QJEGH
Research article
Quarterly Journal of Engineering Geology and Hydrogeology
https://doi.org/10.1144/qjegh2022-106 | Vol. 56 | 2023 | qjegh2022-106

Dissolved sulfate δ34S and the origin of sulfate in coal mine waters; NE England

David Banks[1*] **and Adrian J. Boyce**[2]
[1] James Watt School of Engineering, University of Glasgow, James Watt Building South, Glasgow G12 8QQ, UK
[2] Scottish Universities Environmental Research Centre (SUERC), Rankine Avenue, Scottish Enterprise Technology Park, East Kilbride G75 0QF, UK
DB, 0000-0002-4575-504X
* Correspondence: David.banks@glasgow.ac.uk

Abstract: Coal mine waters have been sampled during a reconnaissance study in the East Midlands, South Yorkshire and Tyneside areas of England. Almost all the mine waters had similar δ^{18}O and δ^{2}H concentrations, indicating a derivation from Holocene recharge (average of −7.9 and −54‰, respectively, excluding two outliers). Most mine waters emerging by shallow gravity drainage have dissolved sulfate δ^{34}S levels of <+10‰, suggesting a derivation of sulfate from the oxidation of pyrite. Deeper mine waters, pumped from boreholes or shafts, tended to be more saline with dissolved sulfate δ^{34}S levels of >+14‰ and, in two cases, >+30‰. The sulfate in these latter waters cannot be readily explained as deriving from pyrite oxidation. Alternative hypotheses (evaporitic or marine brines, evaporite dissolution or partially-closed-system microbial sulfate reduction) can be invoked as explanations. A more general hypothesis proposes that deep groundwaters/mine waters can be regarded as saline 'sinks', whose sulfate δ^{34}S concentration is controlled by a dynamic equilibrium between rates of sulfate mobilization from various sources and sulfate removal by precipitation or microbial reduction.

Supplementary material: Supplementary Material A (a detailed description of sample sites and results) and Supplementary Material B (locations of sample sites) are available at https://doi.org/10.6084/m9.figshare.c.6418981

Received 15 October 2022; **revised** 2 February 2023; **accepted** 2 February 2023

Banks *et al.* (2020), building on hydrochemical studies by Janson *et al.* (2016), Loredo *et al.* (2017) and Burnside *et al.* (2016*a*, *b*), investigated the sulfur isotopic composition of dissolved sulfate in coal mine waters in Spain, Poland and the UK. They found evidence that shallow mine waters were often characterized by a relatively 'light' δ^{34}S isotopic signature (concentrations typically between 0 and +10‰), compatible with a derivation from bulk oxidation of pyrite in coal-bearing strata. Deeper mine waters were often relatively enriched in ^{34}S, with δ^{34}S concentrations around or exceeding +20‰. Rinder *et al.* (2020) documented the same phenomenon from the Ibbenbüren coal mine in Germany. Such elevated δ^{34}S is difficult to reconcile with the commonly accepted hypothesis of pyrite oxidation as a source for sulfate in coal mine waters. Banks *et al.* (2020) proposed several different mechanisms for the high δ^{34}S, including derivation of sulfate from stratigraphically overlying or adjacent evaporites (preferred by Rinder *et al.* 2020, in Germany), infiltration of marine or evaporite brines in the geological past and fractionation due to microbiologically mediated precipitation of ^{34}S-depleted sulfide minerals in deep, reducing environments.

Members of the project team have continued to sample coal mine waters in the UK to investigate this phenomenon further: Walls *et al.* (2022) did not find the same systematic trends in mine waters across the Midland Valley of Scotland (although sample sites were heavily skewed towards shallow mine waters) but they did find evidence of the phenomenon at the UKGEOS mine water research facility in Glasgow (Monaghan *et al.* 2022; Walls *et al.* 2021).

In an older, more complex example, Bottrell *et al.* (2006) sampled coal mine brines from 650 to 750 m depth in the Selby coalfield (North Yorkshire: Sill 1985), and found chloride and sulfate concentrations of 3–10 and 54–57 g l^{-1}, respectively (i.e. not marine brines, due to the large sulfate excess). The full dissolved sulfate stable isotopic dataset (partially reported by Bottrell *et al.* 2006) is shown in Figure 1, with a wide dissolved sulfate δ^{34}S range from +3.9 to +26.4‰ but a very tight interquartile range from +9.8 to +11.7‰ ($N = 13$). S. Bottrell (pers. comm. 2022) notes that the lowest value of +3.9‰ was from a roof inflow near the base of the main drift entrance to the mine, draining unsaturated strata above the drift in a relatively shallow part of the mine. This suggests that the low value was influenced by pyrite oxidation, with the other samples being increasingly influenced by a deeper saline signature.

In order to explore whether the occurrence of ^{34}S-enriched dissolved sulfate in deeper, more saline mine waters is a widespread phenomenon in England, we undertook a brief coal mine water reconnaissance sampling for dissolved sulfate sulfur isotope composition at sites in the East Midlands and the NE of England.

Methods

Between August 2021 and February 2022, around 20 sites were visited, characterized and sampled in the East Midlands (Edwards 1951; Banks *et al.* 1996*a*, *b*, 1997) and in the Tyneside (Smailes 1935; Harrison *et al.* 1989; Gray and Judd 2003; Banks *et al.* 2022) areas of the UK. The sites are detailed in Table 1, Figure 2 and in Supplementary material A: they comprised:

- Coal mine spoil tip leachate (e.g. AST5, Grassmoor Country Park);
- gravity discharges from mostly shallow coal mines in the area around Sheffield in South Yorkshire and Chesterfield in Derbyshire;
- the gravity discharge from the Elsecar Water Drift (also known as the Thorncliffe Water Drift or Sellars Sough), a regional mine water drainage adit collecting mine water overflow from a number of deep interconnected mines in the

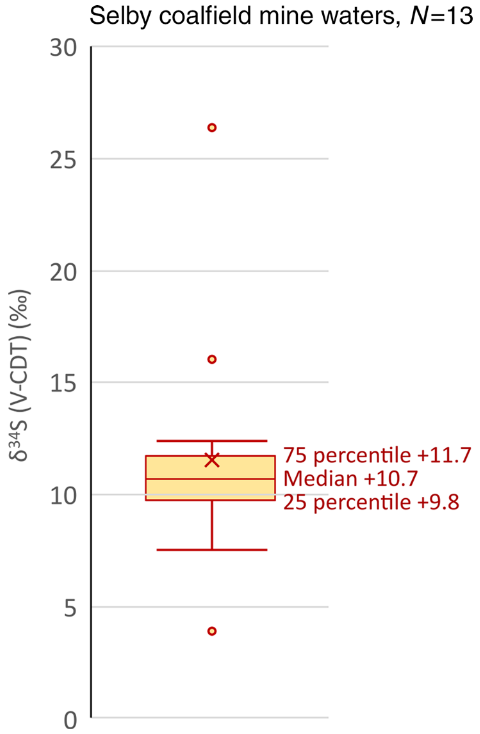

Fig. 1. Dissolved sulfate $\delta^{34}S$ data in underground coal mine waters collected from the Selby interconnected complex of mines by Bottrell *et al.* (2006). The 'X' shows the arithmetic mean of +11.5‰. Data provided and reproduced by kind permission of Prof. S. Bottrell, University of Leeds (pers. comm. 2022). These historical data are not included in the results reported from the current study (i.e. Figs 2–6).

Barnsley–Elsecar area of South Yorkshire (AST21) – the adit's course is detailed in Coal Authority abandoned mine plan M433;

- regional Coal Authority pumping stations at Strafford and Blackwell 'A' Winning, where mine water is pumped and treated for purposes of regional mine water control (AST3 and AST13);
- boreholes drilled into mined Coal Measures strata in the Gateshead area of Tyneside; these included: (i) an abstraction borehole drilled into intact Coal Measures strata at the shallow Lanchester Wines geothermal scheme (Banks *et al.* 2022), sampled by staff of Town Rock Energy Ltd (sample AST01); (ii) pumping test boreholes into mine voids at the Gateshead Baltic mine water geothermal scheme, sampled by staff of the Coal Authority (samples AST15-16); and (iii) observation boreholes drilled into mine workings at Tyneside House and Birtley, and sampled using temporary pumping equipment by staff of the Environment Agency (samples AST18-20); and
- a single sample taken from an adit driven into a hillside comprising lower Namurian (and, possibly, uppermost Visean) shales in Matlock, Derbyshire; this was historically used as a ferruginous spa water, known as Allen Hill Spaw (AST9: Banks 1997*a*; Bradley 2018), and is thus not strictly a coal mine water but is derived from geologically slightly older strata than the coal-bearing uppermost Namurian and Westphalian. The water is regarded as being characterized by the oxidation of sedimentary Carboniferous pyrite, however, and is grouped with shallow mine drainage waters for the purposes of this study.

At each site, water was sampled as close to its discharge point as possible or, in the case of pumped boreholes, directly from the pumped discharge. In the case of the Coal Authority mine water treatment facilities at Blackwell 'A' Winning and Strafford, water was sampled within or at the outfall of passive treatment systems (for reasons of restricted access to the shaft head itself), where iron oxyhydroxide had been removed by oxidation and settlement. We do not believe that any process within the aerobic passive treatment system would have significantly affected chloride, sulfate or sulfur isotopic compositions in the samples.

Full details of sampling localities are provided in Supplementary material A, and a keyhole markup language (.kml) file showing sample site locations is presented as Supplementary material B.

At each site, temperature and temperature-compensated pH and electrical conductivity (EC) were determined in the field using calibrated Apera Instruments EC20 and PH20 probes (or equivalent field probes in the case of the Environment Agency boreholes AST18–AST20). In the case of AST15 and AST16, the determinations of pH and EC were made on arrival of the samples at the laboratory, rather than in the field.

Two duplicate (unfiltered and unpreserved) aliquots of sample were collected in 10 ml glass vials, with screw foil/plastic caps, for subsequent oxygen and hydrogen isotopic analysis. The vials were filled to full capacity, with no air space and sealed with Parafilm® to prevent any possibility of evaporation or gas exchange during transport and storage. The sealed vials were quickly sent to the laboratory where they were refrigerated at 4°C until analysed.

A 1.35 l unfiltered, unpreserved aliquot of sample was collected at each site into a clean plastic flask. On return from the field, water was decanted to a clean 1 l Pyrex beaker and acidified to $pH < 3$ using concentrated hydrochloric acid (to remove bicarbonate from the water and prevent carbonate precipitation during subsequent steps). An excess of 5% barium chloride solution was then added to the beaker to precipitate sulfate as $BaSO_4$ (Carmody *et al.* 1998). The precipitate was repeatedly rinsed with deionized water and, following settlement and decanting of supernatant fluid, was evaporated to dryness in a low-temperature oven. The precipitate was then sent to the laboratory for $\delta^{34}S$ analysis.

