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Sulphides with high $\delta^{34}\text{S}$ from the Late Precambrian Bonahaven Dolomite, Argyll, Scotland

THE Bonahaven Dolomite Formation (BDF) is about 300 m thick and located immediately above the Port Askaig Tillite in the Argyll Group of the Scottish Dalradian Supergroup; it crops out on the northeast coast of Islay. The greenschist facies dolomitic metasediments are of late Proterozoic age and were deposited in a coastal marine environment (Fairchild, 1980) off the south coast of the Laurentian supercontinent (Anderton, 1985). Fairchild (1985) suggested that some quartz-calcite nodules present in the dolomites could represent pseudomorphs after anhydrite. Sulphur isotope analyses of iron sulphides from dolomites with such nodules were therefore undertaken in order to determine whether the sulphur isotopic signature was indicative of the

special evaporitic depositional environment. The part of the sequence sampled, Member 3 of Spencer and Spencer (1972) contains stromatolites. Previous sulphur isotope analyses of sulphides and baryte in mineralized (Willan and Coleman, 1983; Hall *et al.*, 1991) and other unmineralized (Hall *et al.*, 1987, 1988, 1993) Dalradian metasediments suggest that Dalradian (Riphean-Vendian) seawater sulphate was isotopically heavy, with $\delta^{34}\text{S}_{\text{sulphate}}$ at least +30% and possibly as high as +40%, compared to typical Phanerozoic seawater sulphate values of $+15 \pm 5\%$ (Claypool *et al.*, 1980). Such high values were therefore considered to be possible for the BDF iron sulphides, especially if the sulphide sulphur originated by thermal reduction

TABLE 1. Conventional sulphur isotope analysis of pyrite separates

Sample	Nature	$\delta^{34}\text{S}\%$
BON1	Pyrite concentrate	+42.0
BON1	Repeat	+42.1
BON1a	Drilled pyrite (impure)	+38.7
BON1b	Drilled pyrite (impure)	+38.6
BON4a	Pyrite (30 fragments)	+36.5
BON4b	Pyrite (40 fragments)	+37.0

on regional metamorphism of original sulphate. Confirmation of isotopically heavy contemporaneous seawater sulphate is important to studies of Dalradian sulphides but, in addition, this would be significant in relation to estimates of possible variations in bacteriogenic sulphate/sulphide sulphur isotope fractionation through geological time (e.g. Bottomley *et al.*, 1992).

Conventional sulphur isotope analyses

Concentrates of pyrite from dolomitic lithologies sampled from the coastal exposure of BDF, Islay (NR 425733), were analysed using the conventional technique outlined in Hall *et al.*, (1987) and the results are presented in Table 1. The values range from +36.5 to +42.1% and confirm that the pyrite is exceptionally enriched in the heavier isotope of sulphur, ^{34}S , compared to typical $\delta^{34}\text{S}$ of about +15% for Appin and Argyll Group sulphides (Hall *et al.*, 1987, 1988, 1993).

Laser ablation sulphur isotope analyses

An unmounted polished slice (BON1a), about 10 mm², revealed two types of pyrite: (1) fine grained (<50 μm) pyrite as variably recrystallized framboids usually forming small clusters of pyrite crystals; and (2) coarse euhedral pyrite (up

to 500 μm). Coarse pyrite tended to be concentrated into layers within lenses of coarse carbonate. Some coarse pyrite crystals contained cores of 'ghost' inclusions indicating that this coarse pyrite had overgrown aggregates of earlier framboidal pyrite.

The laser technique was used to determine the variation in isotopic composition and locate the isotopically heavy sulphur which had been shown to be present using conventional sulphur isotope analyses.

The laser extraction method at the SURRC has been described by Kelley and Fallick (1990) and, using the more modern and higher precision VG SIRA II[©] mass spectrometer used in the present study, by Fallick *et al.* (1992). Laser light is used to heat to combustion, sulphides held in a chamber containing oxygen; the polished section can be viewed using reflected light microscopy with video camera and monitor during illumination by the 2 watt Nd-YAG laser beam. The sample is moved under the 20 μm beam in order to expose sufficient area of the sulphide which oxidizes to produce SO_2 . The gas in the sample chamber, containing as little as 0.1 μmol , is then processed using the conventional cryogenic gas separation technique and the sulphur isotopic ratios determined by mass spectrometry. Internal standard deviations of the $\delta^{66}\text{SO}_2/\delta^{64}\text{SO}_2$ ratios measured by mass spectrometry were <0.05% for all samples. These ratios are converted to $^{34}\text{S}:^{32}\text{S}$ by calibration with sulphur standards and the results presented as delta (δ) values: $\delta^{34}\text{S}(\%) = [^{34}/^{32}\text{S}_{\text{sample}}/^{34}/^{32}\text{S}_{\text{standard}}] \times 1000$. The corrected values given in Table 2 incorporate a +1 ‰ correction as appropriate from the results for pyrite given by Kelley and Fallick (1990). The analytical uncertainty, taking reproducibility and calibration into account, is about $\pm 0.2\%$, comparable to that of conventional sulphur isotope analyses using powder samples. The CO_2 extracted is monitored because combustion of hydrocarbons can interfere with sulphide combustion and possibly affect the isotopic

