

# Demonstrating deep biosphere activity in the geological record of lake sediments, on Earth and Mars

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## Abstract

The investigation of Gale Crater has highlighted the occurrence of lake sediments in the geological record of Mars. Lacustrine basins include a diversity of potential habitats for life. An analogue terrestrial lacustrine basin of Devonian age in Scotland contains sulphide minerals in several settings where subsurface microbial colonization can be envisaged. Sulphur isotope compositions for the sulphides imply that they were precipitated by microbial sulphate reduction. The data suggest that the search for life in martian lacustrine basins should include investigation of potential subsurface habitats, and that any sulphides in martian lacustrine basins could be useful indicators in the search for life.

## Introduction

The recognition of an extensive deep biosphere on Earth, and the advantages of subsurface niches for putative life on other planets, have contributed to the serious consideration of deep biosphere targets in the search for evidence of life on Mars (Fisk & Giovannoni 1999, Weiss et al. 2000, Michalski et al. 2013). The lacustrine infills of impact craters on Mars are an especially attractive target, as they may once have been sites of elevated heat flow (driving the circulation and surface-expression of liquid water) and nutrient accumulation, enhancing habitability (e.g. Arp 1995). Sulphate minerals have been detected in numerous crater-hosted sediments thought to be groundwater-fed palaeolake deposits, where they have been interpreted as evaporites (sulphate also fills diagenetic veins on Mars; Ehlmann & Edwards 2014 and references therein). The importance of lacustrine deposits on Mars has recently been emphasized by discoveries in Gale Crater by the Curiosity Rover (Grotzinger et al. 2014, 2015), that also include a sulphate-rich lacustrine mudstone unit. The mudstone contains traces of organic matter (Ming et al. 2014) and a cross-cutting sediment injection structure (Grotzinger et al. 2014).

Lacustrine deposits on Earth are natural archives of life in and around lakes (e.g. Buatois & Mángano 1998, Schnurrenberger et al. 2003), preserved as abundant sedimentary organic matter and common carbonaceous fossils. Microfossils are commonly reported within lacustrine sediments including evaporitic sulphates (Schopf et al. 2012). This study sought to investigate whether lacustrine basins can additionally record the presence of the deep biosphere, i.e., microbial populations that develop within the sediments after burial, which might produce geochemical traces in several settings (Fig. 1). Bacterial sulphate reduction (BSR) is known to be a widespread metabolic process in the subsurface (McMahon & Parnell 2014), where along with other microbial activity it is responsible for mineralogical alteration and neoformation (diagenesis) and is a common source of

39 sulphide minerals (e.g. Cavalazzi et al. 2014). The iron sulphide pyrite occurs widely in shales in  
40 particular, where a supply of organic matter fuels microbial activity and biomass growth (Raiswell &  
41 Berner 1986). In this study, sampling of sulphide minerals was undertaken in the Devonian Orcadian  
42 Basin, Scotland (Fig. 2), several aspects of which provide useful analogues for Mars. The basin was  
43 sulphate-rich, and it shows widespread evidence for sulphate precipitation at the sediment surface  
44 and sulphide precipitation in the subsurface (Muir & Ridgway 1975, Duncan & Buxton 1995).  
45 Because bacteria preferentially metabolise the lighter isotope of sulphur ( $^{32}\text{S}$ ), the sulphide minerals  
46 precipitated by BSR are characteristically depleted in the heavier isotope ( $^{34}\text{S}$ ; e.g. Machel, 2001). We  
47 therefore measured the sulphur isotope composition of the sulphides in order to assess if their  
48 precipitation was biologically mediated, and thereby indicative of deep biosphere activity, which  
49 would suggest that the possibility of deep biosphere activity also be considered in martian lacustrine  
50 basins.

