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On the common occurrence of sulphate with elevated δ^{34}S in European mine waters: sulphides, evaporites or seawater?

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Highlights

- Mine water sulphate δ^{34}S characterised in three European coal mining regions.
- Shallow mine waters typically exhibit δ^{34}S characteristic of sulphide oxidation.
- High δ^{34}S in deeper mine waters suggests evaporite / marine derivation.
- Sulphate reduction fractionation may have contributed to elevated sulphate δ^{34}S.
- Is deep mine- / groundwater a dynamic sulphate reservoir analogous to ocean water?

Abstract

The stable isotopic (δ^{34}S, δ^{18}O, δ^{2}H) composition of mine waters has been examined from coal and metal mines, of varying depth, in Spain (Asturias), the UK (north Derbyshire / Yorkshire) and Poland (Bytom, Upper Silesia). δ^{18}O and δ^{2}H data confirm a meteoric origin for all waters. The mine waters have elevated sulphate concentrations relative to recent meteorically-derived groundwaters and have elevated SO_4^{2-}/Cl^- ratios relative to marine water. In the shallower mines and Markham No. 3, the dissolved sulphate δ^{34}S is low, suggesting the sulphate is derived from the oxidation of sulphide minerals. In most of the deeper mines, the dissolved sulphate δ^{34}S is too high (>15‰), to be derived from simple pyrite oxidation. In the deep Polish and Spanish mine waters, the source of sulphate may be evaporite mineral dissolution, but such a mechanism is problematic in the case of the Caphouse (UK) mine. Fractionation associated with sulphate reduction may have contributed to elevated dissolved sulphate δ^{34}S. Elevated sulphate in deep coal mine waters may *not* always be simply derived from pyrite oxidation. The consistent observation of elevated dissolved sulphate δ^{34}S in deep coal mines suggests a distinct genetic pathway, the origin of which as yet remains equivocal.

Key Words: Mine water, sulphate, sulphide, stable isotopes, evaporite, galena, seawater

Introduction

It is often assumed that, in the waters of flooded coal and sulphide ore mines, the dominant hydrochemical process is sulphide oxidation [1]; e.g., for pyrite:

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

$$FeS_2 + 14Fe^{3+} + 8H_2O = 15Fe^{2+} + 2SO_4^{2-} + 16H^+ \qquad (1b)$$

or for sphalerite

$$ZnS + 2O_2 = Zn^{2+} + SO_4^{2-} \qquad (2)$$

The corollary to this assumption is that the majority of the sulphate found in mine waters is derived from sulphide oxidation, whether biologically or abiologically mediated. Hydrochemical data collected during the EU-funded LoCAL [2] project, from several mining environments in Poland, northern Spain (Asturias) and the United Kingdom, have previously been published in separate papers [3, 4, 5, 6]. This paper compares the inorganic chemical data from mine waters in all three areas, adds stable isotopic data and critically examines the assumption that the majority of the sulphate found in mine waters is derived from sulphide oxidation. In opposition to this primary hypothesis, the following opposing hypotheses are considered for the source of sulphate:

1. from marine inundation of the mine host rock (i.e. “fossil” seawater)
2. from dissolution of evaporite minerals, such as gypsum or anhydrite, within the host rock, subjacent or overlying strata (for example, the Permian Zechstein salt deposits, the Triassic Keuper / Mercia Mudstone gypsiferous marls, or Tertiary evaporites, that often overlie Carboniferous coal-bearing strata in a European geological context)
3. from downward density-driven flow of residual brines during evaporite formation in closed evaporitic basins
4. sulphate and other solutes have been concentrated by deep freezing during permafrost conditions associated with the Pleistocene glaciations, a hypothesis that has been advanced to explain deep saline formation waters in British Coal Measures rocks [7], as well as in the Canadian and Fennoscandian shields [8].

In each of the three countries under consideration (Figure 1), the LoCAL data revealed deep mining environments whose waters contain significantly elevated sulphate concentrations, but where the dissolved sulphate ^{34}S isotopic composition is not characteristic of pyrite oxidation. In the case of hypotheses 1, 3 and 4 one would expect elevated concentrations of sulphate to also be accompanied by correspondingly elevated chloride concentrations. In the case of hypothesis 2, chloride would only be elevated if the evaporite deposit contained chloride minerals, but not if it was sulphate-dominated (e.g. gypsum).

Figure 1. Overview map of Europe, showing the locations of the studied mines in the UK, Spain and Poland, together with other locations named in text.

The practical importance of this study is that elevated sulphate concentrations, derived from pyrite oxidation (and implying a dissolved sulphate $\delta^{34}S$ similar to sedimentary sulphide) are widely considered to be diagnostic of coal mine waters [9].

The Mines

Szombierki and Centrum mines, Bytom, Upper Silesian Coal Basin, Poland

Bytom town lies in the western part of the Katowice conurbation, overlying the Carboniferous age Upper Silesian Coal Basin (USCB) synform. The Namurian-Westphalian coal-bearing sequence can reach up to 8500 m in thickness, and comprises sandstones, siltstones, claystones and coals, deposited in a Variscan foredeep basin. It can be subdivided, in descending order, into four Series: the Kraków Sandstones, the Mudstone Series, the Upper Silesian Sandstones, and the Paralic Series [10]. The coal-bearing strata are overlain by Permian, Triassic, Jurassic, Tertiary and Quaternary cover, the Permian and Jurassic strata only being encountered in the north and the Tertiary predominantly in the south. The Triassic strata are more extensive, reaching up to 200 m thick and comprising predominantly dolomites and limestones [11]. These Triassic strata can represent a productive potable groundwater aquifer, but also host workable lead-zinc ore (sulphide) deposits, which were extensively exploited in the Bytom Trough.

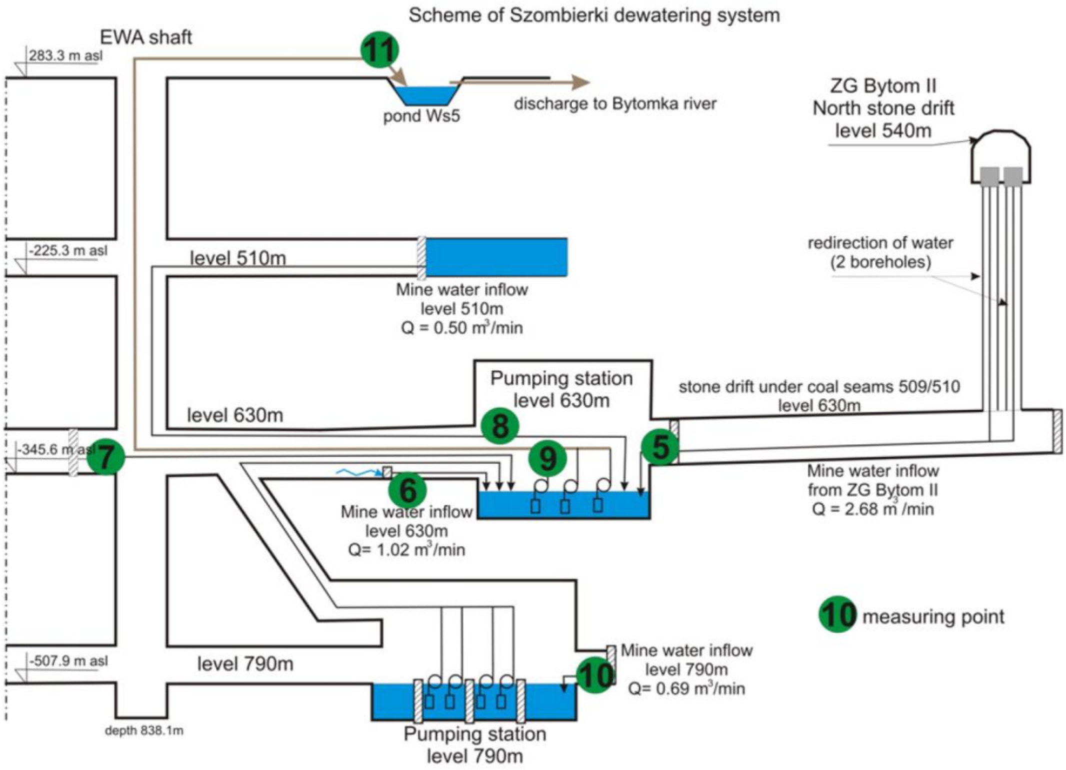

Figure 2. Schematic cross section of the Szombierki mine, showing numbered sampling locations, after [3].

Bytom's Szombierki coal mine [3] was actively mined from 1870 until closure in 1999. It accesses an area of around 10.3 km^2, extending down to c. 950 m below ground level (bgl) / -690 m above sea level (asl). The main seams mined were within the Upper Silesian Sandstone and Paralic Series, with sulphur contents of 0.7 to 1.0% [12]. The mine is kept dewatered by underground pumping stations rather than submersible pumps, in order to control water ingress into adjacent (active) mines, such as the adjacent Centrum / Bobrek mine (50.3548°N, 18.8912°E, which is also dewatered). Szombierki colliery is dewatered via the Ewa shaft (50.3382°N 18.9108°E), with rates of 1.1 to 2.7 million m^3 yr^{-1} (average 35 to 84 L s^{-1}) being recorded since its closure. The water is discharged via a pond termed Ws5, thence ultimately to the Bytomka River. Ewa shaft also receives influxes of water from the adjacent abandoned Bytom II mine at the 630 m level (location 5 on Figure 2) and from the isolated Karol mining area, which enters near location 7 (Figure 2). The mine water hydrochemistry has previously been described by [3].

Bolko Pb-Zn mine pumping station (formerly 'Orzeł Biały'), Bytom, Upper Silesia, Poland

The coal-bearing sequence at Szombierki is overlain by Triassic cover of up to 230 - 250 m thickness, including terrigenous Bunter Sandstone facies and carbonates of Roethian and Muschelkalk type [13, 14, 15, 16]. The mid-Triassic Muschelkalk dolomites contain a lead-zinc sulphide ore body (including both oxidized calamine deposits and sulphide minerals: sphalerite and galena [17, 18, 19]) accessed by around five interconnected mines, ranging in depth from 64 - 100 m [20]. The ores are Mississippi Valley Type, deposited from basinal brines within karst-like features in brecciated Triassic dolomites [21]. The worked areas of the Triassic Pb-Zn mines and Szombierki mines overlap, but are vertically and hydraulically separate. Active Pb-Zn mining ceased in 1989. The 129 m deep Bolko shaft (50.3603°N, 18.9318°E) still acts as a central dewatering station for the Bytom Pb-Zn mine complex. Two galleries, the 1100 m long Western Gallery and 1225 m long Eastern Gallery drain water to a sump and pumping station at the base of the Bolko shaft [13]. In 2003 the average water flow into Bolko was 385 L s^{-1} [20]. In 1999, the water from the western gallery contained 1040 - 1520 mg L^{-1} sulphate, 370 - 800 mg L^{-1} chloride and 5.3 – 12.9 mg L^{-1} zinc, while the water from the eastern gallery was characterised by 930 - 1100 mg L^{-1} SO_4^{2-}, 180 - 220 mg L^{-1} Cl^- and 10.7 - 15.6 mg L^{-1} Zn [16].

Mieres, Asturias, Spain

The studied mines [4, 22, 23] form an interconnected complex of workings along the valley of the River Caudal and its major upstream tributary, the River Turón, in the vicinity of the town of Mieres, Asturias, northern Spain (Figure 1). They are located within the Asturian Central Coal Basin (ACCB), part of the 'Cantabrian Zone' of northern Spain, an easterly directed arcuate thrust and fold belt, formed during the Variscan orogeny [24]. During the early Carboniferous (Mississippian), the Cantabrian Zone comprised a stable, low-sedimentation marine platform; as the orogenic episode gathered momentum during the later Carboniferous, the zone became a foreland basin, infilled by Namurian turbiditic successions in the west and black micritic limestones in the east [25]. In late Namurian and Westphalian times, coal-bearing sequences started to form in alluvial, deltaic and coastal and alluvial settings, and even in intermontane and limnic basins in the Stephanian. The coals range in grade from high-volatile bituminous to anthracite [26].

The studied mines are stratigraphically located within a heavily deformed and steeply dipping [22] Westphalian coal-bearing sequence of shales, greywackes, mudstones, sandstones, conglomerates and limestones. The coals of the c. 3000 m thick Sama Group are generally low-sulphur (0.5 to 1% total S, with occasional outliers up to 2.3%), and overlie the c. 2700 m thick Lena Group [27].

At the downstream end of the mine complex, the Barredo shaft (43.2429°N 5.7747°W) is some 360 m deep and was active from 1926 to 1993. The Figaredo mine (43.2095°N 5.7672°W), in the valley of the River Turón, is 650 m deep [4], and was active until 2007. After 2008, the complex was allowed to partially flood, but water levels are maintained at c. +150 m asl, by pumping from both shafts, at a combined rate of 3.3 to 5.1 million m^3 yr^{-1} (average 4.1 million m^3 yr^{-1} or 130 L s^{-1}). The majority of pumping takes place at Barredo, via 4 submersible pumps: 3 at a depth of c. 100 m and 1 at 200 m depth. The pump at Figaredo is around 100 m deep. Further pumped dewatering occurs at two more mines, Santa Barbara (43.2138°N 5.7182°W) and San José (43.2086°N 5.7379°W), upstream of Figaredo in the Turón valley. The workings of the Barredo-Figaredo complex have an estimated volume of some 5.8 million m^3 (up to the water level of +150 m asl) and underlie an area of some 16.4 km^2 [22].

Shallow workings are also present, including the gravity-drained Mariana mine, driven into the hillside close to Barredo shaft. Rainfall in the area is around 1100 mm yr^{-1}. The mine water hydrochemistry has previously been described by [4].

Caphouse, Yorkshire, United Kingdom

Caphouse Colliery [28] is located near the town of Wakefield, West Yorkshire, United Kingdom. Several shafts are present on site, including the Hope (1.6254°W 53.6418°N), Inman, Furnace and Caphouse (1.6182°W 53.6440°N) shafts and two drifts [29, 30], which are hydraulically interconnected to a wider network of collieries [31, 32]. The colliery typically mined strata between the Flockton Thick and Beeston seams [33] of the Langsettian stage [34] of the Westphalian Lower Coal Measures. The strata comprise coals, mudstones, siltstones and sandstones and were deposited in a "fluvio-lacustrine setting in an embayment distant from the open ocean with limited marine influence" [28]. Caphouse Colliery closed in 1985 as a working mine, but now hosts the National Coal Mining Museum of England

(NCMME). The 197 m deep Hope Shaft is pumped at an average rate of c.3000 m^3 d^{-1} (up to 76 L s^{-1} for 12-16 h day^{-1}), to maintain mine water levels in the range c. 143-156 m bgl (+4 to -9 m asl). This ensures that the museum's underground visitor exhibits remain unflooded and that regional minewater levels are kept low enough to prevent uncontrolled surface minewater outbreaks. The pumped water is treated using a passive oxidation-settlement-wetland system prior to discharge to the river environment [35, 36, 37].

