

## Sm–Nd evidence for the age and origin of a Mississippi Valley Type ore deposit

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**MISSISSIPPI Valley Type (MVT) ore deposits represent the relatively common product of large-scale fluid transport in the continental lithosphere, yet the models for their genesis have been more controversial and unconstrained than those of any other class of giant ore deposit<sup>1,2</sup>. Here we show that Sm–Nd isotope data can be used to determine the age and origin of an MVT deposit. Sm–Nd data for fluorites from the North Pennine orefield are difficult to explain unless some of the mineralization is of Mesozoic rather than the traditionally accepted Palaeozoic age. Furthermore, the Nd and Sr isotopic compositions of the fluorites do not support a variety of recent models that include derivation of the components from the mantle, the Lower Palaeozoic basement or the underlying buried granite which served to focus the flow of hydrothermal fluids.**

The North Pennine orefield (or more strictly, that associated with the Alston block) is zoned above the buried 400-Myr-old Weardale granite<sup>3–6</sup> and has a central fluorite zone (600 km<sup>2</sup>) that gives way abruptly to a barium-minerals zone<sup>7–10</sup> (Fig. 1). The mineralization occurs chiefly in narrow fissure veins in flat-lying Lower Carboniferous limestones, shales and sandstones, but also extends into the Upper Carboniferous sediments and the underlying Lower Palaeozoic basement. Mineral assemblages comprise lead–zinc–iron sulphides, barite, fluorite, ankerite and quartz with minor chalcopryrite, primarily in veins but with many replacement features. The sulphides show a similar zone pattern with a localized central chalcopryrite–pyrite–pyrrhotite assemblage passing outwards into a galena–sphalerite assemblage<sup>11,12</sup>. Maximum temperatures of ore deposition based on fluid-inclusion homogenization temperatures for early quartz indicate 190–230 °C, although most of the fluorite seems to have been deposited over a slightly lower temperature interval of 90–160 °C (refs 12–14). The compositions of the ore fluids approximate NaCl–CaCl<sub>2</sub> brines containing 19–23 wt% NaCl equivalents with Na/Ca ratios of 1.5–3.5 (ref. 13).

Data for twenty samples of fluorite from three veins (Slitt Vein, Ferneygill Vein and Groverake Vein) together with six samples of the underlying Weardale granite, Carboniferous sediments and Whin Sill obtained from the Rookhope borehole are presented in Table 1. Compared to other UK hydrothermal fluorites, the North Pennine fluorites are exceedingly rich in rare-earth elements (REEs) (up to 800 p.p.m. total REEs) and have high Tb/La ratios, typically 0.1–0.5 (ref. 13). Consequently, nearly all the fluorites have Sm/Nd ratios that are greater than (up to twice) chondritic, which allows for important constraints to be placed on the timing of mineralization. The Groverake and Ferneygill Vein fluorites have particularly high Sm/Nd ratios and are especially useful in this regard. Sm–Nd is therefore potentially superior to other isotopic methods such as U–Pb and Rb–Sr in that a major mineralization phase displays relatively large fractionations in parent/daughter ratio.

The  $\epsilon_{Nd}$  values of the fluorite samples are displayed as a function of time in Fig. 2. The fields for Palaeozoic sediments of England and Wales<sup>15</sup> and the northern England Lower

Palaeozoic granites, namely Weardale (Table 1), Shap, Eskdale and Cheviot<sup>16</sup>, are also shown. The latter define a reasonably uniform field with relatively high  $\epsilon_{Nd}$  compared with the Palaeozoic sediments and fluorites. The Whin Sill (a quartz tholeiitic Permo-Carboniferous intrusion thought to be related to a failed rift of the European continent at 290 Myr (refs 17, 18)) has Nd isotopic compositions close to chondritic. This is far more radiogenic than that of the fluorites and immediately rules out the possibility of these tholeiites representing a source for the Nd in the mineralizing fluid.

