The occurrence of elevated $\delta^{34}S$ in dissolved sulfate in a multi-level coal mine water system, Glasgow, UK

David B. Walls [a,b,*], Adrian J. Boyce [c], David Banks [b], Neil M. Burnside [a]

[a] Department of Civil and Environmental Engineering, University of Strathclyde, Glasgow, UK
[b] James Watt School of Engineering, University of Glasgow, Glasgow, UK
[c] Scottish Universities Environmental Research Centre, East Kilbride, UK
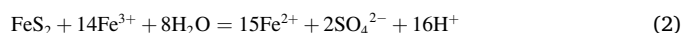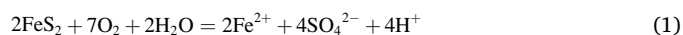
A R T I C L E   I N F O

A B S T R A C T

Stable isotopic compositions of $\delta^{18}O$, $\delta^{2}H$ and dissolved sulfate $\delta^{34}S$ in water from abandoned and flooded coal mines are used to interpret the water's and solutes' origin and interactive history. These isotopic ratios have been determined in mine water from a shallow (<100 m) series of overlapping coal mine workings at the UK Geo-energy Observatories Glasgow Geothermal Energy Research Field Site (UKGEOS GGERFS). Comparison has been made between dissolved sulfate $\delta^{34}S$ of water in mined Carboniferous coal-bearing strata, that of water which had interacted with equivalent unmined strata, and $\delta^{34}S$ in sulfide-bearing minerals (pyrite) in the host sedimentary rocks and local evaporite (gypsum) of the Lower Carboniferous Ballagan Formation. $\delta^{18}O$ and $\delta^{2}H$ confirm a meteoric origin for coal mine waters. The $\delta^{34}S$ arithmetic mean and standard deviation of the pyrite (+5.0 ± 15.5‰) and water from unmined strata (+0.3 ± 2.1‰) were found to be similar, whereas the mine water exhibited elevated isotopic values (+20.3 ± 1.1‰), plotting closer to that of modern-day seawater (+21.2‰) and Ballagan Formation gypsum (+18.9 ± 0.5‰). Whilst the origin of dissolved sulfate in the mine water remains unclear, it is unlikely to be wholly due to simple pyrite oxidation. Influence of evaporite dissolution, fractionation associated with microbial sulfate reduction, and mixing with saline formation waters of marine, evaporitic or of another origin, cannot be ruled out.

1. Introduction

The origin of dissolved sulfate in flooded coal mine waters has typically been considered the result of dissolution of iron sulfide minerals (pyrite) following their oxidation to form dissolved metals and sulfate, often via secondary hydroxysulfate mineral phases (Hammarstrom et al., 2005; Younger, 1995, 1997). Sulfide oxidation occurs during mining operations and groundwater flooding following mine closure, whereby the latter dissolves the products of oxidation (Banks et al., 1997; Burnside et al., 2016a). The electron acceptor for oxidation may be oxygen (Eq. (1)) or ferric iron (Eq. (2)) as oxidants.

$$2FeS_2 + 7O_2 + 2H_2O = 2Fe^{2+} + 4SO_4^{2-} + 4H^+ \qquad (1)$$

$$FeS_2 + 14Fe^{3+} + 8H_2O = 15Fe^{2+} + 2SO_4^{2-} + 16H^+ \qquad (2)$$

The natural variability of the stable sulfur isotope ^{34}S, relative to the most common isotope ^{32}S (measured as $\delta^{34}S$), provides insight into the source and history of mine water sulfate (Banks et al., 2020; Janson

et al., 2016). Oxidation reactions typically proceed with negligible sulfur isotopic fractionation (Chen et al., 2020), meaning produced sulfate should be isotopically similar to the source sulfide, thus, the sulfate produced by reactions 1 and 2 should closely reflect the weighted isotopic average of the oxidised pyrite.

It has been shown that $\delta^{34}S$ values of cleat and banded pyrite in regional Carboniferous coals (East Ayrshire) range between −26.3‰ and +18.4‰ with an overall arithmetic mean and standard deviation of +2.7 ± 9.5‰ ($n = 21$) (Bullock et al., 2018). Thus, oxidation-controlled generation of Scottish mine water sulfate would give a similar $\delta^{34}S$ value, provided this mean is broadly representative of Scottish Carboniferous coals. Previous studies, however, have published data showing significant difference between the isotopic signatures of mine water and of sulfide minerals, whereby deep mine water sulfate $\delta^{34}S$ reaches +20‰ and occasionally higher (Banks et al., 2020; Burnside et al., 2016b; Loredo et al., 2017). Shallower mine waters commonly exhibit lower sulfate $\delta^{34}S$ closer to the sulfide range (Banks and Boyce, 2023; Banks et al., 2020; Walls et al., 2022b). Some researchers have

assigned explanatory narratives to the origins of the elevated S isotopes in mine waters from specific study areas. For example, Chen et al. (2020) conclude that mine waters of the Anhui Province, China obtained elevated sulfate concentrations and dissolved sulfate enriched in $\delta^{34}S$ through the complex influence of high $\delta^{34}S$ evaporite gypsum in the coal bearing sequence. Since seawater and derived evaporite deposits from throughout the Carboniferous period typically have $\delta^{34}S$ values between +13‰ and +21‰ (Kampschulte et al., 2001), resultant $\delta^{34}S$ signatures of groundwaters affected by dissolution of evaporites of that age should match this range. The values associated with Carboniferous sea water are distinctly more enriched in ^{34}S than the mean Carboniferous pyrite from East Ayrshire. More broadly, in Europe, evaporites are notably present in Permian and Triassic strata overlying coal-bearing sequences, with typical values between +10‰ and +20‰ (nearer +10‰ in Permian Zechstein period of massive evaporite deposition (Claypool et al., 1980)). Elevated dissolved sulfate $\delta^{34}S$ in Polish and German coal mine waters has been ascribed to the influence of Triassic or even Miocene evaporites (Banks et al., 2020; Rinder et al., 2020).

This work reports the detailed monitoring of dissolved sulfate in a series of boreholes drilled into abandoned coal mine workings at the Glasgow Geothermal Energy Research Field Site (GGERFS), which is part of the British Geological Survey's (BGS) UK Geoenergy Observatories (UKGEOS). The GGERFS is a unique facility for monitoring, testing and innovation focused on understanding processes within mine water thermal energy systems (Monaghan et al., 2021c) and its setting typifies the geothermal potential in abandoned, flooded coal mines that are widespread beneath many of the UK's towns and cities (Farr et al., 2021). The samples taken in this study effectively represent a baseline for the GGERFS system, taken during initial drilling before any large-scale hydraulic testing. They thus approach being representative of the state of the system following abandonment of the last mine in 1928 (Findlay et al., 2020). This has allowed the structure of the S isotope distribution across a series of mine water boreholes to be explored for the first time.

2. History and description of the mine system

The GGERFS was developed to allow scientific observations of subsurface processes associated with mine water geothermal energy systems, and monitor their effect on the environment (Monaghan et al., 2019). Situated primarily within the Cuningar Loop of the River Clyde, bordering Glasgow City and South Lanarkshire, the location has similarities with many post-industrial areas across the UK including land use, geology and coal mining history (Monaghan et al., 2021c). The GGERFS

is located above the western side of Scotland's extensively mined Central Coalfield (Clough et al., 1926) and hosts a ~ 300 m thick succession of Scottish Upper, Middle and Lower Coal Measures Formations of Westphalian age (British Geological Survey, 1992b). These sequences host seven worked coal seams from the Farme Colliery (main shaft 55.8356°N, 4.2021°W) dating between 1805 and 1928 (Findlay et al., 2020).

There are 12 boreholes at the GGERFS, spread between two locations (Fig. 1): Dalmarnock and Cuningar Loop. The ground elevation is typically c. 10–12 m relative to Ordnance Datum (OD), around 6–8 m higher than the elevation of the River Clyde at Cuningar. Dalmarnock has one seismic observation borehole - GGC01 (55.8411°N, 4.2227°W), drilled to 199 m below ground level (bgl) (Monaghan et al., 2021a). GGC01 spans the entire stratigraphic section covered by the remaining 11 Cuningar Loop boreholes but, importantly, the coal seams encountered by GGC01 are unworked and intact (Kearsey et al., 2019).

The 11 Cuningar Loop boreholes target various geological intervals at a range of depths (Fig. 2), including:

- Five mine water boreholes which access abandoned, flooded workings of the Glasgow Upper Coal or Glasgow Main Coal seams, screened at depths of c. 49 m and c. 85 m bgl respectively: GGA01, GGA04, GGA05, GGA07, and GGA08 (Barron et al., 2020a; Barron et al., 2020b; Monaghan et al., 2020a; Starcher et al., 2020a; Starcher et al., 2020b).
- Five environmental baseline monitoring boreholes, completed into superficial deposits or bedrock above mine workings, drilled to between 16 m and 45 m bgl: GGA03r, GGA06r, GGA09r, GGB04 and GGB05 (Elsome et al., 2020; Shorter et al., 2020b, 2020c; Walker-Verkuil et al., 2020a; Walker-Verkuil et al., 2020b).
- One sensor testing borehole (GGA02) which penetrated abandoned, flooded coal seams during drilling to a maximum depth of 94 m bgl (Monaghan et al., 2020b).

The boreholes at Cuningar Loop are clustered into three groups: Sites 1, 2 and 3, as described in Fig. 2 and Table 1. Mine water boreholes at Cuningar Loop targeted the thickest seams in the area (between 1 and 1.5 m thick) (Hall et al., 1998), where the abandonment plans showed a variety of mining types including pillar and stall, and areas of 'total extraction' (Monaghan et al., 2021c). A comprehensive description of the mining history and borehole array can be found in Monaghan et al. (2021c). It should be noted, that whilst the Glasgow Upper Coal and the Glasgow Main Coal seams are the target horizons for borehole completion, the Glasgow Ell Coal seam was encountered with mining waste or

Fig. 1. Maps showing a) UKGEOS location within Scotland; b) GGC01 borehole and the Cuningar Loop location (red box) in Glasgow's east end; c) The borehole array at Cuningar Loop on the River Clyde. Contains NERC materials ©NERC 2020. Contains OS data © Crown Copyright and database right 2020 (Monaghan et al., 2019). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)
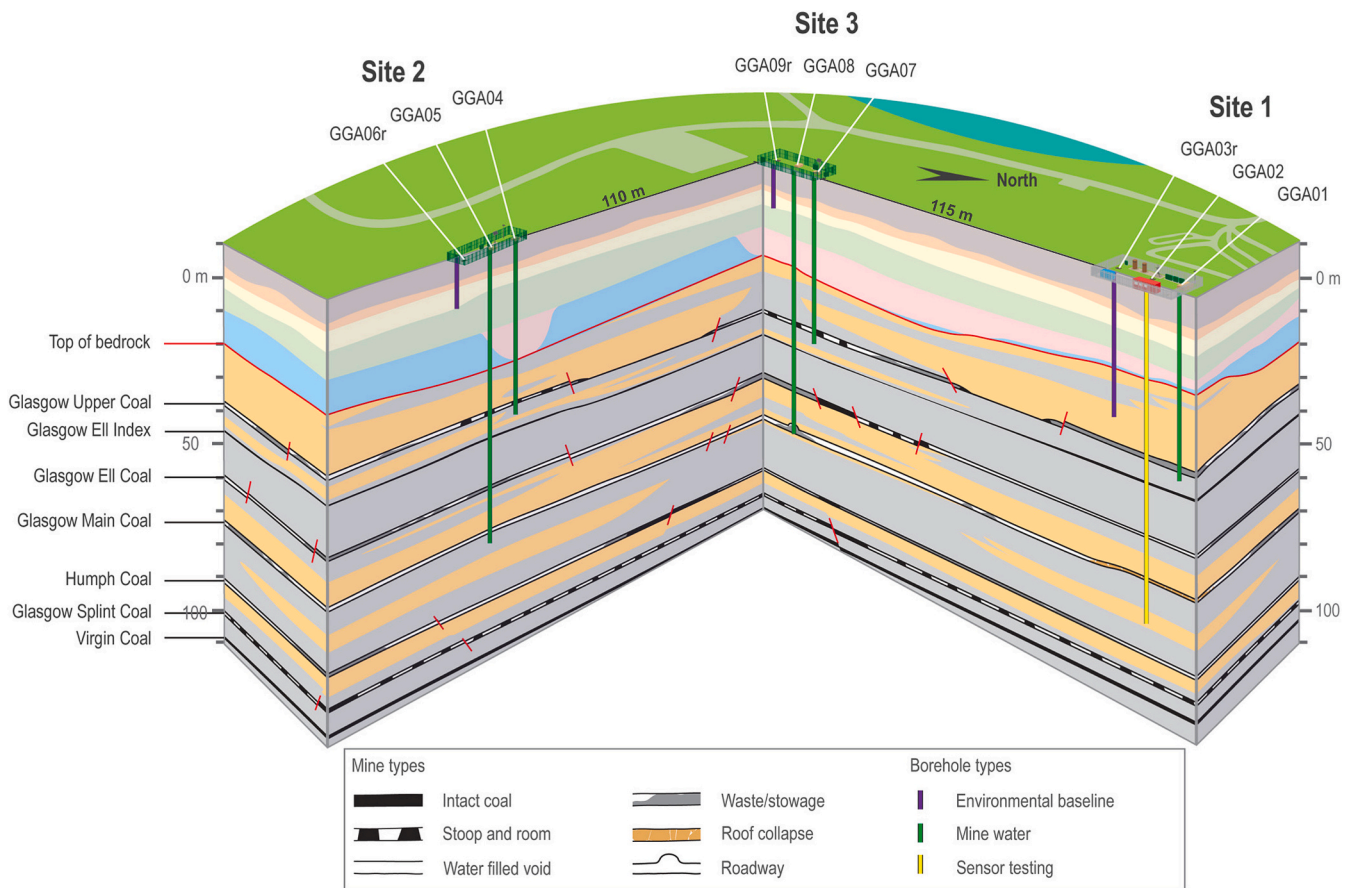
Fig. 2. Block diagram showing the Cuningar Loop borehole array with coal seams labelled. No vertical exaggeration. Note depths are in metres relative to Ordnance Datum (m OD; sea level). Figure originally published by Monaghan et al. (2021c) ©BGS, UKRI 2021.

Table 1
Numbers of water samples collected and analysed by site and sample type.

	Dalmarnock	Cuningar site 1	Cuningar site 2	Cuningar site 3	Cuningar total
	GGC01	GGA01	GGA04	GGA07	
		GGA02	GGA05	GGA08	
		GGA03r	GGA06r	GGA09r	
Borehole fluid samples	14 (2)	11 (11)	14 (8)	22 (19)	47 (38)
Return fluid (routine daily)	12 (6)	10 (7)	13 (6)	14 (9)	37 (22)
Return fluid (rockhead)	N/A	1 (1)	1 (0)	2 (0)	4 (1)
Return fluid (mine water)	N/A	2 (2)	2 (2)	4 (4)	8 (8)
Return fluid total	12 (6)	13 (10)	16 (8)	20 (13)	49 (31)
Pumping test	N/A	3 (3)	5 (5)	5 (5)	13 (13)

Number or samples analysed for $\delta^{34}S$ is in brackets.

voids in each of the 3 deepest boreholes (Figs. 2 and 3) but was subsequently cased off during completion.