The Hope Shaft pumped minewater chemistry has been described previously [5, 38, 39]. It typically a sodium sulphate-(bicarbonate) water of circumneutral pH and with an H_2S odour. It has been suggested [39, 9] that the hydrochemistry results from mixture between an ambient sodium bicarbonate Coal Measures groundwater [40] and an acid sulphate mine water signature. During the past c. 12 years, the mine water quality has improved: SO_4^{2-} concentrations have declined from c. 1200 mg L^{-1} to c. 600 mg L^{-1} and iron concentrations from c. 30 mg L^{-1} to c. 15 mg L^{-1}. Since early 2015, chloride concentrations have increased, for reasons which are not clear, to over 300 mg L^{-1}.

Water seepages to the Secondary Egress Drift at Caphouse, from above the main mine water table, have previously been sampled and published by [38, 41].

Markham Colliery, Bolsover, Derbyshire, United Kingdom

Markham Colliery, located just north of Bolsover, Derbyshire, UK, comprised four main shafts. From the 1880s until its closure in c. 1993, it mined coal between the High Hazels and Blackshale seams of the Duckmantian and Langsettian stages of the Westphalian Coal Measures [42, 43]. Since 2012 until recently, an electrical submersible pump (ESP) was used to supply water from the only remaining accessible shaft (No. 3 shaft; 1.3285°W 53.2424°N), to a heat pump [6, 39]. No.3 shaft was constructed in 1886 to a depth of c. 496 m (the level of the Deep Soft seam), and later backfilled to 429 m (Ell Coal). The shaft hydraulically interconnects with the other Markham shafts (at c. 630 m deep, Shafts 1 and 4 are significantly deeper than No. 3) and thence to a several other nearby collieries across the NE Derbyshire region. Following colliery abandonment, minewater levels are still rising rapidly across the region. In May 2011, the water level in No. 3 shaft was 239.5 m bgl (-167.7 m asl); by February 2016 it was at 136 m bgl and by early 2018, the level was above 92 m bgl (-20 m asl). This equates to an average rise of over 20 m per year.

No. 3 shaft was test-pumped in 2011 with a pump set as deep as 340 m (we refer to this as the *Phase 1 Pumping Regime*), and the water was found to be of a highly saline (electrical conductivity 40,000 µS cm^{-1}), sodium-chloride, reducing nature (ammoniacal nitrogen 14 mg L^{-1} and negligible sulphate, indicating sulphate-reducing conditions) [6].

In 2012, an ESP was installed at c. 235 m depth to supply water at c. 14 - 15 °C to a heat pump system (*Phase 2 Pumping Regime*), with the cooled water being returned to the same shaft via a diffuser at 250 m bgl. The water from this depth was still saline (20,000 – 25,000 µS cm^{-1}, with sodium-chloride composition) and reducing (up to 9 mg L^{-1} dissolved methane and 4 - 5 mg L^{-1} ammoniacal nitrogen), but less so than during *Phase 1* (it now contained 500 - 1700 mg L^{-1} sulphate). In January 2015, the ESP was raised to 170 m bgl (with return diffuser at 153 m bgl; *Phase 3 Pumping Regime*), following which the abstracted water became cooler (13 - 14°C [39]), fresher (EC 2000 - 3000 µS cm^{-1}, but still Na-Cl dominated) and more oxidising (ammonium and methane negligible, significant decline in dissolved Fe and Mn, nitrate at 3 - 5 mg L^{-1}). It thus seems that the water in the Markham shaft is significantly stratified, with fresher, more oxidising recently recharged water 'floating' on denser, saline, reducing water [6, 39].

Shaft No. 3 releases significant quantities of methane gas (indeed, prior to 2012, when water levels were lower, it was used to commercially produce methane), which must be vented at the surface.

Fractionation of Sulphur Isotopes in Marine and Sedimentary Environments

Modern seawater sulphate has a $\delta^{34}S$ around +21‰ CDT [44]. This is higher than the riverine inputs to the world's oceans (estimated as a global flux-weighted mean of 4.4 ±4.5‰ [45], which reflects weathering of sulphur-bearing minerals), due to the preferential removal of ^{32}S by the formation of sulphide minerals in marine sediments by sulphate reduction.

Sulphate precipitates or evaporite minerals derived from seawater [44] have a sulphur isotope composition similar to marine water, with only a very modest positive fractionation (cited between 0 to +2.4‰ by [46]).

Bacterially-mediated sulphate reduction (BSR) in anaerobic sediments typically produces a strong preferential concentration of ^{32}S in the sulphide minerals formed. Thus, sulphide minerals formed in anaerobic systems which are isotopically open to seawater sulphate have a lower $\delta^{34}S$ than the seawater. Fractionation ($\delta^{34}S_{SO4}$ – $\delta^{34}S_{H2S}$) can reach as much as 70‰ in both laboratory studies and real sediments [46, 47, 48, 49, 50]. Thus, pyrite formed by microbial sulphate reduction in conditions that are replete with respect to seawater (i.e. isotopically "open" with respect to sulphate) often has a low to very low (typically negative) $\delta^{34}S$ [51]. Sulphide minerals formed in settings closed with respect to sulphate tend to have a more positive $\delta^{34}S$ which more closely approaches that of the "parent" seawater, as the sulphate present becomes consumed [52]. Thus, pyrite formed under closed conditions, where sulphate is limited (e.g. epigenetic pyrite, formed after burial, after system closure) will thus usually be less depleted in ^{34}S. A typical $\delta^{34}S$ range for marine pyrite is often taken to be between -50 and +15‰ [44, 46]. A study of Cretaceous sediments found that pyrite formed in marine and coastal plain rocks where access to sulphate became progressively "closed" had typical $\delta^{34}S$ up to +18‰, and in some cases even higher [51]. In deeper, higher temperature, abiotic environments, thermochemical sulphate reduction (TSR) may predominate, using hydrocarbons or other reduced species as electron donors [53, 54]. Preferential enrichment of ^{32}S in the sulphide phase by TSR is less extensive than with BSR (0 to 20‰ fractionation commonly cited [55, 56]), but methane-coupled TSR has been suggested as a mechanism for generating elevated $\delta^{34}S$ in fluid sulphates (and related sulphide minerals), with formation of sulphide ores in Zechstein carbonates of Lower Saxony [57] and the Zambian Copper Belt [58].

The seawater $\delta^{34}S$ is governed by the relative rates of mineral weathering input, removal by sulphide formation and removal as sulphate / evaporite minerals. It has thus exhibited systematic variations through geological time [59], with the following values estimated for the geological period relevant to the studied mines. Carboniferous seawater sulphate $\delta^{34}S$ has been estimated to typically range from +18 to +14‰ [46, 60], although values up to c. +23‰ have been reported from the Lower Carboniferous [60, 61]. Higher values are characteristic of the Mississippian period [62], declining through the Upper Carboniferous [63]. In the Permian seawater sulphate $\delta^{34}S$ tended to be less positive at +8 to +14‰ [46]. The late Permian German Zechstein evaporites tend to exhibit a range from +10 to +15‰, with an average of 11.5‰ being suggested for typical late Permian marine sulphate [64]. In the earliest Triassic, the marine sulphate $\delta^{34}S$ abruptly rose to +20 to +30‰, reflecting a transition from an environment of predominant "Zechstein"-type evaporitic sulphate precipitation to an extremely anoxic, euxinic environment, dominated by sulphide formation [65]. Seawater sulphate $\delta^{34}S$ subsequently decreased to below +20‰ in the Middle Triassic to stabilise around +16‰ in the Late Triassic [64]. Global trends in seawater sulphate are also followed by trends in the $\delta^{34}S$ of sulphide minerals produced from such seawater [46].

Seawater salinity has varied through geological time, but not by an order-of-magnitude. Palaeozoic and early Mesozoic chloride salinities are estimated [66] to have been higher than present, while later Mesozoic and Cenozoic salinities were similar to those at present. Concentrations of marine sulphate are generally believed to have been lower than at present [67, 68] through much of geological time, although similar to the present at the Permian-Triassic boundary [69, 70]. Given that the marine SO_4^{2-}/Cl^- ratio has typically been lower in the geological past than at present, a groundwater SO_4^{2-}/Cl^- ratio exceeding modern seawater is a strong indicator of a lithological source of sulphate.

Finally, when sulphide minerals such as pyrite oxidise to sulphate (e.g. when exposed to the atmosphere via mining activities), whether biologically mediated or not [71], there is a general consensus that there is very little sulphur isotopic fractionation, and that the derived sulphate essentially reflects the isotopic composition of the parental sulphide [72].

Sulphide Sulphur Isotopic Composition in the Studied Mining Areas

In the UK, mean pyrite $\delta^{34}S$ of -32. 5‰ and -17.7‰ were recorded in the Namurian Bowland Shales and Caton Shales, respectively [73]. Excluding a single sample (-30.0‰), nine samples of soluble sulphate from these shales returned a mean sulphate $\delta^{34}S$ of -1.7‰, with a range from -8.7 to +3.7‰.

The $\delta^{34}S$ of pyrite in the UK's Coal Measures is very variable, but values of around 0‰ are typical. In Ayrshire (Scotland), the average $\delta^{34}S$ of pyrite in coal was +2.7‰ (range -26.3 to +11.6‰, with one higher outlier; [74]). In Northumberland, the average was +5.1‰ (range -5.4‰ to +12.8‰, with one higher outlier; [62]). A study [75] of a marine incursion in the Westphalian Coal Measures sequence of Yorkshire recorded pyrite $\delta^{34}S$ values ranging from −35.3‰ to +20.4‰. Low values were recorded in marine portions of the succession, (mean −1.2 ± 6.5‰), trending towards higher values in sediments beneath coal seams (+12.7 ± 7.7‰). In summary, UK Coal Measures pyrite typically has a $\delta^{34}S$ range from <-20‰ to around +12‰, but occasionally significantly higher.

In Poland, coals from the USCB are reported [76] to exhibit $\delta^{34}S$ ranging from -6.6‰ to +10.5‰ (mean +3.4‰) in the pyrite fraction, -5.9‰ to 13.7‰ (mean -1.9‰) in the sulphate fraction and from +3.9‰ to +15.9‰ (mean +7.0‰) in the organic fraction. A second study [77] reported a range from +3.5% to +9% in coals the southern USCB.

In the Zn-Pb sulphide ores in the Triassic rocks of the Silesia – Kraków area, the reported $\delta^{34}S$ range is large [21]. $\delta^{34}S$ values in galena, brunckite and sphalerite typically fall in the range -10 to +10‰, although a cluster of brunckite mineralisation yields highly negative values of -20 to -30‰ [18]. [19] confirm the large range of $\delta^{34}S$, but suggest a range from -2 to -15‰ for the later generations of sulphide mineralisation.

No documented values of sulphide $\delta^{34}S$ from the Spanish Asturian coalfield have been located.

Methods

In 2015-2016, water samples were systematically collected under the auspices of the LoCAL project,

- From the pumped Markham No. 3 shaft and the pumped Hope Shaft at Caphouse mine in the United Kingdom, at shaft-top sampling points on the pumped water pipeline.
- From discrete seepages to the Secondary Egress Drift, above the regional mine water table, at Caphouse mine. Some of these seepages had been previously sampled and described by [30, 38]. During the LoCAL project, these seepages, and the bulk water at the Caphouse Furnace Shaft at the bottom of the drift, were analysed for stable isotopes.
- From the Bolko Pb-Zn and Szombierki coal mines, at specific sampling locations underground (in the galleries of the Bolko mine at locations 2, 3 ,4; and as shown in the Szombierki mine in Figure 2). Samples were also taken of the pumped bulk discharge from the Ewa shaft of the Szombierki mine (location 11) and of the pumped bulk discharge of the adjacent Centrum mine to the River Bytomka (location 13, 50.3513°N, 18.8821°E).
- From the Barredo mine (from three 100 m deep ESPs, a single 200 m deep ESP and from the bulk pumped mine water flux from all 4 ESPs), from the Figaredo and San José mine pumped discharges, from the shallow Mariana mine gravity flow of mine water. Samples were also taken from the River Turón upstream of the mine discharges and downstream of the San José mine discharge (but upstream of Figaredo [4]).

Furthermore, samples of meteoric water and run-off were collected for hydrochemical analysis and analysis of ^{18}O and ^{2}H isotopes. These samples were collected from:

- The Holme Brook stream (53.2389°N 1.4442°W) in Chesterfield, East Midlands, UK, representing presumed recent run-off. Stable isotopic data were also downloaded from the IAEA Global Network of Isotopes in Precipitation (GNIP) station [78] at Keyworth, East Midlands, UK (52.8833°N 1.0833°W, data set 1985 to 1996), for comparison.
- Local precipitation to Mieres in Spain. Stable isotopic data were also downloaded from the IAEA GNIP) stations [78] at Léon (42.5883°N 5.6511°W, data set 2000 to 2015) and Santander (43.4911°N 3.8006°W, data set 2000 to 2015), for comparison.
- Precipitation from sites at Bytom and Jaworzno in Poland. Stable isotopic data were also downloaded from the IAEA GNIP) station [78] at Kraków (50.0617°N 19.8486°E, data set 1975 to 2016), for comparison.

Key field parameters (pH, electrical conductivity, redox indicators, temperature) were made in the field using calibrated hand-held instruments by the different national LoCAL teams. Major ions were analysed at national laboratories using methods (typically ion chromatography [IC] and inductively coupled plasma optical emission spectrometry [ICP-OES]) documented in detail in publications by [5, 6] for the Caphouse and Markham (UK) sites, respectively, by [12] for the Polish sites and by [4] for the Spanish sites.

Stable isotopic analysis of water and precipitate samples from all sites was carried out at the Scottish Universities Environmental Research Centre (SUERC). For $\delta^{18}O$ and $\delta^{2}H$ analysis, field samples of water for were taken in duplicate or triplicate using clean 10 ml glass vials with screw caps, sealed with Parafilm. For $\delta^{18}O$ analysis, each sample was over-gassed with a 1% CO_2-in-He mixture for 5 mins and left to equilibrate for a further 24 h. A sample volume of 2 ml was then analysed using standard techniques on a Thermo Scientific Delta V mass spectrometer set at 25°C. Final $\delta^{18}O$ values were produced using the method established by [79]. For $\delta^{2}H$ analysis, sample and standard waters were injected directly into a chromium furnace at 800°C [80], 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 from the V-SMOW standard in standard delta notation. In-run repeat analyses of water standards (international standards V-SMOW and GISP, and internal standard Lt Std) gave reproducibility better than ±0.3‰ for $\delta^{18}O$, ±3‰ for $\delta\ ^{2}H$

For $\delta^{34}S$ analysis, water samples were collected in 1 L plastic bottles. Samples were acidified to pH 3 - 4 using 10% HCl and then dosed with excess 5% $BaCl_2$ solution to precipitate sulphate as barium sulphate [81], which was allowed to settle. The precipitate was recovered from the flask and cleaned repeatedly in de-ionised water and dried. For analysis of the resulting precipitate, SO_2 gas was generated by combustion at 1065°C with excess Cu2O and silica [82], then measured isotopically using a VG Isotech SIRA II mass spectrometer. Results are reported as per mille (‰) variations from the Vienna Canyon Diablo Troilite (V-CDT) standard in standard delta notation. Reproducibility of the results was monitored through the repeated analysis of standards NBS-123 (+17.1‰), IAEA-S-3 (-32.3‰), and SUERC's internal standard CP-1 (−4.6‰), and was typically around ±0.3‰ during these analyses.