A duplicate set of samples was collected from site AST13 (Blackwell 'A' Winning) and analysed 'blind' for O, H and S isotopes.

Stable isotopic analysis of water and precipitate samples from all sites was conducted at the Scottish Universities Environmental Research Centre (SUERC). For $\delta^{18}O$ analysis, each water sample was over-gassed with a 1% CO_2-in-He mixture for 5 min and left to equilibrate for a further 24 h. A sample volume of 2 ml was then analysed using standard techniques on a Thermo Scientific Delta V mass spectrometer set at 25°C. Final $\delta^{18}O$ values were produced using the method established by Nelson (2000). For $\delta^{2}H$ analysis, sample and standard waters were injected directly into a chromium furnace at 800°C (Donnelly *et al.* 2001), with the evolved H_2 gas analysed online via a VG Optima mass spectrometer. Final values for $\delta^{18}O$ and $\delta^{2}H$ are reported as per mille (‰) variations from the V-SMOW standard in standard delta notation. In-run repeat analyses of water standards (international standards V-SMOW and GISP, and internal standard Lt Std) gave reproducibility better than ±0.2‰ for $\delta^{18}O$ and ±3‰ for $\delta^{2}H$.

For $\delta^{34}S$ analysis of the barium sulfate precipitate from the sampled waters, SO_2 gas was generated by combustion at 1125°C with excess Cu_2O and silica (Coleman and Moore 1978), then measured isotopically using a VG Isotech SIRA II mass spectrometer. Results are reported as per mille (‰) variations from the Vienna Canyon Diablo Troilite (V-CDT) standard in standard delta notation. Reproducibility of the results was monitored through the repeated analysis of standards NBS-123 (+17.4‰), IAEA-S-3 (−32.3‰) and SUERC's internal standard CP-1 (−4.6‰), and was typically around ±0.2‰ during these analyses. For three samples (AST15, AST16 and AST19, two of

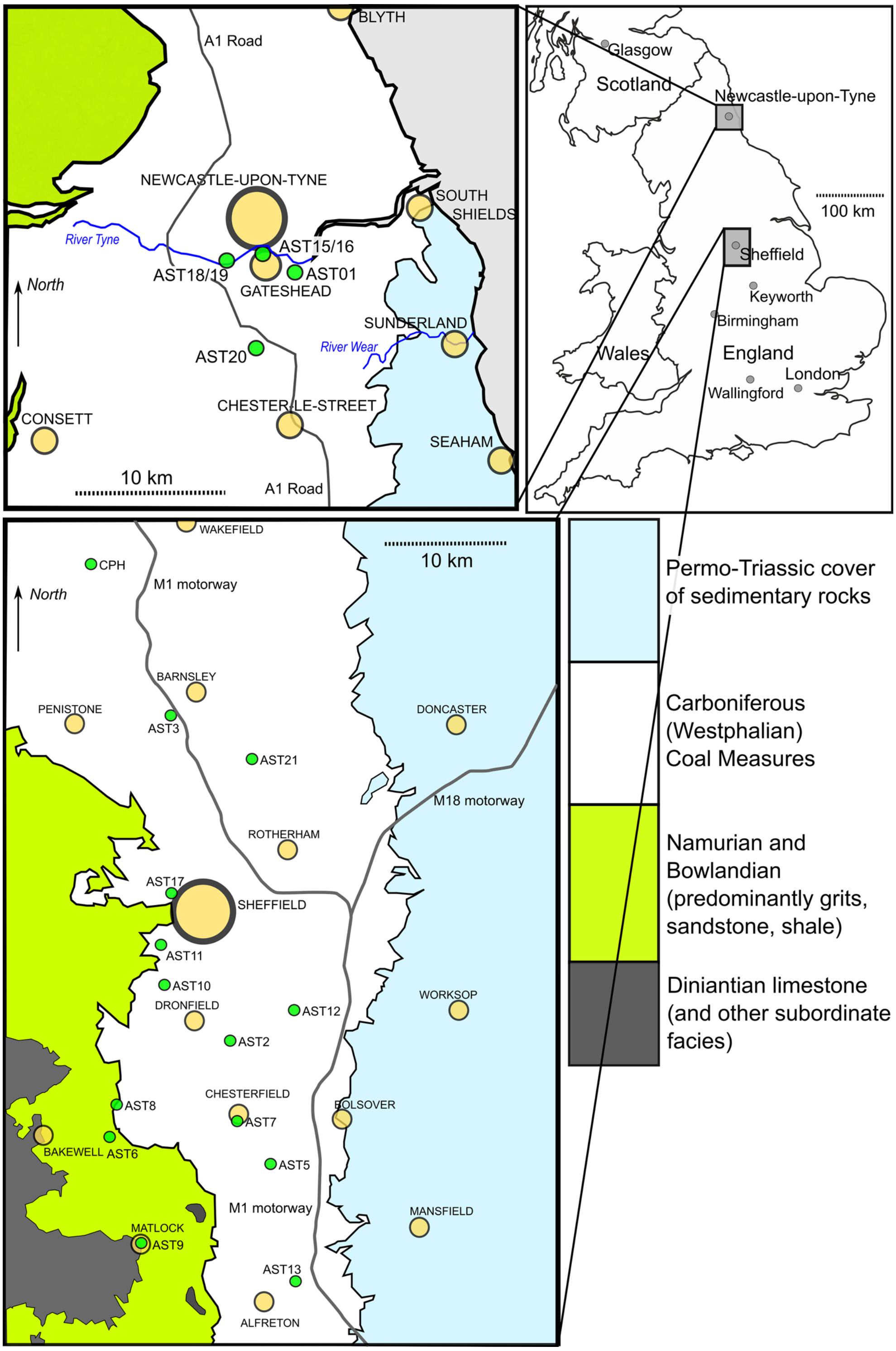

Fig. 2. Simplified geological map of study areas showing sample locations (based on information from the British Geological Survey Geoindex viewer: contains public sector information licensed under the Open Government Licence v3.0).

which returned unusually high $\delta^{34}S$ values), the barium sulfate samples were reanalysed to verify the results.

Many of the study's sampling points (Table 1) had previously been analysed in other studies. Where this was the case, broader hydrochemical analytical results were identified from literature sources and Coal Authority databases. Reported chloride and sulfate concentrations are presented in Table 2.

Finally, the mine water sampled previously from the pumped Hope Shaft at the Caphouse Colliery in Yorkshire (operated by the Coal Authority as a regional mine water control and treatment facility), by Burnside *et al.* (2016*a*) by comparable methods and analysed by the same laboratory, was included in the dataset (sample CPH in Table 1).

Results

The stable isotope results are provided in Table 2, together with chloride and sulfate analyses from available literature.

Duplicate stable isotope sample sets for Blackwell 'A' Winning showed good reproducibility, and the values cited in Table 2 are

Table 1. *Summary of sample sites, with UK National Grid references and previous literature referring to the sample sites*

Sample	Location	Grid Reference	Description
AST1	Abbotsford Road BH2, Gateshead	NZ 28480 62238	Pumped Coal Measures borehole; Lanchester Wines mine water geothermal scheme Banks *et al.* (2022)
AST2	Crow Lane, Unstone	SK 37565 77349	Ochreous gravity mine water discharge from relatively shallow coal workings Banks *et al. (1996a*, 1997); Environment Agency (1996); SWK (1996); Banks and Banks (2001)
AST3	Strafford MWTS	SE 31959 04013	Coal Authority pump Strafford Silkstone shaft for regional mine water control and treatment. Mine water contains H_2S. Sampled at the outfall from the first settlement pond Geroni (2011); Whitworth *et al.* (2012)
AST5	Grassmoor Country Park	SK 41229 67341	Ochreous water drainage, most likely leachate from spoil deposited in the vicinity of the former Grassmoor Colliery
AST6	Stand Wood, Chatsworth	SK 27036 69224	Ochrous gravity mine water discharge from former shallow workings in Baslow Coal Barnatt and Bannister (2009); Derbyshire Heritage (2022)
AST7	Boythorpe / R Hipper, Chesterfield	SK 38251 70642	Ochrous mine water discharge, most likely from the former Boythorpe Colliery, to the River Hipper. Sampled from an overflowing manhole in an adjacent car park Banks *et al.* (1996*a*, 1997); Keeling (2009)
AST8	Robin Hood, Birchen Edge	SK 27765 72112	Ochrous gravity mine water discharge, from former shallow workings in Baslow Coal Barnatt and Bannister (2009); Dalrymple-Smith (2012)
AST9	Allen Hill Spaw, Matlock	SK 29614 60447	Driven adit into pyritiferous Cawdor/Namurian shales for ferruginous spa water Banks *et al.* (1996*a*, *b*, 1997); Banks (1997*a*); Bradley (2018)
AST10	Ecclesall Woods, Sheffield	SK 31793 81764	Ochrous gravity mine water discharge from former shallow workings McCormick (1993); Banks *et al.* (1996*a*, 1997); Dumpleton (2020)
AST11	Whiteley Woods, Greystones, Sheffield	SK 31402 84995	Ochrous gravity mine water discharge from former shallow workings Banks *et al.* (1996*a*, 1997)
AST12	Eckington Moss	SK 43133 79896	Ochrous water. Possibly gravity mine water discharge from former shallow workings, there may be a component of spoil leachate or drainage from natural pyritiferous Coal Measures rocks
AST13	Blackwell 'A' Winning MWTS	SK 43512 57701	Coal Authority pump from the Blackwell 'A' Winning shaft for regional mine water control and treatment. Water sampled at the outfall from the passive treatment system Whitworth *et al.* (2012); Coal Authority (2018)
AST15	Gateshead Baltic High Main (E) borehole	c. NZ 262 635	Sampled by the Coal Authority from a borehole sunk to the worked High Main (E) coal seam. Part of the Gateshead Baltic mine water geothermal scheme Coal Authority (2022)
AST16	Gateshead Baltic Hutton (L) borehole	c. NZ 262 635	Sampled by the Coal Authority from a borehole sunk to the worked Hutton (L) coal seam. Part of Gateshead Baltic mine water geothermal scheme Coal Authority (2022)
AST17	Loxley Bottom No. 1 mine water	SK 32290 89382	Ochreous water draining to the River Loxley. Likely to be shallow mine water gravity drainage, with a probable component of leachate from spoil deposited in a former pond Environment Agency (1996); SWK (1996); Banks and Banks (2001)
AST18	Tyneside House BH1 (R seam)	NZ 23790 62948	Sampled by the Environment Agency from a borehole sunk to the worked Threequarters (R) seam. Bore to 143.5 m depth
AST19	Tyneside House BH2 (K or L seam)	NZ 23788 62948	Sampled by the Environment Agency from a borehole sunk to the worked Brass Thill (K) or Hutton (L) seam. Bore to 47 m depth
AST20	Birtley BH (Q seam)	NZ 25850 56950	Sampled by the Environment Agency from a borehole sunk to the worked Busty (Q) seam. Bore 126 m in depth
AST21	Thorncliffe/Elsecar Water Drift	SE 39032 00465	Regional mine water adit, collecting water overflowing from numerous relatively deep collieries between Tankersley and Elsecar. Sampled at a discharge point north of Elsecar Whitworth *et al.* (2012); Wain (2014); Friends of Hemingfield Colliery (2017)
CPH	Caphouse Hope Shaft	SE 2486 1619	Coal Authority pump from the Hope Shaft at the Caphouse Colliery for regional mine water control and treatment. The mine water contains H_2S Whitworth *et al.* (2012); Wain (2014); Burnside *et al.* (2016*a*); Davies-Vollum *et al.* (2016); Banks *et al.* (2019, 2020)

arithmetic means of the duplicate results. The repeat analyses of AST15, AST16 and AST19 verified the initial analysis, and the average of all runs is presented in Table 2.