TABLE 2. Laser ablation sulphur isotope analysis of pyrite in polished section BON1a

No.	Nature	Number of 40 μm . pits	SO_2 yield μmol s	$\delta^{34}\text{S}\%$ CDT
1	Coarse cubes	20	0.11	39.5
2	Coarse cubes	20	0.08	42.3
3	Disseminated grains	50	0.15	29.9
4	Disseminated grains	50	0.17	30.2
5	Coarse cube cores	25	0.02	—
6	Coarse cube rims	30	0.22	43.3

composition of SO₂ through interference in the mass spectrometer.

Yields of SO₂ were satisfactory except for sample 5, for which no isotopic ratio could be determined. The gas was lost during processing.

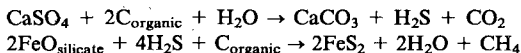
The relatively small grain size of some of the pyrite meant that it was necessary to combust pits or craters in the pyrite and move from grain to grain to accumulate enough SO₂ for analyses. The coarse pyrite combusted well and the time used was about 2–3 s on one spot. A minimum of 20 craters was necessary to give about 0.1 μmols SO₂, sufficient for mass spectrometry. The fine disseminated pyrite grains were all much smaller than the size of the crater developed by the laser in the rock (about 40 μm in diameter). A minimum of 40 pits containing 1 to 3 'grains' of pyrite (up to 10 μm in size) were required to give sufficient SO₂. While CO₂ contamination was low (SO₂/CO₂ ≫ 1) for the coarse pyrite, it was higher (SO₂/CO₂ = 0.1) for the fine pyrite. This could have led to an added uncertainty in the sulphur isotope values of the fine pyrite but the CO₂ was removed effectively and CO₂:SO₂ was < 1:100 as measured using the mass 64 and 44 beams in the mass spectrometer.

It is evident that fine grained pyrite within a carbonate matrix can be analysed satisfactorily. There appears to be a systematic difference between the coarse and fine pyrite with the former having relatively heavy δ³⁴S (+39.5‰ to +43‰), whereas the latter is distinctly isotopically lighter (about +30‰).

Interpretation

There are two possible interpretations of the isotopically heavy sulphur of the iron sulphides in the BDF:

(1) The high δ³⁴S is due to the formation of sulphide on reduction of evaporitic sulphate during progressive regional metamorphism. This can be represented nominally by:



The coarse sulphide inherits the sulphur isotopic signature of the original seawater sulphate, through localized, closed system reduction of evaporitic sulphate within the meta-sedimentary rocks. The local Dalradian (Lower Vendian) seawater therefore contained sulphate of δ³⁴S about +40‰. The lower δ³⁴S of below +30‰ for the fine pyrite indicates the possibility of a distinct sulphide source. The most likely reservoir of isotopically light sulphur would be bacteriogenically reduced seawater sulphate, as

incorporated into framboidal pyrite during early diagenesis. For example, European Jurassic shales from diverse facies proved to contain pyrite with δ³⁴S ranging from about -10 to -40‰ (Fisher and Hudson, 1987) while the δ³⁴S_{sulphate} of Mesozoic seawater was +15 ± 5‰ (Claypool *et al.*, 1980).

However, the textures of the iron sulphides in the BDF suggests that the fine, originally framboidal, pyrite had additional sulphide added during crystallization to pyrite euhedra. This is beyond the resolution of the laser technique. It is therefore likely that the measured isotopic ratio of the pyrite has been increased slightly by the later addition of isotopically heavy sulphur from the same reservoir which formed the coarse pyrite.

(2) All the iron sulphide is of bacteriogenic origin and the high δ³⁴S values are due to sulphide forming by reduction of sulphate in a closed or closing system with limited sulphate supply. The high values are due to residual sulphate becoming isotopically heavy as ³²S is preferentially incorporated into H₂S which is either fixed as iron sulphide or possibly lost by migration from the local system due to a lack of available iron.

On balance, option (1) is preferred because of the textural association of coarser pyrite with carbonate which could well be after original sulphate (Fairchild, 1985) and because nearby finer grained pyrite is isotopically lighter.

Discussion

The data presented here confirm that Vendian seawater had the heaviest sulphate sulphur isotopic ratio; that is the sulphate most enriched in ³⁴S, of the Proterozoic and indeed of any time, as indicated on the 'Claypool curve' of δ³⁴S_{sulphate} for ocean water through geological time (Claypool *et al.*, 1980). There is no evidence for glacial episodes directly affecting the δ³⁴S of sulphate in the oceans (e.g. Claypool *et al.*, 1980). However, given the intimate link between the geochemical S and C–O cycles, and the fact that the latter is certainly affected by glacial episodes, there may be an indirect effect.