## 51 Geological Setting

52 The Orcadian Basin is a 5+ km-thick package of continental sediments, deposited in an extensional  
53 basin of 10s of km wide during the mid-Devonian. The sediments include several kilometres  
54 thickness of lacustrine sediments, deposited in cycles reflecting fluctuations in water level and/or  
55 climate (Donovan 1980, Marshall & Hewett 2003, Andrews & Trewin 2010). The lake sediments are  
56 predominantly siltstones, which interdigitate with fluvial and aeolian sandstones towards the basin  
57 margins. A small proportion of the lake sediments is organic-rich and generated oil during burial  
58 (Trewin 1989, Duncan & Buxton 1995). The sediments include widespread pseudomorphs after  
59 gypsum (Parnell & Janaway 1990, Astin & Rogers 1991), indicating sulphate-rich pore waters.  
60 Offshore, sulphate evaporitic sediments are preserved unreplaced (Duncan & Buxton 1995). In the  
61 middle of the basin is an inlier of the underlying crystalline basement (Strachan 2003), which is a  
62 palaeotopographic high comparable in nature to the central uplift found in larger impact craters  
63 (Kenkmann et al. 2005). As in craters (Osinski et al. 2013), the basement inlier was a focus of  
64 hydrothermal activity during sedimentation, including precipitation of base metal sulphide minerals  
65 (Gallagher et al. 1971, Plant et al. 1986). Further hydrothermal activity occurred after the cessation  
66 of sedimentation, evidenced by widespread calcite veins with traces of sulphides (Gallagher et al.  
67 1971, McMahon et al. 2012, Dichiarente et al. 2016). The lacustrine sediments, sulphate-rich  
68 chemistry and basement high are all characteristics pertinent to Mars. The rocks are well-exposed,  
69 and well-studied, and have proved valuable analogues for planetary science studies (McMahon et al.  
70 2012, Hutchinson et al. 2014)

## 71 Sulphide mineralization

72 The distribution of sulphide minerals in the Orcadian Basin, indicate several settings where  
73 subsurface biological activity could have occurred, and which can be tested by isotopic analysis:

- 74 (i) *Stratabound diagenetic*. The earliest sulphides are pyrite nodules up to 10 cm size, which  
75 grew in the siltstones and sandstones during shallow burial but before significant  
76 compaction. They are locally abundant.
- 77 (ii) Sulphide mineralization that is directly associated with traces of degraded oil within porous  
78 sandstones. Oil was generated from the lacustrine sediments, probably during  
79 Carboniferous time and may have been degraded during subsequent Carboniferous-  
80 Permian uplift (Trewin 1989, Parnell et al. 1998). *Syn-depositional hydrothermal*.

81 Hydrothermal activity which appears to have been syn-diagenetic, i.e. it involved rocks  
82 at and below the contemporaneous sediment surface. This includes the mineralization  
83 of buried stromatolites (cyanobacterial structures), by galena (lead sulphide) and  
84 sphalerite (zinc sulphide), indicating the influx of metals from outside the sedimentary  
85 environment, via a deep hydrothermal system. A well-documented example from  
86 Warebeth, SW Orkney shows sulphide replacement of the stromatolites before  
87 compaction occurred, i.e. very soon after sedimentation ((Muir & Ridgway 1975)). The  
88 later stages of mineralization involve brittle fracture of lacustrine sediment around  
89 sulphide-bearing veins, indicating burial to the subsurface. Such deposits are focussed  
90 around the inlier of basement rock in SW Orkney, which may have channelled fluid flow  
91 and/or heat. Fluid inclusions in the sphalerite are monophasic, indicating temperatures  
92 probably lower than 70 °C (Goldstein & Reynolds 1994), so within the tolerance of  
93 thermophile microbes. Syn-diagenetic sulphide precipitation similarly occurred in the  
94 northern part of the basin in the Shetland Islands at Matta Taing. At this site,  
95 centimetre-scale nodules rich in copper sulphides replaced organic-rich lake sediments,  
96 again before significant compaction (Hall & Donovan 1978).

97 (iii) *Post-depositional hydrothermal*. Later hydrothermal mineralization formed pyrite-bearing  
98 calcite veins (Fig. 3), which cut all rocks, indicating that they post-dated sedimentation in  
99 the basin. The veins occur particularly in the siltstones.

100 (iv) Sulphide mineralization associated with sediment fluidization and injection (Fig. 3B). As in  
101 other basins (Parnell et al. 2013), pyrite is found at the margins of injected sandstone  
102 structures that cut transgressively through the siltstones on a centimetre- to metre-  
103 scale.

