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Enhanced Microbial Activity in Carbon-rich Pillow Lavas, Ordovician, Great Britain and Ireland

--Manuscript Draft--

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Abstract:	There is extensive evidence for the microbial colonization of sea floor basalts in the modern ocean and in the geological record. The sulfur isotope composition of pyrite in the basalts commonly indicates marked isotopic fractionation due to microbial sulfate reduction. Sections through the Nemagraptus gracilis zone (Sandbian, Ordovician) in Great Britain and Ireland are characterized by both widespread pillow lavas and organic-rich seafloor sediment, allowing an exceptional opportunity to assess whether the availability of organic carbon influenced the extent of microbial activity in the basalts in deep geological time. Whole rock data from basalts at ten localities show that there is a relationship between sulfur isotopic composition and the carbon content of the basalt. At two localities where organic carbon was entrained in the basalt, isotopic compositions are relatively heavy compared to compositions in carbon-poor basalt, implying that microbial activity exhausted the supply of seawater sulfate. In most basalt, microbial activity was limited by the supply of carbon, but where the basalt incorporated carbon during emplacement on the seafloor, microbial activity became sulfate-limited.
Response to Reviewers:	G36937 Responses to Reviewers Comments [Responses in square brackets] -------------------- Reviewers' comments: Reviewer #1: In the title maybe consider using Great Britain and Ireland instead of British Isles, it does not rest easy with me when I see Gorumna as part of the British

Isles, the Mineralogical Society use Great Britain and Ireland. I know that this is acceptable internationally this is just a suggestion. Regarding the science figure 3 and 4 are very powerful and support the text very well indeed-excellent ms. [We have adopted terminology suggested by reviewer, in title and text.]

Reviewer #2: Having reviewed this manuscript last year and recommended publication with only minor revisions, I am satisfied that the manuscript has been improved by the revisions and should now be published.
The C and O data from the calcite are a particularly worthwhile addition and clarify that organic matter was being processed within the basalts (presumably a sticking point for one of the other referees in the original submission).
Data from additional localities are also a good addition and reinforce the original findings.

A couple of small queries (probably just typos) Line 73: Should be ten localities now? [Yes, amended to ten]
Line 82: The precision on the C content listed as 0.5%. But even the high carbon content basalts only have 0.21% - maybe an extra 0 is missing? [Yes, amended to 0.05%]
Line 88: Should be 8 low C basalts now? [Yes, amended to eight.]

Reviewer #3:
I found this manuscript is lucid and well presented and contains nothing that I know of that requires major changes, although I have suggested a few recommendations.

My insertions are enclosed in '' and deletions are in ()

108 yeilded a range of 'fractionation' values [‘isotopic’ values clarified.]

Line 109 isotopically light 'Sulphur' (reviewer's note: I assume this is what the authors are referring to) [Yes, ‘sulfur’ inserted to clarify.

Line 110 and near-zero 'isotopic' compositions reflecting a magmatic origin. [Yes, ‘isotopic’ inserted.]

Line 115 which 'in this instance may' be characterized by near-zero values.[No, this qualification would be misleading, as near-zero values are a general composition for magmatic values, not just in this instance.]

Line 132 light,(implying) 'suggesting that this could be the result of biochemical processing' [Amended accordingly]

Authors may wish to consider presenting cluster analysis on the data presented in fig 3 and 4. [Cluster analysis is the division of data sets according to some aspect of the data. This is inherently what we have done, by separating the data into values from carbon-rich and carbon-poor basalts.]

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Enhanced microbial activity in carbon-rich pillow lavas, Ordovician, Great Britain and Ireland

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ABSTRACT

There is extensive evidence for the microbial colonization of sea floor basalts in the modern ocean and in the geological record. The sulfur isotope composition of pyrite in the basalts commonly indicates marked isotopic fractionation due to microbial sulfate reduction. Sections through the *Nemagraptus gracilis* zone (Ordovician) in Great Britain and Ireland are characterized by both widespread pillow lavas and organic-rich seafloor sediment, allowing an exceptional opportunity to assess whether the availability of organic carbon influenced the extent of microbial activity in the basalts in deep geological time. Whole-rock data from basalts at ten localities show that there is a relationship between sulfur isotopic composition and the carbon content of the basalt. At two localities where organic carbon was entrained in the basalt, isotopic compositions are heavy compared to compositions in carbon-poor basalt, implying that microbial activity exhausted the supply of seawater sulfate. In most basalt, microbial activity was limited by

the supply of carbon, but where the basalt incorporated carbon during emplacement on the seafloor, microbial activity became sulfate-limited.

INTRODUCTION

The igneous crust at and below the sea floor may represent one of the largest residences for life on Earth. It is the largest aquifer (Edwards et al., 2011, 2012), and may support an extensive microbial community (Heberling et al., 2010), which before the evolution of land plants would have overwhelmingly dominated the planet's biomass. Microbial activity is facilitated by extensive fluid flow, and water-rock interaction, to provide nutrient and energy sources (Edwards et al., 2011). Evidence for microbial life in this setting today comes from the microbiology and molecular biology of isolates from cores through the ocean floor (Fry et al., 2008; Edwards et al., 2012; Lever et al., 2013). There is also evidence from minerals precipitated by microbial activity, including the iron sulphide pyrite which is found in vesicular basalts below the seafloor of most of the world's oceans (Parnell et al., 2014a). Pyrite survives into the deep geological record, so can provide us with a record of microbial colonization of the sub-seafloor igneous crust, based on the sulfur isotopic composition of the pyrite, which reflects isotopic fractionation associated with microbial sulfate reduction. Thus, the isotopic composition of pyrite in modern and ancient basalts has been used to prove sub-seafloor microbial activity (e.g., Rouxel et al., 2008; McLoughlin et al., 2012; Lever et al., 2013; Parnell et al., 2014a).