δ^2H and δ^{18}O values are plotted in Figure 3. All results lie very close to the relevant local meteoric water lines, suggesting that the water component of the mine waters is overwhelmingly dominated by recent meteoric recharge. Most samples lie towards the isotopically 'lighter' (winter) end of the meteoric water line, suggesting that recharge predominantly occurs in winter. Two samples plot closer to the 'summer' end of the spectrum: the Grassmoor spoil tip leachate (AST5) and the water from the shallow Tyneside House 2 borehole (AST19). Excluding these two samples, the average δ^2H and δ^{18}O values of our dataset are −54 and −7.9‰, respectively, which are statistically indistinguishable from the local meteoric water (the Keyworth precipitation weighted mean for 1985–96 are -54.3 ± 5.9 and -8.0 ± 0.8‰: IAEA/WMO 2022). Furthermore, these values are typical of unconfined groundwaters across England, all of which are interpreted as integrated averages of modern, Holocene meteoric water (Darling and Talbot 2003; Darling *et al.* 2003).

As regards the outlying 'heavy' values, AST5 was sampled from a colliery spoil discharge in summer (August 2021), and its relatively heavy δ^2H and δ^{18}O (−44 and −6.3‰, respectively) may reflect evaporative processes in the spoil heap. The heavy values

Table 2. *Summary of field pH, electrical conductivity (EC) and temperature results, and stable isotope concentrations ($\delta^{18}O$ and $\delta^{2}H$ as ‰ SMOW and as averages of two duplicate samples; $\delta^{34}S$ as ‰ CDT) collected during this study*

Sample No.	Location	Type	pH	Temperature (°C)	EC ($\mu S\ cm^{-1}$)	Source A	$\delta^{18}O$ (‰)	$\delta^{2}H$ (‰)	$\delta^{34}S$ (‰)	Source B	Cl^- ($mg\ l^{-1}$)	SO_4^{2-} ($mg\ l^{-1}$)	SO_4^{2-}/Cl^- (mass ratio)	Source C	H_2S (odour)
AST01	Abbotsford Road	PB	7.7	*c.* 12	1400	[1]	−7.8	−52.8	+14.3	*	235	139	0.59	[1]	
AST02	Unstone	SG	6.9	12.3	586	*	−8.0	−52.7	+10.8	*	35	211	6.03	[2]	
AST03	Strafford	PS	7.5	13.9	255	*	−8.2	−55.8	+18.3	*	65	637	9.85	[3]	Y
AST05	Grassmoor	SP	7.7	12.4	1100	*	−6.3	−43.7	+7.9	*					
AST06	Stand Wood	SG	7.1	11.2	184	*	−7.8	−52.2	−0.5	*					
AST07	River Hipper	SG	4.8	14.1	1340	*	−7.7	−55.5	+5.3	*	27	550	20.37	[4]	
AST08	Birchen Edge	SG	6.1	9.8	228	*	−8.0	−54.0	+5.1	*					
AST09	Allen Hill Spaw	SG	6.8	12.5	816	*	−7.8	−55.5	−11.0	*	83	124	1.49	[2]	
AST10	Ecclesall Woods	SG	6.1	11.4	824	*	−7.9	−54.5	−12.9	*	30	300	10.00	[2]	
AST11	Greystones	SG	6.0	11.5	591	*	−7.9	−54.0	−4.6	*	33	181	5.48	[2]	
AST12	Eckington	SG (+SP?)	7.0	12.0	483	*	−7.4	−53.5	+12.1	*					
AST13	Blackwell 'A'	PS	8.1	11.7	11 480	*	−7.7	−52.5	+14.6	*	3205	1016	0.32	[3]	
AST15	Gateshead (E)	PB	6.9		2730	*	−7.8	−56.0	+6.3	*					
AST16	Gateshead (L)	PB	7.2		6940	*	−7.4	−54.3	+34.1	*					
AST17	Loxley Bottom	SG (+SP?)	6.4	8.0	610	*	−8.3	−55.2	−12.0	*	35	200	5.71	[5]	
AST18	Tyneside House 1	PB	7.0	13.8	5418	*	−7.7	−52.6	+24.2	*	1420	377	0.26	[6]	Y
AST19	Tyneside House 2	PB	6.7	12.6	22 273	*	−4.8	−30.2	+30.8	*	9250	298	0.03	[6]	
AST20	Birtley	PB	6.9	14.2	4131	*	−8.4	−54.6	+19.1	*					
AST21	Elsecar	DG	6.8	11.3	1977	*	−8.2	−55.2	+9.8	*	64	813	12.74	[3]	
CPH	Caphouse	PS	6.9	15	2698		−8.0	−52.0	+21.8	[7]	257	621	2.42	[7], [8]	Y

Two $\delta^{34}S$ re-runs of AST15 returned values of +6.5 and +6.0‰ (average +6.3‰). Four re-runs of AST16 returned values of +34.3, +33.0, +34.7 and +34.5‰ (average +34.1‰). Two re-runs of AST19 returned values of +30.8 and +30.7‰. Cited chloride and sulfate data from the literature sources are also shown, with the data source in the final column. The column marked H_2S notes the presence of a clear H_2S odour in the mine water. Type: PB, pumped borehole; SG, shallow gravity discharge; PS, Coal Authority pumped shaft; SP, spoil leachate; DG, gravity drainage from deeper mines (Elsecar Water Drift). Literature sources: Source A, field EC, temperature and pH data; Source B, stable isotope data; Source C, chloride and sulfate data; *this study; [1] EC, temperature, pH, Cl^- and SO_4^{2-} from Banks *et al.* (2022); [2] Banks *et al.* (1996*a*); [3] Coal Authority water quality database; [4] Keeling (2009); [5] Public domain National Rivers Authority/Environment Agency data cited in SWK (1996); [6] Newcastle University (2018); [7] Banks *et al.* (2020); [8] Burnside *et al.* (2016*a*).

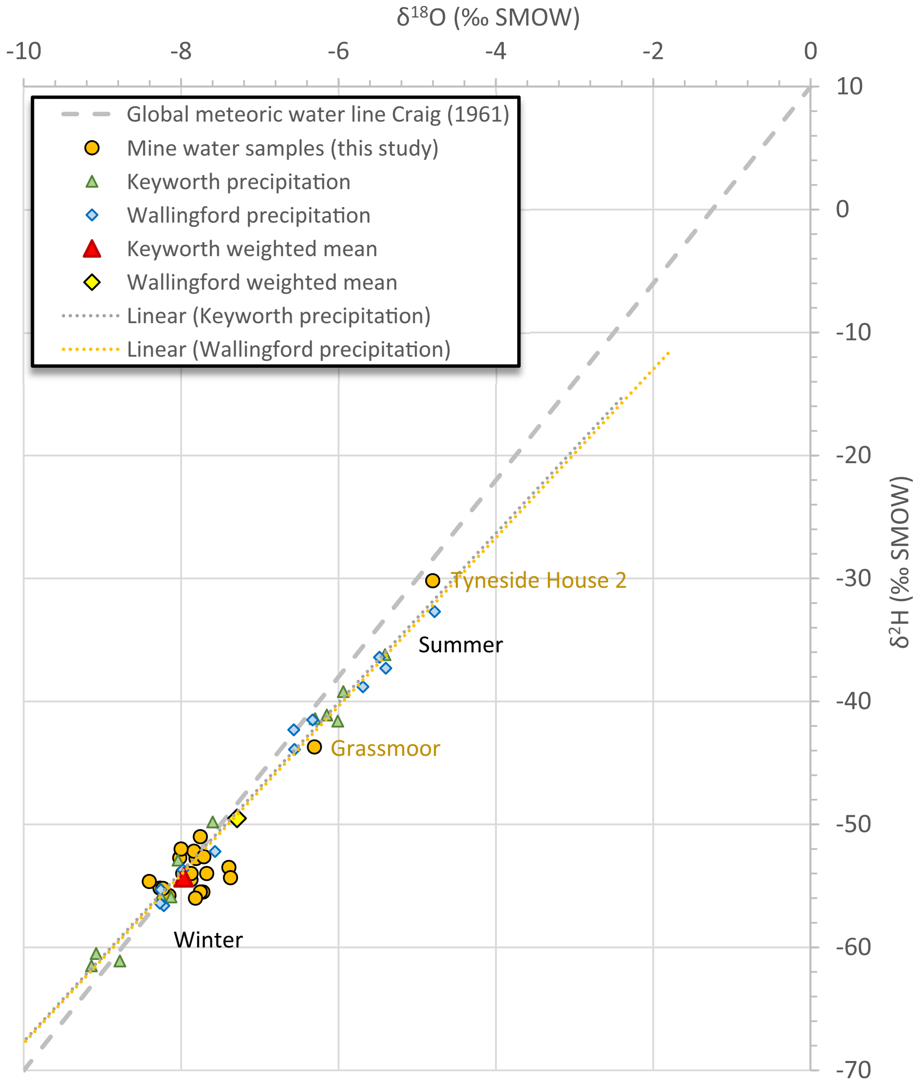

Fig. 3. Bivariate plot of δ^2H v. δ^{18}O in water samples from this study. The global meteoric water line is after Craig (1961); monthly average (and annual weighted mean) isotopic composition of precipitation at Wallingford (Oxfordshire: 1979–2009) and Keyworth (Nottinghamshire: 1985–96) are also shown (see Fig. 2 for the locations), after IAEA/WMO (2022). Summer and winter tendencies relate to the precipitation measurements at Wallingford and Keyworth.

noted in the AST19 Tyneside House 2 borehole (−30 and −4.8‰ for δ^2H and δ^{18}O, respectively) are highly unlikely to be related to evaporation, as the water was sampled from flooded subsurface mine workings in winter (February 2022). The high δ^2H and δ^{18}O concentrations are more likely to be related to the high salinity of the water (22 300 µS cm^{-1}) and possible marine intrusion, or to the observation of gas bubbles in the water sample (degassing could preferentially strip lighter isotopes from the water).

