A sulphur isotope study of iron sulphides in the Late Precambrian Dalradian Easdale Slate Formation, Argyll, Scotland

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Abstract

Pyritic slates from the late Precambrian, Middle Dalradian Argyll Group Easdale Slate Formation, contain mainly quartz, muscovite and chlorite with variable amounts of dolomite, albite and paragonite. Slates from Easdale Island and Cuan Ferry contain pyrite porphyroblasts with $\delta^{34}S = +12$ to $+16‰$. The pyrite grew during a post-tectonic retrogressive event at the expense of pyrrhotine which formed during the main regional metamorphism of the Grampian orogeny by reduction of diagenetic pyrite. Slate from Oban contains abundant diagenetic framboidal pyrite and small syn-tectonic pyrite porphyroblasts with $\delta^{34}S = +22‰$. This pyrite was not all reduced to pyrrhotine on metamorphism so there was little retrogressive growth of pyrite. Metamorphism appears to have homogenized local (cm scale at least) isotopic inhomogeneities and preserved an average seawater-sulphate–sulphide isotopic fractionation value. Middle Dalradian seawater-sulphate had a $\delta^{34}S$ value of about $+35‰$, so the small fractionations are appropriate for bacteriogenic reduction in bituminous sediments, the heavier sulphide in the case of the Oban slate indicating more rapid reduction of sulphate. Lower Dalradian Appin Group, Ballachulish slate contains pyrite with $\delta^{34}S = +15 \pm 2‰$ and is best interpreted as forming in the same manner as the Easdale slates of Easdale Island and Cuan Ferry; the sharp increase in late Precambrian ocean-sulphate sulphur isotope signature from $+15$ to $> +30‰$ therefore occurred by Lower Dalradian Appin Group times.

KEYWORDS: sulphur isotopes, iron sulphide, Dalradian, Argyll, Scotland.

Introduction

THIS study of Middle Dalradian Easdale slates was undertaken to provide a comparison with Lower Dalradian Ballachulish slates and to complement studies of the mineralized Middle Dalradian Ben Eagach Schist. The general aim of this on-going study is to investigate the genesis of iron sulphides in mineralized and unmineralized metasediments in the Dalradian terrain of Scotland.

Pyritic and graphitic slates have long been considered to represent regionally metamorphosed anoxic argillaceous sediments. The iron sulphide is considered to have formed on bacterial reduction of dissolved sulphate by anaerobic bacteria while the graphite represents former organic matter in the sediments. Textural and isotopic studies (Hall, 1982; Hall *et al.*, 1987) of late Vendian (Lower Dalradian) Appin Group Ballachulish slates led to the conclusion that abiological reduction of calcium sulphates is an alternative route for sulphur fixation as iron sulphide; in this case the sulphur isotopic signature of contemporaneous seawater would be inherited by the iron sulphide, whereas sulphide produced by syndiagenetic bacterial reduction would be expected to give sulphur isotope values ($\delta^{34}S$) averaging at least 15‰ lighter and possibly attaining 60‰ lighter than the sulphur of contemporaneous seawater. Although textural and geological considerations support an inorganic mechanism for iron sulphide production in the Ballachulish slates (Hall, 1982), sulphur isotope evidence was inconclusive (Hall *et al.*, 1987), the main reason being that the isotopic signature of