104

## 105 Methodology

106 Sulphide samples were prepared for conventional sulphur isotopic analysis by heavy liquid  
107 and hand picking techniques, at the Scottish Universities Environmental Research Centre (SUERC),  
108 East Kilbride. Heavy liquid separations were undertaken using suspension in bromoform. Sulphide  
109 separates were then analysed by standard techniques (Robinson and Kusakabe, 1975). 5 to 10mg  
110 were utilised for isotopic analysis. SO<sub>2</sub> gas was liberated by combusting the sulphides with excess  
111 Cu<sub>2</sub>O at 1075°C, *in vacuo*. Liberated gases were analysed on a VG Isotech SIRA II mass spectrometer,  
112 and standard corrections applied to raw  $\delta^{66}\text{SO}_2$  values to produce true  $\delta^{34}\text{S}$ . All SO<sub>2</sub> gases were  
113 analysed on a VG Isotech SIRA II mass spectrometer. The standards employed were the international  
114 standard NBS-123 and IAEA-S-3, and SUERC standard CP-1. These gave  $\delta^{34}\text{S}$  values of +17.1‰, -  
115 31.6‰ and -4.6‰ respectively, with 1 $\sigma$  reproducibility better than  $\pm 0.2\%$  around the time of these  
116 analyses. Data are reported in  $\delta^{34}\text{S}$  notation as per mil (‰) variations from the Vienna Canyon Diablo  
117 Troilite (V-CDT) standard.

118

## 119 Results

### 120 Sulphur isotope data

121 The isotopic composition of sulphur in 23 sulphide samples, together with a sample of gypsum from  
122 red bed sediments in the basin, is given in Table 1. The gypsum has a sulphur isotope composition  
123 ( $\delta^{34}\text{S}$ ) of +19.5 ‰, which represents the sulphate in the depositional environment (i.e. the 'parent'  
124 for the sulphides). The sulphides have compositions in the range +18.5 to -26.7 ‰. The stratabound  
125 diagenetic samples (early diagenetic nodules in siltstones, pyrite in sandstones) have compositions  
126 similar to the parent sulphate (Fig. 4). Syn-depositional hydrothermal deposits from 3 localities,  
127 including replacive sulphides in shales and stromatolites, have compositions in the range +0.2 to -6.4  
128 ‰. The post-depositional hydrothermal vein deposits have a wide range of composition from +13.8  
129 to -26.7 ‰. No data were measured for the injectites.

## 130 Discussion

### 131 Lacustrine Basins and Sediments

132 Sediments deposited in large lake basins have several characteristics which are favourable for  
133 microbial growth. They represent reservoirs for nutrients supplied by water flowing into the lake,  
134 incorporated into biomass and then released during decay below the sediment-water interface.  
135 Lacustrine sequences which consist of cyclic packages of sandstone and mudrock, such as in the  
136 Orcadian Basin (Donovan 1980; Andrews & Trewin 2010), contain extensive interfaces between the  
137 sandstone and mudrock. The sandstone is porous and permeable enough to favour microbial  
138 colonization and transport, while the organic-rich mudrock would release nutrients during  
139 compaction, so the interface may be a favoured habitat for life (Parnell et al. 2013). As the  
140 sediments become compacted, their dewatering may cause deformation and mineralization of the  
141 fluid escape pathways, which could include biomineralization where springs emerge at the  
142 contemporary surface and precipitate their solutes. Such mineralized pathways would include  
143 fracture systems and sand injection structures. Many terrestrial lakes accumulate organic carbon,  
144 especially where the water column is seasonally or permanently stratified (Dean & Gorham 1998).  
145 All of these characteristics are feasible on early Mars, although the accumulation of organic carbon is  
146 likely to have been very limited.

