

Characterisation of Organic Matter in the Torridonian Using Raman Spectroscopy

D. K. MUIRHEAD*, J. PARNELL, S. SPINKS, & S. A. BOWDEN.

Department of Geology and Petroleum Geology, University of Aberdeen, Aberdeen AB24 3UE, UK

**Corresponding author (e-mail: dmuirhead@abdn.ac.uk)*

Word count: 3745

Raman applied to Torridonian stratigraphy.

Abstract: The organic carbon preserved in grey-black shales of the Neoproterozoic Torridon Group has been characterized for degree of structural order using Raman spectroscopy. All samples have the compositions of kerogen, rather than graphite, consistent with a low level of metamorphism. Samples of shale from the Diabaig Formation from six widely separated localities exhibit consistently greater structural order than shales from five localities in formations higher in the Torridon Group. This supports previous models invoking an unconformity between the Diabaig Formation and the rest of the Torridon Group. The data further suggest that the Diabaig Formation had experienced an additional episode of heating, in the late stages of Grampian deformation.

The Torridonian Supergroup on the Laurentian foreland represents an important source of information on surface environments, geobiology and geochemistry in the late Mesoproterozoic-early Neoproterozoic. This includes critical data on early eukaryotes (Strother *et al.* 2011), oxygenation of the planetary surface (Parnell *et al.* 2010) and high-resolution sediment cyclicity (Andrews *et al.* 2010). The value of the rocks is enhanced by a high precision date of 1177 ± 5 Ma (Parnell *et al.* 2011) in the lower part of the Supergroup, but the age of the upper part of the succession is weakly constrained. The Supergroup consists of two distinct successions, the lower comprising the Stoer and Sleat Groups and the upper Torridon Group, separated by a marked unconformity, which has been assumed to represent a gap of about 200 million years (Stewart 2002; Kinnaird *et al.* 2007). However, the Torridon Group may include an additional stratigraphic break, between the Diabaig Formation at the base of the group and the overlying Applecross Formation (Fig. 1). The break is indicated by angular discordance, a change from lithological diversity to lithological monotony, a change in detrital mineralogy, and a contrast in diagenesis (Rodd & Stewart 1992; Prave 2002; Kinnaird *et al.* 2007), but currently the Diabaig Formation remains part of the Torridon Group. There is, therefore, uncertainty about the age constraints for this part of the Supergroup. Nevertheless, the growing body of palaeobiological and geochemical data deriving from the Diabaig Formation (Prave 2002; Parnell *et al.* 2011; Callow *et al.* 2011; Battison & Brasier 2012) requires clarity of stratigraphic context.

In the absence of high precision radiometric dates for the Diabaig Formation, one approach to assess time relationships between different parts of the succession is to measure the degree of thermal

alteration. This can be determined on organic carbon, using Raman spectroscopy, which measures degrees of graphitization (high degree of alteration) and carbonization (very low degree of alteration) (Rouzaud et al 2015). Raman is therefore suitable for Precambrian organic matter (Tice *et al* 2004; Schopf *et al* 2005; Allwood *et al.* 2006; Marshall *et al.* 2007; Olcott-Marshall *et al* 2012; Sforza *et al* 2014; Qu *et al* 2015) in rocks such as the Torridonian Supergroup, which have experienced low grade metamorphism. The approach involves comparison of the degree of carbonization (that is, structural order of the carbon) in the Diabaig Formation with that in the underlying Stoer Group and the overlying formations of the Torridon Group.

