EFFECT OF AQUEOUS ALTERATION ON INSOLUBLE ORGANIC CARBON IN CR CHONDRITES.
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Introduction: Using Raman spectroscopy we demonstrate that CR chondrites with little to no aqueous alteration have chemically heterogeneous insoluble organic material (IOM) and that, when aqueous alteration proceeds nearly to completion, the IOM becomes homogenous. We theorize that point-like defects in the graphitic structure of the IOM, which give rise to the D-band in the Raman spectrum, undergo reactions with the fluids present during aqueous alteration of the meteorite parent body. These reactions lower the number of defects in the IOM structure, leading to a less disordered product.

We also test a new model developed by Lucchese et al. [1] (the L model) that describes the relationship between defects and degree of disorder in the IOM structure. The L model builds on the model described by [2] (the FR model), but it more rigorously describes the relationship between defect density, disorder, and the Raman spectral parameters: full width at half maximum of the G-band (FWHM-G) and the ratio of the D to G Band intensities (I_D/I_G). The L model conceptually agrees with the FR model. However, [1] calibrated the L model using ion-bombardment of single graphene sheets. Ion bombardment induces defects within the graphene sheet in a controlled manner. These defects were then imaged by scanning tunneling microscopy in order to measure the defect density.

Sample Preparation: Three Antarctic CR chondrites: QUE99177 (CR3), EET 92161 (CR2), and GRO 95577 (CR1) are used because they represent the full range of aqueous alteration of the CR parent body. These samples were specially prepared without lubricants or water in the cutting or polishing of the chunks (except for a minimal amount of ethanol washing), and the meteorites are not mounted in epoxy.

Methodology: *Raman Spectroscopy.* Twenty Raman spectra were recorded for each meteorite sample in random places in the matrix; ten on the polished side of the sample (if applicable) and ten on the unpolished side. This procedure was intended to a) understand the effects of polishing the sample had on the Raman spectrum, b) determine which correlations arise between aqueous alteration of meteorites and Raman spectral parameters, and c) determine if the chemical composition of the IOM is heterogeneous based on its Raman spectra. This report focuses on (b) and (c).

All Raman data were recorded by a WITec alpha 300 confocal Raman microscope using a 20x microscope objective (~ 7 μm spot size) and a 532 nm exci-

tation laser. A laser power of < 50 μW was obtained using several neutral density filters in series. Spectra were recorded for 240 s x 30 accumulations, for a total of 2 hrs each.

Fitting Procedure & Uncertainties. After a background subtraction, Raman spectra were fitting using the IDL procedure AMOEBA, which minimizes the weighted chi-square statistic. The D-band is fitted using a lorentz line profile, and the G-band is fitted using a skewed lorentz line profile (see [2]). Error bars shown in the figures are 2-sigma, where sigma is the minimum estimated error from the level of noise in each spectrum and the sensitivity of the instrument.

Results & Discussion: Results from the CR1-3 chondrites are shown in Fig 1 and 2. To improve clarity of the plots, the ranges of the CR3, 2, and 1 are circled blue, red, and green, respectively. The raw spectra are characterized by wide D- and G-Bands with shallow inter-band valleys. Background fluorescence is typically high. Signal to noise ratios are consistent (all > 5, most between 10 and 17), indicating that these are good spectra for comparison. There is an anomalous CR3 spectra (labeled A) with much lower intensity ratio and FWHM compared to the rest of the data.

Generally, we find that there is a positive correlation in FWHM of the D- and G-Bands with I_D/I_G, though the ranges of FWHM of both the D- and G-bands are much larger for the CR2-3 samples compared to that of the CR1. The CR3 tends to have more scatter in intensity ratio vs. FWHM-G. The range for the CR1 is small, but it does split into two D-Band groups. CR2-3 samples seem to form multiple groups. The range in FWHM suggests that CR2-3 chondrites' IOM is heterogeneous in chemical composition. The heterogeneity appears to be correlated with the degree of aqueous alteration.