The implications of the interpretation favoured here, that evaporitic sulphate could have contributed to the δ³⁴S of metamorphic pyrite, means that metamorphic pyrite in general cannot be assumed to represent bacteriogenic sulphide and that δ³⁴S determined from extracts of bulk pyrite or total whole-rock sulphide (e.g. Bottomley *et al.*, 1992) could conceal significant variations in the isotopic ratios of the pyrite. This also implies that it is imprudent to make assumptions about variations in the isotopic fractionation of sulphur on

bacteriogenic reduction of sulphate, using whole-rock sulphide data. Although we cannot resolve conclusively the isotopic values of original seawater and diagenetic sulphide, the Bonahaven data can nevertheless be interpreted as being consistent with a reduced fractionation on bacteriogenic reduction of sulphate in the later Proterozoic as suggested by Bottomley *et al.* (1992).

Conclusions

Sulphur isotopic analyses indicate that the Bonahaven Dolomite Formation contains isotopically heavy iron sulphide. Coarse pyrite has $\delta^{34}\text{S}$ values of +39.5 to +43.0‰ consistent with the sulphide forming on closed-system reduction of evaporitic sulphate and inheriting a local seawater sulphate sulphur isotopic ratio of about +40‰. Fine disseminated pyrite is isotopically lighter with $\delta^{34}\text{S}$ about +30‰; this value probably represents a mixture of isotopically lighter sulphide of bacteriogenic origin and heavier sulphide added during the development of overgrowths on the early fine pyrite.

The results indicate that Vendian Dalradian seawater could, at least locally, have contained sulphate enriched in ^{34}S with $\delta^{34}\text{S}_{\text{sulphate}}$ of about +40‰; such isotopically heavy sulphate could have formed the major contribution of sulphate as suggested by Hall *et al.* (1991) to the Aberfeldy synsedimentary baryte deposit which is hosted by Argyll Group graphitic schists. The results confirm the enigmatic ^{34}S -enrichment seen worldwide in late Proterozoic sedimentary sulphides (Bottomley *et al.*, 1992).

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A high-chromium corundum (ruby) inclusion in diamond from the São Luiz alluvial mine, Brazil

DIAMONDS from the São Luiz alluvial deposit, Mato-Grosso state, Brazil, contain a varied assemblage of inclusions with a mineralogy and geochemistry indicative of formation over a wide range of mantle depths. Two unusual groups of inclusions have been recognised (Wilding *et al.*, 1991; Harte, 1992; Harte and Harris, 1993). The first is an eclogitic suite, with assemblages dominated by both normal- and high-silica garnet with associated clinopyroxene. These are thought to represent samples of mantle material with a range of depth of origin down to approximately 400km. The second suite contains inclusions of ferropicrinite–magnesiowustite solid solution compositions indicative of lower mantle conditions (> 650km) (Ringwood, 1982; Scott-Smith *et al.*, 1984).

As part of a study of the inclusion suite in diamonds from São Luiz, a highly chromian corundum (containing over 8 wt. % Cr₂O₃) has been recovered. Corundum is a common accessory mineral in eclogite–grosopydite mantle xenoliths (Dawson and Carswell, 1990), and is stable over a wide range of mantle conditions (Gasparik, 1984; Harley and Carswell, 1990). Kornprobst *et al.*, (1990) described corundum in clinopyroxene–garnet peraluminous eclogitic pyroxenites from the Beni Bousera ultramafic massif, Morocco. Although rare, corundum and corundum xenoliths (Mazzone and Haggerty, 1989) which appear to be related to alkemites, may contain up to 75%

corundum by mode. The only other corundum inclusion so far found, from a cut diamond of unknown origin (Meyer and Gübelin, 1981), was red and contained 1.30 wt. % Cr₂O₃ (see Table 1), and was assigned to the eclogite suite of inclusions because of the association of corundum in eclogite and grosopydite xenoliths.

The São Luiz corundum inclusion comes from a Type II diamond (one which contains no nitrogen, normally a common atomic component in diamond) with a variable $\delta^{13}\text{C}$ (–11.56 to –15.21 against the PDB reference). The inclusion is red, subhedral, approximately 100 μm long and chemically homogeneous. Analyses were performed on a Cameca Camebax Microbeam Electron Microprobe instrument at the Department of Geology and Geophysics, University of Edinburgh. Standards used are a selection of metals, silicates and natural oxides and corrections for matrix effects are made using an on-line $\Phi(\rho z)$ correction program. Analyses were performed for the elements Si, Ti, Al, Cr, Fe, Mn, Mg, Ca, Ni, Na and K at an accelerating voltage of 20 kV and a beam current of approximately 20 nA. An average analysis ($n=8$) is given in Table 1, along with several corundum and chrome-rich corundum (ruby) analyses from the literature. Corundum is a trigonal oxide, typically containing in excess of 97 wt. % Al₂O₃. Chrome-bearing corundum is known as ruby, while Ti- and Fe-bearing varieties are referred to