In the results section (below), isotopic results on duplicate or triplicate aliquots of sample are reported as the mean value.

For the Caphouse Hope Shaft and the Markham No. 3 shaft, the LoCAL project (2015 - 2016) data set is supplemented by earlier hydrochemical analyses (at commercial laboratories) of samples collected by the Coal Authority and the Markham site operator, respectively, as described in [5, 6]. At these sites, stable isotope samples were only collected during the period of the LoCAL project (2015 - 16).

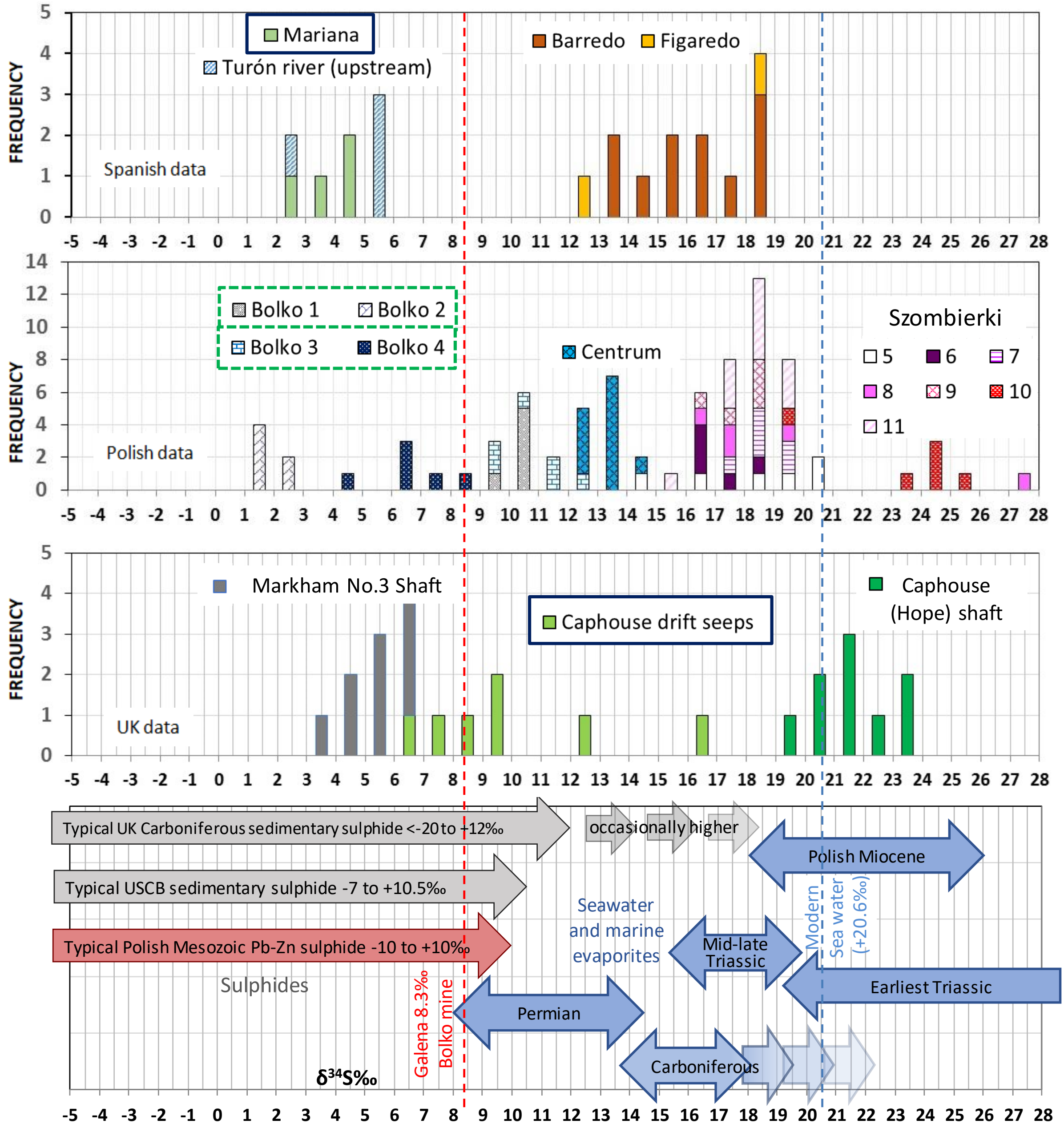

Figure 3. Histogram showing distribution of all $\delta^{34}S$ isotope determinations (average of duplicate/triplicate aliquots) made on dissolved sulphate in mine waters during the LoCAL project. The lowermost panel shows typical distribution of $\delta^{34}S$ in sedimentary sulphide and seawater/evaporites of different geological ages. Note: Bolko 1, 2 etc. refer to locations 1, 2 etc., as described in the legend of Table 1. Sites in solid boxes = shallow gravity-drained mine (Mariana, Caphouse drift), sites in dashed boxes = shallow Pb-Zn mine (Bolko).

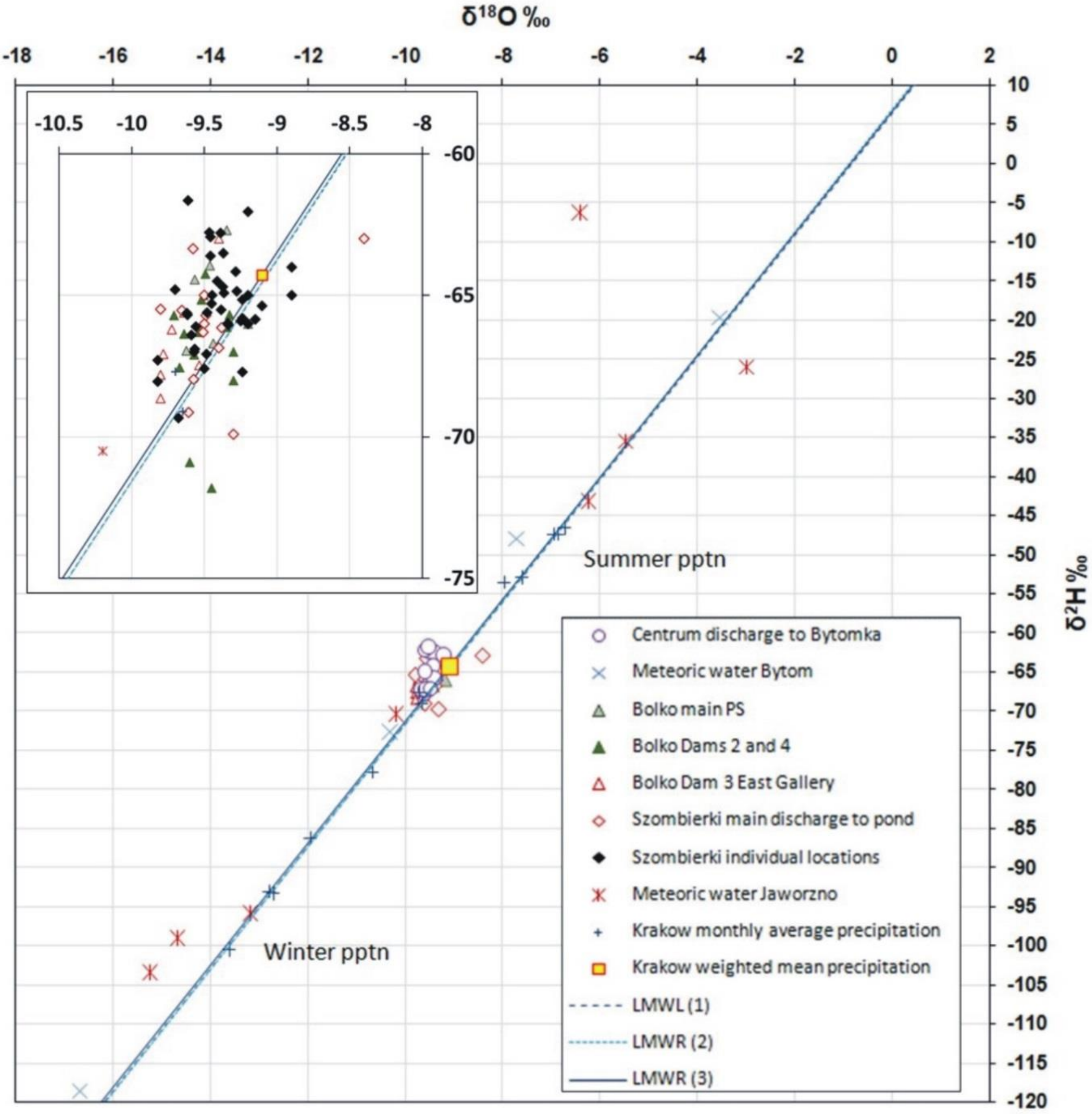

Figure 4. δ18O versus δ2H for the Polish mine waters. Kraków monthly and weighted mean precipitation values derived from [78]. The inset shows the main cluster of mine waters. Some data subsets have been omitted from the inset and the main diagrams for clarity of viewing. LMWR = three variants of proposed local meteoric water line proposed by [78] for Kraków.

Table 1. Arithmetic mean of the hydrochemical characteristics of water samples from Bolko Pb-Zn mine in the period May 2015 – May 2016. Sample locations: (1) Main pumping station (124.4 m depth); (2) Isolating dam no. 2 – Western gallery; (3) Isolating dam no. 4 – Eastern gallery; (4) Isolating dam no. 3 – Eastern gallery.

	Unit	**1**	**2**	**3**	**4**
pH		7.05	7.09	7.10	7.28
Temperature	°C	12.5	12.0	12.4	12.8
Electrical conductivity (EC)	µS cm^{-1}	2535	2584	2516	2494
Total dissolved solids (TDS)	mg L^{-1}	1616	1770	1665	1646
Alkalinity	meq L^{-1}	7.6	7.3	7.0	6.3
Chloride	mg L^{-1} as Cl^-		143	207	130
Sulphate	mg L^{-1} as SO_4^{2-}		1267	977	1200
Nitrate	mg L^{-1} as NO_3^-		4.9	16.3	0.3
Calcium	mg L^{-1} as Ca		376	320	387
Magnesium	mg L^{-1} as Mg		205	142	199
Sodium	mg L^{-1} as Na		91	158	54
Potassium	mg L^{-1} as K		10.9	14.0	3.7
Iron (total)	mg L^{-1} as Fe		1.0	1.9	1.3
Manganese	mg L^{-1} as Mn		1.35	0.36	1.42
Barium	µg L^{-1} as Ba		17	22	13
Strontium	mg L^{-1} as Sr		1.47	1.22	0.97
$\delta^{18}O_{V\text{-}SMOW}$	‰	-9.5	-9.5	-9.5	-9.7
$\delta^{2}H_{V\text{-}SMOW}$	‰	-65.3	-67.3	-66.6	-66.5
$\delta^{34}S_{V\text{-}CDT}$	‰	+10.3	+1.9	+10.7	+6.6
Cl^-/Br^-	Mass ratio		409	331	1182
SO_4^{2-}/Cl^-	Molar ratio		3.38	1.74	3.41
Na^+/Cl^-	Molar ratio		1.00	1.18	0.64
$(Ca^{2+}+Mg^{2+})/SO_4^{2-}$	Eq. ratio		1.35	1.36	1.43
Ca^{2+}/alkalinity	Eq. ratio		2.58	2.23	3.22

Table 2. Arithmetic mean of the hydrochemical characteristics of water samples from Szombierki (Ewa) and Centrum mines in the period May 2015 – June 2016. Sample locations: ($) Bulk water chemistry from Szombierki in 2007 and 2008, cited by [11]; (5) Inflow from Bytom II mine, level 630, Ewa shaft, Szombierki; (6) Inflow to level 630m, Ewa shaft; (7) Inflow from abandoned Karol mine, level 630m, Ewa shaft; (8) Inflow from level 510m (measuring point on level 630m), Ewa shaft; (9) Main pumping station on level 630m, Ewa shaft; (10) Inflow to level 790m, Ewa shaft; (11) Discharge to Ws5 pond from Szombierki pumping station; (13) Discharge from Centrum mine to Bytomka river (see Figure 2 for locations).

	Unit	**$**	**5**	**6**	**7**	**8**	**9**	**10**	**11**	**13**
pH		7.72	6.72	6.72	6.73	7.01	7.28	7.12	7.54	7.99
Temperature	°C	24.5	22.4	22.9	26.5	22.5	24.5	23.6	23.2	13.9*
TDS	mg L^{-1}	8920	7015	3457	5162	3614	5928	4615	5454	3934
Alkalinity	meq L^{-1}	11.7	13.4	14.6	14.4	12.8	14.2	13.4	13.2	7.3
Chloride	mg L^{-1} as Cl^-	3400	2083	723	1100	893	1693	1433	1925	1543
Sulphate	mg L^{-1} as SO_4^{2-}	1640	1453	1733	2600	1833	1967	1567	1729	993
Ammonium	mg L^{-1} as N	0.15								
Nitrate	mg L^{-1} as NO_3^-	0.8	1.6	1.9	1.4	0.5	1.5	0.5	1.8	0.7
Calcium	mg L^{-1} as Ca	315	355	438	384	523	445	283	378	272
Magnesium	mg L^{-1} as Mg	200	109	238	217	263	184	214	175	138
Sodium	mg L^{-1} as Na	2400	1708	583	1423	670	1465	1197	1563	898
Potassium	mg L^{-1} as K	178	64	50	63	66	66	72	66	31
Iron (total)	mg L^{-1} as Fe	0.18	0.71	0.19	0.01	2.84	0.07	0.15	0.10	0.04
Manganese	mg L^{-1} as Mn	0.097	0.53	0.58	<0.005	2.25	0.66	0.26	0.54	0.03
Barium	µg L^{-1} as Ba		0.076	0.033	0.043	0.038	0.054	0.032	0.041	0.023
Strontium	mg L^{-1} as Sr		3.17	4.16	4.34	4.64	4.02	3.29	3.99	3.84
$\delta^{18}O_{V\text{-}SMOW}$	‰		-9.5	-9.4	-9.1	-9.3	-9.4	-9.3	-9.4	-9.5
$\delta^{2}H_{V\text{-}SMOW}$	‰		-65.9	-66.0	-65.3	-64.5	-65.1	-65.0	-66.0	-65.0
$\delta^{34}S_{V\text{-}CDT}$	‰		18.5	16.9	18.6	19.2	17.9	23.6	17.7	14.4
Cl^-/Br^-	Mass ratio		247	275	269	272	251	256	246	231
SO_4^{2-}/Cl^-	Molar ratio		0.34	0.88	0.87	0.76	0.48	0.40	0.35	0.24
Na^+/Cl^-	Molar ratio		1.41	1.25	2.00	1.16	1.37	1.29	1.27	0.90
$(Ca^{2+}+Mg^{2+})/SO_4^{2-}$	Eq. ratio		0.84	1.15	0.68	1.25	0.91	0.98	0.92	1.21
Ca^{2+}/alkalinity	Eq. ratio		1.26	1.49	1.36	2.27	1.64	1.12	1.47	1.87

* the temperature varies seasonally from 7.3 to 19.4°C in the Centrum mine discharge to the Bytomka River, according to our data, suggesting that the point of measurement may be influenced by air temperature conditions.