### 147 Source of sulphides in Orcadian Basin

148 There is widespread evidence for a sulphate-rich depositional environment in the Orcadian Basin, in  
149 pseudomorphs after gypsum that occur on many bedding planes (Parnell & Janaway 1990, Astin &  
150 Rodgers 1991). This sulphate is an obvious source for the sulphides precipitated during burial, and a  
151 direct relationship can be observed where the original gypsum crystals are pseudomorphed by pyrite  
152 (Parnell & Janaway 1990). Where sulphides formed before significant compaction, microbial  
153 sulphate reduction is strongly implicated, as the only widespread sulphide precipitation mechanism  
154 at low temperatures. Together with other examples of syn-diagenetic sulphides in algal breccias  
155 (Parnell & Janaway 1990) and alkaline lake cherts (Parnell 1987), there is extensive evidence for the  
156 precipitation of sulphides in the shallow subsurface environment of the Orcadian lake basin.  
157 Thermochemical sulphate reduction, a non-biological mechanism, is effective at elevated  
158 temperatures from 80-100 °C upwards, but does not generate strong negative isotopic fractionation  
159 (Machel et al. 1995).

160 In the case of sulphides which formed after sedimentation was complete, i.e. those of post-Devonian  
161 age, sulphur could have been available from younger sources, in particular Carboniferous seawater.

162 However, the post-Devonian history is more characterized by deep oxidative weathering (Robinson  
163 1985). The close association of the late sulphide veins with the lacustrine siltstones rather implies  
164 that the sulphide and host carbonate were derived from within the siltstone rather than by  
165 downwards percolation through a thick pile of sediments.

166 The 'stratabound' group of sulphide samples yield data very similar to the parent sulphate. The  
167 similarity is not diagnostic of a specific mechanism of sulphate reduction. It is likely that these  
168 sulphides were a product of microbial sulphate reduction, given the low temperatures typical of  
169 early diagenesis, but this is not conclusively proven by the isotope data. The vein sulphide samples,  
170 by contrast, exhibit a fractionation to a broad range of lighter (more negative) compositions. The  
171 lightest sample, at -26.7 ‰ has a fractionation of -45 ‰ from the parent sulphate. The broad range  
172 and the maximum fractionation are both characteristic features of microbial sulphate reduction  
173 (Machel 2001). The syn-depositional hydrothermal samples have a smaller range of compositions  
174 than the post-depositional hydrothermal samples. They all have a fractionation of about 20‰ from  
175 the parent sulphate, which is typical for microbial sulphate reduction in an open system. The greater  
176 variation in deep hydrothermal samples represents a greater variation in fluid compositions, and  
177 probably variation in the timing of sulphide precipitation. It is likely that the stratabound sulphides  
178 were also a product of microbial sulphate reduction, given the low temperatures typical of early  
179 diagenesis, but that is not conclusively proven by the isotope data.

#### 180 Analogue for Mars

181 Lake sediments may be widespread on Mars (Cabrol & Grin 2010), including in the Valles Marineris  
182 canyon region (Lucchitta 2010, Warner et al. 2013) and the northern plains (Parker et al. 2010), and  
183 particularly in craters. The lacustrine sediments of the Orcadian Basin are a valuable analogue for  
184 those on Mars. Gale Crater, at 140 km width, is of comparable size to the Orcadian Basin (Trewin  
185 1989). The lake system in Gale Crater lasted from thousands to millions of years (Grotzinger et al.  
186 2015), also comparable with the long history of Orcadian lacustrine sedimentation (Andrews &  
187 Trewin 2010, Andrews et al. 2016).

188 Sulphate minerals are widely distributed on Mars (Ehlmann & Edwards 2014), so the sulphate-rich  
189 nature of the lake waters and sediments of the Orcadian Basin make the deposits an especially  
190 pertinent analogue. The occurrence of some sulphides in degraded oil highlights a limitation to the  
191 analogy with Mars or other planets. In this case, microbial activity has used hydrocarbons as a source  
192 of carbon and energy (as is widely observed in oil reservoirs), and the hydrocarbons exist only as a  
193 consequence of earlier carbon fixation by photosynthesis in surface waters. Traces of hydrocarbons  
194 occur in the sulphide-bearing veins, so could have supplied carbon to microbial life. Nevertheless,  
195 the mineral veins in the Orcadian Basin demonstrate that hydrothermal systems can develop in a  
196 lacustrine basin, and circulate fluid and nutrients both during sedimentation and subsequent to it.  
197 The post-sedimentation hydrothermal activity is not mere happenstance; it is a natural consequence  
198 of the expulsion of fluid from a thick, geothermally heated pile of compacting sediment in a long-  
199 lived basin. If there is any microbial activity, hydrothermal settings would be preferred habitats as  
200 they focus nutrient availability and recharge, and activity is promoted at elevated temperatures. This  
201 much can be translated to the exploration of Mars, where the case for investigating the sediment-  
202 fills of crater basins has been well made. Although crater lakes would not undergo continued  
203 subsidence like the extensional Orcadian Basin, the thermal afterglow of the impact itself is