3. Methods

3.1. Drilling and test pumping

3.1.1. Dalmarnock

The cored, seismic monitoring borehole GGC01 was drilled in Dalmarnock (55.8411°N, 4.2227°W) between 19 November and 12 December 2018. Rotary coring was advanced using Glasgow's mains water as the direct flush drilling fluid (described in Section 3.1.2.1); specifically, a Geobore-S system was rotated downhole to drill a borehole of 151 mm outer diameter and recovered core of 102 mm diameter in 3 m lengths (Monaghan et al., 2021a). The mains water drilling fluid

had a geomicrobiological tracer added daily in an attempt to maintain a ratio of tracer to drilling fluid of 1:40,000; alongside this, a drilling additive called Insta-pac supplied by CETCO Europe was added to aid drilling (Monaghan et al., 2021a). Following drilling, GGC01 was open hole wireline logged and reamed out to 156 mm diameter to install a 76.6 mm internal diameter uPVC Boode casing which houses a string of 5 seismometers. The annulus of the borehole was grouted with SP/F6 Portland cement-based grout from Tarmac (Monaghan et al., 2021a; Tarmac, 2016).

3.1.2. Cuningar

The drilling, completion and pumping test methodologies for each of the eleven boreholes at Cuningar Loop are detailed in full in their respective British Geological Survey open reports (Barron et al., 2020a; Barron et al., 2020b; Elsome et al., 2020; Monaghan et al., 2020a;
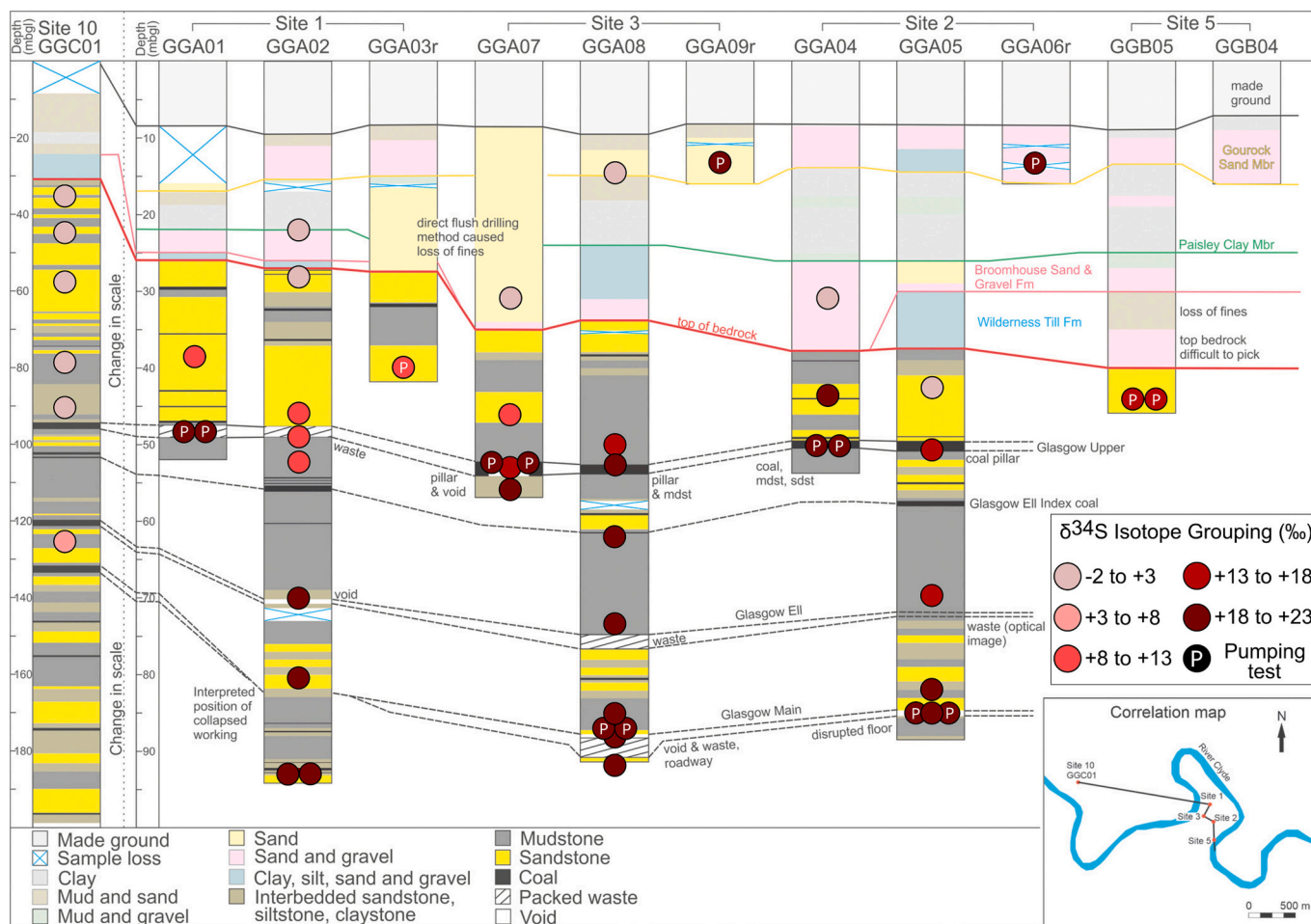
Fig. 3. Lithostratigraphical correlation panel of the Glasgow Observatory boreholes modified from Monaghan et al. (2021c) (©BGS, UKRI 2021) by addition of coloured symbols representing groupings of sulfur isotopic values.

Monaghan et al., 2020b; Shorter et al., 2020b, 2020c; Starcher et al., 2020a; Starcher et al., 2020b; Walker-Verkuil et al., 2020a; Walker-Verkuil et al., 2020b).

3.1.2.1. Drilling fluid and rock samples. The Glasgow mains water which was used as the drilling fluid is ultimately derived (following treatment) from the freshwater Loch Katrine (56.25°N, 4.52°W), around 45 km NNW of Glasgow (Burnet, 1869; Engineering Timelines, 2020). The properties of the water supplied to Cuningar from the Scottish Water plant in Milngavie and of BGS' mains water samples from Dalmarnock are shown in Table 2. During drilling, ingress of formation groundwater

from responsive horizons will have contributed to the overall circulating drilling fluid. Sampled waters from the borehole and the return drilling fluid are most likely a mixture of the initial mains water and formation water. In some instances, bentonite mud was used as drilling fluid where superficial deposits were unstable. During drilling, water or bentonite drilling fluid returned rock chips to the surface; these were separated from the drilling fluid by use of a shaker. Following separation, the drilling fluid was directed into a series of settlement tanks to remove smaller suspended particles before recirculation as "clean" drilling fluid.

3.1.2.2. Made ground and superficial deposits. Each borehole was

Table 2
Mains water quality supplied by Scottish Water to the Cuningar area of Glasgow via Milngavie treatment works, average of 2021 (Scottish Water, 2021); and the average of the two mains water samples taken from the office at the Dalmarnock drilling location (Shorter et al., 2021b).

	Unit	Scottish Water Milngavie mean concentration (2021)	N	BGS Dalmarnock mean concentration (Dec 2018–Jan 2019)	N
pH	pH unit	7.93	36	8.79	2
Electrical conductivity	µS/cm	51	36	60	2
Sodium	mg/L	3.95	8	3.8	2
Calcium	mg/L	n.a.		5.4	2
Ammonium	mg/L as NH_4^+	0.05	36	n.a.	
Iron	mg/L	0.008	36	0.009	2
Manganese	mg/L	0.002	36	0.0004	2
Sulfate	mg/L as SO_4^{2-}	7.55	8	7.08	2
Nitrate	mg/L as NO_3^-	0.7	8	0.47	2
Chloride	mg/L as Cl^-	5.88	8	6.0	2
Alkalinity	meq/L	n.a.		0.15	2

n.a. – not analysed.

progressed through made ground with a BAM piling rig with an 880 mm auger. The made-ground in each was cased-off with permanent steel casing and the annulus was grouted with cement-based grout. The superficial deposits were drilled through to bedrock with tri-cone bits of 558.8 mm for GGA01, GGA02, GGA04, GGA05 and GGA08, and 374 mm for GGA03r and GGB05. GGA08 encountered mobile sands and gravels and hence required redrilling with direct flush duplex drilling method (457 mm outer diameter casing while drilling), GGA07 was drilled using this method to prevent against the same issue (Starcher et al., 2020b). Mains water was used as the drilling fluid whilst progressing through the superficial deposits, except where stability of sand and gravel was an issue, in these instances bentonite mud was used as a drilling fluid, this is true of GGA04, GGA05, GGA08, GGB04 and BBG05. Upon reaching bedrock, the superficial deposits in each borehole were cased-off with permanent steel casing and the annulus was sealed with cement-based grout.

GGA06r, GGA09r and GGB04 were drilled at 191 mm into the superficial deposits and were terminated in the Quaternary Gourock Sand Member, above bedrock. GGA06r has a screened section of 113.8 mm outer diameter Boode BGP™ gravel coated PVC screen with 1 mm slot sizes from +0.31 m to −1.66 m OD, but remains hydraulically open with sand and portions of collapsed borehole in the annulus from +0.51 m to −3.77 m OD (Shorter et al., 2020c). GGA09r has a screened section of 113.8 mm outer diameter Boode BGP™ gravel coated PVC screen with 1 mm slot sizes from −0.01 m to −1.89 m OD, but remains hydraulically open with sand and portions of collapsed borehole in the annulus from +0.02 m to −4.28 m OD (Walker-Verkuil et al., 2020b). GGB04 has a screened section of 113.8 mm outer diameter Boode BGP™ gravel coated PVC screen with 1 mm slot sizes from +1.77 m to −0.13 m OD, but remains hydraulically open with sand and portions of collapsed borehole in the annulus from +1.90 m to −3.60 m OD (Elsome et al., 2020).

3.1.2.3. Bedrock. The five mine water boreholes (GGA01, GGA04, GGA05, GGA07, and GGA08) and the sensor testing borehole (GGA02) were progressed into bedrock with a 406 mm tri-cone bit. The two environmental baseline monitoring boreholes were progressed into bedrock (GGA03r and GGB05) with a smaller 244 mm tri-cone bit. Mains water drilling fluid was used for each of the bedrock sections of the boreholes.

GGA03r and GGB05 were respectively terminated in bedrock c. 8 m and 5 m above the stratigraphically highest coal seam (Glasgow Upper Coal). GGA03r has a screened section of 165 mm outer diameter Boode BGP™ gravel coated PVC screen with 3 mm slot sizes from −26.96 m to −29.77 m OD, but it is hydraulically open with 4–10 mm filter gravel in the annulus from −25.96 m to −30.77 m OD (Shorter et al., 2020b). GGB05 has a screened section of 191 mm outer diameter pipe with 3 mm slot sizes from −30.65 m to −32.45 m OD, but it is hydraulically open with 10 mm gravel in the annulus from −28.45 m to −33.65 m OD (Walker-Verkuil et al., 2020a). Both GGA03r and GGB05 are screened across a sandstone horizon of the Scottish Middle Coal Measures Formation.

3.1.2.4. Glasgow Upper Coal seam. GGA01, GGA04 and GGA07 were drilled as far as the stratigraphically highest coal seam (Glasgow Upper Coal). GGA01 encountered the Glasgow Upper Coal as waste from −36.72 m to −37.98 m OD. It has a screened section of 280 mm outer diameter Boode BGP™ gravel coated PVC screen with 4 mm slot sizes from −34.8 m to −38.4 m OD, but it is hydraulically open from −34.1 m to −41.1 m OD without annulus fill below a rubber annular seal (Monaghan et al., 2020a). GGA04 encountered the Glasgow Upper Coal as an intact or partially collapsed coal pillar and a possibly fractured sandstone roof. The coal was encountered from −37.05 m to −38.19 m OD. It has a screened section of 280 mm outer diameter Boode BGP™ gravel coated PVC screen with 4 mm slot sizes from −35.29 m to −38.89

m OD, but it is hydraulically open from −34.69 m to −41.22 m OD without annulus fill below a rubber annular seal (Starcher et al., 2020a). GGA07 returned coal from the Glasgow Upper Coal seam with some staining and alteration, and thus was interpreted as a pillar in pillar and stall workings. However, the optical camera observed open (stall) portions of the workings, indicating the borehole had penetrated the edge of a pillar. The coal was encountered from −40.57 m to −42.27 m OD. It has a screened section of 280 mm outer diameter Boode BGP™ gravel coated PVC screen with 4 mm slot sizes from −39.57 m to −42.27 m OD, but it is hydraulically open from −38.07 m to −45.27 m OD without annulus fill below a rubber annular seal (Starcher et al., 2020b).

3.1.2.5. Glasgow Ell and Glasgow Main Coal seams. GGA02, GGA05 and GGA08 were drilled to the depth of the Glasgow Main Coal seam, penetrating worked or unworked portions of the Glasgow Upper Coal, and Glasgow Ell Coal seams. Mine water from the level of the Glasgow Upper Coal seam was purged and sampled in GGA02 to meet SEPA sampling requirements. The workings above the Glasgow Main in GGA02 were grouted with a cement-based grout to ensure no flow pathway was created between the different mine water aquifer horizons. This was only performed in GGA02 since GGA05 did not record evidence for worked coal seams above the Glasgow Main. Good and similar water qualities of the Glasgow Upper Coal and Glasgow Main Coal workings were proven prior to GGA08 drilling and hence SEPA were satisfied that drilling could progress without sealing the Glasgow Upper or Glasgow Ell Coal seams. It remained a requirement of the BGS and SEPA that permanent casing ensured a hydraulic seal between the mine workings upon borehole completion.

GGA02 encountered the Glasgow Upper Coal seam as packed waste from −36.89 m to −38.04 m OD, the Glasgow Ell Coal seam as a water filled void from −59.25 m to −59.85 m OD but the Glasgow Main Coal seam was not recognised during drilling and was later interpreted to reflect complete longwall collapse at around −72 m to −73 m OD. During completion cement-based grout entered the inside of the casing and cemented up the screened section of the borehole. GGA02 was repurposed as the sensor testing borehole and was not subject to pumping tests (Monaghan et al., 2020b).

GGA05 encountered the Glasgow Upper Coal seam as intact coal (interpreted as a pillar) from −37.24 m to −38.78 m OD, the Glasgow Ell Coal seam was not identified during drilling and was later observed to be collapsed waste between −59.68 m and − 60.38 m OD, and the Glasgow Main Coal seam was encountered as a void from −72.44 m to −73.14 m OD. GGA05 has a section of 280 mm outer diameter Boode plain PVC™ screen with 4 mm slot sizes from −71.48 m to −74.18 m OD, but it is hydraulically open from −70.88 m to −76.28 m OD without annulus fill below a rubber annular seal (Barron et al., 2020a).