An important constraint for sub-seafloor life, especially in igneous crust, is the availability of organic carbon to provide biomass in heterotrophic organisms. Genetic studies show that active carbon cycling occurs (Edwards et al., 2011). Buried organic matter, in sediments deposited on the sea floor, can provide the necessary carbon (Wellsbury et al., 1997; Edwards et al., 2012), but it is not always accessible to the igneous crust. However, in the geological record, there are episodes when seafloor volcanism occurred within periods of organic-rich sedimentation to leave basalts accompanying black shales. This occurred particularly during the Ordovician, which was a period of both anomalous seafloor volcanic activity and of black shale sedimentation (Vaughan and Scarrow, 2003), exemplified in the *Nemagraptus gracilis* zone (Sandbian stage, Ordovician) rocks of Britain and Ireland. In Scotland, Ireland and Wales, this zone is characterized by black shales (Leggett, 1978) and also includes pillow lavas at numerous localities (Fig. 1; sample details in Data Repository). The pillow lavas are typically basalts consisting of a largely feldspathic groundmass with traces of interstitial opaque minerals (mostly magnetite, some pyrite). At two localities, there is evidence that, during emplacement of the pillow lavas, the magma interacted with organic-rich sediment to produce mobile hydrocarbons which on cooling left a solid carbonaceous residue within basalt. At Helen’s Bay, Northern Ireland (locality in Craig, 1984), the basalt contains numerous clusters of carbon blebs and stringers, associated with chlorite and titanium oxide (Fig. 2), and also millimeter-scale fragments of black shale. At Llanwrtyd Wells, Wales (locality in Stamp and Wooldridge, 1923), the basalt contains millimeter-scale quartz with domains of chlorite intermixed with carbon (Fig. 2), in which the uniform distribution of the carbon in the chlorite indicates that it had unmixed from a carbon-silicate fluid. In both cases, the basalt is crosscut by veinlets of solid carbon (‘bitumen’). The incorporated carbon has resulted in organic carbon contents of up to 0.21% in the basalts. Basalts from five other localities in the *N. gracilis* zone, and three localities less specifically dated to the mid-Ordovician (Fig. 1), where no interaction with organic-rich sediment occurred, have organic carbon contents of 0.03–0.08%. Sulfur in the basalts occurs as pyrite, in vesicle-fills, and crystals disseminated through the groundmass. The occurrence of both carbon-rich and carbon-poor basalts of the same age provides an exceptional opportunity to investigate if the carbon influenced the degree of microbial activity in the lavas, as measured by their sulfur isotope composition.

METHODS AND DATA

Whole rock samples of basalts from the ten localities were measured for sulfur isotope composition, using the chromium reduction method of Canfield et al. (1986). H_2S generated from the reduction of sulfide sulfur by $CrCl_2$ was trapped as Ag_2S in $AgNO_3$ solution. The resulting sulfide was washed, dried and analyzed by conventional procedures, following the method of Robinson and Kusakabe (1975). For carbonate stable isotope analysis, 1 mg sample powders were dissolved overnight in phosphoric acid at 70 °C. Ratios were measured on an AP2003 mass spectrometer. Repeat analyses of the NBS-18 standard are generally better than ±0.2‰ for carbon and 0.3‰ for oxygen. Organic carbon contents were measured using a LECO CS225 elemental analyzer, after decarbonatization with hydrochloric acid, to a precision of ±0.05%. The structural order of the carbon in the basalts and associated shale successions was characterized by laser Raman spectroscopy, using a Renishaw inVia reflex Raman spectrometer, with a Ar+ green laser (wavelength 514.5 nm). Initial analyses were based on accumulations over 3 s scan time on 10% laser power. The extended spectra in Figure 4 were based on four spectra each, accumulated over 10 s scan time with 10% laser power.

The eight low-carbon basalts (< 0.1% total organic carbon [TOC]) yielded $\delta^{34}S$ values from –25‰ to +5‰, to a precision of ±1% (see the GSA Data Repository[1]). The two carbon-bearing basalts (>0.1% TOC) yielded heavier compositions from +14‰ to +42‰ (Fig. 3). The data set as a whole shows a correlation of heavier (more positive) sulfur isotope composition with higher carbon contents of above 0.1% TOC (Fig. 3). Analyses of discrete pyrite crystals in the Llanwrtyd Wells basalt yield comparable compositions of +22‰ to +23‰. Analyses of six samples of calcite from vesicles in low-carbon basalts yielded a mean composition of carbon 0.0‰, oxygen –7.2‰, and seven samples of calcite from carbon-bearing basalt yielded a mean composition of carbon –10.8‰, oxygen –12.2‰ (see the Data Repository). The two sets of data are quite distinct (Fig. 4). Raman spectra for the carbon in both the basalt and shales exhibit well-developed order (G) and disorder (D) peaks, indicating that the carbon is disordered (Fig. DR1 in the Data Repository), and has a composition referable to kerogen, as defined by Wopenka and Pasteris (1993), rather than graphite. This is consistent with conodont alteration indices of ~5 for both localities, characteristic of low-grade metamorphism (Bergström, 1980). Raman spectra for fluid inclusions in cross-cutting mineral veins at Helen’s Bay, and mid-Ordovician seafloor volcanic rocks at Builth Wells, near Llanwrtyd Wells, show volatile hydrocarbons up to C_5 (Metcalfe et al., 1992; Parnell et al., 2014b).

DISCUSSION

Sulfur and Carbon Isotope Fractionation

The sulfur isotope compositions of the basalts can be interpreted in terms of microbial activity in the basalts. The low-carbon samples yielded a range of isotopic values down to −25‰, representing a variable mixture of isotopically light sulfur compositions reflecting microbial reduction of seawater sulfate and near-zero isotopic compositions reflecting a magmatic origin. The light compositions are fractionated from Ordovician seawater sulfate (+25‰ to +30‰; Claypool et al., 1980) to a degree far greater than is possible by abiotic processes (Machel, 2001). A larger data set, for pyrite crystals separated from Ordovician basalts, yielded a similar range of values (Parnell et al., 2014a). The carbon-bearing basalts have isotopic compositions heavier than could be explained by a magmatic origin for the sulfur, which would be characterized by near-zero values. Rather, the relatively heavy composition is typical of settings where the sulfate is progressively fractionated in a closed system to yield isotopically light sulfide (which may escape as hydrogen sulfide) and heavy residual sulfate, which then influences the composition of later-formed sulfides (Schwarcz and Burnie, 1973; Fallick et al., 2012). This represents a greater degree of fractionation of the sulfate than in the low-carbon samples; and implies the immediate availability of organic carbon to further microbial activity. There is evidence from other subsurface environments to show that sulfate reducers can utilize ‘geological’ carbon in anaerobic conditions, including oil reservoirs (Rueter et al., 1994), coal deposits (Wawrik et al., 2012) and black shales (Machel, 2001). These occurrences offer strong support for the inference that basalt containing organic carbon would support sulfate-reducing microbial activity.

