INTERPRETING THE RAMAN SIGNATURE OF UREILITE CARBON

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Ureilite carbon: Ureilites are a distinctive class of meteorite composed primarily of olivine and Ca-low pyroxene [1]. They show an apparently evolved igneous texture, which is difficult to reconcile with their primitive oxygen isotope ratios [2]. Ureilites usually contain up to 6 wt. % carbon, occurring primarily as interstitial material between the silicate grains. The origin of the carbon is also enigmatic, with some indications that the carbon is a primary component of the igneous melt and others that suggest the carbon is a later phase injected as veins into the silicate residue [1, 3, 4]. Carbon may be present as diamond, lonsdaleite, carbide, cohenite, and, more commonly, as graphite displaying varying degrees of structural order. Diamond may have formed from the graphite in response to shock, although an origin in the solar nebula cannot be discounted [1, 5]. It is possible that the carbon is derived from a carbonaceous chondrite precursor, similar to the Allende CV meteorite [1, 6]. A better understanding of the different carbonaceous components is necessary to determine the origin of the graphite. Raman spectroscopy is a widely accepted technique used to characterise the nature of carbonaceous matter. This study compares a range of terrestrial samples with data obtained from ureilite chips and with previously published ureilite data [7]. The initial terrestrial samples analysed were the Dalradian metasediments from the north-east of Scotland previously selected for study [8] as they came from settings where a hot body of magma was known to have interacted with the rocks at a geologically rapid rate, generating a mobile carbonaceous phase. Further analogues were then sought to extend the data set, with a number of bitumen samples being used as a control set. Rocks from the Borrowdale graphite deposit (UK) and from the Erlend Volcanic Complex (off-shore UK) contain carbon nodules that appear to have been generated from a fluid-phase; the carbon from Borrowdale is a paragenetically late phase within an igneous host, whereas the carbon from Erlend is contained within a chlorite matrix and is probably derived from a pre-existing oil of sedimentary origin. Carbon occurs in rocks exhibiting immiscible fluid phases in Jurassic sedimentary rocks from the UK island of Skye (which have been intruded by Tertiary dolerites) and in impact breccias from the Gardnos impact crater in Norway. In the breccias, the carbon occurs only in the melt fragments and is concentrated either at the boundary between two immiscible phases or at the boundary between the breccia matrix and a melt phase. In the Jurassic rocks, the carbon appears to be immiscible with a single aqueous phase [9].

Raman spectroscopy: The aromatic ring stretch experienced by carbon bonds in the graphite structure is Raman active and is detected as a single peak between 1582 cm$^{-1}$ [7] and 1575 cm$^{-1}$ [10]. As the graphite becomes structurally more disordered, peaks are also detected around 1355 cm$^{-1}$ (D1) and 1620 cm$^{-1}$ (D2) [11]. Ratios between peak heights can be used as a proxy for the degree of structural order, with the R1 ratio (D1/G) being particularly useful for more disorganised matter, due to the difficulty in separating the G and D2 spectral bands [12]. Full width at half-maximum (FWHM) values also provide a useful correlation to the degree of structural order, with the most organised material having the narrowest values, although this appears to be a less reliable indicator than the R1 value [12]. Measurements were performed on unpolished chips using a Renishaw inVia Reflex Raman spectrometer. Where it was not possible to use chips, measurements were taken on standard polished thin sections. A reflected light microscope was used to focus an Ar$^+$ green laser with a wavelength of 514.5 nm. The spot size used was typically 1-2 μm in diameter and data was collected over a wavenumber shift of 1100 – 1700 cm$^{-1}$.

Analogue for ureilite carbon: Plotting R1 against FWHM (Fig.1) shows that the Dalradian, Erlend and Borrowdale samples contain carbon that is generally more structurally ordered than the ureilite data, although there is some similarity between the Antarctic ureilite data of Kagi [7] and with the Hajmar data. Conversely, the graphite associated with the immiscible phases from the Jurassic sedimentary rocks and the Gardnos impact breccias is much less structurally ordered than the ureilite carbon. The bitumen results are also a poor fit to the ureilite data.

Implications for ureilite carbon: Hajmar is described as having suffered a high degree of shock, whereas Novo Urei experienced medium shock and North Haig is a polymict breccia [1]. If shock is a potential method of graphitization, it would be expected that Hajmar should show a higher degree of structural order than Novo Urei, with North Haig being a potential intermediary, depending on the clast material analysed. Certainly Novo Urei has a wider spread of values than those for Hajmar but they show no correlation with Kagi’s data for four Antarctic meteorites [7], one of which is also described as having a medium shock state, with the others considered to be low or very low [1]. However, it is known that the effects of shock can be heterogeneous, even on a small scale, so these results are not conclusive. Shocking pre-existing graphite may actually increase the degree of disorder [14].
The spectra obtained from the carbonaceous melts where the carbon is precipitated from an immiscible phase show no correlation with the ureilite data. It is estimated that the melt fragments in suevites form at temperatures > 1500°C [15], considerably higher than the <1300°C postulated for ureilite formation [16]. The rapid quenching of the impact material is likely to result in a high degree of disorder, as the carbon has not had time to equilibrate. The immiscible fluids from Skye, where the rocks were heated by igneous intrusions, would have been generated at significantly lower temperatures. The fluids would have cooled more slowly, allowing greater potential for equilibration and for some degree of structural organisation to be obtained. The ureilites higher degree of structural order suggests that the ureilite carbon has had longer to equilibrate at high temperature than the samples from Gardnos and Skye. The spectra for the C-rich fluids mobile at high temperatures show a good correlation between the data sets. The Dalradian and Erland values are too similar to be subdivided and the Borrowdale data also shows a high degree of structural order. There is some comparability with Kagi’s published data [7] and with the data obtained for Hajmar in this study. Temperature is known to be an important factor in the degree of graphitization [16] and may be more important than the degree of mobilisation. However, the Dalradian – Erland data do show that mobilised carbon can yield a high degree of order. The bitumen group was used as a spectrographic control as it was anticipated that these solid hydrocarbons, formed by low-temperature conversion of organic material, would provide a poor analogue for ureilite carbon and Fig. 1 shows that this is true. The wide range of values seen for the ureilite data and their generally poor fit to the proposed analogue data confirms the complexity of ureilite formation, suggesting that no single factor is responsible for the diversity observed. The use of Raman will allow better terrestrial analogues to be identified and, hence, a better understanding of the processes involved in the formation of ureilite carbon.

Acknowledgements: AW received support from the EPSRC. Ureilite samples (Hajmar BM1980, M19 URE, North Haig BM 1968, 340 and Novo-Urei BM63625) kindly loaned by the Natural History Museum, London. Dr R Wells of the University of Aberdeen is thanked for access to the Raman spectrometer.

References: