

TRACING THE AQUEOUS ALTERATION OF CARBONACEOUS CHONDRITES VIA CARBONATE CLUMPED ISOTOPE AND RAMAN CARBON THERMOMETRY. J. M. Young¹, G. A. Henkes¹, and T. D. Glotch¹ ¹Stony Brook University – Department of Geosciences – 255 Earth and Space Sciences, Stony Brook, NY 11790 (jordan.young@stonybrook.edu)

Introduction: During early solar system history, some chondritic materials were subject varying degrees fluid alteration that changed once primitive olivine/pyroxene mineralogies into a varied host of phyllosilicates, carbonates, sulfates, and other phases associated with alteration. Fluid alteration of chondritic materials is one of the earliest known geologic processes, thought to have occurred in the first 20-50 My after the formation of the solar system [1]. While some work has been done to understand the physio-chemical properties of these early alteration fluids [2][3], they remain poorly constrained. Understanding these properties is critical for tracing the evolution of chondritic materials and their parent bodies. Furthermore, fluid interactions and the products of such interactions may also provide a possible mechanism for the synthesis of complex organic materials, potential building blocks of life, found within carbonaceous chondrites [4][5].

Methods: We used a combined approach of Raman spectroscopy and carbonate clumped isotope measurements to conduct this work.

Raman Spectroscopy. We used confocal micro-Raman spectroscopy to identify and gather spectral parameters from organic materials and carbonate phases contained within each chondrite thin-section sample. We used a WiTEC alpha300R confocal Raman imaging system coupled with a 532 nm (Nd:YAG) green laser. We collected three intensity distribution maps from seven samples, for which each pixel has an associated Raman spectrum (Figure 1.). Each of these images has dimensions 100 μm x 100 μm and is composed of 22,500 pixels. A laser spot size of $\sim 0.8 \mu\text{m}$

results from using a 50x (0.80 NA) objective lens during imaging. We take advantage of the confocal abilities of our system to collect spectra at a depth of 1 μm relative to the thin section surface. This is done to avoid the signatures of processing effects resulting from thin section production and handling. We used a laser power of 1.3 mW during our measurements to avoid thermal oxidation of the samples. We identify relevant phases by imposing a ‘band intensity filter’ on the spectra in an image. The output, shown in Figure 1, is a representative image in which pixel color is dependent on the intensity of the spectrum contained within the boundaries of the filter. We used a filter with a width of 40 cm^{-1} centered at 1090 cm^{-1} and one with width 400 cm^{-1} centered at 1450 cm^{-1} to identify carbonate and organic phases respectively. After we have identified phases, we extract quantitative spectral parameters for each type of material. Initially, map spectra represent a range of $\sim 0\text{-}3500 \text{ cm}^{-1}$. We crop these spectra to new dimensions of 1000-1200 cm^{-1} and 900-2000 cm^{-1} for carbonates and organic phases respectively. We then apply a linear background subtraction to each spectrum. A second-order Savitzky-Golay smoothing filter is then applied to the raw spectra. We then fit each raw spectrum with a Lorentzian band (carbonates) or two Lorentzian bands (organics) to extract a fit spectrum and spectral parameters. We discard all fit spectra with $R^2 < 0.95$ for each fitting procedure. We note that the specific processing/fitting procedure for the separate phases is conducted on separate copies of the original intensity distribution map. We use extracted spectral parameters of observed organic materials to then calculate peak metamorphic temperature estimates for each chondrite [6].

Carbonate Clumped Isotope Geochemistry. Clumped isotope measurements are conducted on CO_2 gas released during the dissolution of carbonate phases within sample. Approximately, 5-10 mg of pure calcium carbonate are required to conduct a single measurement. As such, depending on the carbonate abundance in a given sample, 200-400 mg of powdered chondrite are loaded into an autosampler over an anhydrous phosphoric acid bath. The dissolution reaction occurs at a temperature of $\sim 90 \text{ }^\circ\text{C}$. We collect the evolving CO_2 in a glass U-trap cooled by liquid nitrogen. The glass trap is then heated to $\sim -80 \text{ }^\circ\text{C}$ in order to liberate the CO_2 and remove any residual water left in the trapped CO_2 . In order to perform accurate

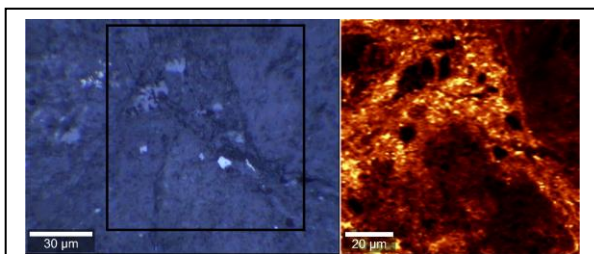


Figure 1. (Left in-set) Reflected light image of sample taken at 50x; (Right in-set) Raman intensity distribution map of sample. Pixel colors for this particular map show the integrated intensity of their corresponding spectrum between 1250 and 1650 cm^{-1} , where yellow pixels show high intensity and black show low intensity.