Secondary calcite mineralization in the basalts occurs as vesicle- and fracture-fillings. The isotopic composition of carbon in the calcite can indicate whether the carbon was derived from organic carbon or seawater bicarbonate. Samples of calcite from the carbon-bearing basalts at Llanwrtyd Wells and Helen’s Bay have carbon isotope compositions quite distinct from samples of calcite from the carbon-poor basalts at Duncannon, Downan Point and Noblehouse (Fig. 4). The calcite from the carbon-bearing basalt is isotopically light, suggesting that this could be the result of biological processing, while the calcite in the other samples is near-zero, similar to seawater composition. These data are strongly consistent with utilization of the carbon in the carbon-bearing basalts by microbial activity.

Magma-Sediment Interaction

The samples represent variable degrees of interaction between magma and sediment. It has become clear that much 'lava' is actually emplaced within wet sediment, causing intermingling of the two components (Hole et al., 2013) in a quasi-intrusive relationship. Where the sediment is organic-rich, this resulted in the generation of hydrocarbons. The potential for interaction with organic-rich sediment was particularly high during the Ordovician because of the relative abundance of both basalts and black shales in the same section, but other examples of hydrocarbons in seafloor basalts in the geological record show that these interactions are not exceptional. There are numerous examples of carbon segregation through interaction between intrusive igneous rocks and organic-rich sediments, as found in the North Atlantic region where Mesozoic shales are altered by Paleocene intrusions (e.g., Lindgren and Parnell, 2006), and in intrusion-related hydrothermal systems on the current sea floor (Kvenvolden and Simoneit, 1990). Mixing within the sediment, rather than at the surface, explains how the high temperature was maintained to allow carbon to become incorporated in the melt at Llanwrtyd Wells.

Availability of Carbon

Although the carbon in the basalts from Helen’s Bay and Llanwrtyd Wells has experienced very high temperatures, and in the latter case has been incorporated in a melt, Raman spectroscopy shows that it remained disordered reduced carbon, and thus was potentially reactive. This is consistent with other studies showing that melting and re-solidification does not cause carbon to become ordered and thus unreactive (Kadik et al., 2004; Parnell and Lindgren, 2006). The succession also experienced low-grade regional metamorphism during the Caledonian Orogeny (Silurian-Devonian), which explains why the carbon in all the basalt and shale samples now has comparable thermal maturity. This implies the carbon may have been more disordered, and reactive, before the orogeny. In younger sequences that have not experienced orogenic heating, seafloor volcanic rocks contain liquid oil (Kvenvolden and Simoneit, 1990). At any stage of thermal maturity, the carbon would additionally release methane. On/below the present day ocean floor, the methane and higher hydrocarbons in volcanic rocks may support microbial communities (Bazylinski et al., 1989; Lizarralde et al., 2011), and we infer that similar microbial activity was possible below the Ordovician seafloor. More generally, other studies show that a deep biosphere can be supported by organic compounds released from kerogen in lithified rocks (Krumholz et al., 2002). Some of the carbon may have been relatively inert, but the presence of liquid hydrocarbons is suggested by the veinlets of solid carbon, and methane and other volatile hydrocarbons are identified in fluid inclusions, both of which could support microbial activity. The carbon-bearing microfractures through the basalt would have facilitated ready access to microbial life. The low-carbon basalts occur in sequences containing black shales, but do not have immediacy of access to the carbon because the carbon was not intermixed in the basalt.

The evidence from sulfur isotope data combines with evidence from bioalteration (McLoughlin et al., 2012) to show that there is a long-term geological record of microbial activity in sub-seafloor basalts. Carbonaceous linings to micro-borings and microbial carbonate precipitates (Furnes et al., 2001) demonstrate the processing of carbon by this activity. The current study emphasizes the importance of carbon availability, and that high carbon contents in basalts can allow a level of microbial activity greater than normal.

The Ordovician Sub-Seafloor Biosphere

This study shows that the incorporation of carbon in Ordovician seafloor basalts allowed them to support anomalous levels of microbial activity. The availability of organic carbon in the sub-seafloor was high in the Lower Paleozoic, when the oceans were anoxic (Saltzman, 2005). This enhanced the chance of carbon becoming entrained in basalts and supporting microbial activity within them. Other studies of Ordovician seafloor deposits have shown evidence for microbial activity in carbonated serpentinites (Lavoie and Chi, 2010) and injected sand complexes (Parnell et al., 2013). Future research should investigate whether sub-seafloor microbial activity has fluctuated through geologic time in conjunction with variations in oceanic oxygenation.

CONCLUSION

This data emphasizes that the cycling of carbon and sulfur in sub-seafloor basalts may be linked. Previous studies show the co-existence of methanogens and sulfate reducers in sub-seafloor basalts (Lin et al., 2012; Lever et al., 2013). In marine sediments, especially anoxic sediments, the carbon and sulfur cycles are clearly linked, and higher contents of metabolizable organic matter engender higher sulfur contents by supporting more microbial sulfide precipitation (Raiswell and Berner, 1986, Lin and Morse 1991). Similarly, this study shows that basalts containing organic carbon allowed more sulfur cycling than in normal low-carbon basalts.

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REFERENCES CITED

Bazylinski, D.A., Wirsen, C.O., and Jannasch, H.W., 1989, Microbial utilization of naturally occurring hydrocarbons at the Guaymas Basin hydrothermal vent site: Applied and Environmental Microbiology, v. 55, p. 2832–2836.

Bergström, S.M., 1980, Conodonts as paleotemperature tools in Ordovician rocks of the Caledonides and adjacent areas in Scandinavia and the British Isles: Geologiska Föreningens i Stockholm Förhandlingar, v. 102, p. 377–392, doi:10.1080/11035898009454495.

Canfield, D.E., Raiswell, R., Westrich, J.T., Reaves, C.M., and Berner, R.A., 1986, The use of chromium reduction in the analysis of reduced inorganic sulphur in sediments and shale: Chemical Geology, v. 54, p. 149–155, doi:10.1016/0009-2541(86)90078-1.