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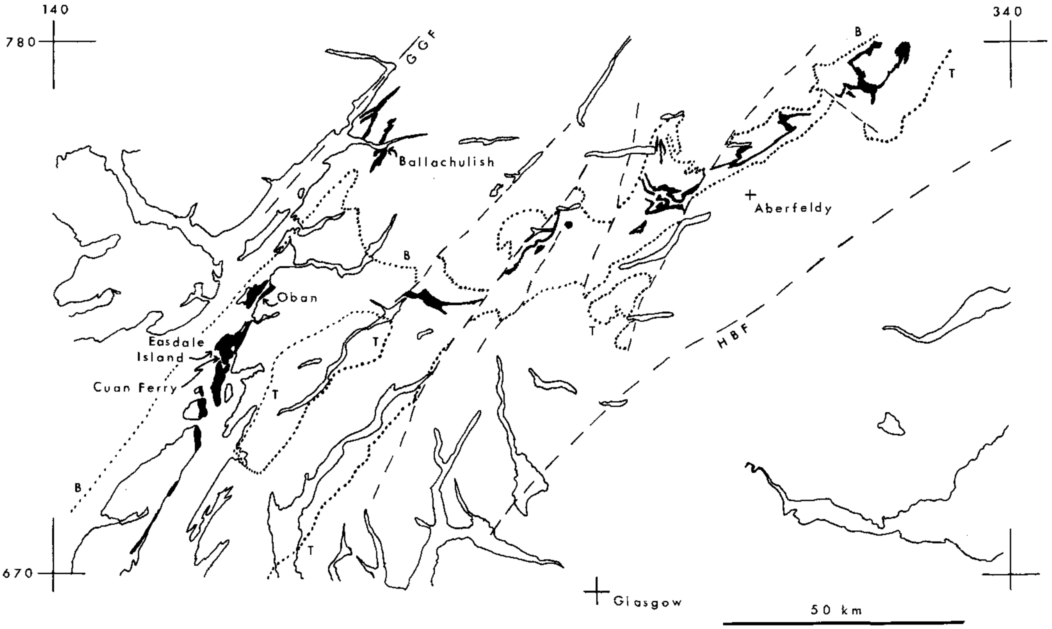


FIG. 1. Map of south-west Scottish Highlands showing localities discussed in the text. The Middle Dalradian, Argyll Group outcrop runs northeast-southwest through the Highlands and is indicated by the dotted lines (B = bottom of sequence, T = top of sequence). Graphitic slate and schist lithologies are particularly abundant in the areas shaded black; this is the Easdale sub-group of the Argyll Group and represents the Easdale slates in the west and the Ben Eagach schist in the central Highlands. The lithologically similar Ballachulish sub-group of the Lower Dalradian, Appin Group is also shaded black and is shown only close to Ballachulish. The synsedimentary baryte mineralization in the Ben Eagach graphitic schist occurs north of Aberfeldy. The Dalradian terrain of Scotland lies between the Highland Boundary Fault (HBF) and the Great Glen Fault (GGF). Major NNE-SSW sinistral strike-slip faults of *c.* 400 Ma are also shown.

Lower Dalradian seawater is unknown. Also, the late Precambrian ocean-sulphate sulphur isotopic signature possibly migrated during early Dalradian times from around +15‰ to 30‰ (Claypool *et al.*, 1980). The narrow range of sulphur isotope values for the Ballachulish slates, +12 to +16‰ was therefore taken to represent either Lower Dalradian seawater or diagenetic bacteriogenic sulphide with isotopic values homogenized by regional metamorphism to at least 15‰ less than seawater of +30‰ or more (Hall *et al.*, 1987).

The Easdale Slate Formation is stratigraphically younger than the Ballachulish Slate Formation and is approximately contemporaneous with the Middle Dalradian Ben Eagach Schist Formation of Perthshire to the east (Fig. 1). Dalradian stratigraphy has recently been reviewed by Anderton (1985). There is strong evidence that Middle Dalradian seawater had a sulphur isotope value of +35‰; the Ben Eagach Schist hosts large stratiform baryte deposits near Aberfeldy and the baryte inherited its sulphate sulphur isotopic signature from local seawater (Pattrick *et al.*, 1979; Willan and Coleman, 1983) when a hydrothermal solution with dissolved barium was debouched into the Dalradian sea (Russell *et al.*, 1984). Abundant pyrite associated with the baryte is also isotopically heavy ($\delta^{34}S > +25$‰; Willan and Coleman, 1983) as expected if hydrothermal sulphide forms by inorganic reduction of seawater sulphate in a hydrothermal system at depth in the Earth's crust (Ohmoto and Rye, 1979). It is noteworthy that sulphates in the early Cambrian K-feldspar-rich dolomites of northwest Scotland also have heavy values in celestite, +31‰ (Allison and Russell, 1985). Study of the Easdale Slate Formation was therefore undertaken with the knowledge that the $\delta^{34}S$ value of seawater was probably about +35‰.