GGA08 encountered the Glasgow Upper Coal seam as possible mine workings from −40.68 m to −41.88 m OD, the Glasgow Ell Coal seam was observed as packed waste −62.88 m and − 64.68 m OD, and the Glasgow Main Coal seam was encountered with a void, wood and mining waste from −75.88 m to −78.88 m OD. GGA08 has a section of 280 mm outer diameter Boode BGP™ gravel coated PVC screen with 4 mm slot sizes −73.71 m to −76.41 m OD, but it is hydraulically open from −72.48 m to −79.55 m OD without annulus fill below a rubber annular seal (Barron et al., 2020a).

3.1.2.6. Purging and pumping tests. Following completion and screen installation, each borehole, except GGA02, was purged with the aim of removing any drilling-related material and fluid from inside the casing. In January and February 2020, after an interval of 1 to 4 months, each borehole was test pumped by a series of 5 step tests and a 5-h constant rate test. Since GGB04 showed very low yield values during purging it was instead selected for a slug test between 17 and 19 February 2020, six months after purging (Elsome et al., 2020).

3.2. Field collection

In this study, all fluid and rock samples from the GGERFS borehole suite were collected by BGS staff on behalf of the authors during construction and testing. Evaporite samples from the Ballagan Formation were collected by the authors.

3.2.1. Rock Samples

The authors were granted access to 1 m of core sample from GGC01 at every 10 m interval. Visual inspection confirmed that one of the intervals contained pyrite-bearing coal from the Glasgow Main Coal seam at 132.6 m bgl. No pyrite was found during screening of the other sample intervals.

During reverse circulation rotary drilling of the boreholes at Cuningar Loop, returned drill cuttings were collected by the BGS from the cutting shaker at 1 m intervals to characterise the stratigraphy of the superficial deposits, intact bedrock and mined coal seams (Fig. 3). Samples which were dominated by pyrite-rich or dark, organic-rich horizons were split into two duplicate subsamples whereby one was collected in plastic sample bags for the authors.

Separate to the GGERFS, Tournaisian (Lower Carboniferous) field samples of gypsum were collected from the Ballagan Formation type locality in Ballagan Glen (55.99°N, 4.29°W, c. 15 km NNW of Cuningar Loop), either side of the Ballagan Glen Fault. These evaporites are the most regionally abundant evaporitic sulfate source within the Carboniferous sequence. Samples from 3 different facies of evaporite deposit were collected with the permission of the National Trust for Scotland. The Ballagan Formation is stratigraphically lower (Tournaisian) than target seams of the GGERFS in the Scottish Middle Coal Measures Formation (Westphalian) (British Geological Survey, 1992b; Monaghan et al., 2017). The Ballagan Formation is expected to be 130 m to 245 m thick (Institute of Geological Sciences, 1978) at c. 1500 m depth below Cuningar Loop. This depth estimate is calculated from the top of the Clyde Plateau Volcanic (CPV) Formation which directly overlies the Ballagan Formation. The CPV Formation is interpreted from gravity surveying and forward modelling to be at c. 1100 m depth (Watson, 2022) and of 300–500 m thickness (Hall et al., 1998).

3.2.2. Water samples

During drilling of each borehole at the GGERFS locations (Cuningar Loop and Dalmarnock), water samples were collected in one litre Nalgene bottles by members of the BGS drilling supervision staff. They were filled with unfiltered, untreated waters and refrigerated until the authors collected the bottles, normally after 1–2 days, but up to one week later. Note that Dalmarnock only had sample types A and Bi collected, but these followed the same procedures as those from Cuningar Loop. The samples were sourced from the following:

Type A – "Borehole fluid": taken from the static water in the borehole, prior to the start of any daily drilling activity (one per borehole per day on days when the borehole was being drilled). Samples were obtained from just below rest water level by gently lowering a 1025 mL disposable plastic hand bailer into the borehole. Once submerged, the bailer was then slowly retrieved, ensuring that it was full of water (Shorter et al., 2021a). There were instances when samples were taken following a long period (weeks or months) without drilling activity, allowing time for settlement or potential stratification of the water column. Samples were collected by the same means before and after the purging activities described above.

Type Bi – "Return fluid": taken from the returning drilling fluid during drilling (one per borehole per day on days when borehole was actively drilled). The bottles were filled from the settling tank, just below the drilling fluid discharge pipe (Shorter et al., 2021a). As described, the drilling fluid was derived from Glasgow's mains tap water, and thus, return fluid samples are likely a mixture of groundwater or mine water with original mains water drilling fluid.

The following sample types were collected from Cuningar Loop only (i.e., all boreholes except GGC01).

Type Bii – "Return fluid – rock head": taken as a return fluid sample upon reaching rock head beneath the superficial deposits.

Type Biii – "Return fluid – mine water": taken as a return fluid sample once mine workings were encountered (as determined by drillers interpretation of subsurface conditions). The only exception for samples of this study was the sample taken from GGA02 in the Glasgow Upper Coal working. Following connection with the mine working, approximately 20 m^3 of water was purged from the borehole by airlifting. Afterwards, the sample was collected via a Hydrasleeve™ discrete bailer, lowered to the depth of the mine working (Shorter et al., 2021a). Air lifting operations in GGA05 post-dated the samples provided to the authors; thus, these were collected by standard return fluid methods.

Type C – "Pumping test water": taken from the sample tap attached to the rising main of the pump used for testing (Palumbo-Roe et al., 2021a). Samples were collected at the midpoint and endpoint of the five-hour constant rate pumping test of each successfully completed borehole. These samples are the best representation of groundwater and mine water derived from the screened intervals, since they have the smallest likelihood of influence by drilling fluids.

Sample types B and C are included in an "active samples" grouping, used in some figures. Sample type A (borehole fluid) is excluded since these were not sampled during active drilling or pumping and therefore had the potential for stratification of the water column.

The depth associated with each of the water samples was taken as metres below ground level (m bgl) by the drilling contractor. The depth of the pumping test water samples is taken as the depth of the hydraulic response interval (open section or screen). These were converted to metres relative to Ordnance Datum (OD; sea level) using data from BGS elevation surveys (Barron et al., 2020a; Barron et al., 2020b; Monaghan et al., 2020a; Monaghan et al., 2021b; Monaghan et al., 2020b; Shorter et al., 2020b, 2020c; Starcher et al., 2020a; Starcher et al., 2020b; Walker-Verkuil et al., 2020a; Walker-Verkuil et al., 2020b).

3.3. Laboratory Analysis

3.3.1. Rock Samples

The single core sample from GGC01 of the Glasgow Main Coal seam was broken along cleat fractures to reveal fresh pyrite. Drill cutting samples were washed with deionised water to remove dust and small debris before being examined for visible pyrite under an incident light binocular microscope. Visible pyrite from both sample types was extracted by scalpel or mineral drill. Ballagan Glen Formation samples were prepared for isotopic analysis by drilling polished samples to obtain powdered gypsum.

3.3.2. Water Samples

Upon receipt of one litre samples from refrigerated drill-site storage, each was transported to the University of Glasgow laboratories and decanted into following aliquots:

1. 0.45 μm filtered into 15 mL polypropylene screw-cap vial for major cation and anion analysis. Filtration was carried out at the laboratory using a 0.45 μm filter capsule mounted on a polypropylene syringe.
2. 100 mL (unfiltered) for determinations of pH, oxidation-reduction potential (ORP) and electrical conductivity (EC) using a handheld Myron P Ultrameter. Readings were automatically temperature corrected to a standard temperature of 25 °C.
3. A 100 mL (unfiltered) for alkalinity determination using a Hach Model 16,900 digital titrator.
4. 0.45 μm filtered (as above) into 15 mL polypropylene screw-cap vial, sealed with Parafilm to prevent sample evaporation, for $\delta^{18}O$ and δ^2H analysis.
5. Remaining volume (c. 770 mL) filtered using 0.45 μm qualitative filter paper and funnel before preparation for $\delta^{34}S$ analysis.

The results following analysis of aliquots 2 and 3 are not presented in this study and hence are not described in detail (but are included in the supplementary material). Dissolved sulfate concentration was determined, alongside that of other major ions from aliquot 1, using ion chromatography on Dionex equipment in the labs of the School of Engineering at the University of Glasgow. For anions a 10 μL sample was passed through a Dionex IonPac AG14A guard column and AS14A-5u analytical column before analysis on an ICS-900, with the aid of displacement chemical regeneration suppression (ACRS 500). A mix of 8 mM sodium carbonate:1 mM bicarbonate eluent and 72 mN H_2SO_4 regenerant was pumped through the system at 0.5 mL/min. For cations a 10 μL sample was passed through a Dionex IonPac CG12A guard column and CS12A analytical column, set to 30 °C, before analysis on an ICS-1100. A 20 mM methanesulfonic acid eluent was pumped through the system at 0.25 mL/min and a CERS 500 was used as an electrolytic suppressor. For both anion and cation analyses a conductivity cell was used for peak detection complete with a 3-level calibration. The standard for anion measurement was a Thermo Scientific™ Dionex™ Combined Seven Anion Standard II and the cation standard was a Dionex™ Six Cation-II solution. Chromeleon 7 software was used for final data analysis and quantification.

Stable isotope analyses of water (aliquot 4), dissolved sulfate (aliquot 5) and sulfur-bearing rock samples were undertaken at the Scottish Universities Environmental Research Centre (SUERC) laboratories, East Kilbride. For $\delta^{34}S$ isotope analysis, gypsum samples were converted to $BaSO_4$ by dissolution in 2.5 M hydrochloric acid, filtration, then precipitation through addition of a 5% BaCl solution. Aliquot 5 was acidified to pH 3–4 using ultrapure concentrated hydrochloric acid and then dosed with excess 5% $BaCl_2$ solution to precipitate sulfate as $BaSO_4$ (Carmody et al., 1998), which was allowed to settle. In both scenarios $BaSO_4$ precipitate was recovered from the sampling vessel, washed repeatedly in deionised water and dried. For analysis of the precipitate, SO_2 gas was liberated from each sample by combustion at 1125 °C with excess Cu_2O and silica, using the technique of Coleman and Moore (1978). For the sulfide mineral (pyrite), combustion at 1075 °C with excess Cu_2O followed the technique of Robinson and Kusakabe (1975). Raw ratios of SO_2 were measured on VG SIRA II mass spectrometer, and standard calculations applied to yield $\delta^{34}S$ ratios reported as per mille (‰) variations from the Vienna Canyon Diablo Troilite (V-CDT) standard.

For water $\delta^{18}O$ analysis, each 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 GasBench and 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, samples and standard waters were injected directly into a chromium furnace at 800 °C (Donnelly et al., 2001), with the evolved H_2 gas analysed on-line via a VG Optima mass spectrometer. Final values for $\delta^{18}O$ and $\delta^{2}H$ are reported as per mille (‰) variations versus standard mean ocean water (V-SMOW) in standard delta notation.

3.4. Quality assurance

Each sample for ion chromatography analysis was run in duplicate with 5-point concentrations of anion and cation standard solutions. Laboratory blanks were created from ultrapure water and subjected to the same laboratory processes as the UKGEOS water samples to check for contamination. All laboratory blanks returned acceptable values which concluded there was no, or minimal interference from the processes of sample preparation and/or laboratory analyses. Duplicate analyses were checked for inconsistencies, if present the sample was run again in duplicate, if the values were consistent, the arithmetic mean was extracted.

Sulfur isotopic data were calibrated using both international (NBS-123 sphalerite: +17.4‰ and IAEA-S-3: −32.3‰) and internal standards

(CP1 chalcopyrite: −4.5‰) and are reported with an error of reproducibility based on repeat analyses of the standards of ±0.3‰. For isotopic analysis of O and H, in-run repeat analyses of water standards (international standard V-SMOW and GISP, and internal standard Lt Std) gave a reproducibility typically better than ±0.3‰ for $\delta^{18}O$, ±3‰ for $\delta^{2}H$.

The Glasgow mains water is low in dissolved solute content (Table 2) and importantly for this study, has a sulfate concentration of 7 mg/L. The starting concentrations for major ions can be used to understand the solute contribution from the surrounding and interacting bedrock or superficial horizons. Most of the Cuningar water samples exhibited dissolved sulfate values far greater than that of the Glasgow mains water, where the 10th percentile was 97 mg/L, median 163 mg/L and 90th percentile 308 mg/L. The samples from Dalmarnock were closer to the mains water concentration of 7 mg/L, but still had dominant concentrations of sulfate contributed from groundwater. This confirms that the dominant signature of the $\delta^{34}S$ was from the formation water.

4. Results

4.1. Sulfide from rock samples

The $\delta^{34}S$ values of the seven pyrite samples from the Dalmarnock and Cuningar Loop boreholes (Table 3) range from −20.5‰ to +30.5‰, with a median of +9.4‰ and an arithmetic mean and standard deviation of +5.0 ± 15.5‰ ($n = 7$). Of the collected rock samples, only coal samples hosted pyrite. The other, dark and organic-rich horizons did not. The wide range of values is similar to that which Bullock et al. (2018) observed in Carboniferous coal bearing units of the Ayrshire Coalfield, where $\delta^{34}S$ ranged from −26.3‰ to +18.4‰ with an overall mean of +2.7 ± 9.5‰ ($n = 21$). The mean values for both pyrite suites are plotted alongside dissolved sulfate $\delta^{34}S$ results in Fig. 4.

4.2. Sulfate from GGC01 water samples

Table 4 shows sulfate $\delta^{34}S$ for the eight borehole and return fluid samples collected from GGC01 at Dalmarnock, which encountered no mined horizons at any depth. Values display a tight range between −2.3‰ and +3.5‰, with a median of −0.1‰ and an arithmetic mean of +0.3 ± 2.1‰ ($n = 8$). The deepest three samples are slightly more enriched in ^{34}S (Fig. 4) starting from 78.5 m bgl (−68.84 m OD), which loosely correlates with the first coal seam observed in GGC01 at c. 75 m bgl (Monaghan et al., 2021a). The mean value for these eight water samples lies comfortably within 1 standard deviation of mean pyrite $\delta^{34}S$ for regional Carboniferous coals from Bullock et al. (2018) (+2.7 ± 9.5‰, $n = 21$), and this study (+5.0 ± 15.5‰, $n = 7$).