Claypool, G.E., Holser, W.T., Kaplan, I.R., Sakai, H., and Zak, I., 1980, The age curves of sulfur and oxygen isotopes in marine sulfate and their mutual interpretation: Chemical Geology, v. 28, p. 199–260, doi:10.1016/0009-2541(80)90047-9.

Craig, L.E., 1984, Stratigraphy in an accretionary prism: the Ordovician rocks in North Down, Ireland: Transactions of the Royal Society of Edinburgh. Earth Sciences, v. 74, p. 183–191, doi:10.1017/S0263593300013651.

Edwards, K.J., Becker, K., and Colwell, F., 2012, The deep, dark energy biosphere: Intraterrestrial life on Earth: Annual Review of Earth and Planetary Sciences, v. 40, p. 551–568, doi:10.1146/annurev-earth-042711-105500.

Edwards, K.J., Wheat, C.G., and Sylvan, J.B., 2011, Under the sea: microbial life in volcanic oceanic crust: Nature Reviews. Microbiology, v. 9, p. 703–712, doi:10.1038/nrmicro2647.

Fallick, A.E., Boyce, A.J., and McConville, P., 2012, Sulphur stable isotope systematics in diagenetic pyrite from the North Sea hydrocarbon reservoirs revealed by laser combustion analysis: Isotopes in Environmental and Health Studies, v. 48, p. 144–165, doi:10.1080/10256016.2012.658791.

Fry, J.C., Parkes, R.J., Cragg, B.A., Weightman, A.J., and Webster, G., 2008, Prokaryotic biodiversity and activity in the deep subseafloor biosphere: FEMS Microbiology Ecology, v. 66, p. 181–196, doi:10.1111/j.1574-6941.2008.00566.x.

Furnes, H., Muehlenbachs, K., Tumyr, O., Torsvik, T., and Xenophontos, C., 2001, Biogenic alteration of volcanic glass from the Troodos ophiolite, Cyprus: Journal of the Geological Society, v. 158, p. 75–84, doi:10.1144/jgs.158.1.75.

Heberling, C., Lowell, R.P., Liu, L., and Fisk, M.R., 2010, Extent of the microbial biosphere in the oceanic crust: Geochemistry Geophysics Geosystems, v. 11, doi:10.1029/2009GC002968.

Hole, M., Jolley, D., Hartley, A., Leleu, S., John, N., and Ball, M., 2013, Lava-sediment interactions in an Old Red Sandstone basin, NE Scotland: Journal of the Geological Society, v. 170, p. 641–655, doi:10.1144/jgs2012-107.

Kadik, A., Pineau, F., Litvin, Y., Jendrzejewski, N., Martinez, I., and Javoy, M., 2004, Formation of carbon and hydrogen species in magmas at low oxygen fugacity: Journal of Petrology, v. 45, p. 1297–1310, doi:10.1093/petrology/egh007.

Krumholz, L.R., Harris, S.J., and Suflita, J.M., 2002, Anaerobic microbial growth from components of Cretaceous shales: Geomicrobiology Journal, v. 19, p. 593–602, doi:10.1080/01490450290098559.

Kvenvolden, K.A., and Simoneit, B.R.T., 1990, Hydrothermally derived petroleum: Examples from Guaymas Basin, Gulf of California, and Escanaba Trough, Northeast Pacific Ocean: AAPG Bulletin, v. 74, p. 223–237.

Lavoie, D., and Chi, G., 2010, An Ordovician “Lost City” – venting serpentinite and life oases on Iapetus seafloor: Canadian Journal of Earth Sciences, v. 47, p. 199–207, doi:10.1139/E10-013.

Leggett, J.K., 1978, Eustacy and pelagic regimes in the Iapetus Ocean during the Ordovician and Silurian: Earth and Planetary Science Letters, v. 41, p. 163–169, doi:10.1016/0012-821X(78)90006-7.

Lever, M.A., Rouxel, O., Alt, J.C., Shimizu, N., Ono, S., Coggon, R.M., Shanks, W.C., Lapham, L., Elvert, M., Prieto-Mollar, X., Hinrichs, K.U., Inagaki, F., and Teske, A., 2013, Evidence for microbial carbon and sulfur cycling in deeply buried ridge flank basalt: Science, v. 339, p. 1305–1308, doi:10.1126/science.1229240.

Lin, H.T., Cowen, J.P., Olson, E.J., Amend, J.P., and Lilley, M.D., 2012, Inorganic chemistry, gas compositions and dissolved organic carbon in fluids from sedimented young basaltic crust on the Juan de Fuca Ridge flanks: Geochimica et Cosmochimica Acta, v. 85, p. 213–227, doi:10.1016/j.gca.2012.02.017.

Lin, S., and Morse, J.W., 1991, Sulfate reduction and iron sulfide mineral formation in Gulf of Mexico anoxic sediments: American Journal of Science, v. 291, p. 55–89, doi:10.2475/ajs.291.1.55.

Lindgren, P., and Parnell, J., 2006, Rapid heating of carbonaceous matter by igneous intrusions in carbon-rich shale, Isle of Skye, Scotland; an analogue for heating of carbon in impact craters: International Journal of Astrobiology, v. 5, p. 343–351, doi:10.1017/S1473550406003442.

Lizarralde, D., Soule, S.A., Seewald, J.S., and Proskurowski, G., 2011, Carbon release by off-axis magmatism in a young sedimented spreading centre: Nature Geoscience, v. 4, p. 50–54, doi:10.1038/ngeo1006.

Machel, H.G., 2001, Bacterial and thermochemical sulfate reduction in diagenetic settings – old and new insights: Sedimentary Geology, v. 140, p. 143–175, doi:10.1016/S0037-0738(00)00176-7.

McLoughlin, N., Grosch, E.G., Kilburn, M.R., and Wacey, D., 2012, Sulfur isotope evidence for a Paleoarchean subseafloor biosphere, Barberton, South Africa: Geology, v. 40, p. 1031–1034, doi:10.1130/G33313.1.

Metcalfe, R., Banks, D., and Bottrell, S.H., 1992, An association between organic matter and localised, prehnite-pumpellyite alteration, at Builth Wells, Wales, U.K: Chemical Geology, v. 102, p. 1–21, doi:10.1016/0009-2541(92)90143-S.