Table 3. Key concentrations and ratios in standard modern oceanic water (salinity c. 34.5 g L^{-1}), from [83, 84, 44] and also, where supplementary or different to these sources, from [85].

	Unit	**Source** [83] [84]	**Source** [85]**,** where differing from previous column
Total dissolved solids	mg L^{-1}	34483	
Alkalinity	meq L^{-1}	2.29	2.33
Chloride	mg L^{-1} as Cl^-	18980	
Sulphate	mg L^{-1} as SO_4^{2-}	2649	
Ammonium	mg L^{-1} as N		0.05
Nitrate	mg L^{-1} as NO_3^-		0.7
Calcium	mg L^{-1} as Ca	400	
Magnesium	mg L^{-1} as Mg	1262	1272
Sodium	mg L^{-1} as Na	10556	10561
Potassium	mg L^{-1} as K	380	
Bromide	mg L^{-1} as Br^-	65	
Lithium	mg L^{-1} as Li	0.17	0.1
Barium	µg L^{-1} as Ba		0.05
Strontium	mg L^{-1} as Sr	13	
Cl^-/Br^-	Mass ratio	292	
SO_4^{2-}/Cl^-	Molar ratio	0.052	
Na^+/Cl^-	Molar ratio	0.858	
$(Ca^{2+}+Mg^{2+})/SO_4^{2-}$	Eq. ratio	2.24	2.26
Ca^{2+}/alkalinity	Eq. ratio	8.70	8.56
$\delta^{34}S_{V\text{-}CDT}$, from [44]	‰	+20.6	

Results - Poland

Typical hydrochemical analyses from the sampling campaign are provided in Tables 2, 3 and Figure 4, while the full results are provided by [86]. The sulphur isotopic results are summarised graphically for all sites in Figure 3.

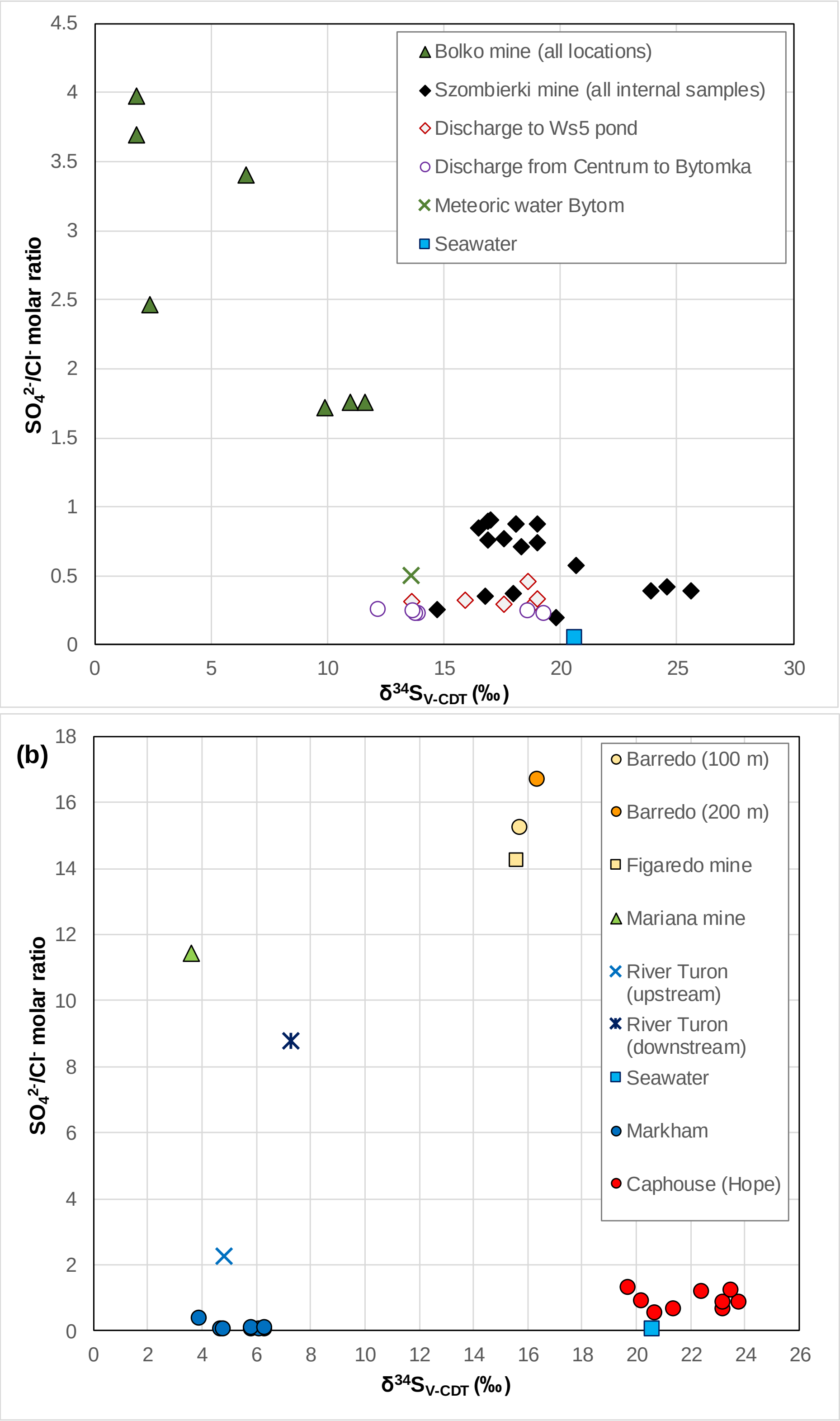

Figure 5. Relationship between the molar SO_4^{2-}/Cl^- ratio and the $\delta^{34}S$ of dissolved sulphate for the (a) Polish and (b) UK / Spanish water samples (arithmetic means shown for Spanish data).

The water pumped from Bolko shaft (Table 1) was a slightly brackish Ca^{2+}-Mg^{2+}-SO_4^{2-} water (total dissolved solids [TDS] c. 1700 mg L^{-1} and chloride 120 - 210 mg L^{-1} at the gallery sampling points) with circumneutral pH. The average molar SO_4^{2-}/Cl^- ratio varied from 1.7 to 3.4, depending on the gallery sampled. The chloride concentrations of a few hundred mg L^{-1} are higher than can be expected from salts in precipitation and the high Cl^-/Br^- ratio (relative to ocean water) suggests a possible derivation from halite dissolution [87]. $\delta^{18}O$ and δ^2H of the mine water exhibited negligible seasonal variability and no depth-related trends. The data fall on the meteoric water line very close to the current mean precipitation value (Figure 4). The bulk dissolved sulphate $\delta^{34}S$ is around +10‰, although the water from individual gallery samples exhibit systematic differences, from location 2 on the Western Gallery (+2‰) to location 3 on the Eastern Gallery (+11‰). A single specimen of galena recovered from the mine was analysed and returned a $\delta^{34}S$ value of +8.3‰.

The water pumped from Centrum mine (Table 2) was a somewhat brackish Na^+-Cl^--(SO_4^{2-}) (TDS c. 3930 mg L^{-1}; chloride 1540 mg L^{-1}) with slightly alkaline pH. The water is less sulphate-rich (c. 990 mg L^{-1}) than Szombierki. The SO_4^{2-}/Cl^- molar ratio (0.23 to 0.26) is around five times higher than seawater (0.052, Table 3).

The water pumped from Ewa shaft (Table 2) was warm (24.5°C) Na^+-Cl^--(SO_4^{2-}) and brackish (mean TDS c. 5500 - 6000 mg L^{-1}; chloride 1700 - 1900 mg L^{-1}), with circumneutral pH. The salinity appears to have declined since 2007 - 2008 [11]. The water is very sulphate-rich (1700 - 1900 mg L^{-1}). The average molar SO_4^{2-}/Cl^- ratio varied from 0.34 to 0.88 in Szombierki, depending on location, again significantly higher than seawater (0.052). Water chemistry varies, depending on sampling point in the mine: the water entering from Bytom II is particularly Na^+-Cl^--rich, while that from Karol mine is especially warm (26.5°C) and SO_4^{2-}-rich (2600 mg L^{-1}).

The Cl^-/Br^- ratios in the coal mine waters are slightly less than standard ocean water ([87], Table 3).

$\delta^{18}O$ and δ^2H of mine waters from both Szombierki and Centrum exhibited negligible seasonal variability and fall on the meteoric water line, very close to the current mean precipitation value. The average dissolved sulphate $\delta^{34}S$ in the combined dewatering flow from Szombierki is rather high at +17.7 to +17.9‰, while that from Centrum is +14.4‰, both showing little temporal variation. There is some systematic location-dependent variation in dissolved sulphate $\delta^{34}S$ in Szombierki mine, with average values varying from +16.9‰ to +23.6‰ in the deepest inflow (location 10).

Overall, in the Polish mines, there is a negative correlation between the sulphate/chloride molar ratio and the $\delta^{34}S$ (Figure 5), such that the higher the sulphate concentration (relative to chloride), the lower the ^{34}S content of the sulphate.

Results - Spain

Typical hydrochemical analyses from the sampling campaign are provided in Table 4 and Figure 6, while additional results are provided by [86].

Table 4. Arithmetic mean of the hydrochemical characteristics of water samples from the Barredo-Figaredo-San José complex. Depths (100m, 200m) refer to pump depth in shaft. For the bulk Barredo minewater for all four installed submersible pumps, the mean $\delta^{18}O$, $\delta^{2}H$ and $\delta^{34}S$ values were -7.5‰, -44‰ and +16.7‰ respectively. < = below detection limit. nd = not determined. The first data column shows results for the River Turón upstream of the mines. ORP = oxidation-reduction potential.

	Unit	**R. Turón (u/s)**	**Mariana**	**San José**	**Figaredo 100 m**	**Barredo 100 m**	**Barredo 200 m**
pH		8.2	7.9	7.1	7.6	7.9	7.8
Temperature	°C	12.9	14.2	18.9	21.6	22.3	22.8
ORP	mV	+39	+27	nd	-48	-35	-52
EC	$\mu S\ cm^{-1}$	431	958	2052	2324	2416	2438
TDS	$mg\ L^{-1}$	302	509	nd	1162	1220	1389
Alkalinity	$meq\ L^{-1}$	3.51	7.31	9.69	12.31	16.18	16.90
Chloride	$mg\ L^{-1}$ as Cl^-	7.4	9.9	12.1	12.8	15.1	14.4
Sulphate	$mg\ L^{-1}$ as SO_4^{2-}	45	306	472	495	624	651
Nitrate	$mg\ L^{-1}$ as NO_3^-	1.9	1.2	0.7	<	<	<
Calcium	$mg\ L^{-1}$ as Ca	53	117	100	136	119	126
Magnesium	$mg\ L^{-1}$ as Mg	13	45	69	60	66	67
Sodium	$mg\ L^{-1}$ as Na	23	109	197	270	431	455
Potassium	$mg\ L^{-1}$ as K	2.5	3.9	8.8	5.3	7.8	7.5
Iron (total)	$mg\ L^{-1}$ as Fe	0.02	0.17	3.70	1.60	1.09	1.56
Manganese	$mg\ L^{-1}$ as Mn	0.06	0.67	0.70	0.40	0.79	1.05
$\delta^{18}O_{V\text{-}SMOW}$	‰	-7.3	-7.2	nd	-7.5	-7.4	-7.2
$\delta^{2}H_{V\text{-}SMOW}$	‰	-42	-41	nd	-47	-44	-43
$\delta^{34}S_{V\text{-}CDT}$	‰	+4.8	+3.6	nd	+15.6	+15.7	+16.3
SO_4^{2-}/Cl^-	Molar ratio	2.26	11.45	14.40	14.27	15.25	16.69
Na^+/Cl^-	Molar ratio	4.76	17.05	25.11	32.53	44.02	48.73
$(Ca^{2+}+Mg^{2+})/SO_4^{2-}$	Eq. ratio	3.97	1.50	1.09	1.14	0.87	0.87
Ca^{2+}/alkalinity	Eq. ratio	0.76	0.80	0.52	0.55	0.37	0.37

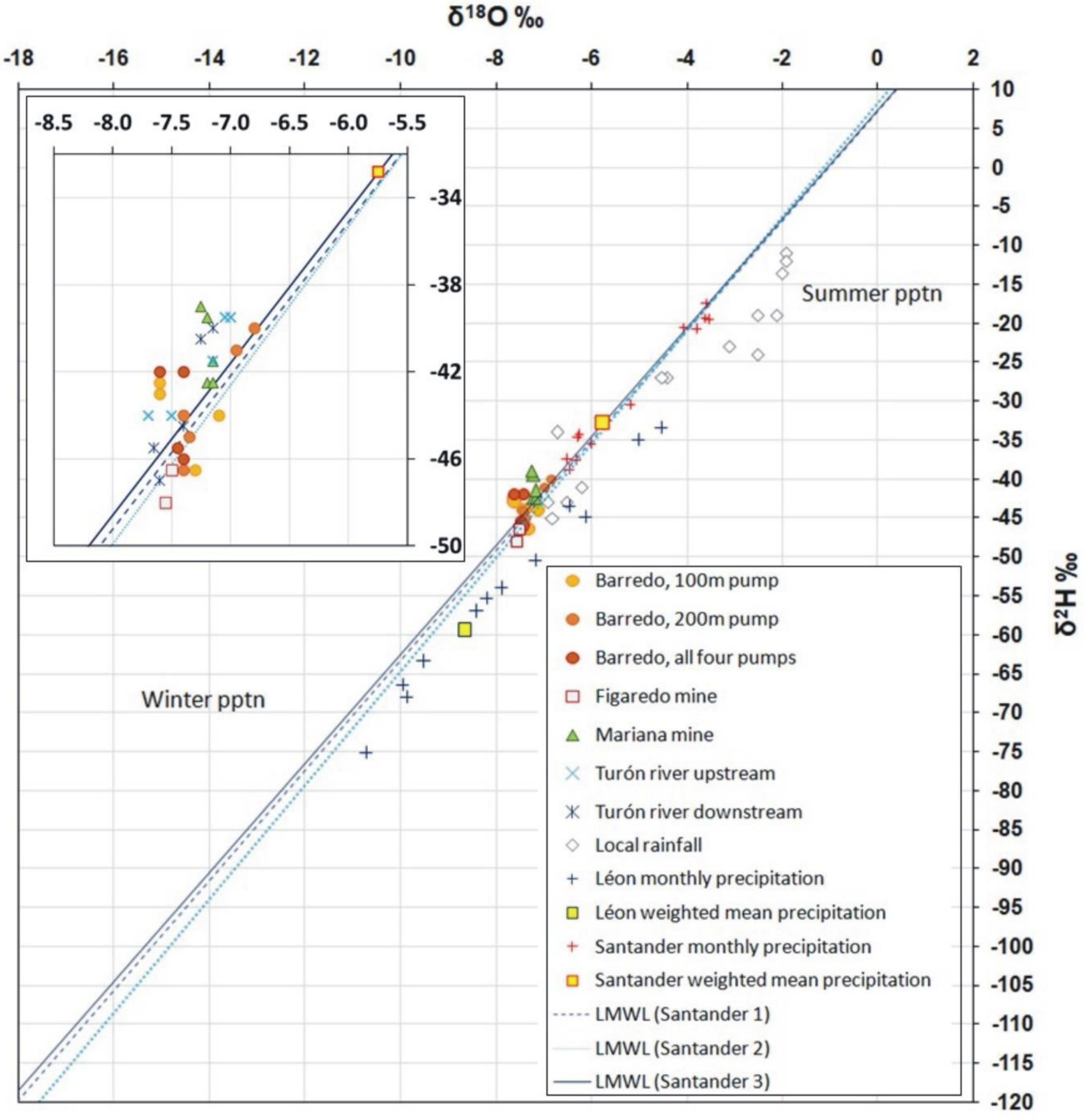

Figure 6. $\delta^{18}O$ versus $\delta^{2}H$ for the Spanish (Asturian) mine waters. The inset shows the main cluster of mine waters. Some data subsets have been omitted from the inset and the main diagrams for clarity of viewing. Other north-Spanish (Léon and Santander) monthly and weighted mean precipitation data derived from [78]. LMWR = three variants of local meteoric water line proposed by [78].

