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.]
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
(Wellbury 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$_2$S
generated from the reduction of sulfide sulfur by CrCl$_2$ was trapped as Ag$_2$S 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 δ^{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 C₅ (Metcalf 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.

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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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Community Support Facility at SUERC. NERC supported the project through Facility
grant IP-1235-0511. The Raman spectroscopy facility at the University of Aberdeen,
is funded by the Biotechnology and Biological Sciences Research Council. We are
grateful to M. Feely, G. Purvis and an anonymous reviewer for helpful criticism.

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and shale: Chemical Geology, v. 54, p. 149–155, doi:10.1016/0009-2541(86)90078-
1.


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).

1GSA 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

Click here to download Figure: Gracilis2 Fig. 1 (14pt).jpg
Figure 4

- $\delta^{13} \text{CPDB (‰)}$
- Solid circles: carbon-bearing basalt
- Open circles: low-carbon basalt

Click here to download Figure: Gracilis2 Fig. 4updated.jpg
GSA DATA REPOSITORY

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

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²Scottish Universities Environmental Research Centre, East Kilbride, Glasgow G75 0QF, UK
³School of Geographical and Earth Sciences, University of Glasgow, Glasgow G12 8QQ, UK

SAMPLE LOCALITIES

Table DR1. Sample localities

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<tr>
<th>Locality</th>
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SULPHUR ISOTOPE DATA

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

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**CARBON and OXYGEN ISOTOPE DATA**

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

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<th>del$^{18}$O (‰)</th>
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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.