Localities sampled

The distribution of the Middle Dalradian Easdale Slate Formation and the stratigraphically equivalent Ben Eagach Schist Formation is shown in Fig. 1. Iron sulphides, especially pyrrhotine, are very susceptible to weathering, so suitable collecting sites are mostly restricted to quarries, recent road-cuttings and some shore sections. The Easdale slate has been quarried on Easdale Island and this formed the principal sampling locality. Samples were also obtained from the shore near Cuan Ferry, where recent blasting had taken place, and a small disused quarry face in Oban. At each locality a search was made for samples representative of the range of occurrence of the iron sulphides. Particular care was taken to locate pyrrhotine.

At Easdale Island and Cuan Ferry the Easdale Slate Formation consists almost entirely of black slates with thin dark dolomitic limestones and a few thin quartzitic beds. Cleavage dips 45–65° east-southeast and is axial-planar to west-facing open recumbent folds. More details of the local geology can be found in Peach *et al.*, 1909. Pyrite is common in the rocks, usually as mm- to cm-sized cubes but occasionally as granular aggregates or stringers. The pyrite is enriched in some horizons, for example within slightly coarser grained slates at Cuan Ferry but also within some typical fine-grained slates.

At the Oban locality fine-grained pyrite occurs as thin mm- to cm-thick layers and as coarser disseminated grains (mm-size) in fine black slate with a poorly developed cleavage.

Analytical techniques

Polished thin sections and blocks were prepared for petrographic examination and energy dispersive X-ray microanalysis (EDX) using a scanning electron microscope (SEM). Powder X-ray diffraction spectrometry (XRD) was used to identify the major components of the matrix as well as to check the purity of separated iron sulphides. Pyrite cubes were separated by hand picking. Magnetic separation failed to provide sufficient pyrrhotine for sulphur isotope analysis. The fine disseminated pyrite in the Oban slate was concentrated using heavy liquids.

Only minor amounts of silicate or carbonate impurity were present in samples used for isotopic analysis at the SURRC, East Kilbride. The technique of conversion to SO_2 is such that non-sulphide contamination presents little problem to the calculation of the sulphur isotope ratio. The gas, SO_2 was produced by reacting an intimate mixture of the sulphide with excess Cu_2O at 1070 °C (after Robinson and Kusakabe, 1975). This usually failed to produce a 100% yield, because of the minor host rock contamination. However, the procedure provided routinely consistent 100% yields from identical combustion of the internal laboratory sulphide standard. The prepared gas was analysed on a 12 cm model double collector mass spectrometer (Isospec 44 modified for SO_2). The ion beams monitored are m/z 66 and 64, with standard correction factors applied to raw $\delta^{34}S$ ratios (e.g. Craig, 1957). The entire instrument is operated at 110 °C. Within run precision of $\delta^{34}S$ ratios is typically $\pm 0.05‰$ ($2\ \sigma$ 10) or better, with a long term reproducibility (including sample preparation) of $\pm 0.27‰$ ($1\ \sigma$, based on 20 analyses of the internal standard). All $\delta^{34}S$ results are reported in ‰ relative to Canyon Diablo troilite. Standards analysed during this study were: Soufre du lac (a pure sulphur standard, supplied by R. Gonfiantini, IAEA) giving a $\delta^{34}S$ of $+16.67‰$; SL-277-6 (a McMaster standard silver sulphide, supplied by H. P. Schwarcz, McMaster University) giving $+22.97‰$; and CP1 (a British Geological Survey standard chalcopyrite, supplied by M. L. Coleman), which has an isotopic value of $-4.56‰$ and was used as our routine internal standard. Calculated yields are given with the results in Table 1. The low yield of sample OB2 is due to abundant impurity slate; the result is considered to be satisfactory because of the good reproducibility of this analysis with the concentrated sample (082).

Mineralogy and petrography

Details of the lithology and mineralogy determined by XRD are given for each sample of slate in Table 1.

