

COMBINED *IN SITU* MICRO X-RAY DIFFRACTION AND RAMAN STUDY OF CARBONACEOUS MATTER IN UREILITES AND TERRESTRIAL MATERIALS. M. R. M. Izawa¹, A. J. Wright², P. J. A. McCausland¹, R. L. Flemming¹, D. K. Muirhead², and J. Parnell². ¹Department of Earth Sciences, University of Western Ontario, London, ON, Canada, (matthew.izawa@gmail.com) ²Dept. of Geology & Petroleum Geology, University of Aberdeen, Kings College Campus, Aberdeen, AB24 3UE, UK

Introduction: It has recently become possible to undertake *in situ* non destructive microanalytical studies of meteorites and other precious materials. Flemming [1] outlines the recent developments made in expanding the applicability of micro X-ray diffraction (μ XRD) for use with Earth and planetary materials. Here we report a reconnaissance study using the complimentary techniques of *in situ* μ XRD and Raman spectroscopy to examine carbonaceous material in two ureilite samples (Dar al Gani 976 and Dar al Gani 1023) and four terrestrial samples (impact suevites from Kara and Gardnos and carbon-rich veins from Torr Mor and the Ereland volcanic complex). The μ XRD analysis was conducted at the University of Western Ontario using the Bruker-AXS D8 Discover diffractometer, with a 50 μ m beam in which diffracted rays are collected using a two dimensional general area diffraction detector system (GADDs), recording textural and crystal structural information. Raman microspectroscopy was carried out at the University of Aberdeen with the 514.5 nm Ar⁺ ion laser beam of a Renishaw inVia Reflex Spectrometer, using a smaller spot size (typically 1-2 μ m) to characterise the carbonaceous material and to provide a proxy for the degree of structural order.

Results: There is generally good agreement between the μ XRD and Raman data, although crystalline graphite seems to be more readily identified using μ XRD (Table 1). Graphite is anisotropic and there may be an orientation effect such that crystalline graphite will only be detected when the Raman laser is perpendicular to the stacked crystallite. The larger beam size used in μ XRD means that there is potentially some overlap between phases and some patterns may be ambiguous (e.g. chaoite). Using a second technique such as Raman microspectroscopy to examine the phases identified by μ XRD provides confirmation and additional information. The μ XRD configuration includes an integrated optical microscope and digital camera system with a HeNe targeting laser. The laser, microscope optics and X-ray beam are aligned such that when the laser is in optical focus, the point on the sample illuminated by the laser is at the centre of diffraction. Image maps can be created prior to analysis and then be used for subsequent Raman imaging and spectroscopy. Fig. 1 shows μ XRD data for one location on the Kara suevite sample. Fig. 2 shows Raman spectra for the same sample, corroborating the presence of amorphous carbon.

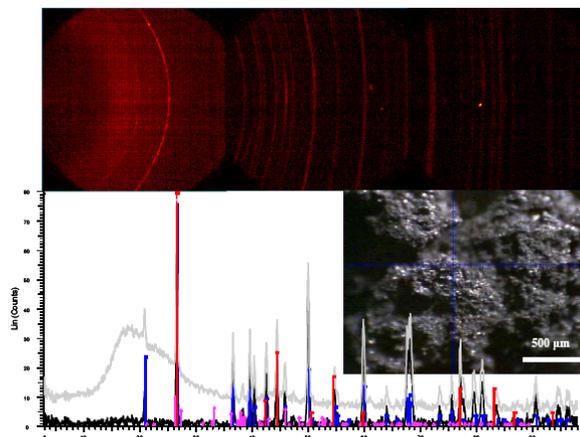


Figure 1. Montage of Kara μ XRD data showing the two dimensional record of diffracted X-rays (top), the integrated diffraction pattern (bottom) and microscope image centered on the spot location (inset). The top image shows “powder rings” indicative of a phase with crystallites in every random orientation, with 2-theta increasing from the left. The raw integrated diffraction pattern (in grey) shows a very broad, diffuse signal from $\sim 12^\circ$ - 25° which is interpreted as amorphous carbon. The background subtracted pattern is shown in black and is overlain with the integrated 1D diffraction pattern. Matching peak locations for graphite are indicated in red, quartz in blue and aragonite in magenta.