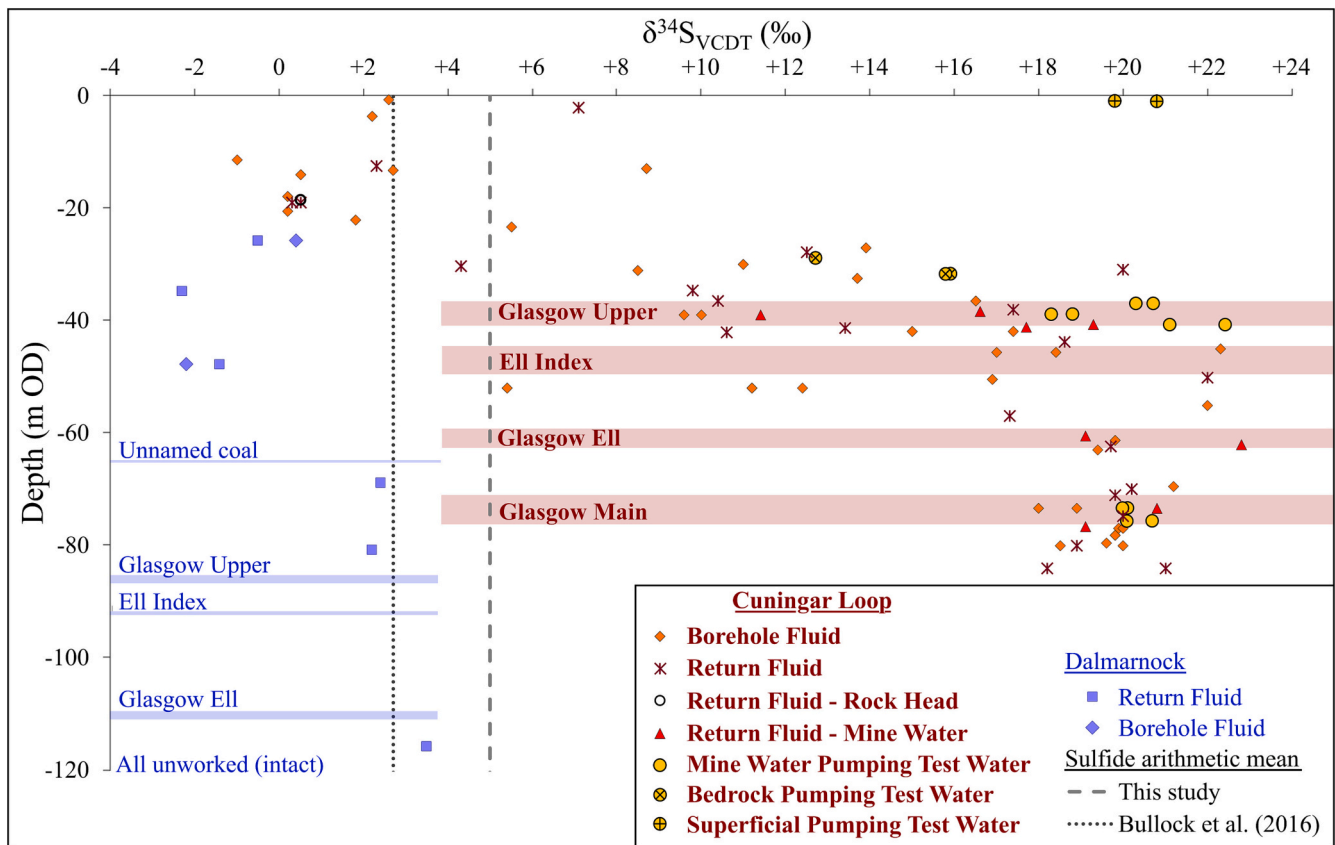### 4.3. Sulfate from Cuningar Loop water samples

Fig. 4 plots $\delta^{34}S$ values from all 84 water samples from the boreholes

Table 3

Sulfide–sulfur isotope data from pyrite separated from coal horizons at the GGERFS ('GGA' Cuningar boreholes – drill cuttings) and stratigraphic and seismic monitoring Dalmarnock borehole (GGC01 – core sample).

Borehole	Depth (m bgl)	Stratigraphic horizon	$\delta^{34}S$ (‰)
GGA02	47–48	Glasgow Upper Coal	+11.8
GGA02	53–54	Ell Index Coal	+6.4
GGA05	49–50	Glasgow Upper Coal	−12.3
GGA07	38–39	Unnamed Coal	−20.5
GGA08	38–39	Unnamed Coal	+9.4
GGA08	52–53	Glasgow Upper Coal	+9.5
GGC01	132.6	Glasgow Main Coal	+30.5
Arithmetic mean and standard deviation ($n = 7$)			+5.0 ± 15.5

Their stratigraphic level is also presented in relation to the mined coal-bearing horizons from which they were collected (see. Fig. 3).

Fig. 4. Plot of $\delta^{34}S$ isotope values versus depth for dissolved sulfate in water samples from both Dalmarnock and Cuningar Loop locations. Arithmetic means of the sulfide sulfur from this study and Bullock et al. (2018) are indicated by vertical dashed lines. Depths of coal seams are shown in blue bands (left) for the Dalmarnock location, and red bands (right) for Cuningar Loop. Note that the y-axis is in metres relative to Ordnance Datum (m OD), ground level is c. 10–12 m OD. Depth of the pumping test samples correlate with the depth of the screened section of the completed borehole. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Table 4

$\delta^{34}S$ isotope data from dissolved sulfate in fluids sampled during the drilling programme for the stratigraphic and seismic monitoring borehole (GGC01) at the Dalmarnock drilling location.

Sample type	Date	Borehole depth (m bgl)	$\delta^{34}S$ (‰)
Borehole fluid	27/11/2018	35.5	+0.4
Borehole fluid	29/11/2018	57.5	−2.2
Return fluid	27/11/2018	35.5	−0.5
Return fluid	28/11/2018	44.5	−2.3
Return fluid	29/11/2018	57.5	−1.4
Return fluid	30/11/2018	78.5	+2.4
Return fluid	03/12/2018	90.5	+2.2
Return fluid	05/12/2018	125.5	+3.5
Arithmetic mean and standard deviation ($n = 8$)			+0.3 ± 2.1

at Cuningar Loop as well as the eight water samples from Dalmarnock (GGC01), against their respective depths. Note that despite being sampled from the surface, the borehole fluid samples are plotted relative to the total borehole depth at the time of sampling.

4.3.1. Borehole fluid and return fluids

The Cuningar Loop boreholes typically intersected coal workings at approximately −37 to −41 m OD (Glasgow Upper Coal seam), −59 to −63 m OD (Glasgow Ell Coal seam) and − 71 to −76 m OD (Glasgow Main Coal seam) (Monaghan et al., 2021c) (Fig. 3). Overall, water samples from Cuningar Loop have $\delta^{34}S$ values which range between −1‰ and +23‰ with a mode at +20‰ (Fig. 5), however, further trends can be identified from Fig. 4. $\delta^{34}S$ values of all Cuningar borehole fluid and return fluid samples taken between surface (c. +10 to +12 m OD)

and − 25 m OD fall within the range of −1‰ to +8.7‰. The mean for these depths (+2.3 ± 2.7‰, $n = 15$) is similar to that of the pyrite from rock samples, and that of the borehole fluid and return fluid samples of GGC01, where coal seams are intact. Below a depth of −25 m OD, the $\delta^{34}S$ values increase towards and cluster around values of +19‰ and +20‰ for the depth interval associated with the Glasgow Upper Coal seam (−37 to −41 m OD). In all Cuningar Loop boreholes, the samples from −65 m OD to the deepest sample locations at −84 m OD have a mean of +19.8 ± 0.9‰ ($n = 21$). The trend of $\delta^{34}S$ with depth in different boreholes can be visualised in Fig. 3, where coloured symbols reflect the different groupings (buckets) of $\delta^{34}S$ values and represented by the histograms for each site in Fig. 5. Sulfate isotopic values at Site 1 have a slightly different trend to the other two sites (2 and 3), where there is an intermediate node, grouped around +10‰ to +13‰, described further in Section 4.3.3.

4.3.2. Cuningar loop pumping test water

All water chemistry results of pumping test mine waters can be found in Palumbo-Roe et al. (2021b). Pumped groundwaters are bicarbonate (HCO_3^-) type with sodium (Na^+) as the dominant cation, except for boreholes GGA03r in bedrock and GGA09r in superficial deposits where calcium (Ca^{2+}) is the main cation (Palumbo-Roe et al., 2021b). Pertinent chemical analyses from the pumping tests and other relevant samples, performed by the BGS, are summarised as arithmetic means presented in Table 5 alongside the major ion composition of typical modern seawater (Lenntech, 2022). Sulfate concentrations in the mains water supply to Dalmarnock are presented for 2021 as mean, minimum and maximum by Scottish Water (2021). They report a mean sulfate concentration of 7.55 mg/L ($n = 8$) with a range between 7.20 and 8.40 mg/L. These

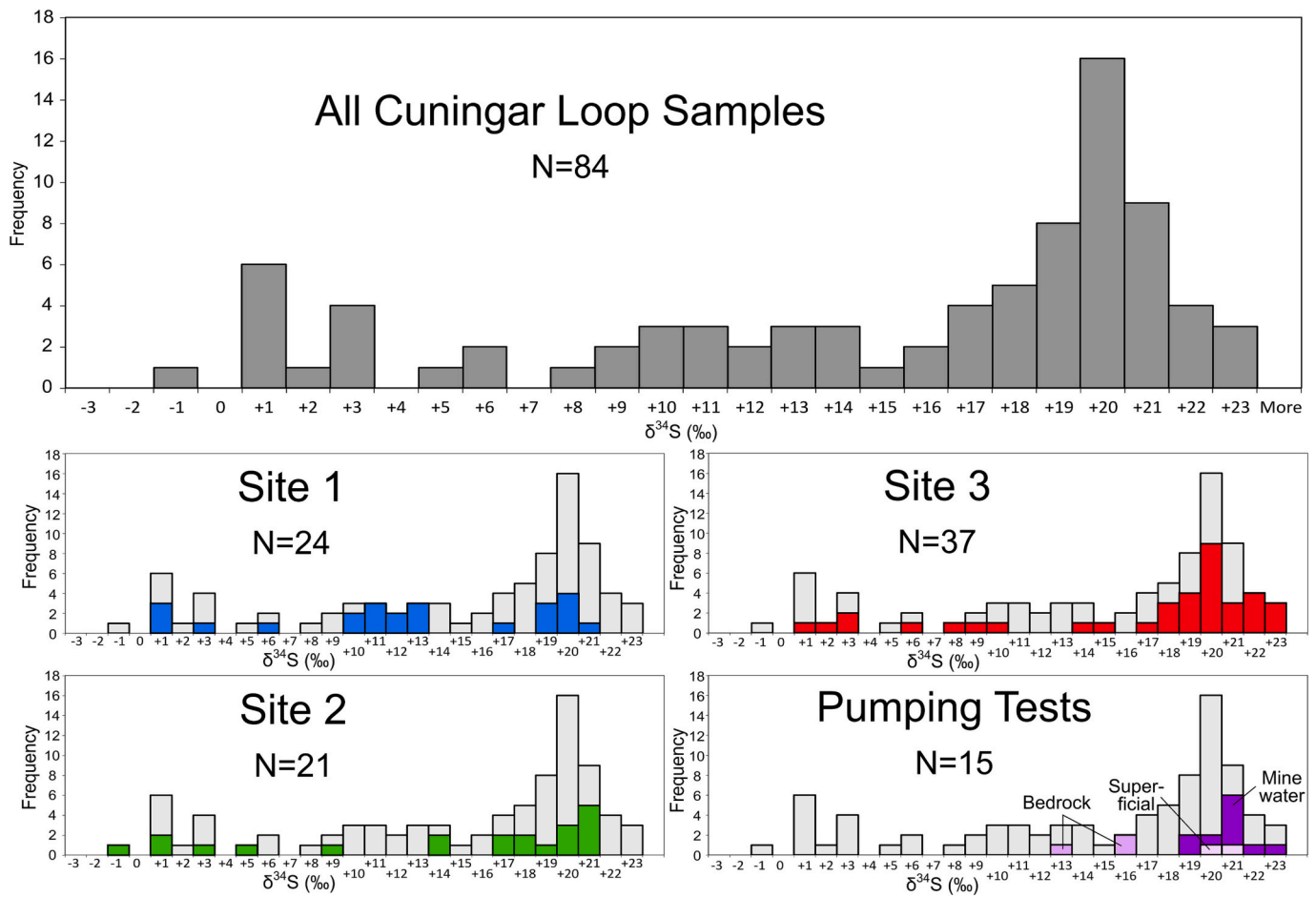**Fig. 5.** Histograms of δ³⁴S isotope values from the Cuningar Loop boreholes. (Top) Active samples (Sample types B and C): all water samples except for borehole fluids as these were not sampled during active drilling or pumping (this histogram is repeated in all other plots as the background). (Bottom) Four plots with titles corresponding to their respective displayed sample types: Site 1; Site 2; Site 3; and Pump test water samples only - all boreholes at Cuningar Loop combined.

Table 5
Arithmetic means of the pump test water samples as grouped by the screen horizon.

		Units	Superficial (n = 2)	Bedrock (n = 3)	Glasgow Upper (n = 6)	Glasgow Main (n = 4)	Seawater from (Lenntech, 2022)
Field data	Temperature	°C	11.8	11.5	12.0	12.4	
	pH	pH units	7.1	7.0	7.1	7.2	
	Electrical Conductivity	µS/cm	1652	1812	1732	1684	
	Eh	mV	+211	+195	+166	+152	
	Alkalinity	meq/L	14.0	12.0	13.3	13.5	
Laboratory chemical data	F^-	mg/L	0.16	0.16	0.17	0.15	1
	Cl^-	mg/L	65.7	62.4	72.4	71.7	18,980
	SO_4^{2-}	mg/L	144	319	181	155	2649
	Br^-	mg/L	0.409	0.548	0.520	0.457	65
	Na	mg/L	139	152	181	174	10,556
	Ca	mg/L	143	131	108	107	400
	Mg	mg/L	49.3	62.5	53.5	54.9	1262
	K	mg/L	21.2	18.1	18.9	19.1	380
	Fe (dissolved)	µg/L	1895	13,030	3738	1910	
	Mn (dissolved)	µg/L	2522	500	409	331	
Chemical ratios	Cl^-/Br^- mass ratio		161	114	139	157	292
	SO_4^{2-}/Cl^- molar ratio		0.811	1.89	0.925	0.799	0.052
	Na/Cl^- molar ratio		3.25	3.75	3.86	3.74	0.858
	$(Ca + Mg)/SO_4^{2-}$ meq ratio		3.72	1.75	2.59	3.05	2.24
	Ca/Mg molar ratio		1.76	1.27	1.23	1.18	0.192
	Ca/Alkalinity meq ratio		0.496	0.565	0.394	0.389	8.70
Iso-topes	δ³⁴S	‰	20.3	14.8	20.3	20.2	21.2

Field and laboratory chemical data from Palumbo-Roe et al. (2021b) compared with seawater from Lenntech (2022). Arithmetic mean sulfur isotopic values are added from this study, and Tostevin et al. (2014) for seawater.

values are low compared to the sulfate concentration in pumping test water samples from the boreholes completed into mine workings ($n = 10$) which exhibit a mean of 171 mg/L and a range between 154 mg/L and 200 mg/L. We thus conclude that potential mixing of a component of drilling fluid in the samples is unlikely to significantly impact the dissolved sulfate $\delta^{34}S$ in the samples. The $\delta^{34}S$ values of dissolved sulfate in the pumping test water samples are shown as yellow circles in Fig. 4 and are presented in Table 6. The boreholes which are completed into mine workings (−37 m OD and deeper) return a mean $\delta^{34}S$ value of $+20.3 \pm 1.1‰$ ($n = 10$). The pumping test samples from bedrock above the coal seams return mean values of $+15.9‰$ ($n = 2$) and $+12.7‰$ ($n = 1$), from screened sections at −34.3 m OD and − 29 m OD respectively. The pumping test water samples from the boreholes completed into the superficial deposits, overlaid by significant thicknesses of made-ground (10-12 m), in GGA06r (12.5 m bgl) and GGA09r (13 m bgl), returned $\delta^{34}S$ values of $+19.8‰$ and $+20.8‰$ respectively. The samples which were taken at the middle and end of each 5-h pumping test proved to be consistent, the greatest difference (1.3‰) was between samples coming from GGA07.