The slates from Easdale Island are dominated by quartz, muscovite and chlorite and contain variable amounts of dolomite and feldspar. Paragonite was identified by XRD only in slates from Easdale Island. In all cases the major XRD peak of feldspar had the characteristics of that of albite; there was no indication of significant K-feldspar or calcic plagioclase. The presence of albite was corroborated by SEM EDX microanalysis. Petrographic study of representative Easdale Island slates revealed a diverse micromineralogy. The main fabric is controlled by mica, chlorite and quartz with grain sizes typically $< 100\ \mu m$. The weak schistosity parallels lithological variations and has been folded and locally sheared to give a variable crenulation and spaced crenulation cleavage. Minor minerals seen in the matrix of the slates include rutile, tourmaline, graphite and apatite. Large elongate masses (up to $1000 \times 3000\ \mu m$) consist typically of coarse polygonal siderite enclosed in coarse polygonal quartz. Scattered micro-inclusions in these masses are pentlandite, pyrrhotine and chalcopyrite and in some cases the amount of pyrrhotine exceeds that of siderite. These masses appear to be texturally early, certainly pre-crenulation and are probably synsedimentary but modified during the development of the first metamorphic fabric. Pyrite porphyroblasts are clearly post-crenulation (Fig. 2) and are typically 1–3 mm in size although some embryonic pyrite porphyroblasts were noted. The pyrite truncates the fabric of the matrix and quartz/carbonate masses and often contains relict inclusions of slate (Fig. 2). Micro-inclusions ($< 20\ \mu m$) in the pyrite are of pyrrhotine, chalcopyrite, sphalerite and galena. It is noteworthy that no iron-bearing Fe–Ti–O phases such as magnetite or ilmenite are present. There is some texturally late fine granular pyrite which occurs in

Table 1 Results of sulphur isotope analysis
The mineralogical composition of each sample
is based on whole-rock X-ray diffraction analysis

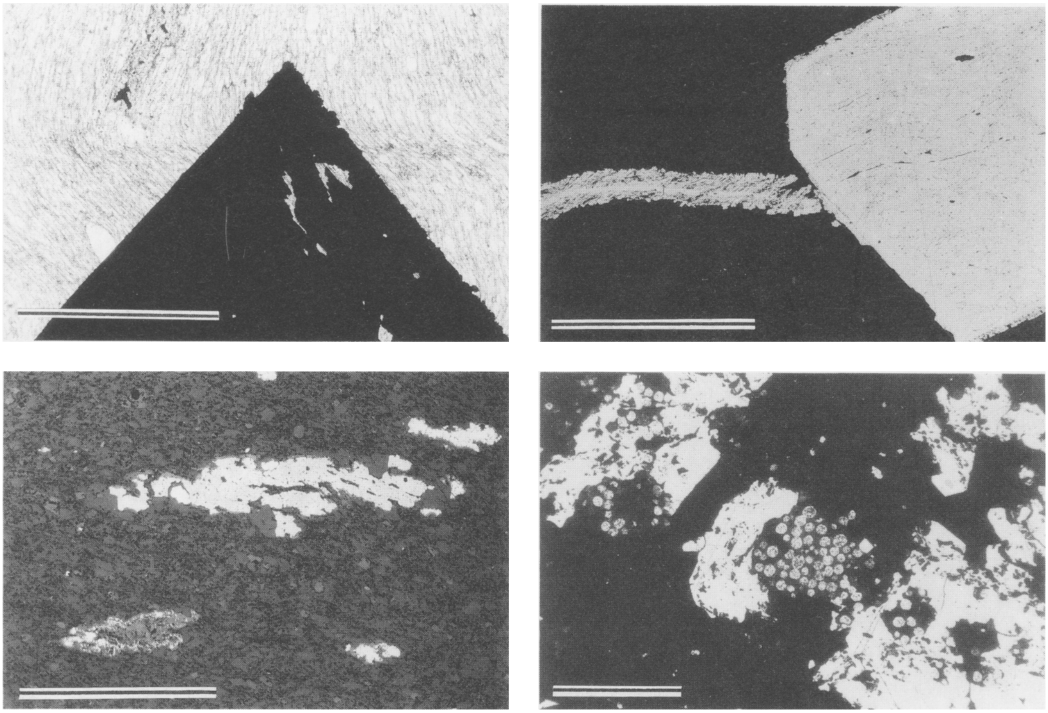
Sample	Lithology	pyrite	yield	$\delta^{34}S$
EI1	GREY PSAMMITIC SLATE major: quartz, chlorite, muscovite, dolomite minor: paragonite, feldspar	abundant small cubes (0.5–1mm)	93%	+12.4‰
EI2	CRENULATED BLACK SLATE major: quartz, muscovite, chlorite, feldspar minor: paragonite, dolomite	abundant cubes (1–2mm)	62%	+13.0‰
EI3	CRENULATED GREY SLATE major: quartz, muscovite, chlorite, feldspar minor: paragonite	cubes (2mm)	101%	+13.9‰
EI4	GREY SLATE major: quartz, muscovite, chlorite, feldspar minor: paragonite, dolomite	abundant cubes (2–4mm)	99%	+14.1‰
CF1	*CRENULATED GREY SLATE* major: dolomite, muscovite, quartz minor: feldspar, chlorite	scarce cubes (3–4mm)	100%	+15.6‰
CF2	CRENULATED GREY LAMINATED SLATE major: quartz, muscovite, chlorite, dolomite, feldspar	abundant cubes (1–2mm)	80%	+13.2‰
CF3	CRENULATED DARK GREY SLATE major: quartz, muscovite, chlorite minor: feldspar, dolomite	scattered aggregates (2–4mm) of cubes (<1mm)	74%	+12.7‰
CF4	CRENULATED PALE GREY SLATE major: quartz, muscovite, chlorite, feldspar minor: dolomite	scattered cubes (2–3mm)	96%	+15.2‰
CF5	LAMINATED COARSE/FINE SLATE major: quartz, dolomite, muscovite, feldspar minor: chlorite	skeletal crystals (2–5mm)	94%	+14.6‰
CF6	CRENULATED DARK GREY SLATE major: dolomite, muscovite minor: quartz, feldspar	scattered cubes (2–3mm)	99%	+14.8‰
OB1	BLACK SLATE major: muscovite, feldspar minor: quartz, chlorite, pyrite	concentrate of framboids, granules and fine crystals	79%	+22.3‰
OB2	BLACK *SLATE*, PYRITIC LAYER major: muscovite, feldspar minor: quartz, chlorite, pyrite	framboids and fine crystals in slate	39% (low yield)	+21.7‰