The Nd isotopic compositions of the fluorites overlap those of the granites only at ages <100 Myr (Fig. 2). Hence, if the Nd were extracted in approximate isotopic equilibrium with its source rocks, the REEs can have been derived only from the underlying Weardale Granite, as suggested by Brown *et al.*<sup>19</sup>, if the mineralization is  $\leq$ 100 Myr old. This seems to be somewhat unlikely because there is no significant mineralization in rocks of Jurassic or younger age anywhere in the United Kingdom. It is also difficult to reconcile with some older K–Ar and <sup>40</sup>Ar–<sup>39</sup>Ar ages for hydrothermal clays of up to ~280 Myr (refs 20, 21). If the Nd in the fluorites was derived in isotopic equilibrium with Lower Palaeozoic sediments, the age of some of the mineralization has to be young, that is, <200 Myr in the case of the Groverake Vein, and <150 Myr in the case of the Ferneygill Vein. The data for the Upper Palaeozoic sediments impose similar constraints on the age of the fluorites except for the Carboniferous shale R110 (Table 1), which has unusually unradiogenic Nd. But even if such a shale contributed Nd to the fluorites, two of the Ferneygill fluorites are still no older than 220 Myr. The data for the Slitt Vein fluorites are far less conclusive in terms of age of the mineralization because of their lower Sm/Nd ratio.

Shepherd *et al.*<sup>13</sup> presented a Rb–Sr isochron age of 206 ± 9 Myr for inclusion fluids in quartz from the Great Sulphur Vein. The initial <sup>87</sup>Sr/<sup>86</sup>Sr of these inclusion fluids is virtually identical to the Sr isotopic compositions of the fluorites reported in Table 1. This, plus the similar fluid-inclusion chemistry, is most easily explained if the fluorite and quartz mineralizations are broadly co-genetic. We therefore consider that the most likely age for the fluorite mineralization is ~200 Myr, consistent with the Sm–Nd data presented above.

The Rb/Sr ratios of the North Pennine fluorites are so low (<0.01) that a genetic interpretation of the Sr isotopic compositions is insensitive to the exact age assumed for the mineralization. In Fig. 3, the Sr and Nd isotopic compositions of the North Pennine fluorites are shown, together with the fields of data for potential source reservoirs, assuming that the fluorites are 200 Myr old. The value of combining the Sr isotopic data

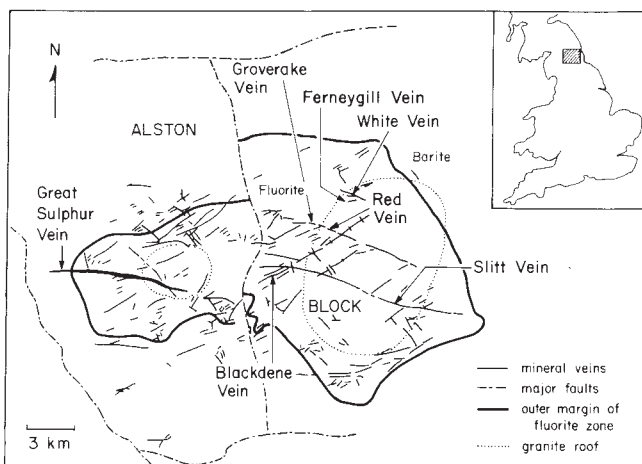


FIG. 1 Map of North Pennine orefield, showing locations of the veins that we sampled.

TABLE 1 Sm-Nd and Rb-Sr isotopic analyses of North Pennine fluorites and whole rock samples from the Rookhope borehole