clumped isotope measurements, the CO_2 gas must be extremely pure. Due to the large carbonaceous component and sulfur-rich nature of carbonaceous chondrite mineral assemblages, necessary purity may be compromised by residual hydrocarbons and hydrogen sulfide. Thus hydrogen sulfide was removed from the CO_2 by running the gas through a silver wool trap. Hydrocarbons and other residual compounds were removed using a 1.2 m Poraplot Q gas chromatography column held at -20°C . Purified CO_2 samples were transferred to a Thermo Scientific MAT 253 Plus gas sourced isotope ratio mass spectrometer. The MAT 253 Plus has been configured to simultaneously measure the CO_2 isotopologues at masses 44, 45, 46, 47, 48, and 49. The ratio of the observed voltages for masses 47 and 44 yields the quantity R^{47} , which is simply the ratio of $^{47}\text{CO}_2$ to $^{44}\text{CO}_2$. $^{47}\text{CO}_2$ is the 'clumped' isotope containing isotopologue of interests, with the ^{13}C - ^{18}O bond. The isotope ratio used to report the abundance of mass 47 isotopologues is Δ_{47} . Δ_{47} is defined as the difference (in per mil, ‰) between the measured R^{47} ratio and that of a stochastic or 'random' distribution of ^{13}C and ^{18}O in the molecules. Δ_{47} has been shown to be dependent on the temperature of formation of the carbonate mineral(s) [2]. In order to calculate the formation temperature from Δ_{47} , we use a contemporary, and widely accepted carbonate temperature calibration [7].

Samples: We analyzed thin-section and rock chip samples of several CM chondrites. One sample was the fall Murray (CM2). The rest were Antarctic meteorite finds, three with weathering grade A and three weathering grade C. Highly weathered samples were included in the work as a control for the effects of terrestrial alteration processes. These heavily altered samples are LAP 03865, LON 94102, MET 01077. The pristine samples are ALH 84042, ALH 85013, and MIL 07700.

Results: Using the clumped isotope thermometer from [7] we report an preliminary carbonate precipitation temperature of 10°C for the chondrite Murray. We compare our collected Δ_{47} and corresponding temperature value to data from [2] in Figure 2. While observed Δ_{47} values are relatively similar between studies, differing slopes between the calibrated thermometer of [6] and the thermometer used in [2] yield a large disparity of calculated temperature values. Using Raman spectral parameters collected from intensity distribution maps we are able to estimate the peak metamorphic temperature (PMT) experienced by each individual chondrite sample. We use the spectral curvature thermometer of [6] to generate PMT values. We report the PMTs for each chondrite sample: 223°C (Murray), 253°C (ALH 84042), 234°C (ALH 85013), 224°C

(LAP 03865), 267°C (LON 94102), 355°C (MET 010777).

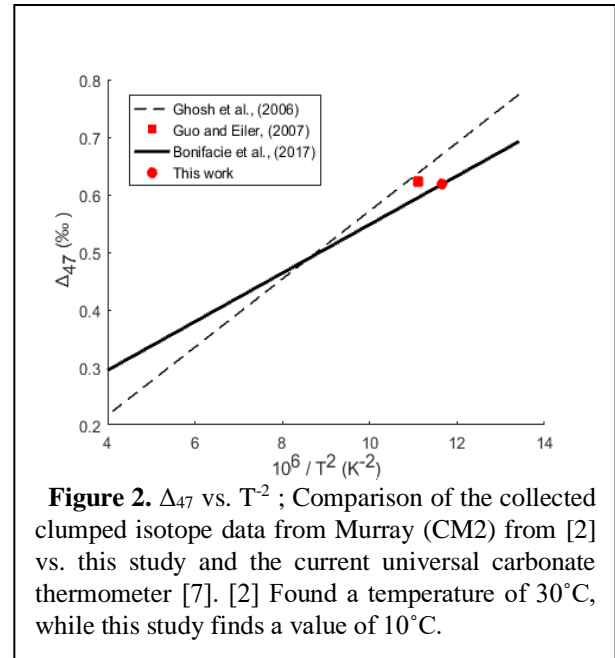


Figure 2. Δ_{47} vs. T^{-2} ; Comparison of the collected clumped isotope data from Murray (CM2) from [2] vs. this study and the current universal carbonate thermometer [7]. [2] Found a temperature of 30°C , while this study finds a value of 10°C .

Discussion: Both carbonate clumped isotope measurements and Raman spectral parameters suggest that CM chondrites were altered under low temperature conditions. However there is disagreement between the temperatures extracted from each method. Our initial carbonate clumped isotope analysis has yielded a temperature of $\sim 10^\circ\text{C}$ for bulk carbonate precipitation in the chondrite Murray. In contrast, Raman spectroscopic measurements suggest that the PMT of the chondrites analyzed is in the range of XXX-XXX $^\circ\text{C}$. This disparity may suggest that bulk carbonate formation occurred after the chondrite parent body had undergone significant cooling from its thermal maximum.

However, more work is required to collect carbonate clumped isotope data from samples that have experienced heavy terrestrial weathering. Correcting for any effects induced by terrestrial weathering is critical for extracting robust carbonate formation temperatures.

References: [1] Endress M. et al. (1996) *Nature*, 379, 701-703 [2] Guo W. and Eiler J. M. (2007) *GCA*, 71, 5565-5575 [3] Lindgren P. et al (2017) *GCA*, 204, 240-251 [4] Watson J. S. and Sephton M. A. (2015) *Astrobiology*, 15, 7887-792. [5] Wdowiak T. J. et al. (1984) *Nature*, 311, 140-142 [6] Young J. et al. (In-Review) *MAPS* [7] Bonifacie M. et al. (2017) *GCA*, 200, 255-279.