Easdale Island (EI); Cuan Ferry (CF); Oban (OB).

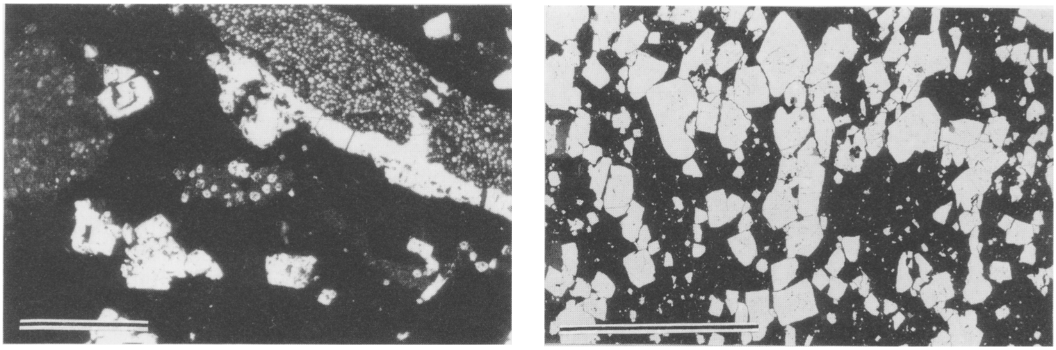
small pockets, in open cleavage spaces and occasionally as sporadic thin overgrowths on pyrite porphyroblasts (Fig. 3). There appears to be no early primary pyrite or other sulphides such as granules or framboids in the slates.