204 expected to have driven hydrothermal activity in craters on Mars as it has on Earth (Rathbun and  
205 Squyres 2002). This is thought to explain the occurrence of post-impact silica and sulphate veins  
206 observed by rovers in Endeavour Crater and Gale Crater on Mars (Arvidson et al., 2014; Grotzinger et  
207 al., 2014). The focus of hydrothermal activity around a basement inlier in the Orcadian Basin is  
208 especially pertinent, as this feature is found in many impact craters (e.g. Mount Sharp in Gale Crater)  
209 and has been identified as a desirable target for astrobiological sampling on Mars.

210 The Orcadian injected sandstone structures (Fig. 3c) are centimetre-scale width and transgress the  
211 stratigraphy, similar to the injected structure in Gale Crater shown by Grotzinger et al. (2014).  
212 Lacustrine successions commonly contain alternating sandstone and mudstone beds, and  
213 disturbances (such as meteorite impacts) could trigger gravitational instability stimulating injections  
214 of the sandstones through the mudstones. Injected structures are conduits for fluid flow, and have a  
215 high surface area of sandstone/mudstone interface, making them good habitats (Parnell et al. 2013).  
216 Such interfaces also occur from where sand fills crack-like structures in adjacent mud layers, which  
217 can open spontaneously during burial and are observed (lithified) both in the Orcadian Basin and in  
218 Gale Crater (Donovan & Foster 1972; Grotzinger et al. 2014; McMahon et al. 2016). Injection and  
219 crack-like structures therefore deserve close attention in the search for life.

220 Both hydrothermal veins and injection structures penetrate to depths of 1-2 km in sedimentary  
221 basins, a depth range that includes most deep biosphere activity (McMahon & Parnell 2014). On  
222 Mars, where gravitational compaction and geothermal gradients are milder than on Earth, there is  
223 no reason to believe that a deep biosphere could not extend to these depths where liquid water is  
224 available (Michalski et al. 2013).

225 The application of sulphur isotopes in this study has served to prove BSR at depth in the Orcadian  
226 Basin, and this the possibility of deep life in lacustrine basins on Mars. The remote measurement of  
227 sulphur isotopes on samples on Mars could also have value in the exploration for biological activity  
228 there (Franz et al. 2011). However, the fractionation of sulphur isotopes 32 and 34 that is the basis  
229 of our conclusion of BSR has evolved over billions of years and is not normally evident in Archean  
230 samples on Earth. Evidence of biological activity is nonetheless possible in Archean samples using  
231 rarer sulphur isotopes 33 and 36 (e.g. Halevy 2013, Marin-Carbonne et al. 2014). The potential of  
232 interrogating Archean sulphide samples is especially pertinent given the equivalent Archean age for  
233 the lacustrine samples on Mars. As an understanding of the sulphur isotope systematics on Mars  
234 improves, so will the evaluation of whether any anomalous isotopic fractionation could be used as  
235 an indicator of possible biology.

236

## 237 **Conclusions**

238 The lacustrine sediments of the Orcadian Basin exhibit evidence for a deep biosphere in several  
239 contexts, including syn-depositional hydrothermal deposits, post-depositional hydrothermal  
240 deposits, and injected sandstones. Hydrothermal deposits are particularly focussed around a  
241 basement uplift. Each of these contexts has potential relevance to Mars. The evidence for microbial  
242 activity in these settings in the Orcadian Basin is in sulphide precipitation, some of which has  
243 diagnostic sulphur isotope compositions. Although the surface of Mars is sulphate-rich, and sulphide  
244 precipitation would be a feasible signature of microbial activity there, this is not essential to the

245 analogy. The critical conclusion is that a lacustrine basin contains deep biosphere habitats, and the  
246 same habitats could occur on Mars.

