IMMATURE CARBONACEOUS MATTER IN CONCORDIA ANTARCTIC MICROMETEORITES.
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Introduction: Antarctic MicroMeteorites (AMMs) represent the dominant source of extraterrestrial matter accreted by Earth today [1]. Some of them are ultra-carbonaceous particles (UCAMMs) [2, 3, 4]. Furthermore, AMMs could have played a role in the origin of life on Earth [e.g. 5]. A better knowledge of their constituent carbonaceous matter could thus shed light on the formation of the organic matter in the early solar system as well as on the origin of life on Earth. We have analysed twenty Antarctic micrometeorites (AMMs) from the 2006 Concordia Collection [6] by Raman micro-spectroscopy, an analytical technique sensitive to the degree of structural order of the carbonaceous matter, and which can identify functional groups like cyanide [7, 8, 9].

Samples and method: AMMs were selected in order to present a gradual thermal alteration developed during hypervelocity deceleration at atmospheric entry, ranging from unmelted AMMs to partially or completely melted ones [10]. A goal of this study was to check whether the carbonaceous matter was transformed during atmospheric entry heating. We have analyzed 8 fine-grained (Fg) AMMs (including 3 ultra-carbonaceous–UCAMMs), 5 intermediate (Fg-Sc), 5 scoriaceous (Sc) and 2 cosmic spherules (CS) [10] (Fig. 1). Raman spectra were obtained with two Labram micro-spectrometers, employing 514 and 244 nm excitation. Only two UCAMMs were analyzed with both excitation wavelengths, as the 244 nm excitation requires high carbon concentration within the sample. The laser power at the sample's surface was set as low as 300 µW in order to avoid thermal alteration. No effect of sample damaging by laser irradiation as a function of acquisition time was observed. The microscope optics provided a spot diameter estimated at 2-3 µm. The experiments were performed in an inert atmosphere (argon) to reduce and stabilize the parameter variations [7]. The most intense bands in a typical Raman spectrum of carbonaceous material are the first order carbon bands, at ~1600 cm^{-1} (G-band) and ~1350 cm^{-1} (D-band) [11]. Two analytical procedures were used. The first consisted in fitting the D and G bands with Lorentzian and Breit-Wigner-Fano (LBWF) profiles, respectively. The second was a Principal Component Analysis (PCA), which accounted for the whole spectral variations. Bulk meteorites and insoluble organic matters (IOM) extracted from pristine carbonaceous chondrites were analysed in the same conditions and used as standards for comparison.

Results and discussion: All AMM spectra exhibit D- and G- bands, with the exception of cosmic spherules. About half of the spectra show a high fluorescence background and were therefore not taken into account. No significant degree of structural order among all textural types (Fg, UCAMMs, Fg-Sc and Sc) are observed after applying LBWF fitting and Principal Component Analysis.

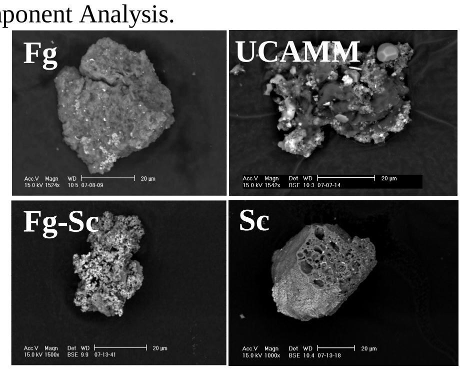

Figure 1: BSE image of the external surfaces of individual fragments of several AMMs that have been analysed (Fg - fine-grained, UCAMM - ultracarbonaceous, Fg-Sc intermediate, and Sc – scoriaceous). See [10] for AMM classification.

No graphite was identified in AMMs and CS by Raman spectroscopy. However, the detection of a specific phase by Raman spectroscopy depends on the volume analyzed by the laser and on the size of the crystals. If the graphite inclusions are smaller than several hundreds of nanometres, they cannot be observed in the Raman spectrum. Using high resolution TEM, we have identifed nanometer sized inclusions of graphite in UCAMM samples [3]. Such phases have been reported in chondritic porous IDPs [12]. Their occurence could indicate the former presence of nanometer-sized inclusions of graphitizable carbonaceous matter, different from the host organic matter, that may have been transformed by a transient high temperature event, but more likely these graphite inclusions are of primordial origin. The spectral parameters that allow to best discriminate between low maturity samples are the full width at half maximum (FWHM) and position of the G-band ($\omega_0 G$) [8]. In this parameter space (Fig. 2.a), two broad families are observed: i) the Fg and UCAMM particles, that span a range going from the CCs to a higher degree of disorder of the carbonaceous matter; ii) the intermediate particles and the scoriaceous samples (triangles and diamonds in Fig. 2) that plot in a different region than the unmelted samples. PCA reveal that fit parameters like FWHM-G definitely account for systematic spectral variations in the data (Fig. 2b). Though there is no clear physical interpretation, those data suggest: 1) structural differences between AMMs and CCs and 2) an effect of atmospheric heating.

The same data plotted in a FWHM-D (width of the D band) vs. ID/IG (ratio of the peak intensities of the D- and G-bands) diagram evidence the lack of significant metamorphism for unmelted to partially melted micrometeorites, compared to what is observed in chondrites with petrologic type 3 [7]. These observations mean that carbonaceous matter in AMMs still preserves a high degree of disorder, even in the partially melted samples.

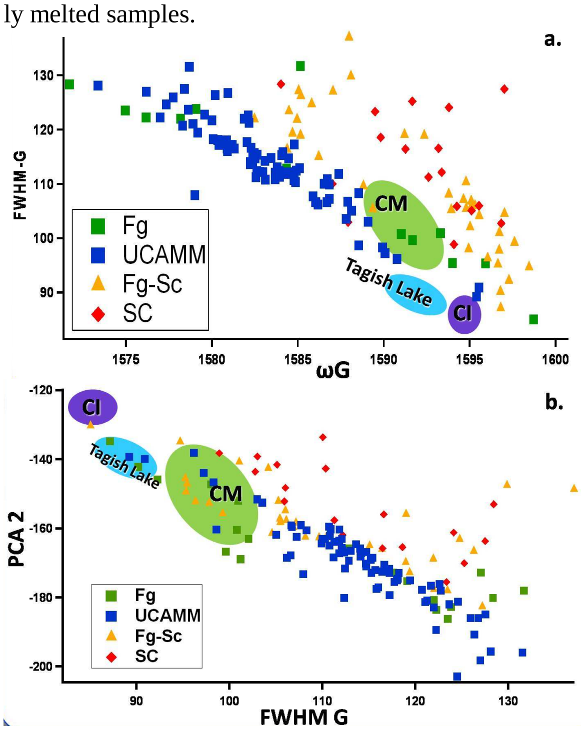

Figure 2. (a) Raman data for carbonaceous matter in AMMs and standards expressed in the parameter space most sensitive to disordered carbonaceous matter (FWHM-G vs ω_G, position of G band); (b) a principal component analysis as a function of FWHM-G for unmelted samples (blue and green squares) and intermediate to partially melted samples (yellow and red symbols).

UV Raman spectra provide further information (Fig. 3). First, the carbon structure in the UCAMM (DC06-09-119) was found different than that of CCs, and more similar to that of some stratospheric IDPs. This observation suggests either different organic precursors and/or an alteration process within the nebula. The Raman spectra also evidence the presence of the cyanide (–CN) functional group (feature peaking at ~2225 cm^{-1}) (Fig. 3). A significant level of –CN have only been reported in some IDPs, and are rare in CCs, as it was solely reported in the CI Alais [9]. The presence of the cyanide functional group could indicate different precursors, but also that CCs precursors experienced different alteration effects, for instance hydrothermalism.

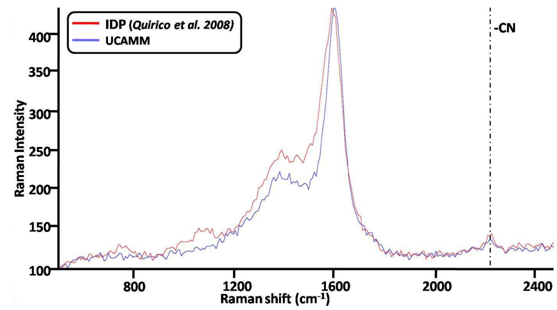

Figure 3. UV Raman spectra (244 nm) of an UCAMM fragment (DC 06-09-119) and an IDP [9]. The -CN functional group is identified in the UCAMM and IDP.

Conclusions: Raman spectroscopy of the carbonaceous matter reveals that all AMMs contain a significant amount of carbonaceous matter that presents a high degree of disorder. No carbon was detected in cosmic spherules. Graphite or poorly graphitized carbon was not detected by this technique, even in the most intensely heated samples (Sc). Nanodomains of graphite are observed by complementary high resolution transmission electron microscopy but it is uncertain whether they originate from atmospheric entry heating [3]. The maturation grade of carbonaceous matter is not significantly different between Fg and UCAMMs. The structure of the carbonaceous matter of UCAMMs is similar to that of IDPs and presents some distinct characteristics from that of CCs. One of the UCAMM sample contains the cyanide functional group. Cyanides are one of the most common classes of molecules observed in the gas phase in interstellar medium [e.g. 13] but are rare in extraterrestrial objects. As they are abundant in comets, there presence in UCAMMs supports a cometary origin of these objets (see also Dobrică et al., and Duprat et al., 2009 this conference).

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