The Cuan Ferry samples are mineralogically and texturally similar to the Easdale Island samples. A variety of elongate quartz, carbonate and sulphide-bearing bodies was again noted. Shapes range from rounded to lozenge-shaped and several resemble the swallow-tail twins of gypsum. Pyrite porphyroblasts resemble those in the Easdale Island samples. The Cuan Ferry samples all contain more late 'spongy' pyrite and appear to be more weathered than the Easdale Island samples. This very late pyrite infills fractures, forms overgrowths on pyrite porphyroblasts, forms porphyroblastic masses and occasionally partially replaces coarse carbonate (Fig. 4). Pyrrhotine blebs, although protected by quartz are often converted to 'spongy' pyrite or weathered out. Limonite tends to be associated with this late pyrite.

The slate from Oban is very rich in fine muscovite with a weak fabric approximately normal to compositional layering and a late weak crenulation and spaced fracture cleavage at an intermediate angle. Samples contain abundant fine-grained pyrite associated with graphite and ranging in concentration from a typical 5% to about 20% in mm- to cm-thick layers which can be seen clearly in hand specimen. Framboids and granules of pyrite (5–50 μm) are present throughout the slate and in small elongate bodies which are almost entirely framboidal pyrite (Figs. 5, 6). These bodies are often fragmented and variably enveloped in relatively coarse quartz or pyrite. Pyrite porphyroblasts (100–300 μm) often contain ghost relict inclusions of framboids as well as micro-inclusions of sphalerite, chalcopyrite and scarce pyrrhotine. Scarce sphalerite and associated chalcopyrite occasionally reach a grain size of 100 μm. The coarser pyrite tends to be elongated parallel to the early weak penetrative fabric (Fig. 7) and both the fine and coarse pyrite tend to be influenced by the late



FIGS. 2–5. FIG. 2 (*top left*). Transmitted-light photomicrograph of crenulated black Easdale Island slate (sample E12) showing microfold in crenulated slaty fabric truncated by late pyrite porphyroblast (black) which contains relict inclusions of slaty matrix. Note the elongate mass with abundant opaque micro-inclusions, mainly pyrrhotine. Scale bar 1000 μm. FIG. 3 (*top right*). Reflected-light photomicrograph of crenulated black Easdale Island slate (sample E12) showing relict folded micro-fabric in pyrite (white) and late 'spongy' pyrite as fracture infill and marginal replacement and as thin overgrowths on the pyrite porphyroblast. Scale 1000 μm. FIG. 4 (*bottom left*). Reflected-light photomicrograph of crenulated pale grey Cuan Ferry slate (sample CF4) showing an irregular elongate mass containing late pyrite (white) and a rim of quartz (grey). A smaller elongate body contains a core of siderite (grey) with a thin irregular rim of pyrite. Scale 1000 μm. FIG. 5 (*bottom right*). Reflected-light, oil-immersion photomicrograph of Oban slate (sample OB1) showing pyrite framboids (white, round) being enveloped in later pyrite crystals. Scale 100 μm.



FIGS. 6 and 7. FIG. 6 (*left*). Reflected-light, oil-immersion photomicrograph of Oban slate (Sample OB1) showing elongate masses of fine granular and framboidal pyrite (white) and later coarse pyrite. Scale 100 μm. FIG. 7 (*right*). Reflected-light photomicrograph of pyritic layer in Oban slate (sample OB2) showing abundant pyrite crystals (white) with a weak elongation and preferred orientation. The mottled texture in many pyrite crystals represents relict framboids. Scale 500 μm.

crenulation cleavage; micro-shear zones rotate mica and graphite grains as well as pyrite. Pressure solution probably accompanied this process that gives rise to the spaced cleavage. It is noteworthy that pyrite framboids have remained undeformed in the slate. The coarsest mica, chlorite, carbonate and pyrite occur in sporadic segregation veins or metamorphic 'sweat-outs'. This and later cross-cutting veins were not sampled for isotopic study. There is no evidence of significant pyrite growth, other than sporadic late 'spongy' pyrite, in the body of the slate after the crenulation event.

In summary, the Easdale Island and Cuan Ferry slates are mineralogically and texturally very similar and they both contain late pyrite porphyroblasts. They differ in that the Easdale Island slates contain minor paragonite while the Cuan Ferry slates tend to be coarser-grained and more weathered. The Oban slate, on the other hand, is very rich in muscovite and contains mainly texturally early pyrite.