4.3.3. Concentration vs $\delta^{34}S$

The deepest borehole at each of the three Cuningar Loop sites (GGA02, GGA05 and GGA08) penetrated the worked Glasgow Main Coal seam (Fig. 2). Comparisons of trends between dissolved sulfate concentration, sulfate $\delta^{34}S$ and depth of each water sample from GGA02, GGA05 and GGA08 are presented in Fig. 6. They illustrate overall increasing $\delta^{34}S$ and sulfate concentration with depth. The sulfate concentration of all samples becomes more consistent with depth, plotting at c. 170 mg/L at depths associated with the Glasgow Main Coal. There is no obvious overall correlation between $\delta^{34}S$ and sulfur concentration. In each of these plots an anomaly is presented by GGA02 (Site 1), whereby the samples associated with the depth of the Glasgow Upper Coal workings (present at −39 m OD) have an elevated sulfate concentration (grouping around 250–400 mg/L) and show intermediate $\delta^{34}S$ values ($+10.2 \pm 2‰$, $n = 9$). Note that some of these intermediate plots are

Table 6
$\delta^{34}S$ values from Cuningar pumping test water samples.

Borehole	Screen depth (m bgl)	Screened horizon	Test stage	Sample date	$\delta^{34}S$ (‰)
GGA06r	−0.9	Superficial deposits	End	31/01/2020	+19.8
GGA09r	−1.1	Superficial deposits	End	11/02/2020	+20.8
GGA03r	−29	Sandstone above workings	Middle	20/01/2020	+12.7
GGB05	−34.3	Sandstone above workings	Middle	14/02/2020	+15.9
GGB05	−34.3	Sandstone above workings	End	14/02/2020	+15.8
GGA04	−37	Glasgow Upper Coal	Middle	28/01/2020	+20.7
GGA04	−37	Glasgow Upper Coal	End	28/01/2020	+20.3
GGA01	−39.3	Glasgow Upper Coal	Middle	15/01/2020	+18.3
GGA01	−39.3	Glasgow Upper Coal	End	15/01/2020	+18.8
GGA07	−40.7	Glasgow Upper Coal	Middle	07/02/2020	+21.1
GGA07	−40.7	Glasgow Upper Coal	End	07/02/2020	+22.4
GGA05	−73.4	Glasgow Main Coal	Middle	23/01/2020	+20.1
GGA05	−73.4	Glasgow Main Coal	End	23/01/2020	+20
GGA08	−75.6	Glasgow Main Coal	Middle	04/02/2020	+20.1
GGA08	−75.6	Glasgow Main Coal	End	04/02/2020	+20.7
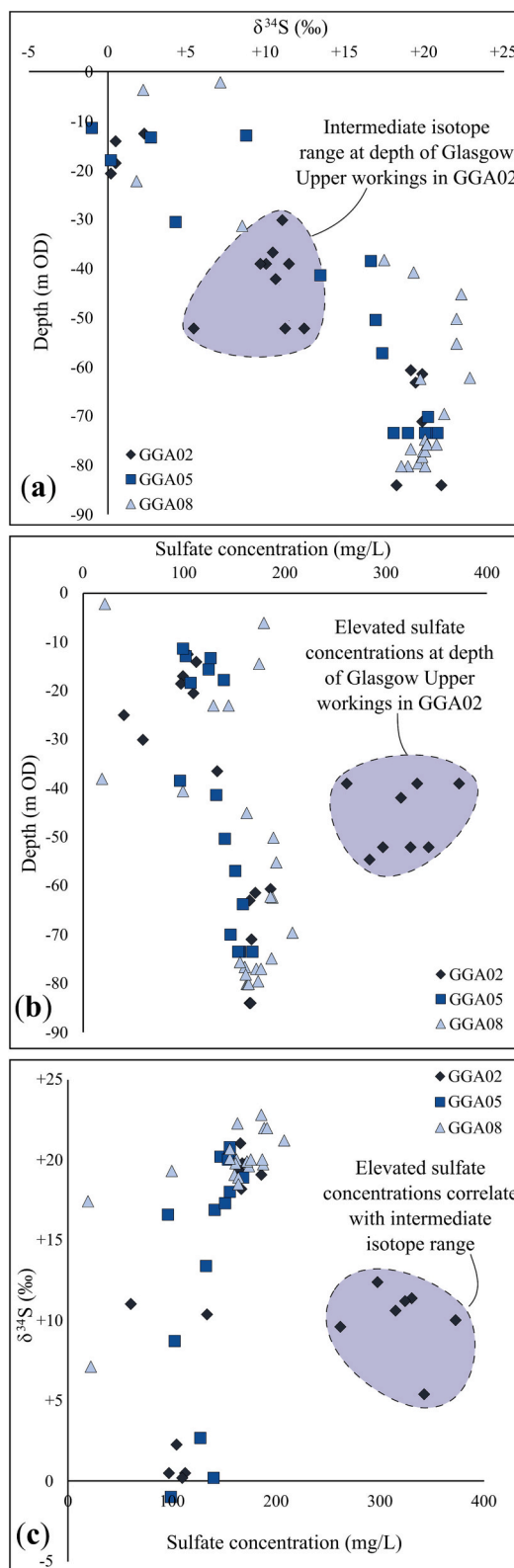
Fig. 6. Plots from the deepest boreholes from each of Site 1, 2 and 3 within Cuningar Loop, showing a) $\delta^{34}S$ values with depth (m OD); b) sulfate concentration with depth; and c) $\delta^{34}S$ values plotted against sulfate concentration. Blue polygons highlight GGC02 anomalies with elevated sulfate concentrations and intermediate $\delta^{34}S$ values. Plot contains all sample types (A, B and C). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

deeper than the quoted horizon for the Glasgow Upper, but since the Glasgow Upper mine water likely dominates the drilling fluid until the next responsive horizon, the signature will likely remain. The Ell Index Coal seam was unworked in GGA02, and thus the next mine water signature was intersected at the Glasgow Ell Coal seam, at c. -60 m OD.

4.4. Sulfate S isotopes in lower Carboniferous gypsum

The sulfur isotope data from the gypsum samples of the Ballagan Formation are shown in Table 7. $\delta^{34}S$ values range from +18.1‰ to +19.9‰, with a mean of +18.9 ± 0.5‰ ($n = 17$). Samples from west and east of the Glen Fault had means of +18.7 ± 0.4‰, $n = 8$ and +19.0 ± 0.5‰, $n = 7$, respectively. As the standard deviations cited on these means all overlap, we conclude that there is little statistically significant difference between sample groups on either side of the fault. Similarly, there is little statistically significant difference between the three facies or the three distinct paragenetic presentations of the gypsum (yellow, orange and platy).

4.5. Oxygen and hydrogen isotopic data

O and H isotopic results of sampled waters are shown in Fig. 7, plotted against the global meteoric water line (GMWL) (Craig, 1961) and a local meteoric water line (LMWL) derived from nearby Glasgow rainwater samples (Walls et al., 2022a). A single mains water sample from January 2019 returned values of −7.3‰ and − 49‰ for $\delta^{18}O$ and $\delta^{2}H$ respectively, plotting on the GMWL and the LMWL. The mean values for the pumping test samples from the mine water boreholes are −7.6‰ and − 49‰ for $\delta^{18}O$ and $\delta^{2}H$ respectively, falling close to the LMWL and GMWL.

5. Discussion

$\delta^{34}S$ analysis of pyrite in coal seams (worked and unworked) in and around the GGERFS show a large range, with a mean value of +5.0 ± 15.5‰ ($n = 7$). The range and mean value are consistent with regional pyrite values, which average + 2.7 ± 9.5‰ ($n = 21$) (Bullock et al., 2018). Borehole fluid and return water sulfate signatures from Dalmarnock (GGC01) show limited variation (+0.3 ± 2.1‰, $n = 8$), plotting within the value range and close to the mean of local pyrite, thus could be reasonably explained as a direct product of pyrite oxidation. A positive correlation between sulfate $\delta^{34}S$ values and depth in GGC01 may suggest subsurface processes driving minor enrichment of ^{34}S in

Table 7
$\delta^{34}S$ values of Ballagan Formation gypsum evaporite samples from Ballagan Glen.

Sample	Facies	Fault side	$\delta^{34}S$ (‰)
BG1 clear	1	West	+18.1
BG1 orange	1	West	+18.7
BG1 orange (repeat)	1	West	+18.7
BG5 red plates	1	East	+19.3
BG5 red plates (repeat)	1	East	+18.4
BG5 red plates (repeat)	1	East	+19.0
BG5 red infill	1	East	+18.6
BG5 red infill	1	East	+19.3
BG5 yellow	1	East	+19.9
BG2 (upper)	2	West	+19.1
BG2 (upper) (repeat)	2	West	+19.2
BG3 (lower)	2	West	+18.1
BG3 (lower)	2	West	+18.3
BG6	2	East	+18.5
BG4	3	West	+19.1
BG4	3	West	+19.1
BLV 1	2	*	+19.5
Arithmetic mean and standard deviation ($n = 17$)			+18.9 ± 0.5

* – museum sample without record of fault side. Facies column indicates chronostratigraphical ordering of sample beds, where 1 is the oldest.

unmined strata. However, return and borehole fluid samples each represent a bulk value of contributions from drilling fluid and all groundwater-bearing bedrock horizons encountered during drilling. Equally, the isotopically elevated values for the deepest three GGC01 samples may reflect a marginally high sulfide $\delta^{34}S$ signature related to the coal seams, indicated on Fig. 4.

Return fluid – mine water samples from the Cuningar Loop boreholes exhibit much higher values (+18.4 ± 3.4‰, $n = 8$) and mine water borehole pumping test water samples, which most closely represent true mine water, have a mean $\delta^{34}S$ value of +20.3 ± 1.1‰ ($n = 10$). These elevated values cannot be simply explained by oxidation of host coal or sedimentary sequence pyrite alone and thus raise three questions:

- Since typical oxidation of sulfide minerals is widely accepted to proceed with negligible isotopic fractionation, what is the source of isotopically elevated sulfate in the mine water?
- Why does it only affect groundwater present in mined coal seams, and not groundwater from unmined strata?
- Why do the pumping test samples from the environmental baseline monitoring boreholes completed into superficial deposits show similarly elevated ^{34}S, and those into bedrock show somewhat elevated (intermediate) isotopic values?

Banks et al. (2020) found elevated sulfate $\delta^{34}S$ in deeper mine waters and found lower values, compatible with oxidised pyrite, in shallow mine waters across several European coalfields and a new study from North East England revealed the same phenomenon (Banks and Boyce, 2023). They concluded that elevated $\delta^{34}S$ in mine waters in Spain and Poland were compatible with evaporite dissolution, but noted that such a source was unlikely to explain elevated values at sites in England (Banks et al., 2020).

The following sources of isotopic sulfate enriched in ^{34}S have been hypothesized (Banks et al., 2020; Chen et al., 2020; Younger et al., 2015):

1. Concentrated brines which percolated into bedrock during formation of sabkhas or evaporites at surface; the evaporites may have since been eroded.
2. Infiltration of geologically recent marine water to the coal bearing strata of Cuningar loop.
3. A residual (connate or derived from marine transgression in post Carboniferous geological time) saline water component in deep mine waters and Carboniferous strata.
4. Concentration of dissolved salts (including sulfate), upon deep freezing by permafrost conditions during Pleistocene glaciations.
5. Dissolution of evaporite minerals (gypsum or anhydrite) present in subjacent or superjacent strata (e.g., Carboniferous Ballagan Formation).
6. Bacterial reduction of sulfate to sulfide, preferentially removing ^{32}S and enriching the remaining sulfate with ^{34}S.

Banks et al. (2020) also propose that an equilibrium in groundwater / mine water may continually shift between $\delta^{34}S$ end members depending on the rates of input/removal of dissolved sulfate by weathering of sulfide and sulfate minerals, and/or bacterial/thermal sulfate reduction to sulfide minerals.

Exploring the potential sources of sulfate requires parallel analysis with other chemical properties, and correlation with local geologic setting/history. When including water chemistry analysis, it is important to understand the nature of the water samples and what they truly represent. Since mains water was used as the drilling fluid, each of the return fluid and borehole samples are a mix of ground water (mining-influenced or not) and mains water, thus elemental concentrations are diluted by the ion-poor mains water presented in Table 2 (Scottish Water, 2021; Shorter et al., 2021b). It is important to note that diluted dissolved sulfate concentrations are unlikely to affect the $\delta^{34}S$ isotopic

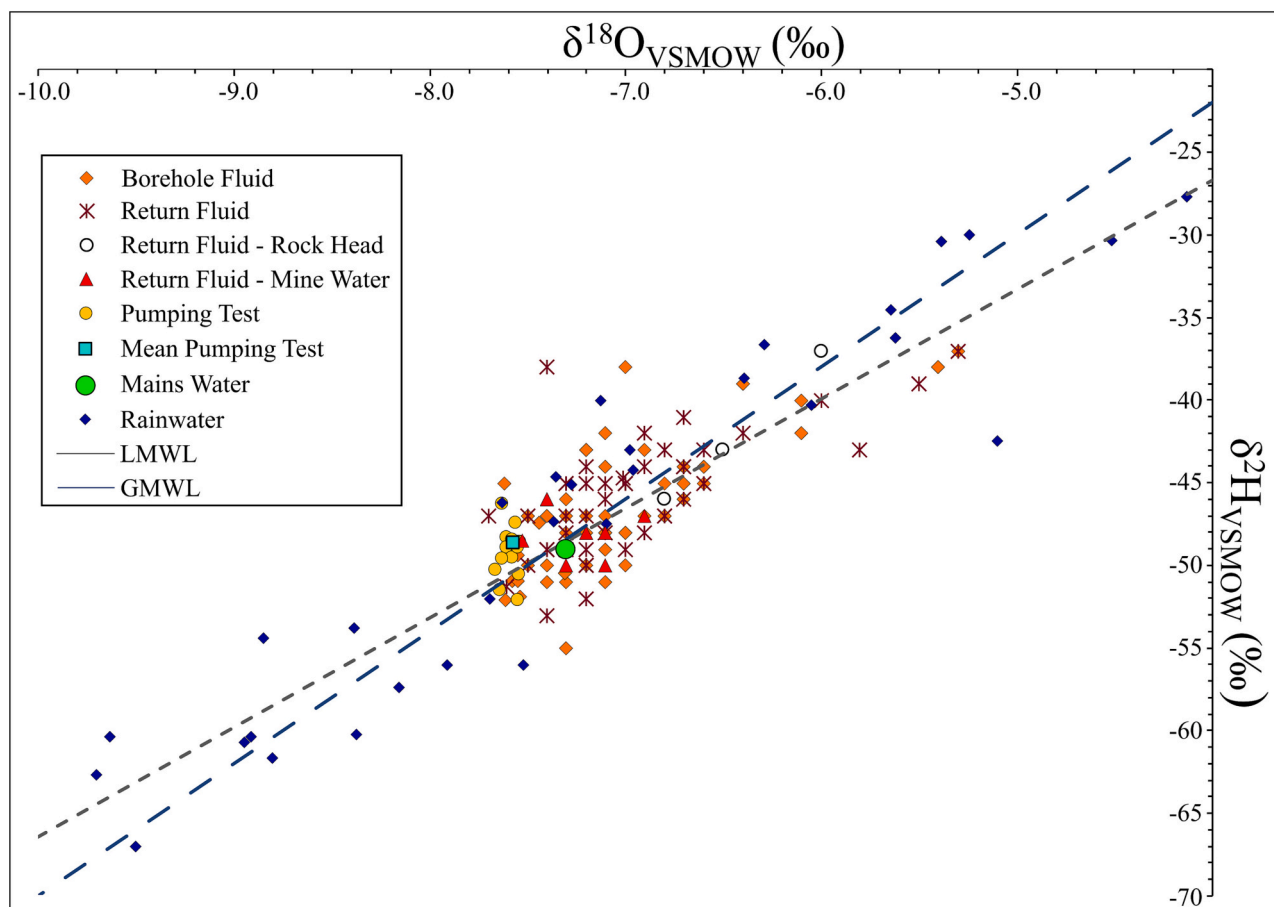**Fig. 7.** Standard $\delta^{18}O$ and δ^2H from all GGERFS water samples (including mains water), plotted against the global meteoric water line (Craig, 1961) and rainwater data collected at the University of Glasgow between December 2016 and February 2020 (Walls et al., 2022a), comprising the local meteoric water line.

signature since the mean concentration in the tap water is only 7.08 mg/L ($n = 2$) according to Shorter et al. (2021b) and around 7.5 mg/L according to Scottish Water (2021) (Table 2), but they will skew $\delta^{18}O$ and δ^2H isotopic ratios towards the mains water values. To avoid the issue of dilution, only pumping test water samples will be discussed, since they represent the truest samples from the target horizons. The following discussion uses the published hydrochemistry datasets for the UKGEOS water samples (Palumbo-Roe et al., 2021b) which correlate with the pumping test water samples for $\delta^{34}S$ analysis in this study; the discussion also refers to baseline monitoring programmes for details on rainwater (O Dochartaigh et al., 2011) and Lenntech's (2022) data for standard ocean water.