Parnell, J., Boyce, A.J., Hurst, A., Davidheiser-Kroll, B., and Ponicka, J., 2013, Long term geological record of a global deep subsurface microbial habitat in sand injection complexes: Scientific Reports, v. 3, p. 1828, doi:10.1038/srep01828.

Parnell, J., Hole, M., and Boyce, A.J., 2014a, Evidence for microbial activity in British and Irish Ordovician pillow lavas: Geological Journal, doi:10.1002/gj.2562.

Parnell, J., McMahon, S., Blamey, N.J.F., Hutchinson, I.B., Harris, L.V., Ingley, R., Edwards, H.G.M., Lynch, E., and Feely, M., 2014b, Detection of reduced carbon in a basalt analogue for martian nakhlite: a signpost to habitat on Mars: International Journal of Astrobiology, v. 13, p. 124–131, doi:10.1017/S1473550413000360.

Parnell, J., and Lindgren, P., 2006, Survival of reactive carbon through meteorite impact melting: Geology, v. 34, p. 1029–1032, doi:10.1130/G22731A.1.

Raiswell, R., and Berner, R.A., 1986, Pyrite and organic matter in Phanerozoic normal marine shales: Geochimica et Cosmochimica Acta, v. 50, p. 1967–1976, doi:10.1016/0016-7037(86)90252-8.

Robinson, B.W., and Kusakabe, M., 1975, Quantitative preparation of SO2 for 34S/32S analysis from sulfides by combustion with cuprous oxide: Analytical Chemistry, v. 47, p. 1179–1181, doi:10.1021/ac60357a026.

Rouxel, O., Ono, S., Alt, J., Rumble, D., and Ludden, J., 2008, Sulfur isotope evidence for microbial sulfate reduction in altered oceanic basalts at OPD Site 801: Earth and Planetary Science Letters, v. 268, p. 110–123, doi:10.1016/j.epsl.2008.01.010.

Rueter, P., Rabus, R., Wilkest, H., Aeckersberg, F., Rainey, F.A., Jannasch, H.W., and Widdel, F., 1994, Anaerobic oxidation of hydrocarbons in crude oil by new types of sulphate-reducing bacteria: Nature, v. 372, p. 455–458, doi:10.1038/372455a0.

Saltzman, M.R., 2005, Phosphorus, nitrogen, and the redox evolution of the Paleozoic oceans: Geology, v. 33, p. 573–576, doi:10.1130/G21535.1.

Schwarcz, H.P., and Burnie, S.W., 1973, Influence of sedimentary environments on sulphur isotope ratios in clastic rocks: A review: Mineralium Deposita, v. 8, p. 264–277, doi:10.1007/BF00203208.

Stamp, L.D., and Wooldridge, S.W., 1923, The igneous and associated rocks of Llanwrtyd (Brecon): Quarterly Journal of the Geological Society, v. 79, p. 16–46, doi:10.1144/GSL.JGS.1923.079.01-04.04.

Vaughan, A.P.M., and Scarrow, J.H., 2003, Ophiolite obduction pulses as a proxy indicator of superplume events?: Earth and Planetary Science Letters, v. 213, p. 407–416, doi:10.1016/S0012-821X(03)00330-3.

Wawrik, B., Mendivelso, M., Parisi, V.A., Suflita, J.M., Davidova, I.A., Marks, C.R., Van Nostrand, J.D., Liang, Y., Zhou, J., Huizinga, B.J., Strapoc, D., and Callaghan, A.V., 2012, Field and laboratory studies on the bioconversion of coal to methane in the San Juan Basin: FEMS Microbiology Ecology, v. 81, p. 26–42, doi:10.1111/j.1574-6941.2011.01272.x.

Wellsbury, P., Goodman, K., Barth, T., Cragg, B.A., Barnes, S.P., and Parkes, R.J., 1997, Deep bacterial biosphere fuelled by increasing organic matter availability during burial and heating: Nature, v. 388, p. 573–576, doi:10.1038/41544.

Wopenka, B., and Pasteris, J.D., 1993, Structural characterization of kerogens to granulite-facies graphite: Applicability of Raman microprobe spectroscopy: The American Mineralogist, v. 78, p. 533–557.

FIGURE CAPTIONS

Figure 1. Localities for pillow lavas analyzed in this study. All localities specifically in the Ordovician *Nemagraptus gracilis* zone, except Gorumna, Rhiw, and Bennane, which are less specifically dated to the mid-Ordovician.

Figure 2. Backscattered electron micrographs of carbon in Ordovician basalts. A: Basalt containing stringers of carbon (dark) and adjacent chlorite (gray), Helen’s Bay, Northern Ireland. B: Quartz (gray)containing carbon-chlorite masses (dark) and pyrite (Bright), Llanwrtyd Wells, Wales. C: Detail of carbon-chlorite masses in B, showing homogenous intermixture of carbon (dark) and chlorite (light).

Figure 3. Cross-plot of whole rock sulfur isotope composition and organic carbon content for Ordovician basalt samples. Data show general trend of heavier isotopic composition with higher carbon content. Be—Bennane; D—Duncannon; DP—Downan Point; G—Gorumna; H—Helen’s Bay, L—Llanwrtyd Wells; N—Noblehouse; R—Raven Gill; T—Tramore; W—Rhiw.

Figure 4. Cross-plot of carbon and oxygen stable isotope compositions for calcite samples from carbon-bearing basalts (solid circles, n = 7) and low-carbon basalts (open circles, n = 6). Calcite from carbon-bearing basalt is isotopically light, consistent with

microbial processing of organic matter. Sample details are provided in the Data Repository (see footnote 1).

[1] GSA Data Repository item 2015xxx, xxxxxxxx, is available online at www.geosociety.org/pubs/ft2015.htm, or on request from editing@geosociety.org or Documents Secretary, GSA, P.O. Box 9140, Boulder, CO 80301, USA.