Raman Spectroscopy of Carbon

Fossil carbonaceous materials within rocks undergo a complex series of reactions when thermally altered, which involve both the formation and reordering of aromatic subunits towards stacked layers such as graphite. Raman spectroscopy has been widely used (Tuinstra & Koenig 1970; Landis 1971; Nemanich & Solin 1979; Knight & White 1989; Ferrari & Robertson 2001; Beyssac *et al.* 2002) as a powerful, non-destructive tool for evaluating the characterisation and thermal alteration of diverse forms of carbonaceous matter (crystalline, nanocrystalline, amorphous). Measurements were based on two broad first order Raman bands (spectral peaks) at $\sim 1585\text{ cm}^{-1}$ (the graphite peak, G) and $\sim 1350\text{ cm}^{-1}$ (the disorder peak, D), produced by Stokes Raman scattering, induced by a laser. Due to the physical properties of carbonaceous materials the bands are produced as a response to the ratio of sp^2 (graphite-like, trigonal planar symmetry) and sp^3 (diamond-like, tetrahedral symmetry) carbon bonds, based on the hybridised atomic orbital configuration of carbon atoms (Robertson 1991).

The $\sim 1585\text{ cm}^{-1}$ graphite peak is a composite of several Raman bands at $\sim 1615\text{ cm}^{-1}$, $\sim 1598\text{ cm}^{-1}$ and $\sim 1545\text{ cm}^{-1}$ (D2, G, D3 respectively) and is treated as one spectral peak in disordered materials until the band narrows, through increasing thermal alteration, to allow clear definition of the shouldered disorder peaks (as exhibited by the Loch Maree sample, a clear D2 shoulder peak allowing for deconvolution). Peak deconvolution is performed on the composite G band, as it is not possible to separate the G and D2 bands in poorly organised carbon (Beyssac *et al.* 2002) such as those in this study. Raman spectral parameters in this study follow those outlined by Olcott-Marshall *et al* (2012) and Quirico *et al* (2009) and fitting procedures follow those outlined in Bonal *et al* (2006).

A number of Raman parameters have been developed over the past few decades that involve measurements made on Raman spectral peaks. Wopenka & Pasteris (1993) measured the position and width of the G peak at $\sim 1585\text{ cm}^{-1}$ for a suite of metamorphic zones. Increased thermal maturation leads to the structural reordering of carbonaceous materials, with an increase in the proportion of aromatic carbon, in turn narrowing the G band and shifting it closer towards 1615 cm^{-1} . If samples are graphitic, narrowing remains similar but with G peak position shifted downwards to $\sim 1598\text{ cm}^{-1}$. It is important to note that in amorphous carbon (*a-C*) initial development of a D band indicates ordering, whereas in graphitic carbon (*ta-C*), the presence of a D band indicates disorder, so Raman parameters must be interpreted with respect to any known information about the carbon feedstock.

The D/G-peak ratios (I_D/I_G , A_D/A_G) decrease with significant thermal maturation and increased structural ordering (Yui *et al.* 1996; Bonal *et al.* 2006; Busemann *et al.* 2007; Quirico *et al.* 2009; Olcott-Marshall *et al.* 2012). Simple graphing of these two ratios can reveal differences in the thermal alteration of the carbonaceous materials (Pasteris & Wopenka, 1991; Jehlicka & Bény, 1992). Early stage thermal alteration can, however, raise the I_D/I_G parameter, particularly in relatively homogenous samples (Rouzaud *et al.* 1983; Muirhead *et al.* 2012). Archaean microfossils exhibit observable Raman spectral characteristics (Wacey *et al.* 2011) and ancient kerogens with long thermal histories have been characterised using Raman spectroscopy with correlation to organic geochemical parameters (Allwood *et al.* 2006; Marshall *et al.* 2007).

Methodology

Sample selection

Representative samples of grey-black shale were collected from six localities in the Diabaig Formation, and five localities in higher formations of the Torridon Group (two Applecross Formation, one Aultbea Formation, two Cailleach Head Formation: Table 1). These sites were selected to give the best possible geographic coverage of the Torridon Group (Fig. 1A). For comparison, additional samples were obtained from two localities in the older Stoer Group and one in the Palaeoproterozoic Loch Maree Group, which the Torridonian Supergroup unconformably overlies (Park *et al.* 2001). All sample localities are remote from any igneous intrusions that might otherwise have enhanced the thermal alteration of the rocks in their immediate vicinity. A sample of quartzose Lochaline Sandstone (Cretaceous) served as a procedural blank.