Sample number	Locality	Lithology	Rb (p.p.m.)	Sr (p.p.m.)	$^{87}\text{Rb}/^{86}\text{Sr}$ (atomic)	$^{87}\text{Sr}/^{86}\text{Sr}$ (atomic)	$^{87}\text{Sr}/^{86}\text{Sr}$ at 200 Myr	Sm (p.p.m.)	Nd (p.p.m.)	$^{147}\text{Sm}/^{144}\text{Nd}$	$^{143}\text{Nd}/^{144}\text{Nd}$ $\pm 2\sigma$	$^{143}\text{Nd}/^{144}\text{Nd}$ at 200 Myr	$\epsilon_{\text{Nd}}$ at 200 Myr
North Pennine orefield													
B5	Slitt Vein	Fluorite	0.318	30.4	0.0303	0.71178 ± 6	0.71169	15.6	43.5	0.2172	0.51221 ± 2	0.51193	-8.9
B13	Slitt Vein	Fluorite	0.186	37.8	0.0142	0.71150 ± 10	0.71046	29.9	81.1	0.2232	0.51218 ± 2	0.51189	-9.6
B44	Slitt Vein	Fluorite	0.0729	53.1	0.00397	0.71138 ± 6	0.71136	38.6	92.8	0.2513	0.51223 ± 2	0.51190	-9.3
B53	Slitt Vein	Fluorite	0.121	28.8	0.0121	0.71094 ± 13	0.71090	6.25	13.3	0.2841	0.51228 ± 2	0.51191	-9.1
B75	Slitt Vein	Fluorite	0.165	41.6	0.0115	0.71139 ± 8	0.71136	3.72	12.0	0.1875	0.51220 ± 2	0.51196	-8.3
B11	Slitt Vein	Fluorite	0.101	35.4	0.00829	0.71091 ± 6	0.71089	9.49	17.9	0.3214	0.51232 ± 2	0.51190	-9.4
B48	Slitt Vein	Fluorite	0.244	44.9	0.0157	0.71166 ± 9	0.71161	25.2	71.0	0.2147	0.51218 ± 2	0.51190	-9.4
B74	Slitt Vein	Fluorite	0.238	60.3	0.0114	0.71360 ± 5	0.71356	7.64	30.0	0.1540	0.51202 ± 2	0.51182	-11.0
B3	Slitt Vein	Fluorite	3.85	30.0	0.372	0.71170 ± 4	0.71064	17.6	53.0	0.2009	0.51216 ± 2	0.51189	-9.5
B46	Slitt Vein	Fluorite	0.0877	41.1	0.00618	0.71149 ± 9	0.71147	26.9	70.9	0.2295	0.51219 ± 2	0.51189	-9.6
B50	Slitt Vein	Fluorite	0.0827	68.3	0.00350	0.71119 ± 6	0.71118	16.4	33.8	0.2936	0.51223 ± 2	0.51184	-10.5
929	Groverake Vein	Fluorite	0.144	41.5	0.0101	0.71092 ± 8	0.71089	14.6	21.9	0.4027	0.51229 ± 2	0.51176	-12.0
480	Groverake Vein	Fluorite	0.134	37.3	0.0104	0.71071 ± 12	0.71068	11.5	26.5	0.2611	0.51226 ± 2	0.51192	-9.0
853	Groverake Vein	Fluorite	0.122	65.9	0.00536	0.71069 ± 6	0.71068	15.1	33.4	0.2738	0.51227 ± 3	0.51191	-9.2
858	Groverake Vein	Fluorite	0.271	32.8	0.0240	0.71082 ± 17	0.71075	11.9	24.3	0.2972	0.51228 ± 3	0.51189	-9.6
933*	Ferneygill Vein	Fluorite						11.1	17.9	0.3763	0.51229 ± 1	0.51180	-11.3
943*	Ferneygill Vein	Fluorite						19.6	55.7	0.2125	0.51215 ± 1	0.51188	-9.9
949*	Ferneygill Vein	Fluorite						5.80	16.7	0.3494	0.51224 ± 1	0.51178	-11.7
951*	Ferneygill Vein	Fluorite						16.3	20.9	0.4712	0.51226 ± 1	0.51164	-14.4
1050	Ferneygill Vein	Fluorite	0.0851	40.7	0.00605	0.71142 ± 6	0.71142	15.8	22.0	0.4357	0.51221 ± 3	0.51164	-14.5
Rookhope borehole													
R105	2,554 ft	Granite	336	129	7.586	0.75273 ± 15	0.73115	3.55	17.4	0.1233	0.51214 ± 2	0.51198	-7.8
R107	1,330 ft	Granite	427	66.2	18.85	0.80331 ± 16	0.74969	3.23	16.5	0.1183	0.51209 ± 2	0.51193	-8.8
R108	1,200 ft	Limestone	1.42	424	0.00970	0.71073 ± 4	0.71070	0.395	1.45	0.1653	0.51207 ± 3	0.51185	-10.4
R110	1,000 ft	Shale	245	376	1.887	0.71823 ± 13	0.71286	8.85	49.4	0.1083	0.51173 ± 3	0.51159	-15.4
R111	847 ft	Dolerite	103	454	0.6570	0.70962 ± 8	0.70776	6.93	31.6	0.1326	0.51249 ± 2	0.51231	-1.3
R116	300 ft	Dolerite	22.1	444	0.1442	0.70655 ± 5	0.70614	6.65	28.4	0.1418	0.51260 ± 2	0.51241	+0.5