Sulphur isotope analyses

The results of the sulphur isotope analyses are given in Table 1 and summarized in Table 2. There is no significant difference in the isotopic values of the Easdale Island and Cuan Ferry pyrites, the values falling within the narrow range of +12 to +16‰. The Oban pyrite, sampled as a concentrate, contains sulphur which is significantly isotopically heavier at +22‰.

Table 2 Summary of sulphur isotope data ($\delta^{34}S$) discussed in text

Middle Dalradian, Argyll Group, Easdale Sub-Group

	pyrite	pyrrhotine	seawater sulphate
Easdale Island, Cuan Ferry	+12 to +16‰	–	?
Oban	+22‰	–	?
Aberfeldy	–	–	+35‰

Lower Dalradian, Appin Group, Ballachulish Sub-Group

	pyrite	pyrrhotine	seawater sulphate
Ballachulish, (East Laroch Quarry)	+15‰	+14‰	?

The Easdale Island and Cuan Ferry slates resemble the Ballachulish slates, but the latter do not contain feldspar or paragonite, and pyrrhotine is much more evident in the latter in the form of disseminated blebs and is concentrated in layers. The early pyrrhotine at Easdale Island and Cuan Ferry could, like that at Ballachulish (Hall, 1982), be interpreted as resulting from thermal inorganic reduction of sedimentary gypsum, perhaps washed in from a shallow-water sabkha-type environment. The carbonate bodies might also represent clasts of early diagenetic carbonate from a similar source. The pyrite ($\delta^{34}S$ = +15‰ ± 2) has clearly grown at the expense of pyrrhotine ($\delta^{34}S$ = +14‰ ± 2) at Ballachulish at a late retrogressive stage of metamorphism (Hall *et al.*, 1987) and this genetic model is appropriate for the pyrite in the Easdale Island and Cuan Ferry slates. Late 'spongy' pyrite is more abundant at Easdale Island and especially Cuan Ferry and this is probably the result of a deep weathering process of sulphide enrichment. It is possible that the range in isotopic values of the hand-picked pyrite crystals is due to admixture of different generations of pyrite but a micro-analytical technique for sulphur isotope analysis will be necessary to test this possibility. In any case, the range is too small to affect significantly the present general interpretation given below.

Genesis of the iron sulphides

The genesis of the pyrite in the Easdale Island and Cuan Ferry slates is similar to that of the pyrite in the Ballachulish slates and can be summarized as follows. The sediments formed in an environment with available seawater sulphate, probably some detrital sulphate, organic matter and available iron, all contributing to the formation of bacteriogenic pyrite on diagenesis. The diagenetic formation of pyrite in such organic-rich sediments has been reviewed recently by Fisher and Hudson (1987). Regional metamorphism during the Grampian orogeny attained greenschist facies conditions and was accompanied by progressive reduction so that disseminated pyrite was reduced to pyrrhotine by a reaction of the type (after Thompson, 1972):

$$2FeS_2 + C + (2FeO)_{silicates} \rightarrow 4FeS + (CO_2)_{fluid}.$$

Such reactions and the role of the metamorphic fluid in closed and open systems have been discussed by Ferry (1981) and reviewed in Hall (1986). The iron sulphide would have been remobilized locally during this process, migrating as metamorphic fluids were expelled from the rocks. Sites suitable for pyrrhotine precipitation would have included pressure shadows, detrital carbonates, graphite or near sources of available iron. Any detrital sulphate would also have been reduced abiologically to provide some isotopically heavy sulphur. Pyrite porphyroblasts grew after a regional crenulation event. This is taken as evidence of relatively oxidizing fluid, probably CO_2-rich, entering microfractures initiated on postmetamorphic uplift. This retrogressive event thus led to further local remobilization of pyrrhotine to form the pyrite porphyroblasts by the reaction (Hall, 1986):

$$8FeS + 5CO_2 + 2H_2O \rightarrow 4FeS_2 + CH_4 + (4FeCO_3)_{solution}.$$

The reactions involving iron sulphides and C–H–O fluids are redox reactions which are driven by the fact that carbon becomes increasingly reducing relative to iron sulphide (and silicate) reactions with increasing temperature (see Hall, 1986, for a detailed explanation). Thus progressive metamorphism led to general reduction whereas retrogressive metamorphism led to general oxidation.