Total Organic Carbon (TOC) analysis

Prior to TOC analyses, powdered rock (~30g) was treated with hydrochloric acid (10 and 25% v/v) in order to remove any carbonate. The dried weight of the recovered material was recorded. The total organic carbon content was calculated using the method outlined by Gross (1971) with a minimum of three analyses per sample, where wt% C was measured with a Carbon-Sulfur analyzer (LECO CS225) at the University of Aberdeen.

Kerogen isolation and Raman spectrometry

Further treatment of the carbonate-free residue with hydrofluoric acid (40% v/v) yielded a kerogen concentrate suitable for analysis by Raman spectrometry. Raman measurements were performed on a Renishaw inVia reflex Raman spectrometer at the University of Aberdeen. A Leica DMLM reflected light microscope was used to focus the Ar⁺ green laser (wavelength 514.5 nm). The laser spot size was approximately 1-2 μm and laser power approx. 0.3 mW at the sample. The scattered light was dispersed and recorded by means of a CCD (Charge Coupled Device) detector. Data were collected between 1100cm^{-1} and 1700cm^{-1} with spectral resolution less than 3cm^{-1} . The duration of accumulations was typically up to 10 seconds for between 3 and 5 accumulations. Care was taken to ensure that the sample did not experience any laser-induced heating, by careful analysis under the microscope before and after heating. All materials were analysed as finely crushed rock chips to avoid erroneous data due to polishing (Mostefaoui *et al.* 2000).

The Renishaw WiRE 2.0 curve-fit software was used for spectral deconvolution. Smoothing and baseline extractions were performed on each sample, including a cubic spline interpolation (to avoid Runge's phenomenon (Runge, 1901)) with peak fitting using a combination of Gaussian and Lorentzian algorithms (Bonal *et al*, 2006). Each sample was deconvolved and data extracted at least three times to ensure reproducibility and the removal of any background signal. Peak position and peak full width at half maximum (FWHM-D, G) are measured in wavenumbers (cm^{-1}), which records the change in vibrational frequency (stretching and breathing) of the Raman-active carbon molecules. Figure 2 summarizes the Raman bands discussed above. Prior to analysis of deconvolved spectra, an initial visual approach to spectral interpretation was adopted (Coates 2000).

Results

The results of the TOC and Raman spectroscopic analyses are summarised in Table 1. All of the Raman data for the Torridonian Supergroup plot within or adjacent to the kerogen field of Wopenka & Pasteris (1993), and well away from the field of graphite (Fig. 3). Figure 4 shows stacked first order representative Raman spectra for all samples in this study (including the procedural blank, Lochaline sandstone). Deconvolved data for the six samples from the Diabaig Formation (in particular their lower FWHM-G values) make them distinct from the other Torridon Group shales (Fig. 5). Furthermore, four of the Diabaig Formation samples (Rubha Reidh, Lower Diabaig, Badachro, Brochel) also exhibit a shift towards lower G band wavelengths (W_G (cm^{-1})). The data from higher formations appear to have some scatter, but only occupy a limited part of the kerogen field. The Stoer Group samples yielded data similar to that for the Diabaig Formation. The lowest I_D/I_G ratios (Table 1) observed in the Diabaig Formation and Stoer Group were 0.41, compared to the lowest I_D/I_G ratios for the higher formations (Applecross Formation) of 0.47. The sample from the Loch Maree Group lies in the graphite field of Wopenka & Pasteris (1993), distinct from the Torridonian Supergroup samples (Fig. 3).

No carbon was found in the procedural blank sandstone sample (Fig. 4), assuring us that contaminating material introduced during sample preparation did not influence the Raman measurements.