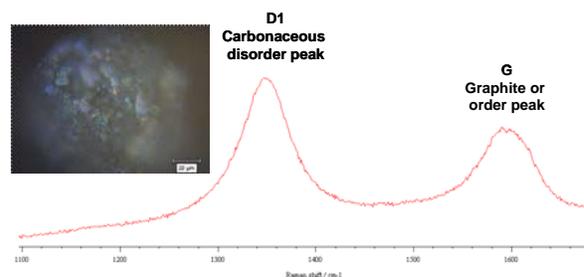


Figure 2. Montage of Raman data showing a spectrum from the Kara sample and (inset) a reflected light image of the point analyzed.

Detailed mapping of the Kara suevite sample using Raman microspectroscopy has yet to confirm the presence of either chaoite or diamond, highlighting the importance of using more than one analytical method to extract sample information.

Fig. 3 shows a Raman spectrum from DaG 976, confirming the presence of diamond in this ureilite, although diamond was not detected in DaG 1023. Lonsdaleite was not found in either sample using Raman microspectroscopy. This should appear as a peak at $\sim 1315 \text{ cm}^{-1}$, slightly lower than that for cubic diamond which occurs at $\sim 1332 \text{ cm}^{-1}$ [2].

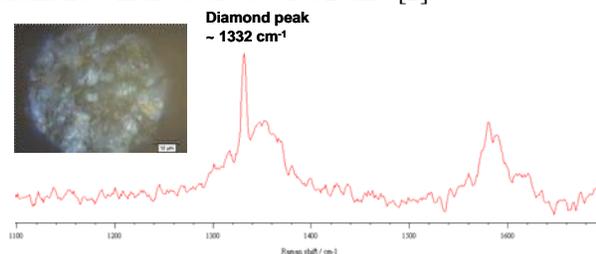


Figure 3. Montage of Raman data for ureilite DaG 976 showing diamond closely associated with the poorly crystalline graphite; (inset) reflected light image of the sample.

MicroXRD analysis indicates that the main carbonaceous phase present in both ureilites is graphite, although the silicate minerals (olivine and clinopyroxene) usually dominate the XRD patterns.

The textural information provided by μ XRD shows that the carbon frequently occurs as fine-grained polycrystalline material in veins surrounding the silicates and that it also occurs in association with metal or metal-sulfide. Raman microspectroscopy shows that the graphite and diamond occur in close spatial proximity; the diamond spectra cannot be

resolved separately, indicating that the diamonds are $< 1 \mu\text{m}$ in diameter (i.e. smaller than the laser spot width).

Conclusions: As both μ XRD and Raman spectroscopy are non destructive techniques, they are ideally suited to the complementary analysis of Earth and planetary samples. Using complimentary techniques to extract information from samples of limited availability, such as ureilites and other rare meteorites, is of particular value: In this study μ XRD readily identified major carbonaceous phases in the ureilites and terrestrial samples and the greater spatial resolution of Raman microspectroscopy enabled the identification of some carbonaceous phases in close proximity to one another. These reconnaissance techniques provide the context (and impetus) for applying other, more conventional techniques, such as electron probe microanalysis or scanning electron microscopy (with sample preparation of a polished thin section or a probe mount) to confirm and further describe the phases present.

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Reference: [1] Flemming, R.L. (2007) *Can J. Earth Sci.*, 44, 1333–1346. [2] Gogotsi, Y.G. et al. (1998) *J. Appl. Phys.*, 84, 1299–1346.

Table 1. Carbonaceous phases identified by μ XRD and Raman analysis.

Sample	Good μ XRD ID	Possible μ XRD ID	Raman ID	Remarks
DaG 976 (ureilite)	graphite, diamond	lonsdaleite	graphite, poorly crystalline graphite, diamond	Lonsdaleite detected using μ XRD only
DaG 1023 (ureilite)	graphite	diamond lonsdaleite	graphite	Diamond and lonsdaleite detected using μ XRD only
Kara suevite (Nenetsia, Russia)	graphite, amorphous C	chaoite, diamond	amorphous C, poorly crystalline graphite	Graphite detected using μ XRD only; further analysis required to confirm possible μ XRD ID for chaoite and diamond
Gardnos suevite (Hallingdal, Norway)	graphite, poorly crystalline C		amorphous C	Graphite detected using μ XRD only
Torr Mor: C vein (Isle of Skye, UK)	graphite, poorly crystalline C	amorphous C	graphite amorphous C	Graphite detected using μ XRD only
Ereland Volcanic Complex (nodules from fluid-phase) offshore UK	graphite		graphite	Sample contains highly crystalline graphite only