The water pumped from Barredo shaft (Table 4) was a warm (22 - 23°C), relatively fresh Na^{+}-HCO_3^{-}-SO_4^{2-} water (typical mean TDS c. 1200 - 1400 mg L^{-1}; chloride 13 - 19 mg L^{-1}), with slightly alkaline pH. The waters from Figaredo and San José were broadly similar, but with progressively lower temperatures, TDS, Na^{+}, SO_4^{2-} and alkalinity contents as one moves up hydraulic gradient through the mine system. In the water from the shallow Mariana mine (in Mieres, close to Barredo), still lower Na^+, SO_4^{2-}, alkalinity and temperatures are observed and the water has a Ca^{2+}-Na^+-Mg^{2+}-HCO_3^--SO_4^{2-} composition. Other trends which can be observed from the deepest Barredo water, via Figaredo and San José, to the shallow Mariana minewater, are a slight tendency to decreasing chloride (although concentrations are low in all mine waters), decreasing Na^+/Cl^- and SO_4^{2-}/Cl^- ratios (Figure 5), and increasing NO_3^- concentrations, suggesting decreasing proportions of deep warm sodium-bicarbonate groundwater and increasing proportions of shallow infiltration. $\delta^{18}O$ and δ^2H of the mine waters exhibited low seasonal variability and plot on the meteoric water line very close to the mid-point between the current mean precipitation values for Léon and Santander (Figure 6), but at the $^{18}O/^2H$-depleted end of the data range for locally sampled precipitation.

The $\delta^{34}S$ values of the different mine waters differ significantly. Barredo returns values in the range +13.4 to +18.5‰, and Figaredo in the range +12.4 to +18.8‰. Mariana mine returns much lower values of +2.1 to +4.4‰, of the same order of magnitude of the River Turón upstream of the mine sites and indicative of sulphide weathering. In the Spanish mines there is a positive correlation between $\delta^{34}S$ and SO_4^{2-}/Cl^- ratio (Figure 5), implying that the greater the sulphate concentration relative to chloride, the higher the $\delta^{34}S$.

Results – United Kingdom

Results are presented in Table 5, Figure 7, and additionally in [86].

As previously stated, the water pumped from Markham shaft was initially (in 2011, *Phase 1 Pumping Regime*) a sodium chloride brine, with total dissolved solids (TDS) exceeding 20 g L^{-1} in one sample, characterised by sulphate-reducing conditions (SO_4^{2-}/Cl^- ratio lower than seawater, and elevated barium [6]). As time progressed, and mine water levels continued to rise in the shaft following mine abandonment, the pump installation was raised to 235 m bgl at the end of 2012 (*Phase 2 Pumping Regime*) and the water became less saline (Table 5). After the pumping/reinjection arrangement was raised to 170 m bgl in February 2015 (*Phase 3 Pumping Regime*), the water's salinity decreased about 10-fold but still retaining a dominant Na^+-Cl^- chemistry (Table 5). Na^+/Cl^- ratios are close to seawater (Table 3) in Phases 1, 2 and 3, suggesting a marine origin for the salinity. SO_4^{2-}/Cl^- ratios are somewhat variable in Phases 2 and 3, but are on average higher than seawater, increasingly so in Phase 3 (Figure 8), suggesting a significant lithological source for sulphate.

Table 5. Arithmetic mean of the hydrochemical characteristics of pumped mine water samples from the Caphouse (Hope shaft) and Markham (No. 3 shaft) mines. Only two samples available for Phase 1 at Markham (from 250 and 340 m depth), so the range is shown, rather than the mean. The LoCAL project (2015) data set is supplemented by earlier commercial analyses of samples collected by the site operators.

		Markham No. 3 shaft			**Caphouse Hope shaft**	
	Unit	**Nov 2008**	**Oct 2012 – Jan 2015**	**Feb-Dec 2015**	**2004-2014**	**Jan 2015 – Jun 2016**
		Phase 1	**Phase 2**	**Phase 3**		
pH		6.6 – 7.0	7.5	7.3	6.98	6.94
Temperature	°C			13.3		
EC	µS cm^{-1}	24200 - 40900	22270	2698	2531	2698
Alkalinity	meq L^{-1}			5.46	8.38	8.67
Chloride	mg L^{-1} as Cl^-	6940 - 11700	6198	700	148	257
Sulphate	mg L^{-1} as SO_4^{2-}	14 - 716	1306	155	915	621
Ammonium	mg L^{-1} as N	4.7 – 14.3	4.4	<0.1	0.93	0.93
Nitrate	mg L^{-1} as NO_3^-			3.4	0.02	0.59
Calcium	mg L^{-1} as Ca	528 - 879	391	133	78	90
Magnesium	mg L^{-1} as Mg	160 - 641	194	47	56	58
Sodium	mg L^{-1} as Na	3830 - 8550	3910	379	493	471
Potassium	mg L^{-1} as K	78 - 106	90	22	11.7	10.8
Iron (total)	mg L^{-1} as Fe	10.8 - 81	15.5	0.52	20.5	14.9
Iron (dissolved)	mg L^{-1} as Fe				16.6	13.0
Manganese	mg L^{-1} as Mn	1.13 – 2.63	3.67	0.03	0.85	0.71
Barium	µg L^{-1} as Ba	0.35 – 19.2	0.15	0.10	<0.02	<0.02
Strontium	mg L^{-1} as Sr	8.27 – 14.1	4.96	0.83	0.75	0.75
$\delta^{18}O_{V\text{-}SMOW}$	‰			-8.1		-8.0
$\delta^{2}H_{V\text{-}SMOW}$	‰			-52		-52
$\delta^{34}S_{V\text{-}CDT}$	‰			+5.5		+21.8
SO_4^{2-}/Cl^-	Molar ratio	0.0007 – 0.02	0.08	0.10	2.27	0.93
Na^+/Cl^-	Molar ratio	0.85 – 1.13	0.98	0.85	5.18	2.89
$(Ca^{2+}+Mg^{2+})/SO_4^{2-}$	Eq. ratio	6.5 - 136	1.74	3.64	0.52	0.72
Ca^{2+}/alkalinity	Eq. ratio			1.23	0.44	0.51

Stable isotope samples were only collected during the *Phase 3* pumping under the auspices of the LoCAL project in 2015 - 16. $\delta^{18}O$ and $\delta^{2}H$ data obtained during *Phase 3* plot very slightly above the local meteoric water line and also close to the mean average values for precipitation at Keyworth, Nottinghamshire (Figure 7), indicating that the water (although not necessarily the salinity) is meteoric in origin. Samples for dissolved sulphate $\delta^{34}S$ were only collected after Feb 2015 (*Phase 3*), and low values of between +3.9 and +6.3‰ were obtained.

In the samples collected from the Caphouse Drift (above the regional water table), sulphate $\delta^{34}S$ values of +6.7‰ to +9.9‰ were typical, with two slightly higher values (+12.5‰ and +16.4‰). The seepages into the Drift are from very specific horizons and may thus carry a sulphur isotope composition specific to the shales or coals in the immediate vicinity. Water $\delta^{18}O$ and $\delta^{2}H$ plot very slightly above the local meteoric water line (Figure 7).

The water pumped from the Caphouse Hope Shaft is a bulk mine water, draining from numerous seams and blocks of mine workings in the vicinity. The SO_4^{2-} concentration has declined quasi-exponentially over time (Figure 8); this is presumed to reflect the flushing out of pyrite oxidation products from the mine workings following abandonment [5, 88, 89]. The water chemistry is, however, still Na^+-SO_4^{2-} in nature, with SO_4^{2-} still significantly exceeding Cl^-. Both SO_4^{2-}/Cl^- and Na^+/Cl^- ratios significantly exceed seawater (Table 3) indicating lithological (non-marine) sources in all samples for Na^+ (tentatively, feldspar weathering) and SO_4^{2-} (usually ascribed to pyrite oxidation, although this explanation is evidently ruled out by the ^{34}S data) in the water. Since May 2015, the chloride content has risen from typical values of 100 - 150 mg L^{-1} to values in excess of 300 mg L^{-1} (leading to declines in the SO_4^{2-}/Cl^- and Na^+/Cl^- ratios; Figure 8), suggesting an increased component of deeper saline water in the minewater. Mine water $\delta^{18}O$ and $\delta^{2}H$ compositions plot in close proximity to the local meteoric water line (Figure 7). High dissolved sulphate $\delta^{34}S$ values of +19.7‰ to +23.8‰ were typical.

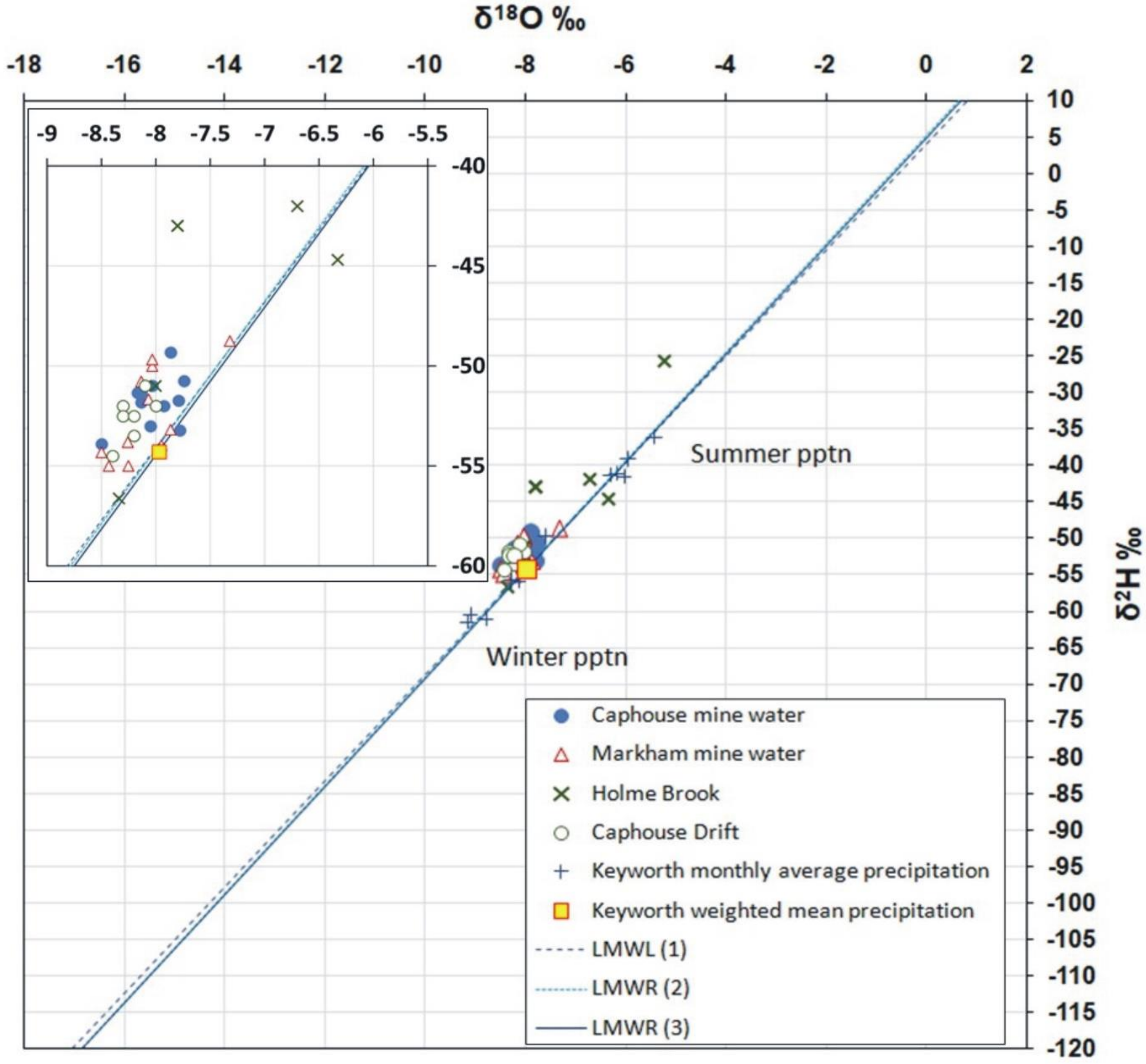

Figure 7. $\delta^{18}O$ versus $\delta^{2}H$ plot for the UK mine waters and the stream water from the Holme Brook in Chesterfield. Keyworth monthly and weighted mean values derived from [78]. The inset shows the main cluster of mine waters. Some data subsets have been omitted from the inset for clarity of viewing. LMWR = three variants of Keyworth local meteoric water line proposed by [78].

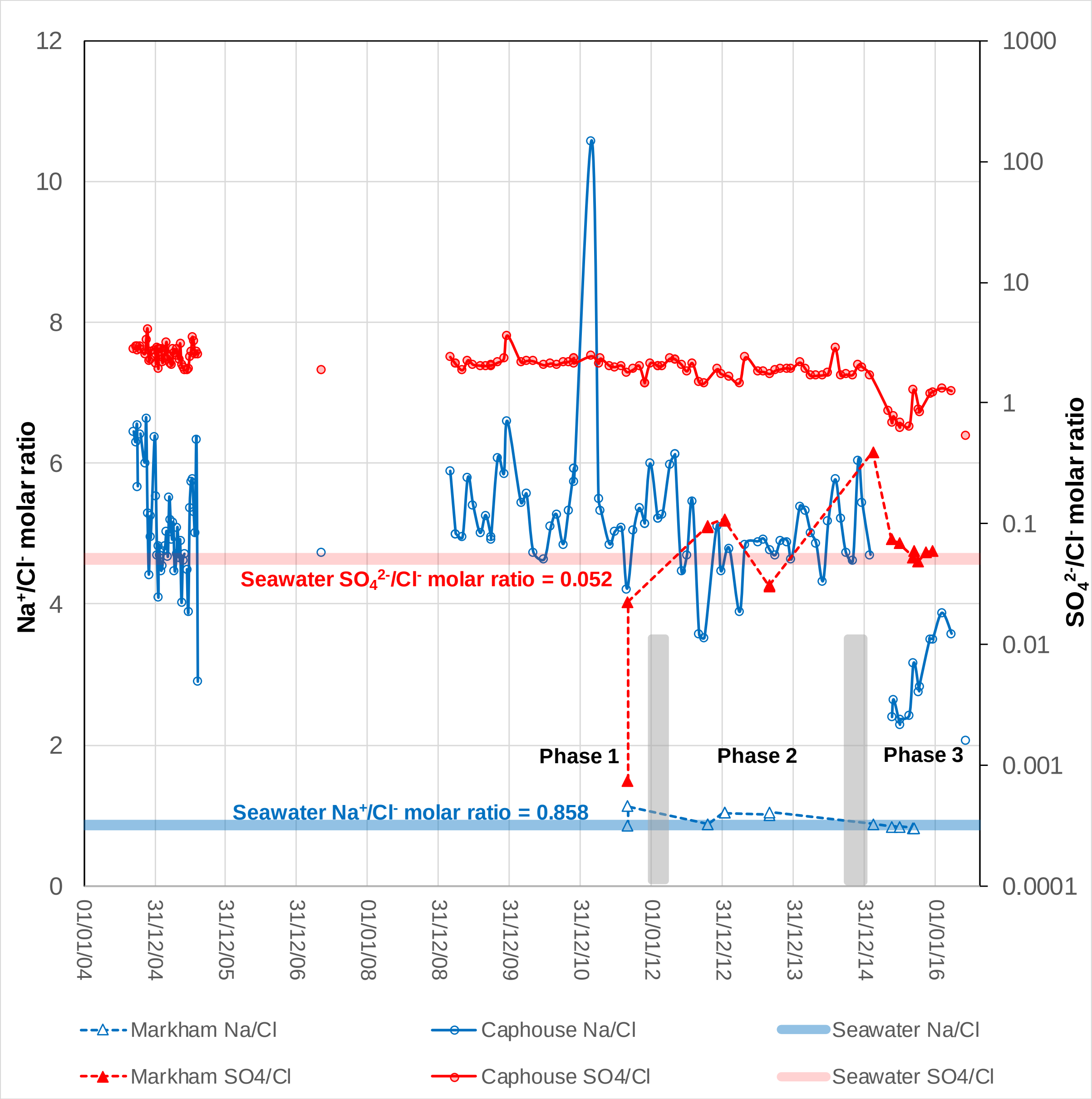

Figure 8. Evolution of molar Na$^+$/Cl$^-$ and SO$_4^{2-}$/Cl$^-$ ratios at Caphouse (Hope) pumping shaft and Marking No. 3 pumping shaft. Note the logarithmic scale for SO$_4^{2-}$/Cl$^-$. The Phases relate to the different pump depths at Markham.

Interpretation – Poland

The various components of the waters pumped from the Pb-Zn mines via Bolko shaft appear to have different origins. The water itself appears to be of modern meteoric origin (δ^{18}O and δ^2H isotopes; Figure 4). Typical dissolved sulphate δ^{34}S values in the range +1.4 ‰ to +12.1‰ (mean +10.3‰ from main pumping station), lie within the plausible range of the S-isotopic composition of sulphide minerals from Mesozoic Polish ore bodies (this study found +8.3 ‰ in galena from Bolko – Figure 3). Given that the mines are relatively shallow and actively dewatered and that the host carbonates are permeable, it seems reasonable to assume that the system is relatively oxidising in nature (as evidenced by the higher nitrate than in the deeper coal mines – Table 1 and 2). The $\delta^{34}S$ is compatible with the majority of the sulphate having an origin in sulphide oxidation. It should be noted that the various sampling points in the mine galleries have rather specific $\delta^{34}S$ values, potentially reflecting specific ore bodies. The somewhat elevated chloride content of the water (120 - 210 mg L^{-1}) appears too high to be explained by salts in rainfall, while the very high Cl^-/Br^- ratios suggest a possible derivation of chloride from evaporite (halite) dissolution. While the sulphate concentrations are well in excess of chloride, a modest component of evaporite-derived sulphate might have a tendency to slightly elevate the $\delta^{34}S$ of the water.

The water from Szombierki mine also appears to be dominated by modern meteoric waters ($\delta^{18}O$ and δ^2H isotopes; Figure 4). The Cl^-/Br^- ratios are similar to ocean water (Table 3), suggesting that chloride (and thus a modest proportion of the sulphate) may be derived from residual seawater in the formation. The dissolved sulphate has rather high $\delta^{34}S$, typically in the range +16‰ to +20‰, although waters from the deepest level (790 m level, location 10) in Ewa shaft have even higher values of +24‰ to +26‰ (Figure 3). The sulphate-to-chloride ratios are too high for the sulphate to be derived directly from past marine inundations or evaporite basin brines (based on chloride content, only 6 to 20% of the sulphate could be derived from a marine source). The lower range of values (+16‰ to +20‰) from the majority of Szombierki mine waters are too elevated to be derived purely from sulphide oxidation, but they are within a range where they could plausibly be derived from post-Carboniferous evaporite minerals (possibly combined with a sulphide oxidation component).

The Upper Silesian Coal Basin has been subject to past marine and evaporite sedimentation; there are thus several potential evaporite sources in the post-Carboniferous stratigraphy for sulphate with a higher $\delta^{34}S$. Thick Permian (Rotliegend, Zechstein) and Triassic evaporites are known throughout much of central Poland, although Upper Silesia arguably lies at the very outer geographical margins of palaeogeographic reconstructions of these basins [90]. However, gypsum, anhydrite and post-evaporitic fabrics (Zellenkalk / Rauhwacke) have been mapped [91] as potential constituents of the Middle-Upper Triassic (Muschelkalk-Keuper facies) sequence of the Upper Silesian Basin [92, 93, 94, 95, 91]. Indeed, Triassic evaporite basin brines are suggested as the most likely source fluids for the Triassic-hosted Pb-Zn ores of the Silesia-Kraków region [96].

Jurassic-Cretaceous brines and Tertiary evaporites are also known in the Upper Silesian region [97, 98]. Gypsum-/anhydrite-bearing strata of Badenian (middle Miocene) age are found in marine (Paratethys) formations in narrow foreland basin environments peripheral to the Carpathian orogen of southern Poland. Extensive Miocene deposits are found to the south of Katowice, but modest inliers have also been mapped around Bytom [99], suggesting previous Miocene cover. The $\delta^{34}S$ of evaporites of this age in Poland and globally range between +18 to +25.7‰ [97], with several examples of Miocene evaporite sulphate minerals from the Upper Silesian region in the range +21 to +25‰ being cited by [98, 97].

Polish researchers have previously found a wide variety of sulphate $\delta^{34}S$ from Upper Silesian coal mine waters. These have been interpreted with the additional assistance of dissolved sulphate $\delta^{18}O$:

- Mine water from the 420 m level of Bolesław Śmiały coal mine had a $\delta^{34}S$ value of +3.0‰ [97]. Similarly, [100] found a $\delta^{34}S$ of +5.8% in mine water sulphate of the Niwka-Modrzejów mine. Both of these were interpreted as reflecting oxidation of sedimentary sulphide minerals in the coal-bearing (Carboniferous) strata.
- Mine water from the deeper 530 m level of Bolesław Śmiały coal mine had a value of +30.7‰. Also, waters from the 330 and 540 m levels in Budryk mine exhibited values of +32.4 to +40.8‰. These were interpreted as being derived from early Triassic-Röt evaporites [97].
- Mine water from the 600 and 690 m levels of Dębieńsko coal mine had a $\delta^{34}S$ of +24.0 to +24.8‰ and was interpreted as being characteristic of derivation from Miocene Zawada Basin evaporites.

On balance, the most likely source for the dissolved sulphate $\delta^{34}S$ in the Szombierki mine waters is a gypsum / anhydrite evaporite, potentially of Mid-Late Triassic age, which typically exhibits $\delta^{34}S$ of +15 to +20‰ globally. Fractionation due to methane-coupled TSR, associated with the formation of Pb-Zn ores in Zechstein carbonates, has been suggested as a mechanism elevating $\delta^{34}S$ in dissolved sulphates in geological environments analogous to Bytom [57]. Hydrocarbons generated during coal basin maturation could plausibly function as electron donors during such a process.

Figure 5 illustrates an inverse correlation between non-marine sulphate excess and $\delta^{34}S$, which implies that the highest SO_4^{2-}/Cl^- ratios are found in the shallow Pb-Zn mines, which are characterised by relatively fresh (low Cl^-) waters in addition to excess sulphate derived from sulphide oxidation (low $\delta^{34}S$). The deeper Szombierki waters are characterised by higher salinity (chloride potentially from marine inundation), a lower (but still elevated relative to marine ratios) SO_4^{2-}/Cl^- ratio related to gypsum/anhydrite dissolution (high $\delta^{34}S$). The waters from Centrum mine appear to be intermediate.

Interpretation – Spain

The fact that the Spanish mine water plots at the ^{18}O-^{2}H-depleted end of the data range for locally sampled precipitation (Figure 6), suggests that it is meteoric water-derived, but with a predominance of winter recharge and/or a preference for groundwater recharge at higher altitude to the system.

Figure 5 does not show the same inverse relationship between non-marine sulphate excess and $\delta^{34}S$ for the Spanish data as was observed in the Polish data. Indeed, all the studied coal mines show very high non-marine sulphate excesses over chloride (molar ratios 11 - 17). The generally very low chloride concentrations (typically 12 - 15 mg L^{-1}), even in the deeper mine waters, are typical of derivation from meteoric recharge and preclude marine or residual evaporative brines as sources of the sulphate in the waters. There does, however, appear to be a bimodal dissolved sulphate $\delta^{34}S$ distribution (Figure 3) suggesting two distinct sources.

The shallow Mariana mine (above the regional mine water table) had dissolved sulphate $\delta^{34}S$ values between +2 to +5‰, which strongly suggest that the sulphate in the water is derived from sulphide oxidation in the coal-bearing strata. The low chloride content, and $\delta^{18}O$ and $\delta^{2}H$ isotopic compositions suggest that the water is derived from relatively recent meteoric recharge. The high Na^+/Cl^- ratio most likely indicates enhanced hydrolysis of silicates (e.g. plagioclase), possibly by protons released from pyrite oxidation. The River Turón upstream samples exhibit similarly low $\delta^{34}S$ values, again suggesting sulphate is likely derived from near-surface oxidation of sedimentary sulphide minerals.

Dissolved sulphate $\delta^{34}S$ values are much higher (+12 to +19‰.) in waters from the deeper Barredo and Figaredo mines. This may suggest derivation in large part from evaporite minerals in post-Carboniferous rocks. A short distance to the north of Mieres, the folded Carboniferous sediments of the ACCB are unconformably overlain by a sequence of post-Variscan Permo-Triassic to Cretaceous sedimentary rocks. Keuper facies evaporites are present in the Triassic sequence, e.g. gypsum within the Upper Triassic and Lower Jurassic sequence of the Trancisión Formation [101]. The area was then deformed by the Late Cretaceous-Miocene Pyrenean-Cantabrian Orogen, with Tertiary sediments being deposited in foreland basins [102]. These Tertiary sediments are predominantly terrigenous clastic and alluvial fan deposits. However, in the Oviedo basin, the lowermost Toral Formation (Eocene) contains lacustrine clays and evaporite deposits, including gypsum [103]. Thus, it is conceivable that the Carboniferous rocks of the Mieres area were once overlain by Triassic or Eocene gypsum-bearing sediments, which could have dissolved to release sulphate to the subjacent rocks. Alternatively, sulphate could be derived from the mid-Carboniferous (Namurian) Barcaliente Formation, comprising micritic carbonates, with evaporite pseudomorphs and breccias [25]. Whatever the age, an evaporite source appears the most plausible explanation for the majority of the sulphate $\delta^{34}S$ in the waters of the deeper Figaredo and Barredo mines.

Interpretation – United Kingdom

The water pumped at Markham No. 3 shaft (*Phase 1 Pumping Regime* [6, 39]) was initially rather saline (up to c. 20 g L^{-1}) and dominated by sodium and chloride. This indicates the present of a deep saline body of groundwater in the Coal Measures aquifer (as has been described in numerous localities in the UK [7, 104, 105]). This deep saline water was deficient in sulphate, indicating sulphate-reducing conditions at depth, although no $\delta^{34}S$ data are available from this phase of pumping to confirm this interpretation. During the shallower *Phase 2 Pumping Regime*, the water samples (2012 – 2013) were less saline, with a higher sulphate content; Figure 8). As the still shallower *Phase 3* pumping regime commenced (Feb 2015 onwards), the water's SO_4^{2-}/Cl^- ratio increased dramatically to a value in excess of modern seawater (Figure 8) and then gradually declined (but still typically demonstrating a modest sulphate excess compared to seawater).

Isotopic determinations at Markham were only made during the third pumping phase. Hydrogen and oxygen isotopic composition indicates indicated a water origin compatible with modern meteoric recharge. Dissolved sulphate $\delta^{34}S$ was generally low (+3.9 to +6.3‰) and within the range of sedimentary pyrite, suggesting that sulphate during this phase originated from pyrite oxidation. We thus hypothesise that as mine water levels recovered in Markham colliery, a redox and salinity stratification developed, with, in ascending order: (i) a deep saline, sulphate-depleted brine, of tentative marine origin, with prevailing highly reducing (sulphate reduction and methanogenic) conditions (*Phase 1 Pumping Regime*); (ii) a saline, less-reducing, sulphate-rich water, of tentative marine origin (*Phase 2 Pumping Regime*); (iii) a much fresher water, more influenced by modern recharge, with a sulphate content dominated by pyrite oxidation, with some admixture with deeper brines (*Phase 3 Pumping Regime*).

The Caphouse Secondary Egress Drift is above the regional water table, with seepages of water related to perched water or unsaturated zone flow in specific stratigraphic horizons. The hydrogen and oxygen isotopic composition indicates a water compatible with modern meteoric recharge (average $\delta^{18}O$ = -8.2‰, $\delta^{2}H$ = -53‰). The sulphur isotopic composition exhibits a variability which reflects the local nature of the seepages, but broadly within the range of sedimentary pyrite observed in UK Coal Measures. We thus conclude that the waters in the Caphouse Drift have a sulphate content predominantly derived from local sulphide mineral oxidation.