Discussion

Raman data

The data for the six Diabaig Formation samples are consistently distinct from the other Torridon Group shales (except perhaps the Cailleach Head B sample). The Diabaig Formation data are shifted in the direction of graphitization (Fig. 5), implying a greater degree of thermal maturity. The scatter in the data, for both sets of shale, is comparable with that in other data sets (Beysac *et al*. 2002). It is clear that the samples from lower formations (Diabaig Formation and Stoer Group) exhibit D bands with a slightly lower intensity and area than those of the younger formations together with a reduction in G band width, indicative of a greater degree of structural order. Lower G band wavelengths (W_G (cm^{-1})) and FWHM-G within four of the Diabaig samples, particularly Badachro and

Brochel Raasay, are consistent with a higher degree of structural order in their dispersed organic matter, attributable to incipient metamorphism of the host rock.

The I_D/I_G ratios for the Diabaig Formation (0.41-0.63) and Stoer Group (0.41-0.46) are lower than those obtained from the younger formations (0.47-1.02: Table 1). This is a further indication of an increase in structural order of their kerogen and hence a higher thermal maturity (Yui *et al.* 1996). Figure 6 summarises the I_D/I_G and A_D/A_G ratios alongside crystallite size (L_a) (Fig. 6 inset) indicating two distinct populations of carbonaceous material (Olcott-Marshall *et al.* 2012), further confirming the higher thermal maturity of the Diabaig Formation. The break between the two populations (Fig. 6) is comparable to the onset of low-grade greenschist (chlorite zone) metamorphism (Fig. 6 inset) (Wopenka & Pasteris, 1993).

Different types of fossil organic matter (e.g. microbial *versus* vascular plant) can be responsible for variations in Raman spectral parameters (Muirhead *et al.*, 2012). However, there is no evidence for such compositional diversity in the organic matter preserved in late Mesoproterozoic to early Neoproterozoic sedimentary rocks. All organic carbon in the Torridon Group is a product of non-marine aquatic prokaryotes or simple eukaryotes (Strother *et al.* 2011; Battison & Brasier 2012). There is also no consistent relationship between Raman parameters and abundance of carbon (%TOC).

The graphitic nature of the Loch Maree kerogen (Table 1, Fig. 3) may be attributed to a significant metamorphic event that affected the Palaeoproterozoic rocks of the study area and predated the deposition of the Torridonian Supergroup (Park *et al.* 2001).

Implications for stratigraphic relationships in the Torridonian Supergroup

The data set as a whole implies that both the Stoer Group and Diabaig Formation have a greater degree of thermal maturity than the overlying formations of the Torridon Group. For this contrast to survive later thermal imprints, including the Caledonian Orogeny, it must represent a significant metamorphic event that had no influence on younger formations. Critically, the degree of structural order of carbonaceous materials is not affected by retrogression and indeed records peak metamorphic conditions up to approx. 650°C (Beyssac *et al.* 2002). The metamorphic event must have occurred after the Diabaig Formation was deposited and prior to deposition of the rest of the Torridon Group. It could not have occurred in the time interval represented by the unconformity separating the Stoer Group and the Diabaig Formation. The consistency of the Raman data across a geographic belt extending more than 45 km along the NW coast of Scotland shows that local phenomena, such as buried igneous intrusions, can be excluded as an explanation for the difference between Diabaig Formation and younger units.

The timing of the inferred thermal event is consistent with the contrast in mineralogy measured by Kinnaird *et al.* (2007), between the illite/sericite/chlorite-bearing Diabaig Formation (Fig. 6, chlorite zone metamorphism) and the younger quartz/feldspar-cemented Applecross Formation, implying a significant discontinuity between them. The Stoer Group was deformed during the late stages of the Grenville Orogeny at about 1100 Ma (Darabi & Piper 2004; Williams & Foden 2011). Constraints on the age of the Torridon Group include a palaeomagnetic pole close to the 1050 to 950 Ma portion of