Figure 1

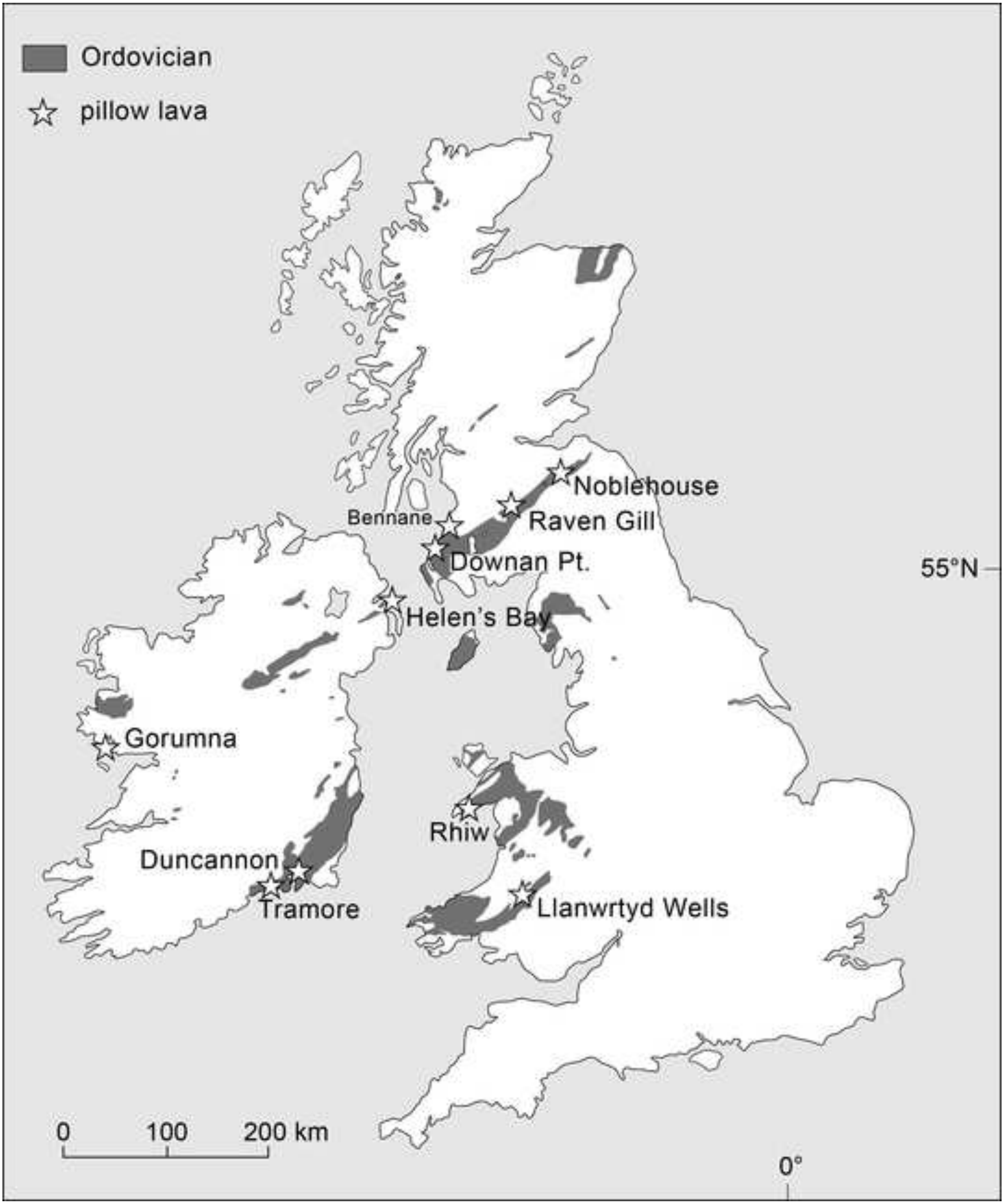

▬ Ordovician
☆ pillow lava
Noblehouse
Raven Gill
Bennane
Downan Pt.
55°N
Helen's Bay
Gorumna
Rhiw
Duncannon
Tramore
Llanwrtyd Wells
0
100
200 km
0°