The pumped Hope Shaft at Caphouse Colliery acts as a regional sink for water from a network of coal mines in the vicinity, working a number of stratigraphic horizons. The water has a chloride content of >100 mg L^{-1} (and up to >300 mg L^{-1}) which is significantly in excess of that observed in typical shallow Coal Measures waters of the area (10 - 40 mg L^{-1} [40]). This suggests a small component derived from a deep saline water body. However, the water is of a Na^+-SO_4^{2-} type, with very high excess sodium and sulphate concentrations (relative to seawater Na^+/Cl^- and SO_4^{2-}/Cl^- ratios). The hydrogen and oxygen isotopic composition indicates a water compatible with modern meteoric recharge. The sulphate $\delta^{34}S$ is very high (typically +20 to +24‰), much higher than the seepages from Caphouse Egress Drift, accessing broadly the same sedimentary strata. The Hope shaft's dissolved sulphate $\delta^{34}S$ is not compatible with a derivation from oxidation of sedimentary sulphide. The high SO_4^{2-}/Cl^- ratio is also incompatible with any derivation from recent or past marine intrusion or from evaporite basin brines. The relatively low chloride content also rules out the brine derivation from freeze-concentration during the Pleistocene ice age [7]. The high sulphate could plausibly be derived from dissolution of evaporite gypsum or anhydrite mineralisation.

Arguably, the Caphouse Hope mine water dissolved sulphate $\delta3^{4}S$ is close to the upper end of the range suggested for Lower Carboniferous seawater / evaporites [60, 61], although evaporites of this age are not documented from the Yorkshire area.

However, sulphate evaporites are known in the Middle and Upper Permian (Zechstein) Marls and Mid-Late Triassic (Mercia Mudstone) sequences of the East Yorkshire area that plausibly could have once overlain the Coal Measures. The early Triassic in Eastern England was characterised by red-bed, predominantly fluvial, lacustrine and aeolian Sherwood Sandstone deposition (although some gypsum and anhydrite is documented, e.g. as cement, within the Sherwood Sandstone of the area [106, 107]).

The origin of saline waters (with high sulphate $\delta^{34}S$, typically of +17.2 to +17.5‰) in the Triassic Sherwood Sandstone of the Selby region of Yorkshire was investigated [108] and possible sulphate sources isotopically characterised. It was found that Triassic Mercia Mudstone evaporites were characterised by a $\delta^{34}S$ of +15.5 to +17.9‰. Sulphate evaporites within Upper and Middle Permian Marls exhibited typical $\delta^{34}S$ in the range +8.2 to +10.2‰. The authors also sampled Coal Measures brines from mines in the Selby area (with chloride ranging from 3 to 10 g L^{-1} and sulphate 54 to 57 g L^{-1}): these were characterised by a $\delta^{34}S$ of +3.9 to +11.7‰. The authors concluded that Triassic evaporites were the most likely source of salinity in the Sherwood Sandstone aquifer.

Opposing the argument for Permo-Triassic evaporites as the source of dissolved sulphate in the Hope shaft mine water is Caphouse's location at the very edge of the Permian-Triassic saline basin palaeogeography [109, 110, 111, 112]. Moreover, throughout much of the Triassic, evaporitic and marine sulphate $\delta^{34}S$ values were around +15 to +17‰, while during the Permian they were even lower.

The global marine sulphate $\delta^{34}S$ was in excess of +20‰ during the earliest Triassic. Subsequent to the earliest Triassic, global marine sulphate did not reach +20‰ before the Tertiary, according to [113]. The elevated dissolved sulphate $\delta^{34}S$ in Caphouse Hope Shaft's mine water thus seems incompatible with the obvious candidate sources for evaporite derivation.

The water pumped from Caphouse Hope shaft does, however, have an odour of hydrogen sulphide [5], indicating sulphide-reducing niches somewhere within the mine or aquifer system connected to the Hope shaft. If sulphide is being formed and precipitated within the Caphouse mine/aquifer system, the residual fluid would become enriched in ^{34}S. Thus, one can propose two alternative scenarios for the generation of the very high $\delta^{34}S$ in the Caphouse Hope Shaft mine water:

1) Generation of sulphate and acidity by pyrite oxidation. Acidity consumed by weathering of silicate and carbonate minerals. Admixture with sodium-bicarbonate, high pH Coal Measures groundwater [40, 114]). Dissolved sulphate in water enriched in ^{34}S by ongoing sulphide mineral precipitation in sulphate-reducing niches in mine (and/or in the aquifer over geological time).
2) Dissolution of sulphate from Permian or Triassic gypsum or anhydrite (which have subsequently been removed by erosion). Admixture with ambient groundwater. Dissolved calcium removed from solution by processes of either cation exchange or precipitation of calcite [114, 115]. Dissolved sulphate in water enriched in ^{34}S by fractionation associated with sulphate reduction, as above.

A mechanism of sulphate reduction to explain high $\delta^{34}S$ values in groundwaters has been invoked by, for example, [116], in the context of deep Jurassic and Cretaceous aquifer brines in Poland. For this to be a convincing explanation for the mine water pumped from Caphouse's Hope Shaft (which, being a regional pumping station, is difficult to envisage as a system closed with respect to sulphur), however, the rate of sulphate reduction would need to be of at least a similar order of magnitude to the rate of sulphate dissolution / generation and throughflow from other parts of the mine or aquifer system. Given the large water throughflows, the high sulphate content of the water, and the seeming lack of closure with respect to sulphate, this seem intuitively unlikely.

Conclusions

Mine waters in three study areas have been sampled and analysed for hydrochemical parameters and the stable isotopes ^{18}O, ^{2}H (water molecule) and ^{34}S (dissolved sulphate). The hydrochemistry of these mines has been published in detail elsewhere [3, 4, 5, 6, 39] and this paper focusses on the stable isotope data. In all cases, the $\delta^{18}O$, $\delta^{2}H$ data are compatible with waters being derived from relatively recent meteoric recharge.

The sulphate $\delta^{34}S$ data do suggest that the conventional assumption [1] that dissolved sulphate in minewater is usually derived from oxidation of sulphide minerals is incorrect (or, at least, incomplete) in many of the mines studied. In each of the mine areas, a bimodal distribution of sulphate $\delta^{34}S$ is observed. Sulphate $\delta^{18}O$ would have undoubtedly enhanced the value of this data set and aided interpretation: this parameter is highly recommended in addition to $\delta^{34}S$ in subsequent studies.

In all three regions, deep regional coal mine waters have been documented with elevated dissolved sulphate $\delta^{34}S$ compositions, unlikely to be derived directly from sulphide oxidation, leading us to suspect that such a phenomenon is more widespread than previously recognised.

In shallow mines, presumed to be well-flushed with recent recharge water, the dissolved sulphate $\delta^{34}S$ suggests oxidation of sulphide minerals as the main sulphate source. Examples include the Mariana coal mine (Asturias, Spain), the Caphouse Secondary Egress Drift (Yorkshire, UK) and the Bolko Pb-Zn sulphide mine (Bytom, Poland). Also, in the relatively deep Markham mine (Derbyshire, UK), low salinity water in the upper part of the stratified mine water body had a dissolved sulphate $\delta^{34}S$ compatible with oxidation of pyrite.

At Szombierki coal mine, Bytom, Poland, sulphate $\delta^{34}S$ are compatible with derivation from dissolution of gypsum/anhydrite evaporite minerals in overlying Triassic strata.

At Figaredo and Barredo coal mines, Asturias, Spain, the sulphate $\delta^{34}S$ are compatible with derivation from dissolution of gypsum/anhydrite evaporite minerals. Sources have not been clearly identified, but Upper Triassic / Lower Jurassic, or Eocene evaporites are known from the region.

At Caphouse coal mine (Hope Pumping Shaft), the dissolved sulphate $\delta^{34}S$ is too high to be readily explained by evaporite dissolution, and such an evaporite source has not been clearly identified in the area. The fact that dissolved H_2S is observed in pumped water lead us to speculate whether an initial sulphate source (either derived from primary sulphide oxidation, or evaporites) has been preferentially depleted in the light isotope (^{32}S) by bacterial sulphate reduction to sulphide within the mine or aquifer system, over geological or anthropic time, leaving the residual water enriched in ^{34}S. We acknowledge that the quantitative aspects of this hypothesis are problematic, given (a) the mine water's high sulphate content and (b) the large pumping rate and throughflow of water in the mine workings.

In all three regions studied, deep mine waters have been found which have sulphate δ^{34}S values that appear too high to attribute solely to pyrite oxidation. Thus, contrary to accepted belief, isotopic evidence suggests that we should not automatically assume that sulphate in mine waters from coal mines is inevitably derived from pyrite oxidation. The practical implications of this finding are that: (1) a dissolved sulphate δ^{34}S similar to sedimentary pyrite is not a diagnostic characteristic of coal mine waters; (2) elevated sulphate concentrations may be characteristic of deep groundwaters in Carboniferous sedimentary basins and not be restricted to, or characteristic of, mining environments.

It is tempting, in these cases, to postulate a component of dissolved sulphate derived from dissolution of overlying or subjacent evaporite minerals to account for these elevated sulphate δ^{34}S values. In the Polish and Spanish cases, this explanation is certainly plausible (although it is arguably somewhat *too* plausible to be a demonstrable hypothesis). The fact that viable evaporite sources have not been identified for the Caphouse (Hope) mine water suggests there are aspects of mine water sulphate isotope geochemistry that we still do not fully understand. Fractionation by bacterial sulphate reduction processes (and enrichment of residual waters in ^{34}S) may play a role. In the geological past, under conditions where the coal-bearing strata were deeply buried, methane-coupled thermal sulphate reduction and associated fractionation could also have played a role in producing fluids with a high δ^{34}S [57]. Indeed, a future study might usefully examine any relationship between coal grade and the δ^{34}S of dissolved sulphate and sedimentary pyrite, within a single coal basin.

We tentatively postulate that the deep groundwater/minewater environment may represent an isotopically enriched reservoir for sulphate sulphur, directly analogous to the ocean. In this reservoir there may be a dynamic, and shifting, equilibrium between inputs of sulphate from shallow weathering of sulphide and sulphate minerals, and removal of sulphate by precipitation of sulphate minerals and bacterial (or thermal) sulphate reduction, which preferentially remove ^{34}S-depleted sulphide in deep anoxic hydrochemical niches, leaving the remaining groundwater reservoir isotopically enriched in ^{34}S.

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Data Availability

A data file of raw hydrochemical and isotopic data [86] is available via the Mendeley repository.

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References

[1] D. Banks, P. Younger, R. Arnesen, E. Iversen and S. Banks, "Mine-water chemistry: the good, the bad and the ugly," *Environmental Geology,* vol. 32, no. 3, p. 157–174, 1997.

[2] G. Gzyl, D. Banks, P. Younger, M. Głodniok, N. Burnside, B. Garzon and A. Skalny, "Low Carbon After-Life –overview and first results of project LoCAL," in *Drebenstedt, C. & Paul, M. (eds) "Mining meets water – conflicts and solutions", Proceedings of the 2016 International Mine Water Association (IMWA) Conference, Leipzig, Germany*, Leipzig, Germany, 2016.

[3] E. Janson, A. Boyce, N. Burnside and G. Gzyl, "Preliminary investigation on temperature, chemistry and isotopes of mine water pumped in Bytom geological basin (USCB Poland) as a potential geothermal energy source," *International Journal of Coal Geology,* vol. 164, pp. 104-114, 2016.

[4] C. Loredo, A. Ordóñez, E. Garcia-Ordiales, R. Álvarez, N. Roqueñi, P. Cienfuegos, A. Peña and N. Burnside, "Hydrochemical characterization of a mine water geothermal energy resource in NW Spain," *Science of the Total Environment,* vol. 576, pp. 59-69, 2017.

[5] N. Burnside, D. Banks and A. Boyce, "Sustainability of thermal energy production at the flooded mine workings of the former Caphouse Colliery, Yorkshire, United Kingdom," *International Journal of Coal Geology,* vol. 164, pp. 85-91, 2016.

[6] N. Burnside, D. Banks, A. Boyce and A. Athresh, "Hydrochemistry and stable isotopes as tools for understanding the sustainability of thermal energy production from a ‘standing column’ heat pump system: Markham Colliery, Bolsover, Derbyshire, UK," *International Journal of Coal Geology,* vol. 164, pp. 85-91, 2016.

[7] P. Younger, A. Boyce and A. Waring, "Chloride waters of Great Britain revisited: from subsea formation waters to onshore geothermal fluids," *Proceedings of the Geologists' Association,* vol. 126, pp. 453-465, 2015.

[8] R. Stotler, S. Frape, T. Ruskeeniemi, P. Pitkänen and D. Blowes, "The interglacial–glacial cycle and geochemical evolution of Canadian and Fennoscandian Shield groundwaters," *Geochimica et Cosmochimica Acta,* vol. 76, p. 45–67, 2012.

[9] D. Banks, S. Burke and C. Gray, "Hydrogeochemistry of coal mine drainage and other ferruginous waters in north Derbyshire and south Yorkshire, UK," *Quarterly Journal of Engineering Geology ,* vol. 30, pp. 257-280, 1997.

[10] D. Banks, A. Frolik, G. Gzyl and M. Rogoż, "Modeling and monitoring of mine water rebound in an abandoned coal mine complex: Siersza Mine, Upper Silesian Coal Basin, Poland," *Hydrogeology Journal,* vol. 18, no. 2, pp. 519-534, 2009.

[11] E. Janson, G. Gzyl and D. Banks, "The occurrence and quality of mine water in the Upper Silesian Coal Basin, Poland," *Mine Water and the Environment,* vol. 28, no. 3, pp. 232-244, 2009.

[12] E. Janson, G. Gzyl, M. Głodniok and M. Markowska, "Use of geothermal heat of mine waters in Upper Silesian Coal Basin, Southern Poland – possibilities and impediments," in *"Mine Water and Circular Economy", Proceedings of the Conference of the International Mine Water Association 2017*, Lappeenranta, Finland, 2017.

[13] J. Kropka, "Quantitative analysis of supply from anthropogenic sources to mine workings of closed zinc-lead ore mines in the Bytom Trough (southern Poland)," in *Uranium in the Aquatic Environment*, Berlin-Heidelberg, Springer, 2002, pp. 1075-1082.

[14] A. Kowalczyk and A. Witkowski, "Groundwater recharge of carbonate aquifers of the Silesian-Cracow Triassic (southern Poland) under human impact," *Environmental Geology,* vol. 44, pp. 235-246, 2008.

[15] J. Kropka and A. Witkowski, "Groundwater quality degradation in the area of abandoned Zn-Pb ore mine (Bytom syncline - southern Poland)," in *Proceedings of the 5th Congress of the International Minewater Association (IMWA), Nottingham, UK, September 1994*, Nottingham, UK, 1994.