The dissolved sulfate δ^{34}S exhibits a large range, from almost −13‰ in the mine water draining from the shallow workings of Dore Colliery into the Limb Brook in Ecclesall Woods, Sheffield (AST10) to over +30‰ in the Tyneside House 2 (AST19) and the Gateshead Baltic Hutton (AST16). Interestingly, both of these boreholes access the Hutton (‘L’) coal seam of the Tyneside coalfield (Banks *et al.* 2022).

A clear trend appears when sulfur isotopes are plotted against water type (Fig. 4), with the shallow gravity discharges typically yielding dissolved sulfate δ^{34}S clustered around 0‰ and ranging from around −13 up to +11‰. The pumped boreholes and regional Coal Authority pumped shafts returned waters with typically much higher δ^{34}S values, clustered around +20‰ and ranging from +14 to +34‰, with one low outlier (the shallow Gateshead Baltic High Main borehole at +6.3‰) (Fig. 4).

When plotted against the mine waters’ electrical conductivity (EC: Fig. 5), which can be regarded as a proxy for salinity, a trend of increasing δ^{34}S with increasing salinity emerges. Almost all the shallow coal mine drainages have low salinity and low δ^{34}S, while the δ^{34}S values of around and above +20‰ are typically found in waters of EC > 2500 µS cm^{-1}.

Finally, Figure 6 plots dissolved sulfate δ^{34}S against the mass ratio of sulfate/chloride, where these concentrations are known from historical analyses.

Discussion

It is very commonly assumed that the dissolved sulfate in most coal mine waters is derived from the oxidation of sulfide minerals such as pyrite (Banks *et al.* 1996*b*, 1997). Under most circumstances, little sulfur isotope fractionation occurs when pyrite is oxidized to dissolved sulfate (Taylor *et al.* 1984). Indeed, authors such as Bottrell *et al.* (2000), Dold and Spangenburg (2005), Tostevin *et al.* (2016) and Dogramaci *et al.* (2017) used dissolved sulfate δ^{34}S as a tracer for the influence of sulfide or pyrite oxidation in the groundwater environment. Thus, the dissolved sulfate δ^{34}S of coal mine waters (if the assumption is correct) should reflect a bulk average isotopic composition of available oxidized sulfide in the Carboniferous mined sequence.

The δ^{34}S of the pyrite content of British coal-bearing strata is not especially well documented. Such pyrite can have a wide variation in δ^{34}S, and can even exhibit multiple generations of δ^{34}S due to isotopic fractionation in the depositional environment or to secondary mineralization. Microbial sulfide reduction produces a strong fractionation effect, often of several tens of per mille, with the solid sulfide phase being depleted in ^{34}S and the remaining

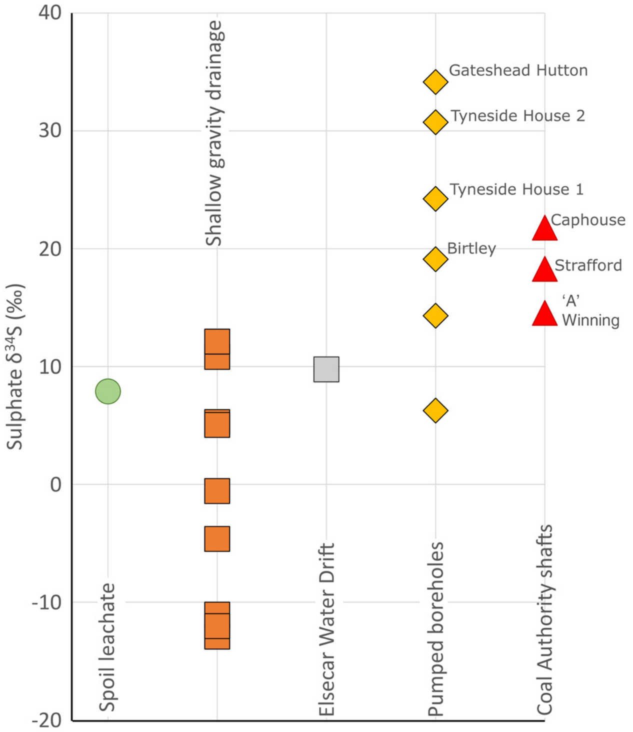

Fig. 4. Distribution of dissolved sulfate δ^{34}S in waters from this study, according to the type of discharge.

dissolved phase enriched (Rees 1973; Chambers and Trudinger 1979; Strauss 1997; McKay and Longstaffe 2003; Brunner and Bernasconi 2005; Sim *et al.* 2011; Leavitt *et al.* 2013). Fike *et al.* (2015) regarded a fractionation of −40‰ as being typical between seawater sulfate and sedimentary marine pyrite. If the reduction system is closed with respect to sulfate, early sulfide minerals produced by sulfate-reducing bacterial (SRB) processes will have a very low δ^{34}S but ^{34}S will accumulate in the residual porewater, meaning that the last fraction of sulfide mineral to be precipitated can have a high δ^{34}S (Schwarcz and Burnie 1973).

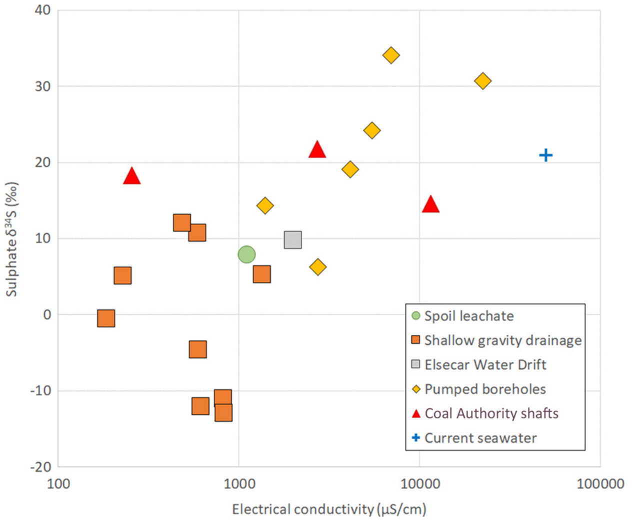

Fig. 5. Dissolved sulfate δ^{34}S plotted against electrical conductivity (EC) of waters from this study (temperature compensated to 25°C). The electrical conductivity of seawater around the British coast is 35 000–40 000 µS cm^{-1} at ambient temperature (Tyler *et al.* 2017), and around 50 000 µS cm^{-1} at the standard reference temperature of 25°C (Sauerheber and Heinz 2015).

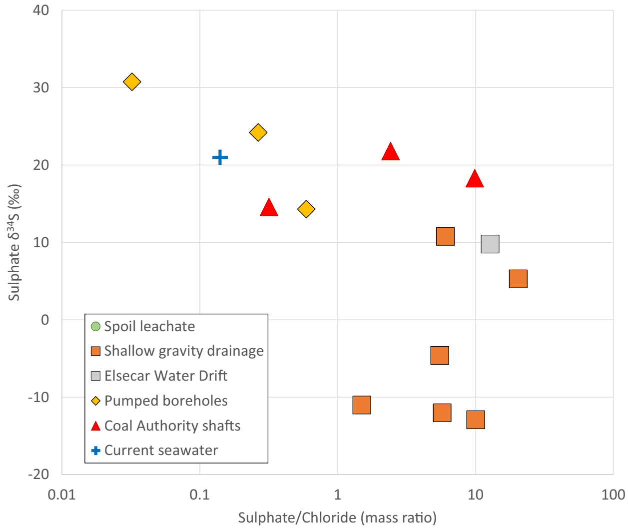

Fig. 6. Dissolved sulfate δ^{34}S plotted against the mass ratio of sulfate/chloride in waters from this study (where these concentrations are reported from the literature). The sulfate and chloride concentrations of standard ocean water are 2712 and 19 353 mg kg^{-1} (Millero *et al.* 2008).

In the British Namurian Bowland Shale and Caton Shale, Dean (1994) recorded mean pyrite δ^{34}S concentrations of −32.5 and −17.7‰, respectively. Excluding a low outlier (−30.0‰), nine samples of soluble sulfate from these shales returned a mean sulfate δ^{34}S concentrationof −1.7‰, with a range from −8.7 to +3.7‰.

In the British Westphalian, Turner and Richardson (2004) studied pyrite δ^{34}S in the Northumberland coalfield and cited an average of +5.1‰ and a typical range of −5.4 to +12.8‰, with a single high outlier exceeding +30‰. They regarded the sulfur isotopic composition as possibly having been influenced by secondary pyrite formation from sulfate-rich brines mobilized by Permian Variscan transpression and emplacement of the Weardale granite batholith. The same mineralization effect may have led to abnormally high barium contents in coals. Indeed, Clowes (1889) and Gray and Judd (2003) noted the elevated barium contents of mine waters in the Newcastle-upon-Tyne, Sunderland and coastal Durham area. Bullock *et al.* (2018) noted δ^{34}S values ranging from −20.6 to +11.7‰ in four pyrite samples from the Low Main/Plessey seam stratigraphic interval at Shotton in the Northumberland coalfield.

Love *et al.*'s (1983) study of a marine incursion in a Lower Coal Measures sequence near Penistone, South Yorkshire, recorded pyrite δ^{34}S values ranging from −35.3 to +20.4‰. Low values were recorded in marine portions of the succession (mean −1.2 ± 6.5‰), trending towards higher values in sediments beneath coal seams (+12.7 ± 7.7‰). In Coal Measures strata of Ayrshire (Scotland), pyrite δ^{34}S concentrations ranged from −26.3 to +11.6‰ with one higher outlier and an overall mean of +2.7‰ ($n = 21$). Walls *et al.* (2021) found a similar range in Glaswegian coal-bearing strata, albeit with a single very high value of >+30‰.

In summary, UK Coal Measures pyrite can exhibit a wide range of δ^{34}S, from <−20‰ up to around +12‰ and, rarely higher. Mean values tend to be in the range *c.* 0 to +5‰.

Thus, if the dissolved sulfate δ^{34}S of mine waters is derived from pyrite oxidation, one would expect a dissolved sulfate δ^{34}S value of typically 0 to +5‰, reflecting the average sulfide content of the Carboniferous mined sequence, with some variation outside this range due to local stratigraphic variation. Indeed, our data show this is indeed the case for shallow, non-saline gravity drainage waters in Table 2 and Figure 4, also for the spoil leachate and for the shallow Gateshead Baltic High Main borehole (AST15).

As has been found in the pan-European study of mine waters (Banks *et al.* 2020), many of the deeper and more saline mine waters were characterized by considerably higher dissolved sulfate δ^{34}S concentrations that cannot be wholly ascribed to conventional oxidation of sedimentary pyrite. One can invoke several hypotheses to explain the origin of the elevated dissolved sulfate δ^{34}S in such deeper waters:

1. Residual marine water in the sedimentary sequence: seawater δ^{34}S levels have varied from around +10 to +24‰ throughout geological time since the Carboniferous, with excursions exceeding +30‰ at the Permo-Triassic boundary (Strauss 1997; Present *et al.* 2020). Current marine sulfate has a δ^{34}S level of +21‰ (Tostevin *et al.* 2014). Microbial sulfate reduction processes in marine sediments, see hypothesis (5) below, can push δ^{34}S concentrations in interstitial waters considerably higher (Böttcher *et al.* 1999). If seawater were the source of the sulfate and elevated δ^{34}S, one would expect a high chloride/sulfate ratio approaching that of seawater.
2. Dissolution of evaporite minerals in suprajacent or subjacent strata: here the chloride/sulfate ratio would depend on the evaporite composition but a pure gypsum/anhydrite sequence could generate a high sulfate, low chloride salt solution, with high δ^{34}S concentrations reflecting the palaeoseawater composition from which the evaporites were deposited (Otero and Soler 2002). Bottrell *et al.* (2006) documented δ^{34}S mostly in the range of +8 to +11‰ in Permian (Zechstein) evaporites and reported corresponding signatures in Permian Magnesian Limestone groundwaters. They reported δ^{34}S of +15.5 to +18‰ in Triassic Mercia Mudstone evaporites and associated groundwaters. Elevated δ^{34}S in Polish coal mine waters is often ascribed to Triassic or Tertiary evaporite dissolution (Banks *et al.* 2020) and could be a factor for some coastal Northumberland/Tyneside/Durham mine waters, where Permian evaporite sequences overlie (or have overlain) Coal Measures. It is more difficult to argue this hypothesis for the exposed coalfield of central England (Yorkshire/Derbyshire), however, where extensive Permo-Triassic evaporite deposition is unlikely. Gunn *et al.* (2006), however, postulated Lower Carboniferous evaporites to explain elevated dissolved sulfate δ^{34}S concentrations in the thermal groundwaters of Matlock; indeed, Dunham (1973) proved the existence of such Tournasian sabkha anhydrite at around 1730 m depth in the Eyam borehole in Derbyshire.
3. Residual evaporite brines, which may have sunk into the deep Carboniferous rocks under gravity during evaporite formation (e.g. in the Permo-Triassic). Even in continental environments, where thick sedimentary evaporites are implausible, sabkha-like environments could have generated dense brines.
4. Mineralization events and residual fluids, such as the Variscan Pennine mineralization event evoked by Turner and Richardson (2004) to explain pyrite δ^{34}S in Northumberland: such explanations are, of necessity, only regionally convincing and cannot necessarily be evoked to explain elevated mine water δ^{34}S in the East Midlands, in Glasgow or elsewhere in Europe.
5. Isotopic fractionation associated with sulfate reduction to sulfide within mine water systems, removing ^{32}S as sulfide minerals and leaving mine water dissolved sulfate enriched in ^{34}S: microbially mediated sulfate reduction can cause fractionations well in excess of −46‰ (Brunner and Bernasconi 2005). Appropriate redox conditions are most likely to exist in niches in the deepest mines. Hydrogen sulfide was explicitly noted at Caphouse, AST03 and AST18, all of which exhibit elevated δ^{34}S levels.

We note, from Figures 5 and 6, that three of the Newcastle-upon-Tyne/Gateshead samples (AST16, AST18 and AST19) exhibit dissolved sulfate δ^{34}S exceeding modern seawater, rendering hypotheses (2) and (3) implausible, unless one were to invoke marine or evaporitic influence dating from the Permian–Triassic boundary. The fact that the sample in Figure 6 with the high δ^{34}S level (AST19) exhibits a sulfate/chloride ratio well below modern seawater suggests that the water has been depleted in sulfate and that mechanism (5) is a strong candidate in this case.

These mechanisms have already been discussed in detail as plausible hypotheses for enriched ^{34}S in coal mine waters by Banks *et al.* (2020, 2021). The relative merits of these mechanisms will thus not be discussed in more detail here. While several of these hypotheses for generating ^{34}S-enriched mine waters can be invoked in local or regional settings, they are in danger of becoming ‘Just So’ stories (Kipling 1902), lacking universal explanatory power.

It should finally be mentioned that Pellerin *et al.* (2019) identified a mechanism by which large positive δ^{34}S fractionations, of +12.5‰ or more, can indeed be generated during sulfide oxidation. However, the bacterium responsible (*Desulfurivibrio alkaliphilus*) tends to thrive in alkaline lacustrine environments, and oxidizes sulfide in anaerobic environments using nitrate and CO_2 as electron acceptors. These conditions mean that the bacterium seems an implausible candidate for most coal-mining environments; however, not impossible, given that deep Coal Measures strata are typically anaerobic and can be alkaline (Banks 1997*b*; Banks *et al.* 1997). Deep mine waters can also be enriched in ammonium (Demin *et al.* 2010), potentially a product of nitrate reduction, although the source of the ammonium is normally regarded as being lithological (ammonium within the mineral structures of clays and feldspars: Manning and Hutcheon 2004). Further research is needed to ascertain whether such microbes can thrive in deep Coal Measures environments.

A provisional hypothesis

It is widely recognized that global seawater acts as a dynamic ‘sink’ for soluble ions, including sulfate. Concentrations of sulfate and their isotopic composition depends on the dynamic equilibrium between sulfate sources (Leavitt *et al.* 2013; Fike *et al.* 2015) (Fig. 7):

- continental dissolution of evaporite minerals and sulfate salts;
- sulfate salts in rainfall, transported via rivers and windborne dust;
- continental weathering: oxidation of primary and sedimentary sulfides (e.g. pyrite), dissolution and transport to the sea (typically low δ^{34}S, reflecting sulfide composition); note that the current global flux-weighted mean δ^{34}S for riverine-transported sulfate to the ocean is estimated at +4.4 ± 4.5‰ (Burke *et al.* 2018), suggesting that the weathering of sulfide minerals is more significant than continental evaporite sulfate dissolution;
- primary emissions of sulfides (e.g. mid-ocean vents)

and sulfur sinks:

- deposition of sulfate from seawater as evaporites (e.g. gypsum and anhydrite), typically in semi-closed basins, or removal as carbonate-associated sulfate (CAS); and
- microbial reduction of sulfate and precipitation as sedimentary sulfide, primarily in deep-sea organic sediments, with fractionation (depletion of the remaining dissolved sulfate pool in ^{32}S).

Because the present marine environment forms an interconnected global body, the marine sulfur isotope signature is spatially

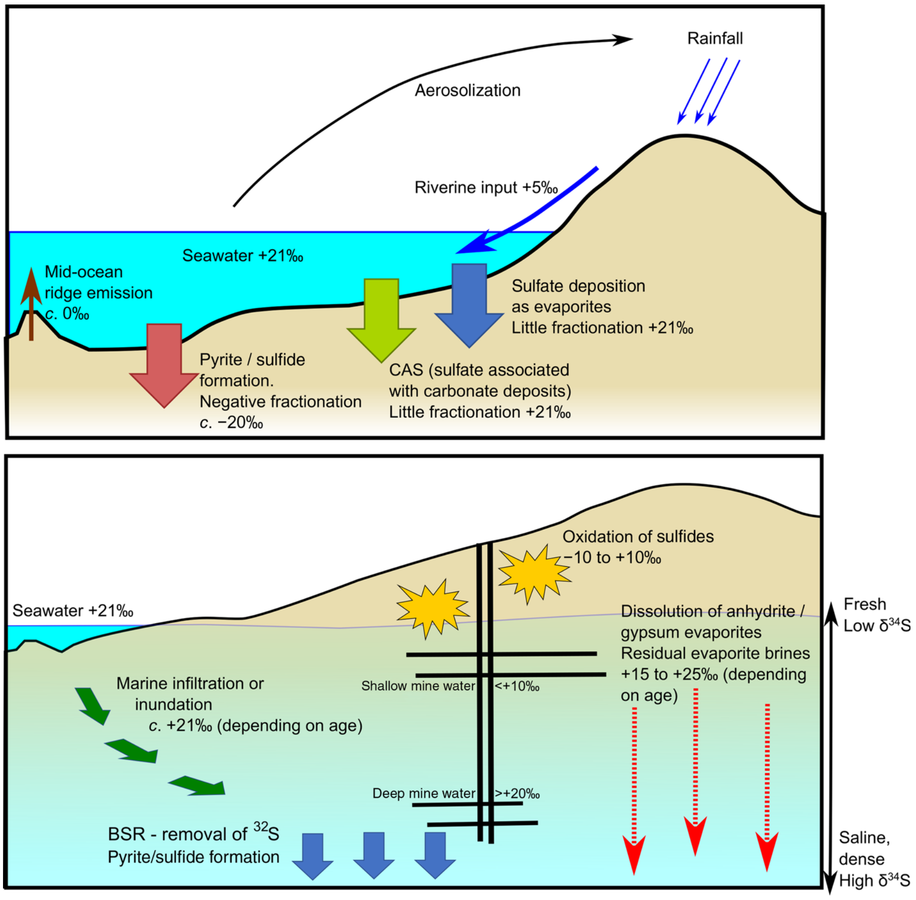

Fig. 7. Conceptual models of (**a**) seawater as a dynamic reservoir of sulfate, whose $\delta^{34}S$ concentration is determined by relative source and sink rates, as suggested by, for example, Fike *et al.* (2015); and (**b**) analogous conceptual model of groundwater as a stratified dynamic reservoir of sulfate, whose $\delta^{34}S$ is determined by relative source and sink rates. Suggested values for the $\delta^{34}S$ concentration of mid-ocean ridge emissions is from Shanks *et al.* (1995), for modern seawater from Tostevin *et al.* (2014), for river run-off from Burke *et al.* (2018), and for evaporites, carbonate-associated sulfate (CAS) and sedimentary pyrite from Fike *et al.* (2015). BSR, bacterial sulfate reduction.

homogeneous but temporally dependent on the balance between the weathering and deposition of sulfates and sulfides. In particular, it is dependent on the rate of the main fractionation process, microbial sulfate reduction and sulfide deposition in the deep marine environment. For example, it is widely accepted that the highly elevated $\delta^{34}S$ levels in marine sulfate at the Permo-Triassic boundary is due to widespread anoxia and euxinia removing and trapping ^{32}S due to reduction of sulfate to sulfide in the reduced sediments (Meyer *et al.* 2008).

One can propose that deep groundwater fulfils a similar function as a dynamic 'sink' for soluble salts. It is widely recognized that deep groundwater is highly saline, and the source of this salinity is much debated (e.g. Pauwels *et al.* 1993; Fritz 1997). Whatever the source (residual connate water, subsequent marine inundation, evaporite brines, ultrafiltration or radiogenesis), excess density means that such deep brines could remain in place for considerable periods of geological time in the absence of any overwhelming orogenic or thermal event causing them to migrate by forced or free convection. Like seawater, we thus propose that the sulfate content of such deep brines, and the sulfur-isotopic signature thereof, will reflect the dynamic balance of the sulfur sources and sinks: pyrite oxidation, marine/brine infiltration, sulfate dissolution in suprajacent and adjacent strata, and sulfate removal via inorganic precipitation of sulfate salts or by microbial or thermochemical sulfate reduction.

In shallow areas of active groundwater throughflow (e.g. Coal Measures outcrop areas in the UK) one would expect conditions to be broadly oxidizing and for residual marine or evaporitic sulfate salts to have been flushed away by dissolution. One might thus expect groundwater sulfate signatures to be dominated by sulfide or pyrite oxidation (typically low $\delta^{34}S$ in the range of −10 to +10‰). In deeper groundwater, one would expect dissolved sulfate-rich brines from evaporite dissolution or marine inundation to accumulate (in the range +15 to +25‰) and for microbial sulfate reduction to become progressively more important as the environment becomes depleted in oxidizing species, resulting in sulfur isotope fractionation and enrichment of the residual dissolved phase in ^{34}S (where the system becomes partially closed with respect to, or experiences restricted availability of, sulfate).

Because the groundwater is system is not well interconnected either vertically or globally (in the way that seawater is), there would be no homogeneous isotopic signal, merely a local sulfur isotopic profile with a tendency toward enrichment of ^{34}S with depth, relative to ^{32}S (Fig. 7).

A possible objection to this hypothesis is the $\delta^{18}O$ and $\delta^{2}H$ isotopic signatures of our sampled mine waters, which suggest a derivation from modern rainfall (Fig. 3). Whilst samples of brackish–saline groundwaters from deep Triassic and Permian basins in the UK return rather variable $\delta^{18}O$ and $\delta^{2}H$ values (suggesting a complex evolutionary history: Darling *et al.* 1997), unconfined modern groundwaters reflect a dominance of integrated values of 'modern' Holocene meteoric water (Darling and Talbot 2003; Darling *et al.* 2003), with no evidence of evapotranspiration impacting on the O and H isotope values. It is therefore unsurprising that mine waters, whose hydrogeology has been open to surface-water recharge at least since the start of mining, also largely reflect modern meteoric water values (e.g. Burnside *et al.* 2016*a*, *b*; this study). It would, however, only take a small fraction of deep saline groundwater or porewater in a modern mine water flow to significantly affect the sulfate-S isotopic composition, without necessarily having a major impact on the bulk isotopic composition of the water molecules. Whilst the O and H in these waters is an integrated measure of recent surface-water values, the salinity in these waters may not be controlled by surface recharge but may, instead, be reflecting deep groundwaters.

Conclusion

Around 20 ferruginous groundwaters have been sampled from mined Carboniferous strata in the Tyneside and East Midlands coalfields of the UK, and the dissolved sulfate content has been analysed for δ^{34}S. Shallow, gravity-drained mine waters tend to exhibit dissolved sulfate δ^{34}S concentrations of <+10‰, which is regarded as compatible with derivation from the oxidation of sedimentary Carboniferous pyrite.

Deeper waters, derived from the sampling of boreholes or deep shafts, pumped for purposes of regional mine water control, tend to be more saline and also exhibit dissolved sulfate δ^{34}S concentrations of >+14‰ and, in two cases, >+30‰. These values are highly unlikely to be explained purely by pyrite oxidation and are more compatible with a derivation from marine water/evaporite brines, dissolution of evaporite salts or, conceivably, by microbially facilitated sulfide oxidation by bacteria such as *Desulfurivibrio alkaliphilus* (which are hitherto unrecorded in deep subsurface environments but which are demonstrated to favour saline, alkaline, anoxic environments: Pellerin *et al.* 2019). The very highest values >+30‰ are unlikely to have been derived wholly from pyrite or from marine/evaporite sources (unless from marine salts deposited around the Permo-Triassic boundary). To explain the highest sulfur isotope values, some form of isotopic fractionation seems necessary, most probably by ongoing microbial sulfate reduction to sulfide (preferentially removing ^{32}S and leaving the residual dissolved phase enriched in ^{34}S).

No single explanatory factor can be advanced to explain the depth- and salinity-related trends in δ^{34}S in the mine waters. We suggests that deep groundwater be regarded as a dynamic reservoir for soluble salts such as chloride and sulfate, whose sulfur isotope composition depends on relative source and sink rates. Density favours the accumulation of evaporite- or marine-derived brines at depth, and anoxic conditions favour microbial sulfate reduction: both factors in turn result in elevated dissolved-phase δ^{34}S concentrations. Shallow groundwater systems in Carboniferous British upland areas have been flushed of residual marine/evaporite salts and more oxidizing conditions favour a derivation of sulfate from sulfide oxidation, typically resulting in lower δ^{34}S values.

Other published research (Banks *et al.* 2020; Rinder *et al.* 2020) suggests that the sulfur isotopic stratification of mine water is internationally widespread, having been reported from Spain, Poland and Germany in addition to the UK. Moreover, the phenomenon may not be restricted to mine water but may occur more universally in groundwater systems, as evidenced by thermal waters in the limestones of Derbyshire, UK (Bottrell *et al.* 2000; Gunn *et al.* 2006) and from the deep Pohang geothermal reservoir in Korea (Banks *et al.* 2021).

Scientific editing by Jonathan Smith

Acknowledgements The authors would like to thank Diane Steele, Groundwater Technical Specialist, and her colleagues at the Groundwater, Hydrology and Contaminated Land team, NE Area, Environment Agency for kindly sampling the Tyneside House and Birtley observation boreholes. The authors also thank John Gordon of the Coal Authority for providing samples of mine water from the Gateshead Baltic Geothermal Scheme, Dr Anke Neumann of Newcastle University for providing historical hydrochemical data for the Tyneside House boreholes and David Townsend of Town Rock Energy Ltd for assisting with sampling the Abbotsford Road geothermal scheme. The water chemistry (chloride and sulfate) data for 'A' Winning, Strafford and Elsecar Water Drift have been reproduced in Table 2 with permission of the Coal Authority (© The Coal Authority, all rights reserved). The authors also thank Prof. Simon Bottrell of the University of Leeds for provision, and permission to reproduce, the Selby data in Figure 1. The authors would like to thank the reviewers of this paper for their valuable comments.

Author contributions **DB**: conceptualization (lead), data curation (lead), project administration (equal), writing – original draft (lead), methodology (equal); **AJB**: conceptualization (supporting), data curation (supporting), formal analysis (lead), methodology (equal), project administration (equal), resources (equal), writing – review & editing (equal).

Funding This pilot study was carried out without external project funding. However, staff time was funded by the University of Glasgow (DB) and by SUERC and the NERC NEIF Facility at SUERC (AJB, under their pilot analyses scheme). Isotopic analyses were carried out at the NEIF-Geoscience-High T Facility at SUERC (Grant: NERC Facility contract NE/S011587/1).

Competing interests The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability The data generated by this study is contained in full in Supplementary material A of this paper.

References

Banks, D. 1997*a*. The spas of England. *In:* Albu, M., Banks, D. and Nash, H. (eds) *Thermal and Mineral Groundwater Resources*. Springer, Dordrecht, The Netherlands, 235–280, https://doi.org/10.1007/978-94-011-5846-6_10

Banks, D. 1997*b*. Hydrogeochemistry of Millstone Grit and Coal Measures groundwaters, south Yorkshire and north Derbyshire, UK. *Quarterly Journal of Engineering Geology and Hydrogeology*, **30**, 237–256, https://doi.org/10.1144/GSL.QJEG.1997.030.P3.06

Banks, D., Burke, S.P. and Gray, C.G. 1996*a*. *Hydrogeochemistry of Coal Mine Drainage and Other Ochre Waters in North Derbyshire and South Yorkshire, UK*. NGU Report 96.140. Norges Geologiske Undersøkelse, Trondheim, Norway, https://www.ngu.no/upload/Publikasjoner/rapporter/1996/96_140.pdf

Banks, D., Younger, P.L. and Dumpleton, S. 1996*b*. The historical use of mine-drainage and pyrite-oxidation waters in Central and Eastern England, United Kingdom. *Hydrogeology Journal*, **4**, 55–68, https://doi.org/10.1007/s100400050091

Banks, D., Burke, S.P. and Gray, C.G. 1997. Hydrogeochemistry of coal mine drainage and other ferruginous waters in North Derbyshire and South Yorkshire, UK. *Quarterly Journal of Engineering Geology and Hydrogeology*, **30**, 257–280, https://doi.org/10.1144/GSL.QJEG.1997.030.P3.07

Banks, D., Athresh, A., Al-Habaibeh, A. and Burnside, N. 2019. Water from abandoned mines as a heat source: practical experiences of open- and closed-loop strategies, United Kingdom. *Sustainable Water Resources Management*, **5**, 29–50, https://doi.org/10.1007/s40899-017-0094-7

Banks, D., Boyce, A.J., Burnside, N.M., Janson, E. and Roqueñi Gutierrez, N. 2020. On the common occurrence of sulphate with elevated δ^{34}S in European mine waters: sulphides, evaporites or seawater? *International Journal of Coal Geology*, **232**, 103619, https://doi.org/10.1016/j.coal.2020.103619

Banks, D., Boyce, A.J., Westaway, R. and Burnside, N.M. 2021. Sulphur isotopes in deep groundwater reservoirs: evidence from post-stimulation flowback at the Pohang geothermal facility, Korea. *Geothermics*, **91**, 102003, https://doi.org/10.1016/j.geothermics.2020.102003

Banks, D., Steven, J., Black, A. and Naismith, J. 2022. Conceptual modelling of two large-scale mine water geothermal energy schemes: Felling, Gateshead, UK. *International Journal of Environmental Research and Public Health*, **19**, 1643, https://doi.org/10.3390/ijerph19031643

Banks, S.B. and Banks, D. 2001. Abandoned mines drainage: impact assessment and mitigation of discharges from coal mines in the UK. *Engineering Geology*, **60**, 31–37, https://doi.org/10.1016/S0013-7952(00)00086-7

Barnatt, J. and Bannister, N. 2009. *The Archaeology of a Great Estate: Chatsworth and Beyond*. Oxbow Books, Oxford, UK.

Böttcher, M.E., Bernasconi, S.M. and Brumsack, H.J. 1999. Carbon, sulfur, and oxygen isotope geochemistry of interstitial waters from the western Mediterranean Basin. *In:* Zahn, R., Comas, M.C. and Klaus, A. (eds) *Proceedings of the Ocean Drilling Program, Scientific Results, Volume 161*. Ocean Drilling Program, College Station, TX, 413–421, https://doi.org/10.2973/odp.proc.sr.161.229.1999

Bottrell, S.H., Webber, N., Gunn, J. and Worthington, S.R.H. 2000. The geochemistry of sulphur in a mixed allogenic–autogenic karst catchment, Castleton, Derbyshire, UK. *Earth Surface Processes and Landforms*, **25**, 155–165, https://doi.org/10.1002/(SICI)1096-9837(200002)25:2<155::AID-ESP55>3.0.CO;2-P

Bottrell, S.H., West, L.J. and Yoshida, K. 2006. Combined isotopic and modelling approach to determine the source of saline groundwaters in the Selby Triassic sandstone aquifer. *Geological Society, London, Special Publications*, **263**, 325–338, https://doi.org/10.1144/GSL.SP.2006.263.01.19

Bradley, R. 2018. *Secret Matlock and Matlock Bath*. Amberley Publishing, Stroud, UK.

Brunner, B. and Bernasconi, S.M. 2005. A revised isotope fractionation model for dissimilatory sulfate reduction in sulfate reducing bacteria. *Geochimica et Cosmochimica Acta*, **69**, 4759–4771, https://doi.org/10.1016/j.gca.2005.04.015

Bullock, L.A., Parnell, J., Perez, M., Armstrong, J.G., Feldmann, J. and Boyce, A.J. 2018. High selenium in the Carboniferous Coal Measures of

Northumberland, North East England. *International Journal of Coal Geology*, **195**, 61–74, https://doi.org/10.1016/j.coal.2018.05.007

Burke, A., Present, T. *et al.* 2018. Sulfur isotopes in rivers: insights into global weathering budgets, pyrite oxidation, and the modern sulfur cycle. *Earth and Planetary Science Letters*, **496**, 168–177, https://doi.org/10.1016/j.epsl.2018.05.022

Burnside, N.M., Banks, D. and Boyce, A.J. 2016*a*. Sustainability of thermal energy production at the flooded mine workings of the former Caphouse Colliery, Yorkshire, United Kingdom. *International Journal of Coal Geology*, **164**, 85–91, https://doi.org/10.1016/j.coal.2016.03.006

Burnside, N.M., Banks, D., Boyce, A.J. and Athresh, A. 2016*b*. Hydrochemistry and stable isotopes as tools for understanding the sustainability of minewater geothermal energy production from a 'standing column' heat pump system: Markham Colliery, Bolsover, Derbyshire, UK. *International Journal of Coal Geology*, **165**, 223–230, https://doi.org/10.1016/j.coal.2016.08.021

Carmody, R., Plummer, L., Busenberg, E. and Coplen, T. 1998. *Methods for Collection of Dissolved Sulfate and Sulfide and Analysis of Their Sulfur Isotopic Composition*. United States Geological Survey Open-File Report, **97-234**, https://doi.org/10.3133/ofr97234

Chambers, L. and Trudinger, P. 1979. Microbiological fractionation of stable sulfur isotopes: a review and critique. *Geomicrobiology*, **1**, 249–293, https://doi.org/10.1080/01490457909377735

Clowes, F. 1889. Deposits of barium sulphate from mine water. *Proceedings of the Royal Society of London*, **46**, 368–369, https://doi.org/10.1098/rspl.1889.0046

Coal Authority 2018. *A-Winning Mine Water Treatment Scheme*. Coal Authority, Mansfield, UK, https://www.gov.uk/government/case-studies/a-winning-mine-water-treatment-scheme [accessed 1 July 2022].

Coal Authority 2022. *Mine Water Energy Scheme at Gateshead*. Coal Authority, Mansfield, UK, https://www2.groundstability.com/major-grant-to-connect-gateshead-homes-to-coal-authority-mine-water-energy-scheme/ [accessed 1 July 2022].

Coleman, M. and Moore, M. 1978. Direct reduction of sulfates to sulfur dioxide for isotopic analysis. *Analytical Chemistry*, **50**, 199–260, https://doi.org/10.1021/ac50033a056

Craig, H. 1961. Isotopic variations in meteoric waters. *Science*, **133**, 1702–1703, https://doi.org/10.1126/science.133.3465.1702

Dalrymple-Smith, D. 2012. *Notes on Baslow coal*. Baslow History website, https://baslowhistory.files.wordpress.com/2021/03/robin-hood-coal-mine.pdf

Darling, W.G. and Talbot, J.C. 2003. The O and H stable isotope composition of freshwaters in the British Isles. 1. Rainfall. *Hydrology and Earth System Sciences*, **7**, 163–181, https://doi.org/10.5194/hess-7-163-2003

Darling, W.G., Edmunds, W.M. and Smedley, P.L. 1997. Isotopic evidence for palaeowaters in the British Isles. *Applied Geochemistry*, **12**, 813–829, https://doi.org/10.1016/S0883-2927(97)00038-3

Darling, W.G., Bath, A.H. and Talbot, J.C. 2003. The O and H stable isotope composition of freshwaters in the British Isles. 2. Surface waters and groundwater. *Hydrology and Earth System Sciences*, **7**, 183–195, https://doi.org/10.5194/hess-7-183-2003

Davies-Vollum, K.S., Guion, P.D., Knight, J.A. and Smith, A. 2016. Geology of Caphouse Colliery, Wakefield, Yorkshire, UK. *Proceedings of the Yorkshire Geological Society*, **61**, 97–108, https://doi.org/10.1144/pygs2015-372

Dean, S.P. 1994. *A Study of the Organic and Inorganic Geochemistry of Sulphur in Shales*. PhD thesis, University of Leeds, Leeds, UK, https://core.ac.uk/reader/42605110

Demin, O.A., Dudeney, A.W.L. and Tarasova, I.I. 2010. Remediation of ammonia-rich minewater in constructed wetlands. *Environmental Technology*, **23**, 497–514, https://doi.org/10.1080/09593332308618388

Derbyshire Heritage 2022. *Beeley Moor coal pits* Derbyshire Heritage website, https://derbyshireheritage.co.uk/industrial/mines/coal-mines/beeley-moor-coal-pits/ [accessed 14 July 2022].

Dogramaci, S., McLean, L. and Skrzypek, G. 2017. Hydrochemical and stable isotope indicators of pyrite oxidation in carbonate-rich environment; the Hamersley Basin, Western Australia. *Journal of Hydrology*, **545**, 288–298, https://doi.org/10.1016/j.jhydrol.2016.12.009

Dold, B. and Spangenburg, J.E. 2005. Trends of water-soluble sulfates in mine tailings profiles. *Environmental Science and Technology*, **39**, 5650–5656, https://doi.org/10.1021/es040093a

Donnelly, T., Waldron, S., Tait, A., Dougans, J. and Bearhop, S. 2001. Hydrogen isotope analysis of natural abundance and deuterium-enriched waters by reduction over chromium on-line to a dynamic dual inlet isotope-ratio mass spectrometer. *Rapid Communications in Mass Spectrometry*, **15**, 1297–1303, https://doi.org/10.1002/rcm.361

Dumpleton, S. 2020. *Discussion on SK3181: A rusty spring*. Geograph website, SK3181, https://www.geograph.org.uk/photo/6437730 [accessed 14 July 2022].

Dunham, K.C. 1973. A recent deep borehole near Eyam, Derbyshire. *Nature*, **241**, 84–85, https://doi.org/10.1038/physci241084a0

Edwards, W. 1951. *The Concealed Coalfield of Yorkshire and Nottinghamshire*. 3rd edn. Memoirs of the Geological Survey (Coalfield). HMSO, London.

Environment Agency 1996. *Environmental Assessment of Selected Abandoned Mine Waters in the North East Region*. Environment Agency, Bristol, UK, http://www.environmentdata.org/archive/ealit:636/OBJ/19000963.pdf

Fike, D., Bradley, A. and Rose, C. 2015. Rethinking the ancient sulphur cycle. *Annual Review of Earth and Planetary Sciences*, **43**, 593–622, https://doi.org/10.1146/annurev-earth-060313-054802

Friends of Hemingfield Colliery 2017. *Friends in the Field, or Catching the drift*. Blog entry. Friends of Hemingfield Colliery website, https://hemingfieldcolliery.org/2017/01/12/2017-happy-new-year/

Fritz, P. 1997. Saline groundwater and brines in crystalline rocks: the contributions of John Andrews and Jean-Charles Fontes to the solution of a hydrogeological and geochemical problem. *Applied Geochemistry*, **12**, 851–856, https://doi.org/10.1016/S0883-2927(97)00074-7

Geroni, J.N. 2011. *Rates and Mechanisms of Chemical Processes Affecting the Treatment of Ferruginous Mine Water*. PhD thesis, University of Cardiff, Cardiff, UK, https://core.ac.uk/works/23155659

Gray, G. and Judd, A.G. 2003. Barium sulphate production from mine waters in South East Northumberland. *British Mining*, **73**, 72–88, https://www.nmrs.org.uk/wp-content/uploads/2019/06/Barium-Sulphate-Production-from-mine-waters.pdf

Gunn, J., Bottrell, S.H., Lowe, D.J. and Worthington, S.R.H. 2006. Deep groundwater flow and geochemical processes in limestone aquifers: evidence from the thermal waters in Derbyshire, England, UK. *Hydrogeology Journal*, **14**, 868–881, https://doi.org/10.1007/s10040-006-0022-7

Harrison, R., Scott, W.B. and Smith, T. 1989. A note on the distribution, levels and temperatures of minewaters in the Northumberland and Durham coalfield. *Quarterly Journal of Engineering Geology*, **22**, 355–358, https://doi.org/10.1144/GSL.QJEG.1989.022.04.08

IAEA/WMO 2022. *Global Network of Isotopes in Precipitation. The GNIP Database*. International Atomic Energy Agency (IAEA)/World Meteorological Organization (WMO), https://nucleus.iaea.org/wiser

Janson, E., Boyce, A.J., Burnside, N. and Gzyl, G. 2016. Preliminary investigation on temperature, chemistry and isotopes of mine water pumped in Bytom geological basin (USCB Poland) as a potential geothermal energy source. *International Journal of Coal Geology*, **164**, 104–114, https://doi.org/10.1016/j.coal.2016.06.007

Keeling, R. 2009. *A Field Evaluation of the American Standard Method for the Determination of Alkalinity, Acidity and Net Acidity in Mine Waste Waters*. MSc thesis, University of Leeds, Leeds, UK.