The following sections (5.1–5.5) address the six $\delta^{34}S$ enrichment process hypotheses outlined above and assess their potential influence on observed $\delta^{34}S$ values in the GGERFS system. Section 5.6 explores the mechanisms responsible for distributing elevated $\delta^{34}S$ sulfate through mine workings, whereas Section 5.7 addresses the sulfate concentration and isotopic anomaly observed at Site 1. Section 5.8 and 5.9 postulate a source of high $\delta^{34}S$ in superficial and bedrock aquifer pumping test water samples respectively.

5.1. Hypothesis 1

Walls et al. (2022a) detail the geological setting of the Midland Valley of Scotland following the deposition of the Coal Measures strata. They suggest that evaporitic conditions from the Permian to Cretaceous could have led to percolating residual saline brines or dissolved paleo-evaporites, which in turn could contribute an isotopically elevated seawater/evaporite signature to the groundwater. Such brines are

unlikely to be a major source of water molecules to the groundwater since $\delta^{18}O$ and δ^2H isotopic ratios indicate that pumping test waters have not undergone significant fractionation from the GMWL and suggest a recent, Holocene meteoric origin (Darling et al., 2003). Nonetheless the sulfate from a small amount of concentrated brine could represent a significant component of the overall mine water sulfate concentration and influence its $\delta^{34}S$ signature. The dominance of modern meteoric water is typical for mine waters analysed for S isotopes across Europe (Banks et al., 2020). Influence of a concentrated evaporitic brine which contributes sulfate enriched in ^{34}S in high enough concentrations to dominate the $\delta^{34}S$ isotopic signature without skewing the $\delta^{18}O$ and δ^2H signatures, cannot be ruled out.

5.2. Hypothesis 2

Recent marine water ingression would impart a significant chloride content on mine waters. The chloride concentrations of the 10 pumping test waters from the Glasgow Upper and Main Coal seams range between 70.9 and 75.9 mg/L (Palumbo-Roe et al., 2021b), which are elevated compared to the probable chloride concentration of infiltrating rainwater, c. 7 mg/L (O Dochartaigh et al., 2011), even when evapotranspirative upconcentration is considered. Although it should be remembered that sulfate and chloride concentrations in rainfall would have been substantially greater in the period following the industrial revolution (Fowler et al., 1982), with values as high as 70 mg/L sulfate being reported in Glasgow rainfall by Smith (1872).

The observed chloride concentrations from UKGEOS also exceed the 75th percentile value for unmined Coal Measures groundwater (50 mg/L) (O Dochartaigh et al., 2011), suggesting that there is an additional

source of chloride in the mine waters, beyond that of infiltrating rain-water. They exceed the range for the River Clyde (16–40 mg/L) but plot within the range of the Tollcross Burn (41–138 mg/L, mean 65 mg/L) (Fordyce et al., 2021), suggesting that chloride in the stream may be introduced by water influenced by urban activities e.g., salting roads. The Clyde adjacent to Cuningar Loop has a water level of c. +3 m OD and is non-tidal and fresh, the tidal limit being the tidal weir adjacent to Glasgow Green, built in 1901 at NS 59511 64374. It is interesting to speculate as to the degree tidal and marine (and hence saline) influence may have extended up the Clyde prior to its construction. Historically, the Clyde was tidal and navigable as far upstream as Rutherglen (Secret Scotland, 2023; Undiscovered Scotland, 2023). One should further note that the published geological maps show raised marine and glaciomarine silts and clays as far inland as Cuningar, indicating marine inundation in Pleistocene times (British Geological Survey, 1992a).

The mine water samples all have sulfate/chloride molar ratios (mean = 0.87) much greater than modern seawater (0.05) (Lenntech, 2022), similarly, sodium/chloride molar ratios are greatly elevated (mean = 3.81) versus seawater (0.86) (Table 5). These ratios indicate that sulfate and sodium have been added to the system without chloride, i.e., from a source which is not of recent marine origin. The chloride/bromide mass ratios of the mine waters (mean = 147) are half that of seawater (292) (Lenntech, 2022), and within the range of typical shallow groundwater (100−200) (Davis et al., 1998). Whilst the sulfur isotopic composition of modern seawater is similar to that found in the mine waters, the other aspects are distinct. This evidence is enough to eliminate recent marine ingression as a controlling factor on mine water $\delta^{34}S$ signature.

5.3. Hypotheses 3 and 4

The moderately low chloride content diminishes the possible role of percolating freeze-out concentrated groundwaters formed during Pleistocene permafrost formation. Moreover, although cryoconcentration could increase chloride and sulfate concentrations, it would not be expected to systematically elevate the $\delta^{34}S$. Similarly, the modest chloride concentrations argue against the influence of deeper chloride-rich saline waters, known to affect mine waters elsewhere in the UK, particularly the NE of England (Younger et al., 2015).

5.4. Hypothesis 5

Ballagan Formation gypsum samples exhibit a narrow $\delta^{34}S$ range between +18.1‰ and + 19.9‰ (mean + 18.9 ± 0.5‰) (n = 17), well within the range of $\delta^{34}S$ for Lower Carboniferous seawater sulfate (Claypool et al., 1980), strongly suggesting that the sulfate source for Ballagan Formation gypsum deposits is contemporaneous marine sulfate. Dissolution of these evaporite deposits by groundwater would impart a distinct $\delta^{34}S$ isotopic signature on dissolved sulfate around 1.5‰ to 2‰ lower than the solid phase, thus around +16.9‰ to +17.4‰ (Driessche et al., 2016). Dissolution of gypsum would contribute calcium to the waters whilst enriching the sulfate $\delta^{34}S$ isotopic signature; however, no clear correlation is observed between $\delta^{34}S$ and calcium concentration. Whilst these findings do not support evaporite dissolution, it should be noted that other processes including calcite saturation can suppress calcium concentrations, meaning that a correlation can be lost even with a shared genetic origin.

The Ballagan Formation evaporite minerals are primarily gypsum, but there are anhydrite and halite present (Millward et al., 2018). Dissolution of gypsum would contribute sulfate with the high $\delta^{34}S$ signature described above, whilst dissolution of halite would contribute chloride and importantly, impart a chloride/bromide ratio as high as 1000–10,000 (Davis et al., 1998). As discussed for hypothesis 2, the mine water chloride/bromide ratios are below the values of seawater (292), and thus are well below these evaporite signatures. If halite comprises only a very minor portion of the evaporite solutes or are

entirely absent, then the chloride/bromide ratio may not be affected, or may be buffered by elevated bromide in coals (Davis et al., 1998). Furthermore, it cannot be ignored that the Ballagan Formation, despite being the most regionally abundant sulfate source within the Carboniferous sequence, has a significant c. 1500 m stratigraphical separation from the Middle Coal Measures Formation and a mechanism for upwards evaporite brine migration from the Ballagan formation would need to be proposed for this to be a realistic hypothesis. Each of these points indicate that evaporite dissolution is an unlikely source for the enriched $\delta^{34}S$ isotopic signature, but it cannot be ruled out entirely.

5.5. Hypothesis 6

Detection of H_2S at the surface whilst penetrating mined coal seams during drilling (Barron et al., 2020a; Monaghan et al., 2020b) suggests that sulfate-reducing bacteria are present in the mine water at the site. It is accepted that bacterial fractionation can shift the bulk $\delta^{34}S$ of the dissolved sulfate phase towards its elevated end member, by preferential removal of ^{32}S. However, whether this process is significant enough to fractionate the hypothetical initial sulfate signature from oxidised pyrite (+5.0 ± 15.5‰, n = 7) to the higher values in measured mine water samples (+20.3 ± 1.1‰, n = 10) remains unclear. For this to be a viable hypothesis, the rate of bacterial sulfate reduction needs to be of a similar order of magnitude to that rate of sulfate introduction to groundwater (e.g., by pyrite oxidation). It is hypothesized that the rate of pyrite oxidation in completely flooded mine workings is likely to be relatively low (Younger, 1997). The data indicate that the $\delta^{34}S$ signature is relatively consistent at all levels of mine workings at the GGERFS, where all samples deeper than −65 m OD have a mean of +19.8 ± 0.9‰ (n = 21) and the pumping test water samples exhibit a mean of +20.3 ± 1.1‰ (n = 10) indicating that the mined system is well mixed.

$\delta^{34}S$ values and alkalinity for all samples exhibit an overall positive correlation, whereby the pumping test samples have the highest values of both. This trend can be an indication of activity by sulfate-reducing bacteria in relatively stagnant, anoxic groundwater (Brown et al., 2002). However, the trend may not be unique to sulfate reduction, since evaporite dissolution of the Ballagan Formation would require deep-seated, long residence time waters, evoking high alkalinity.

5.6. Movement of waters with elevated dissolved sulfate $\delta^{34}S$

Should elevated $\delta^{34}S$ observed in the mine water have originated from deeper ("sulfate-rich, chloride-poor") groundwaters, e.g., those affected by evaporite brines or dissolution (Hypotheses 1 and 5), then their upwards transport must be explored. A potential migration pathway to the Scottish Coal Measures Formation strata is via discrete permeable features, such as the Shettleston Fault, 1–2 km to the north of Cuningar Loop (British Geological Survey, 1992b). Following vertical transfer, these fluids might flow slowly through Upper Carboniferous aquifers of relatively modest permeability. Alternatively, mined coal strata would provide preferential flow pathways for such fluids. This may explain why sulfate in the water samples of the unmined sequence (GGC01) do not return any elevated $\delta^{34}S$ values, while water in mined workings has been able to transmit the elevated $\delta^{34}S$ to the Cuningar area.

Furthermore, one could hypothesise that waters with elevated sulfate-$\delta^{34}S$ reflect longer residence times in deeper, reducing, oxygen poor mine waters where bacterial sulfate reduction may occur, removing sulfur as ^{32}S-enriched pyrite and leaving the residual dissolved sulfate enriched in ^{34}S. Waters with short residence times may be associated with pyrite oxidation dominated $\delta^{34}S$ since these waters will have been most recently in contact with the atmosphere, inducing oxidation. Networks of mined strata, connected by shafts and drifts, provide a potential throughflow and mixing environment with high lateral and vertical connectivity, allowing a component of longer residence high $\delta^{34}S$ sulfate-rich brines to manifest in the near surface environment.

5.7. Alternative contribution in Site 1

Water samples from borehole GGA02, within Site 1 at Cuningar Loop (see Fig. 2), exhibit three distinct populations which increase in $\delta^{34}S$ with depth (Fig. 6a). Shallow samples (to c. -20 m OD) reflect typical values of oxidised pyrite in the coal-bearing strata, similar to those seen through the entire sequence in the unmined strata of GGC01. Deep samples, from c. -60 m OD and below, likely influenced by the Glasgow Main Coal seam at -84 m OD, returned $\delta^{34}S$ values of sulfate between $+19‰$ and $+20‰$. The middle sequence of samples (from c. -30 to -52 m OD), which are likely influenced by the Glasgow Upper Coal seam (-39 m OD), exhibit $\delta^{34}S$ values of intermediate range ($+10.2 \pm 2‰$, $n = 9$).

Water samples taken during drilling through superficial deposits and bedrock above the first worked coal seam (Glasgow Upper Coal) contain sulfate concentrations with an arithmetic mean of 110 mg/L. Values from GGA05 and GGA08 show a gradual increase towards 170 mg/L in the basal Glasgow Main Coal samples. Glasgow Upper Coal related samples from GGA02 (arithmetic mean of 320 mg/L) stand apart from the rest of the data (Fig. 6b). With their intermediate $\delta^{34}S$ values, these samples could be explained by either (a) a mixture of isotopically enriched ^{32}S-sulfate derived from intense pyrite oxidation with a component of deeper, ^{34}S-enriched groundwater, or (b) a lesser degree of bacterial sulfate reduction (BSR) relative to pyrite oxidation, resulting in a niche with higher sulfate concentrations and a correspondingly lower degree of BSR-related fractionation enrichment of ^{34}S in the dissolved sulfate.

Further relevant factors may be that GGA02 was the only borehole which used borehole purging to sample the Glasgow Upper Coal seam groundwater during drilling, potentially mixing stratified waters. It is noted that GGA05 was also purged but following collection of samples for this study. Otherwise, GGA02 was the only borehole subject to cement-based grouting in between drilling episodes, done to prevent connection of the Glasgow Upper and the other worked coal seams and mixing of the mine waters from different horizons as per SEPA requirement (Monaghan et al., 2020b).

Portland cement often contains a small amount of sulfate (1–3% SO_3 as a percentage of total oxides), typically as a result of addition of gypsum during milling (Bogue, 1929, Builders Booklet, 2021, Kirby and Kanare, 1988, Zhang, 2011). Despite this, intermediate $\delta^{34}S$ values for three samples ($+10.4$ to $+11.4‰$), and elevated sulfate for the one return fluid - mine water sample (331 mg/L) pre-date the grouting episodes in GGA02, suggesting that grouting is unlikely to be a plausible explanation for the observations.