Aqueous alteration appears to decrease I_D/I_G, FWHM-D and -G, and the heterogeneity of the IOM chemistry. It is well known that I_D/I_G alone cannot fully describe the degree of disorder in the IOM structure (e.g. [2]), but FWHM-G always increases with the increase in defects in the structure of graphene [3]. Fig 3 describes the relationship between I_D/I_G and the typical distance between point-like defects, L_D, for two models (Cançado in red and Lucchese in purple) in graphene described by [2].

As the number of internal defects in the honeycomb lattice of the carbon structure increases, L_D decreases [3]. For $L_D > 10$ nm, the intensity ratio general-

ly conforms to the TK model [4], or stage 1 of the FR model (e.g. $I_D/I_G \propto 1/L_D$). For $L_D < 10$ nm, the effect of defects on the Raman spectra begins to deviate from the TK model and it eventually reaches a maximum (where the defect density is saturated). The location of the saturation point depends on model parameters; two examples are given in Fig 3. For L_D to the left of the maximum, the intensity ratio will decrease rapidly with respect to defect density (Stage 2 of the FR model) as the defects start to coalesce and dominate the structure.

As we can see in Fig 3, the I_D/I_G values may indicate either a very low L_D or a range of mid to large L_D values. High FWHM-G always indicates high disorder. Therefore, because there is a direct and positive correlation in Fig 1 of the FWHM-G and I_D/I_G, the CR1 IOM has less disorder than the CR2 and CR3 IOM. We can also conclude that all of the IOM in these meteorites are in stage 1, or low defect density. Since we are in a low defect regime, we can estimate L_D as demonstrated by [3], shown as data points in Fig 3, inset.

We suggest that the lack of distinct spectral groups and the low range of parameter spectral values for the CR1 spectral data set (Figs 1-2) indicate that the CR1 IOM is less chemically heterogeneous than the CR2-3 chondrite IOM. Thus, aqueous alteration chemically alters the IOM. Homogenization may occur as the most reactive defects in the IOM structure are altered or destroyed. The resultant graphitic IOM (which is what Raman can actually measure) has fewer defects, and therefore less disordered.

Conclusions: We demonstrate that the L model is a convenient way to describe the structure of the IOM by measuring its Raman spectrum. It allows us to predict how the Raman spectra for this particular set of IOM would behave if aqueous alteration were to continue, or if further defects were introduced to the structure. The model more rigorously describes the chemical structure and the nature of the defects in the IOM. It would be interesting to test this model by measuring IOM spectra in other classes of carbonaceous chondrites. Our hypothesis is that high water-to-rock ratios lead to homogenous IOM, while primitive chondrites will have the most chemically heterogeneous IOM. This would have broad implications for how the IOM formed and processed in the solar nebula.

We also demonstrate that CR1 IOM is chemically homogeneous, but the CR2-3 IOM is not. Furthermore, we theorize that the CR1 IOM is a reaction product of a defect-rich disordered IOM with the aqueous alteration fluids. The CR3 IOM data overlap with the CR2 data, which may be further indication that the CR3 has undergone a small amount of aqueous alteration, as suggested by [5]. If the CR3 experienced no aqueous alteration, we would expect the CR3 IOM to have greater scatter, larger band widths, and larger I_D/I_G, but that is not what we observe.

References: [1] Lucchese M. M. et al. (2010) *Carbon, 48,* 1592-7. [2] Ferrari A. C. and Robertson J. (2000) *Phys. Rev. B, 61,* 14095-107. [3] Cançado L. G. et al. (2011) *NanoLett., 11,* 3190-6. [4] Tuinstra F. and Koenig J. L. (1970) *J. Chem. Phys., 53,* 1126-30. [5] Bonal L. et al. (2013) *GCA* in press.

Fig 1 — I_D/I_G vs G-band FWHM (cm^{-1})

Fig 2 — I_D/I_G vs D-Band FWHM (cm^{-1})

Fig 3 — I_D/I_G vs L_D (nm)