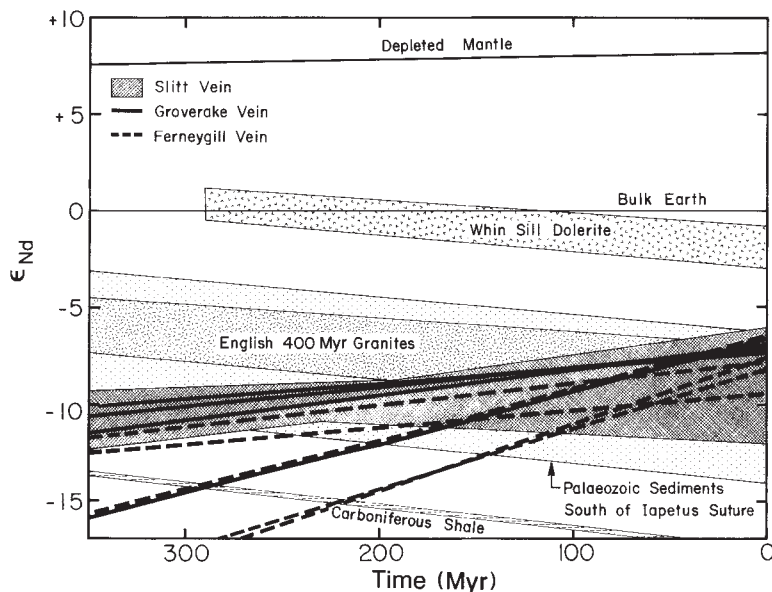
Rb, Sr, Sm and Nd were separated using standard ion-exchange procedures. All concentration measurements were performed using isotope dilution. Analyses marked with an asterisk in Table 1 were conducted at the University of Michigan using a VG Sector mass spectrometer as outlined elsewhere<sup>39</sup>. All other analyses were performed at the Scottish Universities Research and Reactor Centre, East Kilbride, on a VG Isomass 54E mass spectrometer as described elsewhere<sup>40</sup>.

with the Nd isotopic data is that it allows discrimination between potential source reservoirs that are not resolvable using Nd data alone. Although there is no very clear relationship between the Nd and Sr isotopic compositions of the North Pennine fluorites, the variations could reflect mixing of components from different reservoirs with different Sr/Nd ratios and isotopic compositions. The scatter observed does not support simple two-component fluid-mixing models, but rather suggests minor amounts of interaction between the fluid and a number of reservoirs. The North Pennine fluorites seem to have derived very little of their Nd or Sr (hence rare-earth and alkaline-earth budget) from the under-

lying Weardale granite, as has been advocated<sup>19</sup>. It is clear, however, that the Lower Carboniferous sediments are an ideal source reservoir for both Nd and Sr. The Sr isotopic compositions are important evidence in this respect because they distinguish the clastic-dominated black shale and turbidite Lower Palaeozoic successions from the carbonate-dominated platform and shelf Upper Palaeozoic successions with relatively unradiogenic Sr.

The chemical similarity between oilfield brines and the aqueous fluids trapped in fluid inclusions<sup>22,23</sup> has led to basin-brine expulsion models<sup>24-28</sup> for Mississippi Valley Type

FIG. 2 Plot of  $\epsilon_{\text{Nd}}$  as a function of time for North Pennine fluorites and main crustal reservoirs in central Britain. Data from Table 1 and refs 15 and 16.



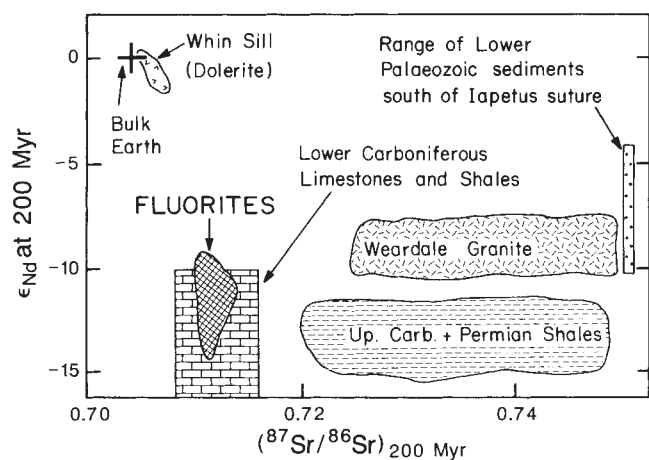


FIG. 3 Plot of  $\epsilon_{Nd}$  against  $^{87}Sr/^{86}Sr$  at 200 Myr for North Pennine fluorites and potential source reservoirs. Data from Table 1 and refs 13, 15 and 16.