the polar wander curve for Laurentia (Piper & Darabi 2005), a youngest detrital zircon suggesting a maximum age for the Applecross Formation of 1060 ± 18 Ma (Rainbird *et al.* 2001), and a Rb-Sr age from mudrocks in the Diabaig Formation of 994 ± 48 Ma which probably reflects diagenesis (Turnbull *et al.* 1996). These data allow the possibility that the Diabaig Formation rocks could have been heated by an event at about 1100-1050 Ma. The Torridon Group as a whole is attributed to a syn-collisional phase in the assembly of the Rodinia Supercontinent (Cawood *et al.* 2007, 2010), when heat pulses could have been generated as the assembly progressed. Other basins on the Laurentian foreland show evidence of volcanic activity consistent with this (Cawood *et al.* 2007). The metamorphic event is possibly the result of late stage Grenvillian foreland thrusting *c.* 1.0 Ga (Sherlock *et al.* 2008), post-dating Stoer Group deposition and prior to or concomitant with deposition of the Applecross Formation. The affinity in the Raman data between the Stoer Group and Diabaig Formation suggests they both attained broadly the same level of thermal maturation, thus distinguishing them from formations higher in the Torridon Group. Data presented herein further confirm that the Stoer and Diabaig shales have a thermal history distinct from that of the Applecross, Aultbea and Cailleach Head Formations (Kinnaird *et al.* 2007).

This new insight into the stratigraphy of the Torridonian Supergroup emphasizes the need for additional high resolution radiometric dating, mineralogical and provenance studies.

Conclusions

Raman spectroscopy was successfully applied to a suite of Torridon Group shales, revealing that:

- (i) Their organic matter content are amenable to structural characterization, through measurement of the order and disorder peaks of carbon.
- (ii) All samples, except one from the Loch Maree Group, have a composition referable to kerogen rather than graphite, consistent with a low level of metamorphism.
- (iii) Organic carbon in the Diabaig Formation is markedly more ordered than that in younger units of the Torridon Group, implying that the latter rocks were not exposed to the same metamorphic event.
- (iv) This distinction is consistent with a marked stratigraphic break between the Diabaig Formation and the rest of the Torridon Group.

Finally, we have shown that Raman spectroscopy is a valuable tool for elucidating stratigraphic uncertainties associated with the complexity of Proterozoic sedimentary successions and tectonic histories when high-precision dates are unavailable or unattainable.

References

ALLWOOD A.C., WALTER M.R., & MARSHALL C.P. 2006. Raman spectroscopy reveals thermal palaeoenvironments of c.3.5 billion-year-old organic matter. *Vibrational Spectroscopy* **41**, 190-197.

