyond the crystal boundary.

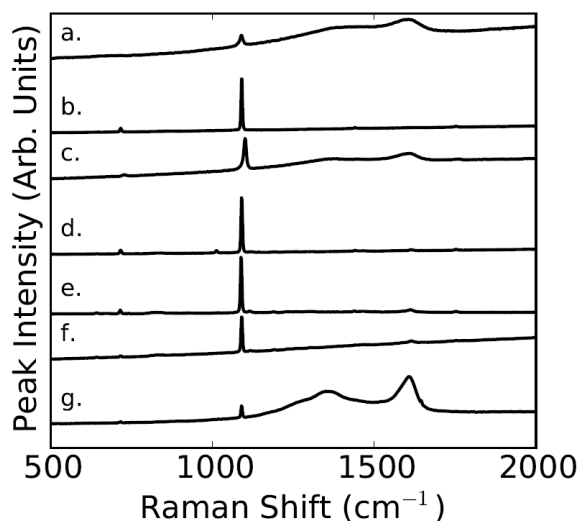


Figure 2: Raman spectra showing the first-order regions of the carbonates in the CMs: (a) WIS 91600; (b) Santa Cruz; (c-d) Nogoya; (e) Murchison; (f-g) Jbilet.

The spectra of the carbonates in Jbilet, Nogoya and WIS 91600 are characterized by their broad D and G bands, which indicate the presence of highly disordered aromatic materials. Visual examination of the overall shape of the Raman spectra shows that these chondrites have experienced low peak metamorphic temperatures (PMT). Jbilet has experienced the lowest PMT among the analyzed CMs ($\sim 200^\circ\text{C}$, which is calculated with the full width

at half maximum [FWHM] of the D1 band $\sim 130\text{ cm}^{-1}$, and applying the geothermometer derived by Kouketsu et al. [6] for the PMT range of $200\text{--}400^\circ\text{C}$).

The occurrence of organic matter in carbonates can be correlated to the degree of alteration. Nogoya and WIS 91600 have experienced higher thermal ($<500^\circ\text{C}$) and aqueous alteration as opposed to Murchison [1, 13]. The Poorly Characterized Phases (PCP) index in Jbilet also supported a more extensive aqueous alteration than other CMs [7]. The organic materials could have been produced prior to or concurrently with the alteration process in Jbilet, Nogoya and WIS 91600, when the carbonates were formed as late-stage alteration replacement product. These carbonates probably served to entrain or adsorb organic materials during or after their formation.

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References

- [1] Bunch T.E. and Chang S.: *Geochimica et Cosmochimica Acta*, Vol. 44, pp. 1543-1577, 1980.
- [2] Carter P.W. and Mitterer R.M.: *Geochimica et Cosmochimica Acta*, Vol. 42, pp. 1231-1238, 1978.
- [3] Cloots R.: *Spectrochimica Acta Part A: Molecular Spectroscopy*, Vol. 47, pp. 1745-1750, 1991.
- [4] Cronin J.R. and Pizzarello S.: *Science*, Vol. 275, pp. 951-955, 1997.
- [5] Grady M.M. *et al.*: *Geochimica et Cosmochimica Acta*, Vol. 52, pp. 2855-2866, 1988.
- [6] Kouketsu Y. *et al.*: *Island Arc*, Vol. 23, pp. 33-50, 2014.
- [7] Pernet-Fisher J. *et al.* (2014) *Lunar and Planetary Institute Science Conference Abstracts*, 2386.
- [8] Sephton M.A. *et al.*: *Geochimica et Cosmochimica Acta*, Vol. 67, pp. 2093-2108, 2003.
- [9] Smith J. and Kaplan I.: *Science*, Vol. 167, pp. 1367-1370, 1970.
- [10] Suess E.: *Geochimica et Cosmochimica Acta*, Vol. 34, pp. 157-168, 1970.
- [11] Suess E.: *Geochimica et Cosmochimica Acta*, Vol. 37, pp. 2435-2447, 1973.
- [12] Thomas M.M. *et al.*: *Chemical Geology*, Vol. 109, pp. 201-213, 1993.
- [13] Yabuta H. *et al.*: *Meteoritics & Planetary Science*, Vol. 45, pp. 1446-1460, 2010.