Kipling, R. 1902. *Just So Stories for Little Children*. Macmillan & Co., London.

Leavitt, W., Halevy, I., Bradley, A. and Johnston, D. 2013. Influence of sulfate reduction rates on the Phanerozoic sulfur isotope record. *Proceedings of the National Academy of Sciences of the United States of America*, **110**, 11244–11249, https://doi.org/10.1073/pnas.1218874110

Loredo, C., Ordóñez, A. *et al.* 2017. Hydrochemical characterization of a mine water geothermal energy resource in NW Spain. *Science of The Total Environment*, **576**, 59–69, https://doi.org/10.1016/j.scitotenv.2016.10.084

Love, L., Coleman, M. and Curtis, C. 1983. Diagenetic pyrite formation and sulphur isotope fractionation associated with a Westphalian marine incursion, northern England. *Transactions of the Royal Society of Edinburgh: Earth Sciences*, **74**, 165–182, https://doi.org/10.1017/S0263593300009822

Manning, D.A.C. and Hutcheon, I.E. 2004. Distribution and mineralogical controls on ammonium in deep groundwaters. *Applied Geochemistry*, **19**, 1495–1503, https://doi.org/10.1016/j.apgeochem.2004.01.019

McCormick, J.P. 1993. Mining sites of Dore. *Dore to Door. Dore Village Society*, **30**, 8–9, https://dorevillage.co.uk/documents/download/59ae6082-55b8-4b49-a960-3366816b3dfb

McKay, J. and Longstaffe, F. 2003. Sulphur isotope geochemistry of pyrite from the upper Cretaceous Marshybank Formation, Western Interior Basin. *Sedimentary Geology*, **157**, 175–195, https://doi.org/10.1016/S0037-0738(02)00233-6

Meyer, K.M., Kump, L.R. and Ridgwell, A. 2008. Biogeochemical controls on photic-zone euxinia during the end-Permian mass extinction. *Geology*, **36**, 747–750, https://doi.org/10.1130/G24618A.1

Millero, F.J., Feistel, R., Wright, D.G. and McDougall, T.J. 2008. The composition of Standard Seawater and the definition of the Reference-Composition Salinity Scale. *Deep Sea Research Part I: Oceanographic Research Papers*, **55**, 50–72, https://doi.org/10.1016/j.dsr.2007.10.001

Monaghan, A.A., Bateson, L. *et al.* 2022. Time zero for net zero: a coal mine baseline for decarbonising heat. *Earth Science, Systems and Society*, **2**, 10054, https://doi.org/10.3389/esss.2022.10054

Nelson, S. 2000. A simple, practical methodology for routine VSMOW/SLAP normalization of water samples analyzed by continuous flow methods. *Rapid Communications in Mass Spectrometry*, **14**, 1044–1046, https://doi.org/10.1002/1097-0231(20000630)14:12<1044::AID-RCM987>3.0.CO;2-3

Newcastle University 2018. *Water Quality in the Tyneside House Boreholes*. Report from the sampling campaign 20 February 2018, carried out jointly by the Environment Agency and Newcastle University (fieldwork component of module CEG8111), 28 June 2018. Newcastle University, Newcastle, UK.

Otero, N. and Soler, A. 2002. Sulphur isotopes as tracers of the influence of potash mining in groundwater salinisation in the Llobregat Basin (NE Spain). *Water Research*, **36**, 3989–4000, https://doi.org/10.1016/S0043-1354(02)00125-2

Pauwels, H., Fouillac, C. and Fouillac, A.M. 1993. Chemistry and isotopes of deep geothermal saline fluids in the Upper Rhine Graben. Origin of compounds and water–rock interactions. *Geochimica et Cosmochimica Acta*, **57**, 2737–2749, https://doi.org/10.1016/0016-7037(93)90387-C

Pellerin, A., Antler, G. *et al.* 2019. Large sulfur isotope fractionation by bacterial sulfide oxidation. *Science Advances*, **5**, eaaw1480, https://doi.org/10.1126/sciadv.aaw1480

Present, T.M., Adkins, J.F. and Fischer, W.W. 2020. Variability in sulfur isotope records of Phanerozoic seawater sulfate. *Geophysical Research Letters*, **47**, e2020GL088766, https://doi.org/10.1029/2020GL088766

Rees, C. 1973. A steady-state model for sulphur isotope fractionation in bacterial reduction processes. *Geochimica et Cosmochimica Acta*, **37**, 1141–1162, https://doi.org/10.1016/0016-7037(73)90052-5

Rinder, T., Dietzel, M., Stammeier, J.A., Leis, A., Bedoya-González, D. and Hilberg, S. 2020. Geochemistry of coal mine drainage, groundwater, and brines from the Ibbenbüren mine, Germany: a coupled elemental-isotopic approach. *Applied Geochemistry*, **121**, 104693, https://doi.org/10.1016/j.apgeochem.2020.104693

Sauerheber, R. and Heinz, B. 2015. Temperature effects on conductivity of seawater and physiologic saline, mechanism and significance. *Chemical Sciences Journal*, **6**, 1000109, https://www.hilarispublisher.com/open-access/temperature-effects-on-conductivity-of-seawater-and-physiologic-salinemechanism-and-significance-2150-3494-1000109.pdf

Schwarcz, H. and Burnie, S. 1973. Influence of sedimentary environments on sulfur isotope ratios in clastic rocks: a review. *Mineralium Deposita*, **8**, 264–277, https://doi.org/10.1007/BF00203208

Shanks, W.C., Böhlke, J.K. and Seal, R.R. 1995. Stable isotopes in mid-ocean ridge hydrothermal systems: interactions between fluids, minerals, and organisms. *American Geophysical Union Geophysical Monograph Series*, **91**, 194–221, https://doi.org/10.1029/GM091p0194

Sill, M. 1985. The Selby coalfield project: progress to 1984. *Geography*, **70**, 69–71, https://www.jstor.org/stable/pdf/40571498

Sim, M.S., Bosak, T. and Ono, S. 2011. Large sulfur isotope fractionation does not require disproportionation. *Science*, **333**, 74–77, https://doi.org/10.1126/science.1205103

Smailes, A.E. 1935. The development of the Northumberland and Durham Coalfield. *Scottish Geographical Magazine*, **51**, 201–214, https://doi.org/10.1080/14702543508554344

Strauss, H. 1997. The isotopic composition of sedimentary sulfur through time. *Palaeogeography, Palaeoclimatology, Palaeoecology*, **132**, 97–118, https://doi.org/10.1016/S0031-0182(97)00067-9

SWK 1996. *Coal Authority Study of Gravity Drainage from Abandoned Mines*. Scott Wilson Kirkpatrick (SWK) for the Coal Authority, Chesterfield, UK.

Taylor, B., Wheeler, M. and Nordstrom, D. 1984. Stable isotope geochemistry of acid mine drainage: experimental oxidation of pyrite. *Geochimica et Cosmochimica Acta*, **48**, 2669–2678, https://doi.org/10.1016/0016-7037(84)90315-6

Tostevin, R., Turchyn, A., Farquhar, J., Johnston, D., Eldridge, D., Bishop, J. and McIlvin, M. 2014. Multiple sulfur isotope constraints on the modern sulfur cycle. *Earth and Planetary Science Letters*, **396**, 14–21, https://doi.org/10.1016/j.epsl.2014.03.057

Tostevin, R., Craw, D., Van Hale, R. and Vaughan, M. 2016. Sources of environmental sulfur in the groundwater system, southern New Zealand. *Applied Geochemistry*, **70**, 1–16, https://doi.org/10.1016/j.apgeochem.2016.05.005

Turner, B.R. and Richardson, D. 2004. Geological controls on the sulphur content of coal seams in the Northumberland Coalfield, Northeast England. *International Journal of Coal Geology*, **60**, 169–196, https://doi.org/10.1016/j.coal.2004.05.003

Tyler, R.H., Boyer, T.P., Minami, T., Zweng, M.M. and Reagan, J.R. 2017. Electrical conductivity of the global ocean. *Earth, Planets and Space*, **69**, 156, https://doi.org/10.1186/s40623-017-0739-7

Wain, K. 2014. *The Coal Mining Industry of Barnsley, Rotherham and Worksop*. Amberley Publishing. Stroud, UK.

Walls, D.B., Burnside, N.M. and Boyce, A.J. 2021. *During drilling and test pumping - S isotopes*. British Geological Survey Online Workshop, UKGEOS Glasgow Hydrobiogeochemistry Workshop, 13 April 2021, British Geological Survey.

Walls, D.B., Banks, D., Peshkur, T., Boyce, A.J. and Burnside, N.M. 2022. Heat recovery potential and hydrochemistry of mine discharges from Scotland's coalfields. *Earth Science, Systems and Society*, **2**, 10056, https://doi.org/10.3389/esss.2022.10056

Whitworth, K., England, A. and Parry, D. 2012. *Overview of Mine Water in the UK Coalfields*. White Young Green Engineering Report for the Coal Authority. White Young Green (WYG), Annesley, UK, https://www.whatdotheyknow.com/request/690399/response/1652459/attach/7/Overview%20of%20Mine%20Water%20in%20the%20UK%20Final%20Report%20by%20WYG%20Nov2012.pdf