Figure 2

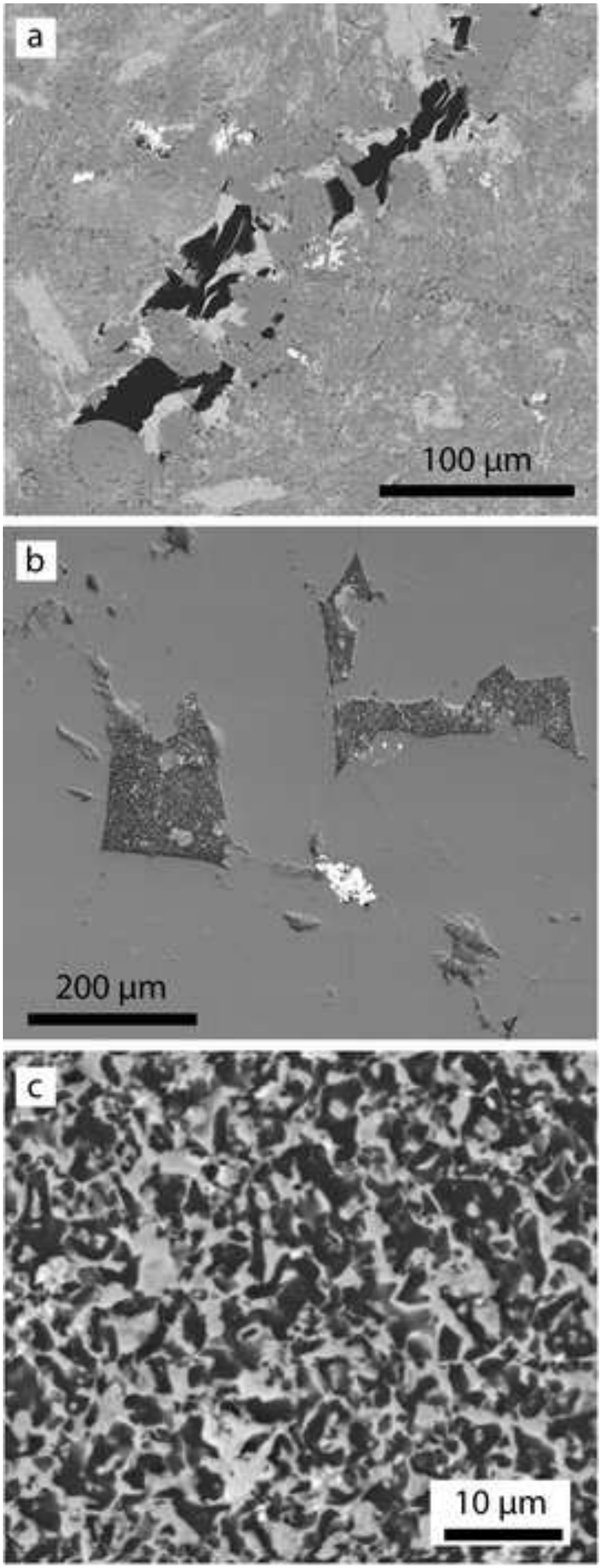


Figure 3

Click here to download Figure: Gracilis2 Fig. 3.jpg

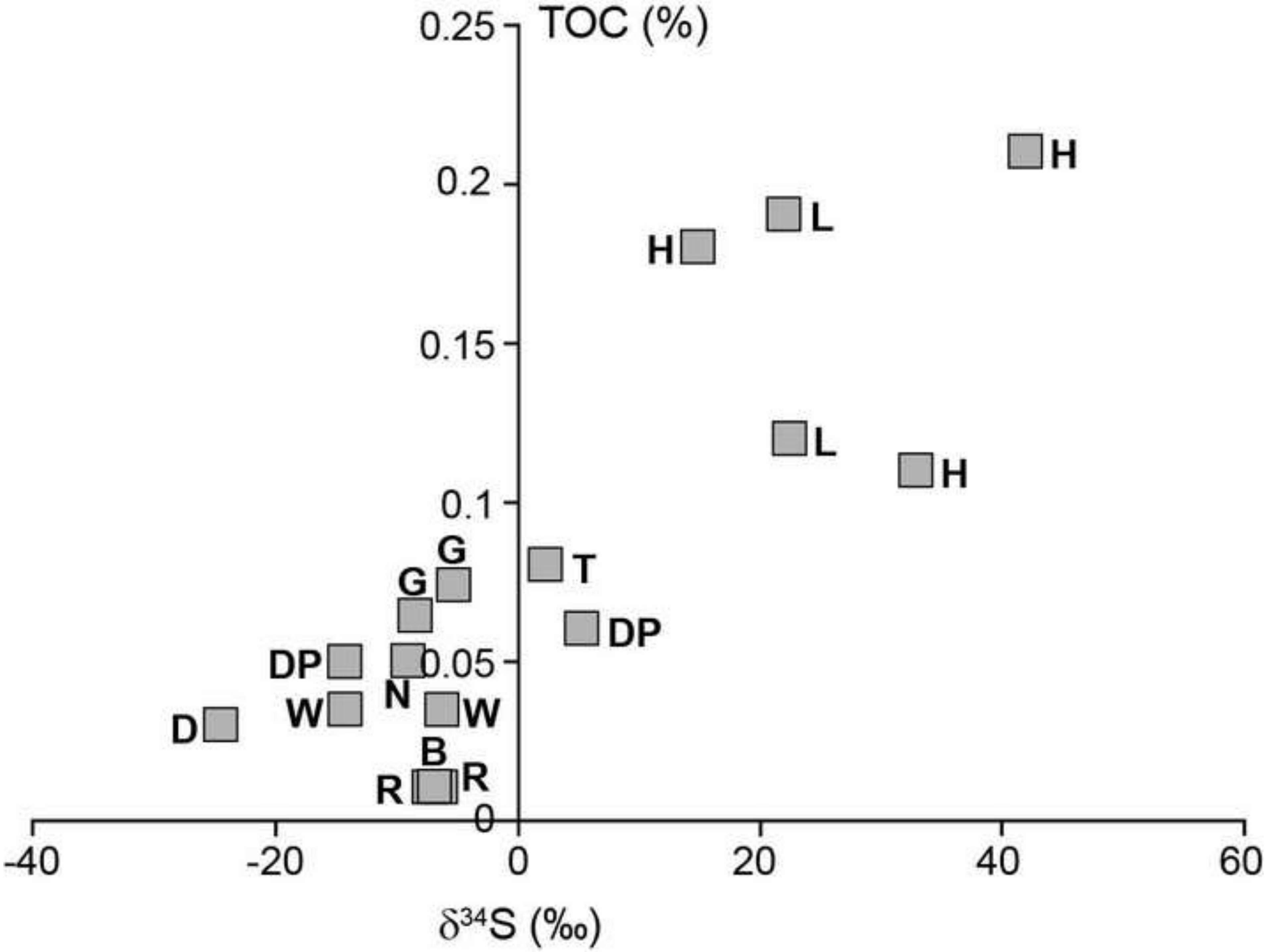
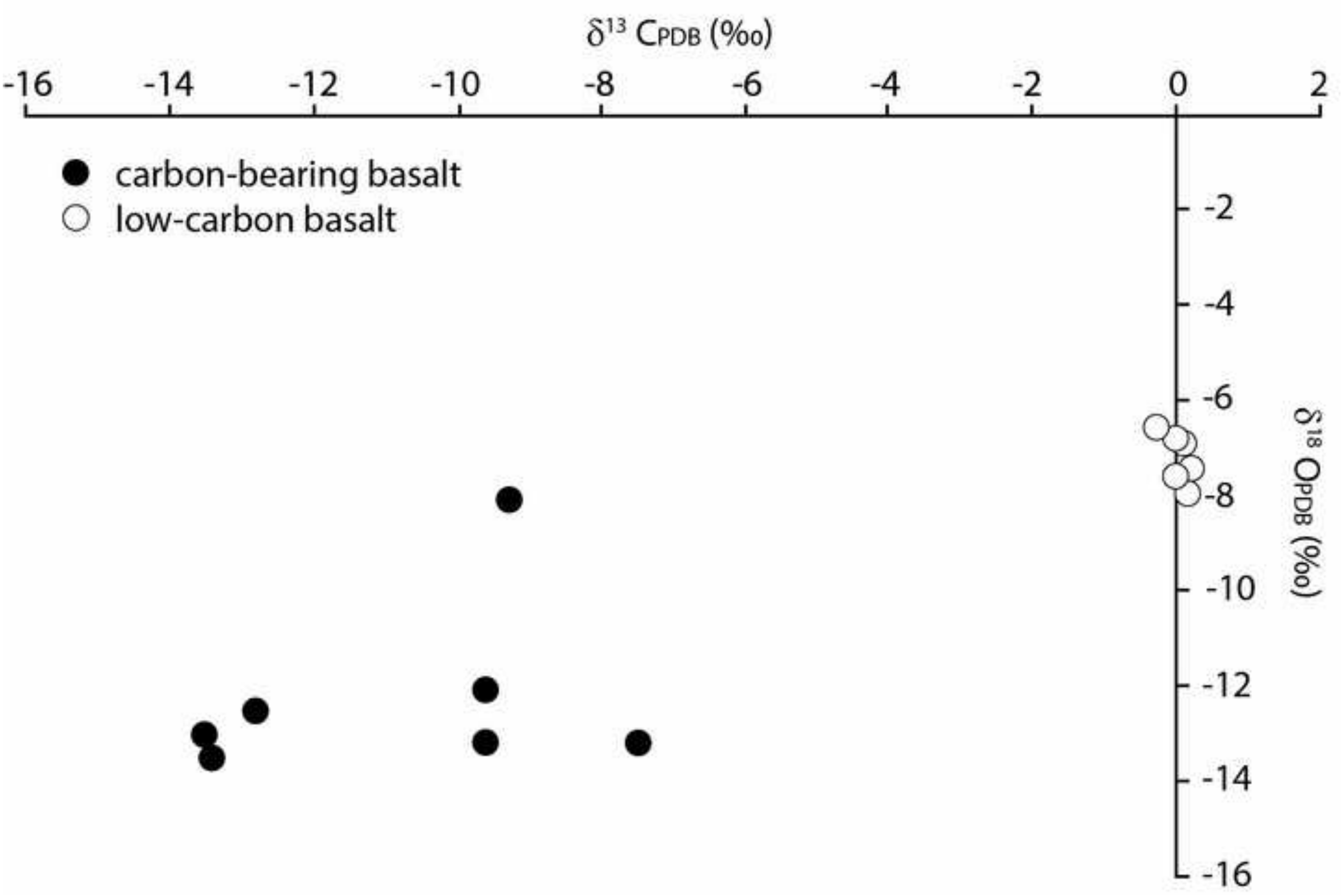