deposits, which supersede the granite-related magmatic models of 20 years ago. The fluorite-rich Rossiclare- and Pennine-type deposits have proved distinctive and especially enigmatic<sup>2</sup>, however, not least because of the problem of generating fluorine-rich basin brines at temperatures of up to 200 °C. For these, the older magmatic hypotheses have been remodelled to incorporate rifting or crypto-volcanic structures and the proximity of alkaline magmatism at depth to account for fluorine<sup>29,30</sup>. For the North Pennine orefield, various basin-brine expulsion models, or refinements thereof, have been proposed<sup>7,13,19,31,32</sup>, although the difficulty in identifying an unequivocal source for the fluorine has led to hybrid models that combine aspects of both basin-brine and rift-related hypotheses<sup>33</sup>.

Although the exact age of mineralization has yet to be resolved, the range of K-Ar, <sup>40</sup>Ar-<sup>39</sup>Ar and Rb-Sr ages, endorsed by the Sm-Nd data, are consistent with fluid movements triggered by regional tectonic processes between the Carboniferous and the Jurassic. There is no regional evidence to support models of major lateral squeezing of fluids from the crust during the Mesozoic, which has been proposed as an explanation for formation of the MVT deposits of central and eastern United States in Upper Palaeozoic times<sup>34-36</sup>. Neither is there any evidence for coeval magmatic activity in the area. There is abundant evidence, however, for relatively sudden crustal-tension events and for widespread coeval hydrothermal activity<sup>37,38</sup>. We consider it most likely, therefore, that the MVT deposits of the North Pennines were produced by anomalously deep penetration of the crust by fluids, concomitant with the production and reactivation of fracture permeability induced by unusual regional lithospheric tension. The Weardale Granite<sup>3</sup>, above which the mineralization is zoned<sup>4-6</sup>, clearly provided much of the geothermal energy for the hydrothermal activity. However, the data are difficult to reconcile with the hypothesis that the underlying granite dominates certain chemical characteristics (such as the REE budget) of the mineralization<sup>19</sup>. □

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## Hydroperoxides in plants exposed to ozone mediate air pollution damage to alkene emitters

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**OZONE is phytotoxic: it is damaging to cell integrity and photosynthesis<sup>1,2</sup>, causing leaf necrosis<sup>3</sup> and reducing crop yield<sup>4</sup>. It has been implicated in forest decline<sup>5</sup>, perhaps through interactions with stress ethene<sup>6</sup>. Here we show that organic hydroperoxides (ROOH), which are products of ozone-alkene reactions<sup>7-9</sup>, are present in the leaves of isoprene-emitting plants after exposure to ozone, but are not found in control plants grown in clean air. On the basis of earlier studies<sup>6,7,10</sup>, we suggest that this reaction of ozone with biogenic alkenes to produce toxic ROOH could be one of the mechanisms by which damage to plants occurs. This could be particularly important in areas experiencing acidic deposition, where the stability of ROOH will be enhanced. This model may explain in part the die-back of tree species producing reactive alkenes, such as the red spruce, which emits isoprene<sup>11-15</sup> and monoterpenes<sup>16</sup>, and the Norway spruce and silver fir, which are both prolific monoterpene emitters<sup>17</sup>.**

We have used HPLC with a hydroperoxide-specific detection system, which allows the separation and quantification of nine organic hydroperoxides and hydrogen peroxide in biological samples; the detection limit is  $5 \times 10^{-9}$  M as the ROOH<sup>18,19</sup>. California poppies (*Eschscholzia californica*) were grown from seed in Teflon chambers housed in a controlled environment growth cabinet (at a temperature of 28 °C and a light regime of 12 h at intensity  $250 \mu\text{mol m}^{-2} \text{s}^{-1}$  and 12 h dark). Clean air

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