A potential explanation may be that the elevated sulfate and intermediate $\delta^{34}S$ results have arisen from greater rates of sulfide oxidation in the Glasgow Upper Coal seam and the surrounding strata, connected by extensive fracture networks. Site 1 is the only of the three to be mined via total extraction techniques, whereby older, elongated pillar and stalls were "robbed" (Monaghan et al., 2020b), both Sites 2 and 3 were worked using the pillar and stall method (Barron et al., 2020a; Barron et al., 2020b). It may be that roof strata collapse and fracturing, not seen in Sites 2 and 3, allow a good hydraulic connection for meteoric waters to maintain oxidising conditions in the shallow Glasgow Upper Coal seam whilst simultaneously granting access to the overlying fine grained sandstone which hosts occasional pyrite and traces of iron staining (Monaghan et al., 2020b). It is also noted that subsequent groundwater sampling from the Glasgow Upper Coal seam by the BGS in an adjacent hole in Site 1, GGA01 (Fig. 2) shows remarkably increased and on-going sulfate production from September 2020 to May 2021 rising from 1157 mg/L to a maximum of 1409 mg/L (Bearcock et al., 2022). This correlates with an increase in iron concentration across the same timeline, further suggesting extensive pyrite oxidation.

5.8. Superficial groundwater dissolved sulfate $\delta^{34}S$

The groundwater from the superficial deposits have a high dissolved solute content, where pumping test water samples from GGA06r and GGA09r have arithmetic mean electrical conductivity values of 1675 μS/cm, interpreted as a result of anthropogenic inputs from the urban and industrial environment (Palumbo-Roe et al., 2021a). High $\delta^{34}S$ values of the two pumping test water samples ($+19.8‰$ and $+20.8‰$) and where calcium is the dominant cation in GGA09r suggest influence of waters affected by dissolution of gypsum in building materials (plaster, cement). Gypsum for construction materials has been mined in the UK from primarily Permian and Triassic age deposits (Bell, 1994), and thus would host $\delta^{34}S$ between $+10.9‰$ and $+25.8‰$ (Kampschulte and Strauss, 2004). The superficial horizon accessed by these two environmental monitoring boreholes is the Gourock Sand Member. It exhibits moderate hydraulic conductivity values (median of 1.027 m day^{-1} (Williams et al., 2017)) and lies directly beneath the anthropogenic made-ground, thus anthropogenically-altered groundwater can be expected to be sampled as part of the test pumping programme in GGA06r and GGA09r. Beneath the Gourock Sand Member are c. 11 m deposits of the Paisley Clay Member and c. 7 m of the Wilderness Till Formation with median hydraulic conductivities of 0.062 m day^{-1} and 0.032 m day^{-1} respectively (Williams et al., 2017). It is likely that these are hydraulic barriers which prevent superficial groundwater flow from reaching bedrock in this locality. Furthermore, Shorter et al. (2020a) report resting groundwater head for superficial, bedrock and mine water aquifers which indicate the presence of an upwards hydraulic gradient. This source of elevated $\delta^{34}S$ should not be considered for the values exhibited by the samples from the mine workings.

5.9. Bedrock groundwater dissolved sulfate $\delta^{34}S$

The dissolved sulfate $\delta^{34}S$ of the test pumping samples from each of the two environmental baseline monitoring boreholes were $+12.7‰$ for GGA03r, and two samples of $+15.9$ and $+15.8$ ‰ for GGB05 These boreholes were terminated in bedrock c. 8 m (GGA03r) and 5 m (GGB05) above the stratigraphically highest coal seam (Glasgow Upper Coal). Upon test pumping, GGB05 gave a high transmissivity value of 580 m^2 day^{-1}, rare for Carboniferous sandstones (Ó Dochartaigh et al., 2015) and expected to be associated with extensive fracturing. It is suggested that the fracturing is induced by the mining beneath (Shorter et al., 2020a), and it is likely that the fractures allow a portion of mine water to be abstracted during pumping. It is postulated that addition of a portion of mine water with elevated sulfate-$\delta^{34}S$ during pumping is responsible for increasing the $\delta^{34}S$ towards its ^{34}S enriched end member.

The bedrock test pumping samples exhibit the highest sulfate concentrations which suggests a considerable input from pyrite oxidation. The isotopic equilibrium between sulfate from oxidising pyrite and that from mine water influence is likely to be different for GGA03r. It has a calculated transmissivity value of 2.6 m^2 day^{-1}, indicating that fractures are less dominant. GGA03r did, however, show responses to pumping in each of the three boreholes completed in the Glasgow Upper Coal workings (Shorter et al., 2020a) and hence is not hydraulically separate from the mine workings.

6. Conclusion

Mine waters from the UK Geoenergy Observatory's Glasgow Geothermal Energy Research Field Site have been sampled from multiple mined coal seams upon first entry via drilling at Cuningar Loop, and the $\delta^{34}S$ signature of their dissolved sulfate has been determined. Alongside samples of mine water, drilling fluids which had interacted with portions of mined and unmined strata of the same horizons were collected from the GGC01 borehole in Dalmarnock, as well as sulfide bearing minerals (pyrite) in the host bedrock and local evaporite (gypsum) deposits from the Ballagan Formation.

Samples of water which had interacted with the 199 m unmined sequence of Scottish Middle Coal Measures in GGC01 show dissolved sulfate-δ^{34}S values ($+0.3 \pm 2.1‰$, $n = 8$) consistent with a sulfide oxidation origin ($+5.0 \pm 15.5‰$, $n = 7$). A markedly different and higher dissolved sulfate δ^{34}S is observed in water from mined coal seams at the Cuningar Loop sites ($+20.3 \pm 1.1‰$, $n = 10$). This is consistent with observations from previous European coal mine systems and suggests that the origin of dissolved sulfate in coal mine waters cannot be fully explained by pyrite oxidation.

Across six boreholes at Cuningar Loop, drilled through three worked coal seams, the strongest influence of pyrite oxidation was observed in borehole GGA02 at the level of the Glasgow Upper Coal workings. This was indicated by intermediate δ^{34}S values and elevated sulfate concentrations and underlines the importance of spatial and temporal monitoring of flooded mine workings to identify the varied geochemical niches which may be present.

Potential explanations for the elevated dissolved sulfate δ^{34}S in most mine waters include incorporation of fluids derived from evaporite brines or dissolved (evaporite) minerals. The former involves contribution of elevated sulfate-δ^{34}S from ancient evaporitic brines, retained in Carboniferous bedrock following erosion of their (e.g., Mesozoic) parent sedimentary successions. A small component of brine could dominate the sulfur isotopic signature, without δ^{18}O and δ^2H diverging from the recent meteoric signals demonstrated by mine water samples. Any influence of evaporitic minerals likely requires δ^{34}S-enriched sulfate derived from the most regionally abundant sulfate source in the Carboniferous sequence - the Ballagan Formation. However, there remains a large vertical separation (c. 1500 m) between the Lower Carboniferous Ballagan Formation and the Upper Carboniferous Middle Coal Measures which hosts the GGERFS. Moreover, the δ^{34}S values of the UKGEOS mine waters ($+20.3 \pm 1.1‰$, $n = 10$) are marginally higher than the Ballagan evaporites ($+18.9 \pm 0.5‰$, $n = 17$). Both of these hypotheses remain theoretically feasible, but their influence as controlling sources is largely unlikely.

Finally, the extent of bacterial reduction and fractionation of sulfate is not clear but remains a potential influencing factor on sulfur isotopic signatures. Whether such fractionation can be significant enough to elevate typical pyrite oxidation derived sulfate-δ^{34}S values up to around $+20‰$ remains uncertain and will depend on the relative rates of pyrite oxidation and bacterial sulfate reduction. The presence of hydrogen sulfide gas in the UKGEOS mine waters provides evidence for the activity of sulfate reducing bacteria. Overall, sulfate-δ^{34}S signatures likely reflect residence time of the mine waters, where elevated signatures may indicate long residence times in reducing, oxygen-poor conditions promoting fractionation by bacterial sulfate reduction. Short residence times indicate more oxidising recently recharged waters, favouring sulfate-δ^{34}S values indicative of pyrite oxidation.

Author contributions

DBW: conceptualisation (supporting), project administration (lead), methodology (supporting), investigation (lead), data curation (lead), formal analysis (lead), writing – original draft (lead), writing – review and editing (equal).

AJB: conceptualisation (equal), funding (supporting), methodology (lead), investigation (supporting), data curation (supporting), formal analysis (equal), writing – review and editing (equal), supervision (equal).

DB: writing – review and editing (equal), formal analysis (supporting), supervision (equal).

NMB: conceptualisation (equal), funding (lead), methodology (supporting), project administration (supporting), formal analysis (supporting), writing – review and editing (equal), supervision (equal).

Declaration of Competing Interest

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

Any data not presented in the manuscript has been shared as a supplementary material file.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.coal.2023.104248.

References

Banks, D., Boyce, A.J., 2023. Dissolved sulphate δ34S and the origin of sulphate in coal mine waters; NE England. Q. J. Eng. Geol. Hydrogeol. https://doi.org/10.1144/qjegh2022-106.

Banks, D., Younger, P.L., Arnesen, R.-T., Iversen, E.R., Banks, S.B., 1997. Mine-water chemistry: the good, the bad and the ugly. Environ. Geol. 32 (3), 157–174. https://doi.org/10.1007/s002540050204.

Banks, D., Boyce, A.J., Burnside, N.M., Janson, E., Roqueñi Gutierrez, N., 2020. On the common occurrence of sulphate with elevated δ34S in European mine waters: Sulphides, evaporites or seawater? Int. J. Coal Geol. 232, 103619 https://doi.org/10.1016/j.coal.2020.103619.

Barron, H.F., Starcher, V., Monaghan, A.A., Shorter, K.M., Walker-Verkuil, K., 2020a. Mine water characterisation and monitoring borehole GGA05, UK Geoenergy Observatory, Glasgow. In: British Geological Survey Open Report, OR/20/025, 36 p.

Barron, H.F., Starcher, V., Walker-Verkuil, K., Shorter, K.M., Monaghan, A.A., 2020b. Mine water characterisation and monitoring borehole GGA08, UK Geoenergy Observatory, Glasgow. In: British Geological Survey Open Report, OR/20/028, 35 p.

Bearcock, J.M., Walker-Verkuil, K., Mulcahy, A., Palumbo-Roe, B., MacAllister, D.J., Gooddy, D., Darling, W.G., 2022. UK Geoenergy Observatories: Glasgow baseline groundwater and surface water chemistry dataset release September 2020–May 2021. In: British Geological Survey Open Report, OR/22/038, 151 p.

Bell, F.G., 1994. A survey of the engineering properties of some anhydrite and gypsum from the north and midlands of England. Eng. Geol. 38 (1), 1–23. https://doi.org/10.1016/0013-7952(94)90021-3.

Bogue, R.H., 1929. Calculation of the compounds in portland cement. Ind. Eng. Chem. Anal. Ed. 1 (4), 192–197. https://doi.org/10.1021/ac50068a006.

British Geological Survey, 1992a. Airdrie. Scotland Sheet 31W. Drift Geology. 1:50000. British Geological Survey, Keyworth, Nottingham.

British Geological Survey, 1992b. Airdrie. Scotland Sheet 31W. Solid. 1:50 000 Geology Series.

Brown, M.M.E., Jones, A.L., Leighfield, K.G., Cox, S.J., 2002. Fingerprinting mine water in the eastern sector of the South Wales Coalfield: Mine Water Hydrogeology and Geochemistry. Geol. Soc. Lond., Spec. Publ. 198, 275–286. https://doi.org/10.1144/GSL.SP.2002.198.01.18.

Builders Booklet, 2021. Chemical composition of Portland Cement. https://www.buildersbooklet.com/concrete/chemical-composition-of-portland-cement/. Date Accessed:

Bullock, L.A., Parnell, J., Perez, M., Boyce, A., Feldmann, J., Armstrong, J.G.T., 2018. Multi-stage pyrite genesis and epigenetic selenium enrichment of Greenburn coals (East Ayrshire). Scott. J. Geol. 54 (1), 37–49. https://doi.org/10.1144/sjg2017-010.

Burnet, J., 1869. History of the water supply to Glasgow, from the commencement of the present century. Glasgow. https://wellcomecollection.org/works/hjwduews.

Burnside, N.M., Banks, D., Boyce, A.J., 2016a. Sustainability of thermal energy production at the flooded mine workings of the former Caphouse Colliery, Yorkshire,

United Kingdom. Int. J. Coal Geol. 164, 85–91. https://doi.org/10.1016/j.coal.2016.03.006.

Burnside, N.M., Banks, D., Boyce, A.J., Athresh, A., 2016b. 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. Int. J. Coal Geol. 165, 223–230. https://doi.org/10.1016/j.coal.2016.08.021.

Carmody, R.W., Plummer, N., Busenberg, E., Coplen, T.B., 1998. Methods for Collection of Dissolved Sulfate and Sulfide and Analysis of their Sulfur Isotopic Composition, 97–234.

Chen, X., Zheng, L., Dong, X., Jiang, C., Wei, X., 2020. Sources and mixing of sulfate contamination in the water environment of a typical coal mining city, China: evidence from stable isotope characteristics. Environ. Geochem. Health 42 (9), 2865–2879. https://doi.org/10.1007/s10653-020-00525-2.

Claypool, G.E., Holser, W.T., Kaplan, I.R., Sakai, H., Zak, I., 1980. The age curves of sulfur and oxygen isotopes in marine sulfate and their mutual interpretation. Chem. Geol. 28, 199–260. https://doi.org/10.1016/0009-2541(80)90047-9.

Clough, C.T., Hinxman, L.W., Wright, W.B., Anderson, E.M., Carruthers, R.G., 1926. The Economic Geology of the Central Coalfield of Scotland, Description of Area V, Glasgow East, Coatbridge and Airdrie. Memoir of the Geological Survey of Scotland.

Coleman, M.L., Moore, M.P., 1978. Direct reduction of sulphates to Sulphur dioxide for isotopic analysis. Anal. Chem. 28, 199–260.

Craig, H., 1961. Isotopic variations in meteoric waters. Science 133 (3465), 1702–1703. https://doi.org/10.1126/science.133.3465.1702.

Darling, W.G., Bath, A.H., Talbot, J.C., 2003. The O and H stable isotope composition of freshwaters in the British Isles. 2. Surface waters and groundwater. Hydrol. Earth Syst. Sci. Discuss. 7 (2), 183–195. https://hal.archives-ouvertes.fr/hal-00304768.

Davis, S.N., Whittemore, D.O., Fabryka-Martin, J., 1998. Uses of chloride/bromide ratios in studies of potable water. Groundwater 36 (2), 338–350. https://doi.org/10.1111/j.1745-6584.1998.tb01099.x.

Donnelly, T., Waldron, S., Tait, A., Dougans, J., 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 Commun. Mass Spectrom. 15 (15), 1297–1303. https://doi.org/10.1002/rcm.361.

Driessche, A.E.S.V., Canals, A., Ossorio, M., Reyes, R.C., García-Ruiz, J.M., 2016. Unraveling the sulfate sources of (giant) gypsum crystals using gypsum isotope fractionation factors. J. Geol. 124 (2), 235–245. https://doi.org/10.1086/684832.

Elsome, J., Walker-Verkuil, K., Starcher, V., Barron, H.F., Shorter, K.M., Monaghan, A.A., 2020. Environmental baseline characterisation and monitoring borehole GGB04, UK Geoenergy Observatory, Glasgow. In: British Geological Survey Open Report, OR/20/030, 22 p.