Pyrite porphyroblasts that grow on retrogressive metamorphism would be expected to inherit a sulphur isotope value which is homogenized by local remobilization and re-equilibration with local metamorphic fluid. The present narrow range in values for the pyrite, $\delta^{34}S = +12$ to $+16‰$, therefore probably represents a former greater range in the original sedimentary sulphur reservoir. Bacteriogenic sulphate reduction is likely to produce a seawater-sulphate–sulphide fractionation of at least 25‰ in organic-rich lithologies (Fisher and Hudson, 1987) with the lowest fractionation occurring in restricted environments. The sulphur isotope values of the Easdale Island and Cuan Ferry pyrites are therefore appropriate for sulphide which formed mainly by bacteriogenic reduction in an environment with limited sulphate replenishment (accepting $\delta^{34}S$ of the seawater $= +35‰$) so that a small sulphate–sulphide fractionation resulted (20‰). The detrital sulphate may have contributed slightly to an increase in the isotopic value of the pyrite.

The pyrite in the Oban slate has not undergone total reduction but only some remobilization. Preservation of early diagenetic pyrite textures, the best recorded from the Dalradian, probably results from there being insufficient local metamorphic fluid to reduce all the pyrite. In other words, the abundance of the pyrite buffered the local metamorphic fluid to a state of higher sulphur fugacity. The syntectonic growth of pyrite crystals, often incorporating framboidal pyrite, is evidence that iron and sulphur were taken into solution but reprecipitated locally as pyrite. That this was accomplished by reduction of pyrite to give FeS in solution is indicated by the presence of scarce pyrrhotine micro-inclusions in the syntectonic pyrite. There was no significant retrogressive growth of pyrite porphyroblasts because the main metamorphism failed to produce abundant pyrrhotine.

The Oban pyrite could only be sampled in bulk because of the small grain size, so any range in sulphur isotope values will be concealed. However, the two samples gave almost identical values and it is probable that there was local re-equilibration and homogenization of the sulphur isotope values as pyrite was taken into solution and reprecipitated during metamorphism. The relatively heavy $\delta^{34}S$ value of $+22‰$ indicates that more complete reduction of seawater sulphate took place on bacteriogenic reduction (Rye and Ohmoto, 1979) than in the case of the Cuan Ferry and Easdale Island slates. The diagenetic environment must have been amenable to sulphate reduction with an ample supply of sulphate, organic matter and iron, although it is noteworthy that the Oban slate is muscovite-, rather than chlorite-rich. It is surprising therefore that the isotope values are not much lighter; since fractionation is also influenced by kinetic factors such as reaction rate and is well known to be inversely proportional to reaction rate, it seems likely that the isotopically heavy nature of the Oban pyrite is due to a small fractionation caused by rapid bacteriogenic sulphate reduction. An alternative explanation is the possibility of local isotopically heavy seawater.

Implications of the results

It is clear from this study of the Easdale slates that it is incorrect to generalize about the isotopic behaviour of iron sulphides in metasediments. The iron sulphides have behaved quite differently in slightly different lithologies in similar metamorphic environments. In addition, it is apparent that homogenization of isotopic values is likely to take place if sulphides are remobilized on metamorphism and this may help interpretation of the original diagenetic environment by reducing original small-scale variations.

The isotopic analyses do not support textural indications that early pyrrhotine in the Easdale Island and Cuan Ferry slates might have formed mainly after detrital sulphate. This conclusion makes it unlikely that the Ballachulish pyrrhotine sulphur came entirely from original sulphate. If this had been the case and the $+15‰$ pyrite values had represented contemporaneous seawater then we would have to account for the lack of isotopically very light sulphur in the Dalradian and the Oban results would have been particularly anomalous. It is therefore concluded that Lower Dalradian seawater was similar isotopically to Middle Dalradian seawater with $\delta^{34}S = +35‰$ and the Late Precambrian sharp migration of ocean-water sulphate $\delta^{34}S$ value of around $+15‰$ to above $+30‰$ had taken place before the start of Lower Dalradian Appin Group sedimentation.

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