- ANDREWS, S.D., TREWIN, N.H., HARTLEY, A.J. & WEEDON, G.P. 2010. Solar variance recorded in lacustrine deposits from the Devonian and Proterozoic of Scotland. *Journal of the Geological Society, London*, **167**, 847-856.
- BATTISON, L. & BRASIER, M.D. 2012. Remarkably preserved prokaryote and eukaryote microfossils within 1 Ga-old lake phosphates of the Torridon Group, NW Scotland. *Precambrian Research*, **196-197**, 204-217.
- BEYSSAC, O., GOFFE, B., CHOPIN, C. & ROUZAUD, J.N. 2002. Raman spectra of carbonaceous material in metasediments: a new geothermometer. *Journal of Metamorphic Geology*, **20**, 859-871.
- BONAL L., QUIRICO E., BOUROT-DENISE M., AND MONTAGNAC G. (2006) Determination of the petrologic type of CV3 chondrites by Raman spectroscopy of included organic matter. *Geochimica et Cosmochimica Acta* **70**, 1849-1863.
- BUSEMANN, H., ALEXANDER, C.M.O'D., & NITTLER, L.R. 2007. Characterisation of insoluble organic matter in primitive meteorites by microRaman spectroscopy. *Meteoritics and Planetary Science*, **42**, 1387 – 1416.
- CALLOW, R.H.T., BATTISON, L. & BRASIER, M.D. 2011. Diverse microbially induced sedimentary structures from 1 Ga lakes of the Diabaig Formation, Torridon Group, northwest Scotland. *Sedimentary Geology*, **239**, 117-128.
- CAWOOD, P.A., NEMCHIN, A.A., STRACHAN, R., PRAVE, T. & KRABBENDAM, M. 2007. Sedimentary basin and detrital zircon record along East Laurentia and Baltica during assembly and breakup of Rodinia. *Journal of the Geological Society, London*, **164**, 257-275.
- CAWOOD, P.A., STRACHAN, R., CUTTS, K., KINNY, P.D., HAND, M. & PISAREVSKY, S. 2010. Neoproterozoic orogeny along the margin of Rodinia: Valhalla orogen, North Atlantic. *Geology*, **38**, 99-102.
- COATS, J. 2000. Interpretation of Infrared Spectra, A Practical Approach. In: MAYERS, R.A. (eds) *Encyclopedia of Analytical Chemistry*, 10815-10837.
- DARABI, M.H. & PIPER, J.D.A. 2004. Palaeomagnetism of the (Late Mesoproterozoic) Stoer Group, Northwest Scotland: implications for diagenesis, age and relationship to the Grenville Orogeny. *Geological Magazine*, **141**, 15-39.
- FERRARI, A. C. & ROBERTSON J. 2001. Resonant Raman spectroscopy of disordered, amorphous and diamondlike carbon. *Physical Review B* **64**, pp 13.
- GROSS, M.G. 1971. Carbon determination. In: *Procedures in Sedimentary Petrology*. Edited by: Carver R.C. Wiley-Interscience: London and New York. pp 573-596.
- JEHLICKA, J. & BÉNY, C. 1992. Application of Raman microspectrometry in the study of structural changes in Precambrian kerogens during regional metamorphism. *Organic Geochemistry*, **18**, 211-213

- KINNAIRD, T.C., PRAVE, A.R., KIRKLAND, C.L., HORSTWOOD, M., PARRISH, R. & BATCHELOR, R.A. 2007. The late Mesoproterozoic – early Neoproterozoic tectonostratigraphic evolution of NW Scotland: the Torridonian revisited. *Journal of the Geological Society, London*, **164**, 541-551.
- KNIGHT D.S. & WHITE W.B. 1989. Characterization of diamond films by Raman spectroscopy. *Journal of Material Research*, **4**, 385-393
- LANDIS C.A. 1971. Graphitisation of dispersed carbonaceous material in metamorphic rocks. *Contribution to Mineralogy and Petrology*, **30**, 34-45.
- MARSHALL C.P., LOVE G.D., SNAPE C.E., HILL A.C., ALLWOOD A.C., WALTER M.R., VAN KRANENDONK M.J., BOWDEN S.A., SYLVA S.P., & SUMMONS R.E. 2007. Structural characterization of kerogen in 3.4 Ga Archaean cherts from the Pilbara Craton, Western Australia. *Precambrian Research*, **155**, 1-23.
- MOSTEFAOUI S., PERRON C., ZINNER E., & SAGON G. 2000. Metal-associated carbon in primitive chondrites: Structure, isotopic composition, and origin. *Geochimica et Cosmochimica Acta*, **64**, 1945-1964.
- MUIRHEAD, D. K., PARNELL, J., TAYLOR, C., & BOWDEN, S. A. 2012. A kinetic model for the thermal evolution of sedimentary and meteoritic organic carbon using Raman spectroscopy. *Journal of Analytical and Applied Pyrolysis*, **96**, 153-161.
- NEMANICH, R.J. & SOLIN, S.A. 1979. First and second order Raman scattering from finite-size crystals of graphite. *Physical Review B*, **20**, 392-401.
- OLCOTT MARSHALL A., EMRY J. R., AND MARSHALL C. P. (2012) Multiple generations of carbon in the Apex Chert and Implications for preservation of microfossils. *Astrobiology* **12**, 160-166.
- PARK, R. G., TARNEY, J., & CONNELLY J, N. 2001. The Loch Maree Group: Palaeoproterozoic subduction-accretion complex in the Lewisian of Northwest Scotland. *Precambrian Research*, **105**, 205-226.
- PARNELL, J., BOYCE, A.J., MARK, D., BOWDEN, S. & SPINKS, S. (2010) Early oxygenation of the terrestrial environment during the Mesoproterozoic. *Nature*, **468**, 290-293.
- PARNELL, J., MARK, D., FALICK, A.E., BOYCE, A. & THACKREY, S. (2011) The age of the Mesoproterozoic Stoer Group sedimentary and impact deposits, NW Scotland. *Journal of the Geological Society, London*, **168**, 349-358.
- PASTERIS, J.D. & WOPENKA, B.1991. Raman spectra of graphite as indicators of degree of metamorphism. *Canadian Mineralogist*, **29**, 143-153.
- PIPER, J.D.A. & DARABI, M.H. 2005. Palaeomagnetic study of the (late Mesoproterozoic) Torridon Group, NW Scotland: Age, magnetostratigraphy, tectonic setting and partial magnetic overprinting by Caledonian orogeny. *Precambrian Research*, **142**, 45-81.
- PRAVE, A.R. 2002. Life on land in the Proterozoic: Evidence from the Torridonian rocks of northwest Scotland. *Geology*, **30**, 811-814.
- QU, Y., ENGDahl, A., ZHU, S., VAJDA, V., MCLOUGHLIN, N. (2015) Ultrastructure heterogeneity of carbonaceous material in ancient cherts: Investigating biosignature origin and preservation. *Astrobiology*, **15**, 825-842.