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252

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- 377 Figure captions
- 378 Fig. 1. Schematic cross-section across a lacustrine basin, showing diversity of settings which may  
 379 support subsurface microbial activity.
- 380 Fig. 2. Map of central part of Orcadian Basin, northern Scotland, showing localities for sulphide and  
 381 sulphate samples. Outcrop of basement uplift occurs in SW Orkney. Localities A, Achanarras, B,  
 382 Broadhaven, C, Castlehill, E, East Scapa, G, Graemsay, K, Ackergill, N, Breck Ness, P, Pennyland, S,  
 383 Spittal, SH, Wick South Head, W, Warebeth, X, Staxigoe.

384 Fig. 3. Settings for sulphide mineralization in the sediments of the Orcadian Basin. A, Concretionary  
 385 stromatolites replaced by galena (lead sulphide), Warebeth. Field width 2 cm. B, Margin of calcite  
 386 vein through siltstone, with pyrite at interface (arrowed), Spittal. C, Sandstone injection structure  
 387 cross-cutting siltstone host, The Haven (transgressive relationship arrowed). Pyrite occurs at  
 388 sandstone/siltstone boundary at a microscopic level. Compass scale 5 cm wide.

389 Fig. 4. Histogram of sulphur isotope data from sulphides in the Orcadian Basin.

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392 Table 1. Samples of sulphide and sulphate minerals used for sulphur isotope analysis.

Locality	Lab code	Mineral	setting	style	$\delta^{34}\text{S}$ (‰)
East Scapa	61	gypsum	Massive in red beds	Primary sulphate (stratabound)	19.5
Ackergill	2109	pyrite	Nodule in black shale	Stratabound diagenetic	14.4
Castlehill	2110	pyrite	Nodule in shale	Stratabound diagenetic	14.5
Pennyland	2113	pyrite	Nodule in sandstone	Stratabound diagenetic	18.5
Pennyland	2114	pyrite	Nodule in sandstone	Stratabound diagenetic	17.3
Pennyland	2115	pyrite	Nodule in shale	Stratabound diagenetic	16.1
Breckness	20	pyrite	Nodule in sandstone	Stratabound diagenetic	17.3
Matta Taing	SS28	Cu sulphides	Replacive in shale	Syn-depositional hydrothermal	-4.1
Warebeth	SS29	galena	Replacive in stromatolite	Syn-depositional hydrothermal	-0.6
Warebeth	145	galena	Vein in shale	Syn-depositional hydrothermal	0.0
Graemsay	146	galena	Replacive in stromatolite	Syn-depositional hydrothermal	-0.6
Warebeth	147	galena	Vein in shale	Syn-depositional hydrothermal	-0.1
Warebeth	148	galena	Replacive in stromatolite	Syn-depositional hydrothermal	0.2
Matta Taing	149	Cu sulphides	Replacive in shale	Syn-depositional hydrothermal	-1.8
Matta Taing	150	Cu sulphides	Replacive in shale	Syn-depositional hydrothermal	-6.4
Achanarras	ACH	pyrite	Vein through shale	Post-depositional hydrothermal	7.9
Achanarras	ACH32	pyrite	Vein through shale	Post-depositional hydrothermal	-3.8
Staxigoe	135	pyrite	Vein through shale	Post-depositional hydrothermal	6.9

Wick South Head	136	pyrite	Vein through shale	Post-depositional hydrothermal	13.8
The Haven	137	pyrite	Vein through shale	Post-depositional hydrothermal	-26.7
Broadhaven	138	pyrite	Vein through shale	Post-depositional hydrothermal	9.5
The Haven	SS2	pyrite	Vein through shale	Post-depositional hydrothermal	10.1
Spittal	2111	pyrite	Vein through shale	Post-depositional hydrothermal	4.3
The Haven	2112	pyrite	Vein through shale	Post-depositional hydrothermal	-11.1

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