Engineering Timelines, 2020. Loch Katrine and its aqueducts. Engineering Timelines website. http://www.engineering-timelines.com/scripts/engineeringItem.asp?id=1244, Date Accessed: 1/11/2022. https://web.archive.org/web/20210614191914/.

Farr, G., Busby, J., Wyatt, L., Crooks, J., Schofield, D.I., Holden, A., 2021. The temperature of Britain's coalfields. Q. J. Eng. Geol. Hydrogeol. 54 (3) https://doi.org/10.1144/qjegh2020-109 p. qjegh2020-109.

Findlay, C., McDonald, B., Cunningham, J., 2020. A History of Coal Mining in Rutherglen and Cambuslang. Rutherglen Heritage Society.

Fordyce, F.M., Shorter, K.M., Walker-Verkuil, K., Barlow, T., Sloane, H.J., Arrowsmith, C., Hamilton, E.M., Everett, P.A., 2021. UK Geoenergy Observatories, Glasgow Environmental Baseline Surface Water Chemistry Dataset 1. Open Report OR/20/061.

Fowler, D., Cape, J.N., Leith, I.D., Paterson, I.S., Kinnaird, J.W., Nicholson, I.A., 1982. Rainfall acidity in northern Britain. Nature 297 (5865), 383–385. https://doi.org/10.1038/297383a0.

Hall, I.H.S., Browne, M.A.E., Forsyth, I.H., 1998. Geology of the Glasgow district. In: Sheet 30E (Scotland). Memoir of the British Geological Survey, British Geological Survey, Keyworth, 117 p.

Hammarstrom, J.M., Seal, R.R., Meier, A.L., Kornfeld, J.M., 2005. Secondary sulfate minerals associated with acid drainage in the eastern US: recycling of metals and acidity in surficial environments. Chem. Geol. 215 (1), 407–431. https://doi.org/10.1016/j.chemgeo.2004.06.053.

Institute of Geological Sciences, 1978. IGS Boreholes 1977. Report of the Institute of Geological Sciences. No.78/21.

Janson, E., Boyce, A.J., Burnside, N., 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. Int. J. Coal Geol. 164, 104–114. https://doi.org/10.1016/j.coal.2016.06.007.

Kampschulte, A., Strauss, H., 2004. The sulfur isotopic evolution of Phanerozoic seawater based on the analysis of structurally substituted sulfate in carbonates. Chem. Geol. 204 (3), 255–286. https://doi.org/10.1016/j.chemgeo.2003.11.013.

Kampschulte, A., Bruckschen, P., Strauss, H., 2001. The Sulphur isotopic composition of trace sulphates in Carboniferous brachiopods: implications for coeval seawater, correlation with other geochemical cycles and isotope stratigraphy. Chem. Geol. 175 (1), 149–173. https://doi.org/10.1016/S0009-2541(00)00367-3.

Kearsey, T., Gillespie, M., Entwisle, D., Damaschke, M., Wylde, S., Fellgett, M., Kingdon, A., Burkin, J., Starcher, V., Shorter, K., Barron, H., Elsome, J., Barnett, M., Monaghan, A., 2019. UK Geoenergy Observatories Glasgow: GGC01 Cored, seismic monitoring borehole – intermediate data release. In: British Geological Survey Open Report, OR/19/049.

Kirby, R.K., Kanare, H.M., 1988. Portland Cement Chemical Composition Standards (Blending, Packaging and Testing). US National Bureau of Standards special publication v. 260–110. https://nvlpubs.nist.gov/nistpubs/Legacy/SP/nbsspecialpublication260-110.pdf. v. 260–110.

Lenntech, 2022. Composition of Seawater. https://www.lenntech.com/composition-seawater.htm. Date Accessed: 03/03/2022.

Loredo, C., Ordonez, A., Garcia-Ordiales, E., Alvarez, R., Roqueni, N., Cienfuegos, P., Pena, A., Burnside, N.M., 2017. Hydrochemical characterization of a mine water geothermal energy resource in NW Spain. Sci. Total Environ. 576, 59–69. https://doi.org/10.1016/j.scitotenv.2016.10.084.

Millward, D., Davies, S.J., Williamson, F., Curtis, R., Kearsey, T.I., Bennett, C.E., Marshall, J.E.A., Browne, M.A.E., 2018. Early Mississippian evaporites of coastal tropical wetlands. Sedimentology 65 (7), 2278–2311. https://doi.org/10.1111/sed.12465.

Monaghan, A.A., O Dochartaigh, B., Fordyce, F., Loveless, S., Entwisle, D., Quinn, M., Smith, K., Ellen, R., Arkley, S., Kearsey, T., Campbell, S.D.G., Fellgett, M., Mosca, I., 2017. UKGEOS – Glasgow Geothermal Energy Research Field Site (GGERFS): Initial Summary of the Geological Platform. British Geological Survey, Nottingham, UK, p. 205.

Monaghan, A.A., Starcher, V., Ó Dochartaigh, B., Shorter, K., Burkin, J., 2019. In: British Geological Survey (Ed.), UK Geoenergy Observatories: Glasgow Geothermal Energy Research Field Site; Science Infrastructure Version 2. British Geological Survey, Keyworth, Nottingham, p. 49. UKGEOS Report G0100, BGS Open Report OR/19/032.

Monaghan, A.A., Barron, H.F., Starcher, V., Shorter, K.M., Walker-Verkuil, K., 2020a. Mine water borehole GGA01, UK Geoenergy Observatory, Glasgow. In: British Geological Survey Open Report, OR/20/021, 28 p.

Monaghan, A.A., Starcher, V., Barron, H.F., Shorter, K.M., Walker-Verkuil, K., 2020b. Borehole GGA02, UK Geoenergy Observatory, Glasgow. In: British Geological Survey Open Report, OR/20/022, 31 p.

Monaghan, A.A., Damaschke, M., Starcher, V., Fellgett, M.W., Kingdon, A., Kearsey, T., Hannis, S., Gillespie, M., Shorter, K., Elsome, J., Barnett, M., 2021a. UK Geoenergy Observatories Glasgow: GGC01 cored, seismic monitoring borehole – final data release. In: British Geological Survey Open Report, OR/21/031 (64 p).

Monaghan, A.A., Damaschke, M., Starcher, V., Fellgett, M.W., Kingdon, A., Kearsey, T., Hannis, S., Gillespie, M., Shorter, K., Elsome, J., Barnett, M., 2021b. UKGEOS Glasgow GGC01 Final Borehole Information Pack: NERC EDS National Geoscience Data Centre. https://doi.org/10.5285/e38c58a6-48ec-4ad1-a996-6c6144968d7d.

Monaghan, A.A., Starcher, V., Barron, H.F., Shorter, K., Walker-Verkuil, K., Elsome, J., Kearsey, T., Arkley, S., Hannis, S., Callaghan, E., 2021c. Drilling into mines for heat: geological synthesis of the UK Geoenergy Observatory in Glasgow and implications for mine water heat resources. Q. J. Eng. Geol. Hydrogeol. https://doi.org/10.1144/qjegh2021-033 p. qjegh2021-2033.

Nelson, S.T., 2000. A simple, practical methodology for routine VSMOW/SLAP normalization of water samples analyzed by continuous flow methods. Rapid Commun. Mass Spectrom. 14 (12), 1044–1046. https://doi.org/10.1002/1097-0231(20000630)14:12<1044::Aid-rcm987>3.0.Co;2-3.

O Dochartaigh, B.E., Smedley, P.L., MacDonald, A.M., Darling, W.G., Homoncik, S., 2011. Baseline Scotland: groundwater chemistry of the Carboniferous sedimentary aquifers of the Midland Valley. In: British Geological Survey Open Report, OR/11/021, p. 105. http://nora.nerc.ac.uk/id/eprint/14314/, p. 105.

Ó Dochartaigh, B.E., MacDonald, A.M., Fitzsimons, V., Ward, R., 2015. Scotland's aquifers and groundwater bodies. In: British Geological Survey Open Report, OR/15/028, p. 76.

Palumbo-Roe, B., Shorter, K.M., Fordyce, F.M., Walker-Verkuil, K., Ó Dochartaigh, B., Gooddy, D., Darling, W.G., 2021a. UK Geoenergy Observatories: Glasgow Borehole Test Pumping - Groundwater Chemistry. In: British Geological Survey Open Report, OR/21/030 (73 p).

Palumbo-Roe, B., Shorter, K.M., Fordyce, F.M., Walker-Verkuil, K., Ó Dochartaigh, B., Gooddy, D., Darling, W.G., 2021b. UKGEOS Glasgow Test Pumping Groundwater Chemistry Data Release. https://doi.org/10.5285/53ded3f2-a4e9-4f49-8084-2c8b3b485268.

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

Robinson, B.W., Kusakabe, M., 1975. Quantitative preparation of sulfur dioxide, for sulfur-34/sulfur-32 analyses, from sulfides by combustion with cuprous oxide. Anal. Chem. 47 (7), 1179–1181. https://doi.org/10.1021/ac60357a026.

Scottish Water, 2021. Water Register; Date Range of Sample: 01/01/2021 to 31/12/2021; Regulation Zone = Milngavie C2. https://www.scottishwater.co.uk/-/media/ScottishWater/Water-Quality/Data/73/202209/Water-202101-Milngavie-C2-Calendar-Year.pdf.

Secret Scotland, 2023. Clyde Tidal Weir. https://www.secretscotland.org.uk/index.php/Secrets/ClydeTidalWeir. Date Accessed: 28/01/2023.

Shorter, K.M., MacDonald, A.M., Ó Dochartaigh, B.E., Elsome, J., Burke, S., 2020a. Data release and initial interpretation of test pumping of boreholes at the Glasgow UK Geoenergy Observatory. In: British Geological Survey. Open Report, OR/21/016, 104pp., 104 p.

Shorter, K.M., Starcher, V., Barron, H.F., Walker-Verkuil, K., Monaghan, A.A., 2020b. Environmental baseline characterisation and monitoring borehole GGA03r, UK Geoenergy Observatory, Glasgow. In: British Geological Survey Open Report, OR/20/023, 23 p.

Shorter, K.M., Starcher, V., Barron, H.F., Walker-Verkuil, K., Monaghan, A.A., 2020c. Environmental baseline characterisation and monitoring borehole GGA06r, UK Geoenergy Observatory, Glasgow. In: British Geological Survey Open Report, OR/20/026, 23 p.

Shorter, K.M., Palumbo-Roe, B., Ó Dochartaigh, B.E., Fordyce, F., Walker-Verkuil, K., 2021a. UK Geoenergy Observatories Glasgow: Groundwater chemistry data collected

during the borehole construction phase. In: British Geological Survey Open Report, OR/21/015, 45 p.

Shorter, K.M., Palumbo-Roe, B., Ó Dochartaigh, B.E., Fordyce, F., Walker-Verkuil, K., 2021b. UKGEOS Glasgow Construction Phase Groundwater Chemistry Data Release. NERC EDS National Geoscience Data Centre. (Dataset). https://doi.org/10.5285/295984e5-5f2a-43aa-aa3d-6995a80ac8ed.

Smith, R.A., 1872. Air and Rain: The Beginnings of a Chemical Climatology. Longmans, Green, and Company.

Starcher, V., Barron, H.F., Monaghan, A.A., Shorter, K.M., Walker-Verkuil, K., 2020a. Mine water characterisation and monitoring borehole GGA04, UK Geoenergy Observatory, Glasgow. In: British Geological Survey Open Report, OR/20/024, 28 p.

Starcher, V., Walker-Verkuil, K., Shorter, K.M., Monaghan, A.A., Barron, H.F., 2020b. Mine water characterisation and monitoring borehole GGA07, UK Geoenergy Observatory, Glasgow. In: British Geological Survey Open Report, OR/20/027, 29 p.

Tarmac, 2016. Technical Data Sheet Flow Modified Grout Range. https://www.pozament.co.uk/wp-content/uploads/2013/02/Flow-Modified-Grout-Range-Technical-Datasheet-July-2016.pdf.

Tostevin, R., Turchyn, A.V., Farquhar, J., Johnston, D.T., Eldridge, D.L., Bishop, J.K.B., McIlvin, M., 2014. Multiple sulfur isotope constraints on the modern sulfur cycle. Earth Planet. Sci. Lett. 396, 14–21. https://doi.org/10.1016/j.epsl.2014.03.057.

Undiscovered Scotland, 2023. Rutherglen. https://www.undiscoveredscotland.co.uk/glasgow/rutherglen/index.html. Date Accessed: 28/01/2023.

Walker-Verkuil, K., Starcher, V., Barron, H.F., Shorter, K.M., Elsome, J., Monaghan, A.A., 2020a. Environmental baseline characterisation and monitoring borehole GGB05, UK Geoenergy Observatory, Glasgow. In: British Geological Survey Open Report, OR/20/031, 23 p.

Walker-Verkuil, K., Starcher, V., Barron, H.F., Shorter, K.M., Monaghan, A.A., 2020b. Environmental baseline characterisation and monitoring borehole GGA09r, UK

Geoenergy Observatory, Glasgow. In: British Geological Survey Open Report, OR/20/029.

Walls, D.B., Banks, D., Peshkur, T., Boyce, A.J., Burnside, N.M., 2022a. Heat Recovery Potential and Hydrochemistry of Mine Discharges from Scotland's Coalfields. In Press.

Walls, D.B., Banks, D., Peshkur, T., Boyce, A.J., Burnside, N.M., 2022b. Heat recovery potential and hydrochemistry of mine water discharges from Scotland's Coalfields. Earth Sci. Syst. Soc. 2 https://doi.org/10.3389/esss.2022.10056.

Watson, S.M., 2022. An Investigation of the Geothermal Potential of the Upper Devonian Sandstones beneath Eastern Glasgow. PhD Thesis,. University of Glasgow. https://doi.org/10.5525/gla.thesis.82687.

Williams, J.D.O., Dobbs, M.R., Kingdon, A., Lark, R.M., Williamson, J.P., MacDonald, A. M., Ó Dochartaigh, B.É., 2017. Stochastic modelling of hydraulic conductivity derived from geotechnical data; an example applied to Central Glasgow. Earth Environ. Sci. Trans. Roy. Soc. Edinb. 108 (2–3), 141–154. https://doi.org/10.1017/S1755691018000312.

Younger, P.L., 1995. Hydrogeochemistry of minewaters flowing from abandoned coal workings in County Durham. Q. J. Eng. Geol. 28 (2), S101–S113. https://doi.org/10.1144/GSL.QJEGH.1995.028.S2.02.

Younger, P.L., 1997. The longevity of minewater pollution: a basis for decision-making. Sci. Total Environ. 194-195, 457–466. https://doi.org/10.1016/S0048-9697(96)05383-1.

Younger, P.L., Boyce, A.J., Waring, A.J., 2015. Chloride waters of Great Britain revisited: from subsea formation waters to onshore geothermal fluids. Proc. Geol. Assoc. 126 (4–5), 453–465. https://doi.org/10.1016/j.pgeola.2015.04.001.

Zhang, H., 2011. 4 - Cement. In: Building Materials in Civil Engineering. Woodhead Publishing, pp. 46–423, 978-1-84569-955-0.