- QUIRICO, E., MONTAGNAC, G., ROUZAUD, J.-N., BONAL, L., BOUROT-DENISE, M., DUBER, S & REYNARD, B. 2009. Precursor and metamorphic condition effects on Raman spectra of poorly ordered carbonaceous matter in chondrites and coals. *Earth and Planetary Science Letters*, **287**, 185-193.
- RAINBIRD, R.H., HAMILTON, M.A. & YOUNG, G.M. 2001. Detrital zircon geochronology and provenance of the Torridonian, NW Scotland. *Journal of the Geological Society, London*, **158**, 15-27.
- ROBERTSON, J. 1991. Hard amorphous (diamond-like) carbons. *Prog. Solid State Chemistry*, **21**, 199.
- RODD, J.A. & STEWART, A.D. 1992. Geochemistry, weathering and diagenesis of the Diabaig Formation (Torridon Group) in NW Scotland. *Scottish Journal of Geology*, **28**, 27-35.
- ROUZAUD, J.N., OBERLIN, A., & BENY-BASSEZ, C. 1983. Carbon films: structure and microtexture (optical and electron microscopy, Raman spectroscopy). *Thin Solid Films*, **105**, 75-96.
- ROUZAUD, J., DELDICQUE, D., CHARON, E., PAGEOT, J. (2015) Carbons at the heart of questions on energy and environment: A nanostructural approach. *Comptes Rendus Geoscience*, **347**, 124-133.
- RUNGE, c. 1991. Über empirische Funktionen und die Interpolation zwischen äquidistanten Ordinaten. *Zeitschrift für Mathematik and Physik* **46**, 224-243.
- SCHOPF, J.W., KUDRYAVTSEV, A.B., AGRESTI, D.G., CZAJA, A.D., WADOWIAK, T.J. (2005) Raman imagery: A new approach to assess the geochemical maturity and biogenicity of erpmineralized Precambrian fossils. *Astrobiology*, **5**, 333-371.
- SFORNA, M.C., VAN ZUILEN, M.A., PHILIPPOT, P. (2014) Structural characterization by Raman hyperspectral mapping of organic carbon in the 3.46 billion-year-old Apex chert, Western Australia. *Geochimica et Cosmochimica Acta*, **124**, 18-33.
- SHERLOCK, S.C., JONES, K.A., & PARK, G. 2008. Grenville-age pseudotachylite in the Lewisian: laserprobe $^{40}\text{Ar}/^{39}\text{Ar}$ ages from the Gairloch region of Scotland (UK). *Journal of the Geological Society, London*, **165**, 73-83.
- STEWART, A.D. (2002) The later Proterozoic Torridonian rocks of Scotland: their sedimentology, geochemistry and origin. *Geological Society, London, Memoir* **24**.
- STROTHER, P.K., BATTISON, L., BRASIER, M.D. & WELLMAN, C.H. 2011. Earth's earliest non-marine eukaryotes. *Nature*, **473**, 505-509.
- TICE M., BOSTICK B. C., AND LOWE D. R. (2004) Thermal history of the 3.5-3.2 Ga Onverwacht and Fig Tree Groups, Barberton greenstone belt, South Africa, inferred by Raman microspectroscopy of carbonaceous material. *Geology* **32**, 37-40.
- TUINSTRAN, F. & KOENIG J.L. 1970. Raman spectrum of graphite. *Journal of Chemical Physics*, **53**, 1126-1130.
- TURNBULL, M.J.M., WHITEHOUSE, M.J. & MOORBATH, S. 1996. New isotopic age determinations for the Torridonian, NW Scotland. *Journal Geological Society of London*, **153**, 955-964.