Figure 4


δ13 CPDB (‰)
-16
-14
-12
-10
-8
-6
-4
-2
0
2
● carbon-bearing basalt
○ low-carbon basalt
-2
-4
-6
-8
-10
-12
-14
-16
δ18 OPDB (‰)

GSA DATA REPOSITORY

Enhanced Microbial Activity in Carbon-rich Pillow Lavas, Ordovician, Great Britain and Ireland

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SAMPLE LOCALITIES

Table DR1. Sample localities

Locality	Nation	National Grid Reference
Llanwrtyd Wells	Wales	SN870470
Rhiw	Wales	SH223285
Helen's Bay	Northern Ireland	J459831
Duncannon	Republic of Ireland	S727082
Tramore	Republic of Ireland	S580008
Gorumna	Republic of Ireland	L855230
Bennane	Scotland	NX 091865
Downan Point	Scotland	NX067803
Raven Gill	Scotland	NS921199
Noblehouse	Scotland	NT186499

SULPHUR ISOTOPE DATA

Table DR2. Sulphur isotope and organic carbon compositions for Ordovician basalts

Locality	Lab No.	del34S (‰)	TOC (wt.%)
Downan Point	JPWR1	5.1	0.06
Downan Point	JPWR2A	-14.4	0.05
Noblehouse	JPWR4	-9.2	0.05
Bennane Head	JPWR10	-6.9	0.01
Helen's Bay	JPWR11	41.8	0.21

Helen’s Bay	JPWR12	32.8	0.11
Helen’s Bay	JPWR32	14.6	0.18
Rhiw	JPWR13	-5.3	0.04
Rhiw	JPWR14	-14.6	0.04
Duncannon	JPWR18	-24.6	0.03
Gorumna	JPWR21	-7.9	0.07
Gorumna	JPWR22	-5.5	0.08
Raven Gill	JPWR23	-7.4	0.01
Raven Gill	JPWR24	-6.5	0.01
Tramore	JPWR24A	2.0	0.08
Llanwrtyd Wells	JPWR30	21.7	0.19
Llanwrtyd Wells	JPWR31	22.2	0.12

CARBON and OXYGEN ISOTOPE DATA

Table DR3. Stable isotope data for samples of calcite in Ordovician basalts

Locality	Lab No.	del13C (‰)	del18O (‰)
Llanwrtyd Wells	LLHB7	-9.3	-8.1
Llanwrtyd Wells	LLHB8	-12.8	-12.5
Helen’s Bay	LLHB9	-7.5	-13.2
Llanwrtyd Wells	LLHB14	-13.5	-13.0
Llanwrtyd Wells	LLHB15	-9.6	-12.1
Llanwrtyd Wells	LLHB16	-9.6	-13.2
Llanwrtyd Wells	LLHB17	-13.4	-13.5
Downan Point	JPSM9	0.2	-7.5
Downan Point	LLHB18	0.0	-6.8
Downan Point	LLHB19	0.2	-8.0
Duncannon	LLHB20	0.1	-6.9
Noblehouse	LLHB21	-0.3	-6.6
Noblehouse	LLHB22	0.0	-7.6

RAMAN SPECTROSCOPY

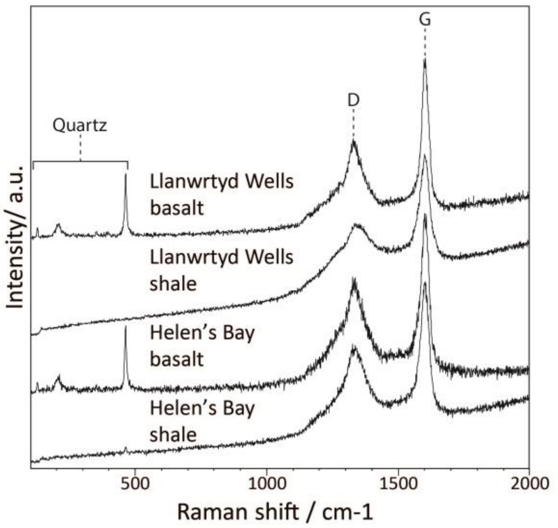

Fig. DR1. Raman spectra for carbon in basalts and associated shales from Helen’s Bay and Llanwrtyd Wells. D and G are main carbon peaks. All spectra show pronounced disorder (D) peaks, despite heating by basalt and later regional metamorphism.