WACEY, D., KILBURN, M.R., SAUNDERS, M., CLIFF, J. AND BRASIER, M.D., 2011. Microfossils of sulphur-metabolizing cells in 3.4-billion-year-old rocks of Western Australia. *Nature Geoscience*, **4**(10), 698-702.

WILLIAMS, G.E. & FODEN, J. 2011. A unifying model for the Torridon Group (early Neoproterozoic), NW Scotland: Product of post-Grenvillian extensional collapse. *Earth-Science Reviews*, **108**, 34-49.

WOPENKA, B. & PASTERIS, J.D. 1993. Structural characterization of kerogens to granulite-facies graphite: Applicability of Raman microprobe spectroscopy. *American Mineralogist*, **78**, 533-557.

YUI, T-F., HUANG, E. & XU, J. 1996. Raman spectrum of carbonaceous material: a possible metamorphic grade indicator for low-grade metamorphic rocks. *Journal of Metamorphic Geology*, **14**, 115 – 124.

Figure captions

Fig. 1. (a) Geological map showing generalised outcrop of Torridonian rocks (modified after Stewart 2002). Circled letters represent localities of all material studied. (b) Map of Scotland showing the location of the Torridonian rock outcrop from map A. (c) Legend indicating stratigraphy. (d) Generalised stratigraphy of the Torridonian Supergroup (modified after Stewart 2002). The Sleaf Group does not occur at localities investigated.

Fig. 2. Summary of Raman spectral features for very disordered carbon (top) with broad D1 and merged G and D2 peaks; disordered graphite with small D1 and shoulder D2 peak; and ordered graphite with single G peak (middle two); diamond (bottom).

Fig. 3. Raman spectroscopy data envelopes for all Torridonian Supergroup and Loch Maree Group data relative to the kerogen and graphite fields of Wopenka & Pasteris (1993).

Fig. 4. Representative stacked first order Raman scans for each formation or group. CHF: Cailleach Head Formation; AuF: Aultbea Formation; ApF: Applecross Formation; DF: Diabaig Formation; SG: Stoer Group; LMG: Loch Maree Group; LS: Lochaline Sandstone (procedural blank).

Fig. 5. Raman cross-plot of FWHM-G (cm^{-1}) and G band position (W_G , cm^{-1}) for all Torridonian Supergroup samples.

Fig. 6. Raman cross-plot of averaged I_D/I_G and A_D/A_G for all Torridonian Supergroup samples. Inset: Raman cross-plot of $(A_D / A_D + A_G) \times 100$ and crystallite size (L_a). Chlorite zones after Wopenka & Pasteris (1993).

Table 1. *Locations, total organic carbon contents and Raman spectrometric data for selected Torridonian and Lewisian shales.*