[16] J. Motyka and A. Witkowski, "Sulphates in groundwater of the karst-fractured Triassic aquifers in areas of intensive mining drainage (the Olkusz and the Bytom regions)," in *Proceedings of the Congress of the International Mine Water Association (IMWA), Sevilla, Spain*, Sevilla, Spain, 1999.

[17] W. Heijlen, P. Muchez, D. Banks, J. Schneider, H. Kucha and E. Keppens, "Carbonate-hosted Zn-Pb deposits in Upper Silesia, Poland: origin and evolution of mineralizing fluids and constraints on genetic models," *Economic Geology,* vol. 98, no. 5, pp. 911-932, 2003.

[18] C. Harańczyk, "Sulfur isotope models of genesis of the Silesian-Cracow Zn-Pb ore deposits," *Geological Quarterly (Polish Geological Institute),* vol. 37, no. 2, pp. 307-322, 1993.

[19] V. Coppola, M. Boni, H. Gilg and B. Strzelska-Smakowska, "Nonsulfide zinc deposits in the Silesia–Cracow district, southern Poland," *Mineralium Deposita,* vol. 44, p. 559–580, 2009.

[20] J. Kropka, "Changes in mine-water hydrology during the shut-down process of the zinc-lead ore mines in the Bytom region (S Poland)," in *Proceedings of the International Minewater Association Symposium 2004 (IMWA 2004), Newcastle-upon-Tyne, UK*, Newcastle-upon-Tyne, UK, 2004.

[21] D. Leach and J. Viets, "Comparison of the Cracow-SilesianMississippi Valley-type district, southern Poland, with Mississippi Valley-type districts in North America," US Geological Survey Open-File Report OF/92-704, Denver, USA, 1992.

[22] S. Jardón, A. Ordóñez, R. Álvarez, P. Cienfuegos and L. J., "Mine Water for Energy and Water Supply in the Central Coal Basin of Asturias (Spain)," *Mine Water and the Environment,* vol. 32, no. 2, pp. 139-151, 2013.

[23] J. Loredo, A. Ordóñez, S. Jardón and R. Álvarez, "Mine water as geothermal resource in Asturian coal mining basins (NW Spain)," in *Proc. Congress International Mine Water Association IMWA 2011 "Mine Water – Managing the Challenges"*, Aachen, Germany, 2011.

[24] B. Ábalos, J. Carreras, E. Druguet, J. Viruete, M. Pugnaire, S. Alvarez, C. Quesada, L. Fernández and J. Gil-Ibarguchi, "Chapter 9. Variscan and Pre-Variscan tectonics," in *The geology of Spain*, Geological Society of London, 2002, pp. 155-183.

[25] E. Villa and L. Sánchez de Posada, "Chapter 3. Carboniferous of the Cantabrian Zone," in *Spanish Geological Frameworks and Geosites. An approach to Spanish geological heritage of international relevance*, Madrid, Spain, Instituto Geológico y Minero de España, 2009, pp. 45-55.

[26] J. Colmenero, L. Fernández, C. Moreno, J. Bahamonde, P. Barba, N. Heredia and F. González, "Chapter 7. Carboniferous," in *The Geology of Spain*, Bath, UK, The Geological Society, London, 2002, pp. 93-116.

[27] M. Díaz-Somoano, I. Suárez-Ruiz, J. Alonso, J. Encinar, M. López-Antón and M. Martínez-Tarazona, "Lead isotope ratios in Spanish coals of different characteristics and origin," *International Journal of Coal Geology,* vol. 71, no. 1, pp. 28-36, 2007.

[28] K. Davies-Vollum, P. Guion, J. Knight and A. Smith, "Geology of Caphouse Colliery, Wakefield, Yorkshire, UK," *Proceedings of theYorkshire Geological Society,* vol. 61, pp. 97-108, 2015.

[29] I. Brown and J. Goodchild, "The coal mines of the Flockton area, near Horbury, West Yorkshire," *Bulletin of the Peak District Mines Historical Society,* vol. 7, no. 3, pp. 169-173, 1979.

[30] N. Kruse, "Simulation of hydrogeochemical processes in abandoned underground mines. PhD thesis, School of Civil Engineering and Geosciences, University of Newcastle," University of Newcastle, Newcastle-upon-Tyne, 2007.

[31] INWATCO, "Integrated water management in former coal mining regions: guidance to support strategic planning," EU Life Environment Programme, 2005.

[32] INWATCO, "Integrated water management in former coal mining regions: non-technical summary," EU Life Environment Programme, 2005.

[33] R. Lake and E. Hough, "The Pennine Lower and Middle Coal Measures formations of the Barnsley district. British Geological Survey Internal Report IR/06/135," British Geological Survey, Keyworth, UK, 2006.

[34] N. Kruse and P. Younger, "Sinks of iron and manganese in underground coal mine workings," *Environmental Geology,* vol. 57, no. 8, p. 1893–1899, 2009.

[35] S. Banks, "The UK Coal Authority minewater-treatment scheme programme: performance of operational systems," *Water and Environment Journal,* vol. 17, no. 2, pp. 117-122, 2007.

[36] PIRAMID Consortium, "Engineering guidelines for the passive remediation of acidic and/or metalliferous mine drainage and similar wastewaters," University of Newcastle, Newcastle-upon-Tyne, 2003.

[37] M. Faraldo Sanchez, "Thermal balance of minewater treatment lagoons and wetlands. MSc thesis in Environmental Engineering, School of Civil Engineering and Geosciences, University of Newcastle," University of Newcastle, Newcastle-upon-Tyne, UK, 2007.

[38] N. Kruse and P. Younger, "Sinks of iron and manganese in underground coal mine workings," *Environmental geology,* vol. 57, p. 1893–1899, 2009.

[39] D. Banks, A. Athresh, A. Al-Habaibeh and N. Burnside, "Water from abandoned mines as a heat source: practical experiences of open- and closed-loop strategies, United Kingdom," *Sustainable Water Resources Management,* vol. 5, no. 1, pp. 29-50, 2019.

[40] D. Banks, "Hydrogeochemistry of Millstone Grit and Coal Measures groundwaters, south Yorkshire and north Derbyshire, UK," *Quarterly Journal of Engineering Geology,* vol. 30, pp. 237-256, 1997.

[41] N. Kruse, "Simulation of hydrogeochemical processes in abandoned undergorund mines. PhD thesis, School of Civil Engineering and Geosciences, Newcastle University, UK," Newcastle University, Newcastle-upon-Tyne, 2007.

[42] healeyhero, "Markham Colliery - 1973. Background information - the colliery," 2019. [Online]. Available: http://www.healeyhero.co.uk/rescue/pits/markham/markham_73_1.htm. [Accessed 12 6 2019].

[43] T. Sheppard, "A stratigraphical framework for the Upper Langsettian and Duckmantian of the East Pennine coalfields. British Geological Survey Internal Report IR/05/070," British Geological Survey, Keyworth, UK, 2005.

[44] R. Tostevin, A. Turchyn, J. Farquhar, D. Johnston, D. Eldridge, J. Bishop and M. McIlvin, "Multiple sulfur isotope constraints on the modern sulfur cycle," *Earth and Planetary Science Letters,* vol. 396, pp. 14-21, 2014.

[45] A. Burke, T. Present, G. Paris, E. Rae, B. Sandilands, J. Gaillardet, B. Peucker-Ehrenbrink, W. Fischer, J. McClelland, R. Spencer, B. Voss and J. Adkins, "Sulfur isotopes in rivers: insights into global weathering budgets, pyrite oxidation, and the modern sulfur cycle," *Earth and Planetary Science Letters,* vol. 496, pp. 168-177, 2018.

[46] H. Strauss, "The isotopic composition of sedimentary sulfur through time," *Palaeogeography, Palaeoclimatology, Palaeoecology,* vol. 132, pp. 97-118, 1997.

[47] L. Chambers and P. Trudinger, "Microbiological fractionation of stable sulfur isotopes: a review and critique," *Geomicrobiology,* vol. 1, no. 3, pp. 249-293, 1979.

[48] C. Rees, "A steady-state model for sulphur isotope fractionation in bacterial reduction processes," *Geochimica et Cosmochimica Acta,* vol. 37, no. 5, pp. 1141-1162, 1973.

[49] M. Sim, T. Bosak and S. Ono, "Large sulfur isotope fractionation does not require disproportionation," *Science,* vol. 333, no. 6038, pp. 74-77, 2011.

[50] W. Leavitt, I. Halevy, A. Bradley and D. Johnston, "Influence of sulfate reduction rates on the Phanerozoic sulfur isotope record," *Proceedings of the National Academy of Sciences of the USA,* vol. 110, no. 28, pp. 11244-11249, 2013.

[51] J. McKay and F. Longstaffe, "Sulphur isotope geochemistry of pyrite from the upper Cretaceous Marshybank Formation, Western Interior Basin," *Sedimentary Geology,* vol. 157, pp. 175-195, 2003.

[52] H. Schwarcz and S. Burnie, "Influence of sedimentary environments on sulfur isotope ratios in clastic rocks: a review," *Mineralium Deposita,* vol. 8, p. 264–277, 1973.

[53] P. Li, H. Zou, F. Hao and X. Yu, "Sulfate sources of thermal sulfate reduction (TSR) in the Permian Changxing and Triassic Feixianguan formations, Northeastern Sichuan Basin, China," *Geofluids,* pp. Article ID 5898901, 13 pages, 2019.

[54] L. Jia, C. Cia, H. Yang, H. Li, T. Wang, B. Zhang, L. Jiang and X. Tao, "Thermochemical and bacterial sulfate reduction in the Cambrian and Lower Ordovician carbonates in the Tazhong Area, Tarim Basin, NW China: evidence from fluid inclusions, C, S, and Sr isotopic data," *Geofluids,* vol. 15, p. 421–437, 2015.

[55] H. Machel, "Bacterial and thermochemical sulfate reduction in diagenetic settings - old and new insights," *Sedimentary Geology,* vol. 140, pp. 143-175, 2001.

[56] Y. Kiyosu and H. Krouse, "The role of organic acid in the abiogenic reduction of sulfate and the sulfur isotope effect," *Geochemical Journal,* vol. 24, pp. 21-27, 1990.

[57] M. Sośnicka and V. Lüders, "Super-deep, TSR-controlled Phanerozoic MVT type Zn-Pb deposits hosted by Zechstein-2 gas reservoir carbonate (Ca2), Lower Saxony Basin, Germany," *Chemical Geology,* vol. 508, p. 62–77, 2019.

[58] R. McGowan, S. Roberts, R. Foster, B. A.J. and D. Coller, "Origin of the Cu-Co deposits of the Zambian Copperbelt: an epigenetic view from Nchanga," *Geology,* vol. 31, no. 6, pp. 497-500, 2003.

[59] D. Fike, A. Bradley and C. Rose, "Rethinking the ancient sulphur cycle," *Annual Review of Earth and Planetary Sciences,* vol. 43, pp. 593-622, 2015.

[60] G. Claypool, W. Holser, I. Kaplan, H. Sakai and I. Zak, "The age curves of sulfur and oxygen isotopes in marine sulfate and their mutual interpretation," *Chemical Geology,* vol. 28, pp. 199-260, 1980.

[61] A. Fallick, J. Ashton, A. Boyce, R. Ellam and M. Russell, "Bacteria were responsible for the magnitude of the world-class hydrothermal base-metal orebody at Navan, Ireland," *Economic Geology,* vol. 96, pp. 883-888, 2001.

[62] B. Turner and D. Richardson, "Geological controls on the sulphur content of coal seams in the Northumberland Coalfield, Northeast England," *International Journal of Coal Geology,* vol. 60, pp. 169-196, 2004.

[63] H. Strauss, "Geological evolution from isotope proxy signals — sulfur," *Chemical Geology,* vol. 161, p. 89–101, 1999.

[64] S. Bernasconi, I. Meier, S. Wohlwend, P. Brack, P. Hochuli, H. Bläsi, U. Wortmann and K. Ramseyer, "An evaporite-based high-resolution sulfur isotope record of Late Permian and Triassic seawater sulfate," *Geochimica et Cosmochimica Acta,* vol. 204, p. 331–349, 2017.

[65] K. Meyer, L. Kump and A. Ridgwell, "Biogeochemical controls on photic-zone euxinia during the end-Permian mass extinction," *Geology,* vol. 36, no. 9, pp. 747-750, 2008.

[66] L. Knauth, "Salinity history of the Earth's ocean," in *Encyclopedia of Geobiology, 2011 edition*, Springer, 2011, pp. 769-772.

[67] N. Planavsky, A. Bekker, A. Hofmann, J. Owensa and T. Lyons, "Sulfur record of rising and falling marine oxygenand sulfate levels during the Lomagundi event," *Proceedings of the National Academy of Sciences of the United States of America,* vol. 109, no. 45, pp. 18300-18305.

[68] N. Holt, J. García-Veigas, T. Lowenstein, P. Giles and D. Williams-Stroud, "The major-ion composition of Carboniferous seawater," *Geochimica et Cosmochimica Acta,* vol. 134, pp. 317-334, 2014.

[69] B. Gill, T. Lyons and M. Saltzman, "Parallel, high-resolution carbon and sulfur isotope records of the evolving Paleozoic marine sulfur reservoir," *Palaeogeography, Palaeoclimatology, Palaeoecology,* vol. 256, no. 3-4, pp. 156-173, 2007.

[70] J. Horita, H. Zimmermann and H. Holland, "Chemical evolution of seawater during the Phanerozoic: Implications from the record of marine evaporites," *Geochimica et Cosmochimica Acta,* vol. 66, p. 3733–3756, 2002.

[71] S. Glynn, R. Mills, M. Palmer, R. Pancost, S. Severmann and A. Boyce, "The role of prokaryotes in supergene alteration of submarine hydrothermal sulfides," *Earth and Planetary Science Letters,* vol. 244, pp. 170-185, 2006.

[72] B. Taylor, M. Wheeler and D. Nordstrom, "Stable isotope geochemistry of acid mine drainage: Experimental oxidation of pyrite," *Geochimica et Cosmochimica Acta,* vol. 48, no. 12, pp. 2669-2678, 1984.

[73] S. Dean, "A study of the organic and inorganic geochemistry of sulphur in shales.," PhD thesis, University of Leeds, 1994.

[74] L. Bullock, J. Parnell, M. Perez, A. Boyce, J. Feldmann and J. Armstrong, "Multi-stage pyrite genesis and epigenetic selenium enrichment of Greenburn coals (East Ayrshire)," *Scottish Journal of Geology,* vol. 54, no. 1, pp. 37-49, 2018.

[75] L. Love, M. Coleman and C. Curtis, "Diagenetic pyrite formation and sulphur isotope fractionation associated with a Westphalian marine incursion, northern England," *Transactions of the Royal Society of Edinburgh: Earth Sciences,* vol. 74, pp. 165-182, 1983.

[76] A. Chmielewski, R. Wierzchnicki, M. Derda and A. MikoПajczuk, "Sulfur isotope composition of selected Polish coals," *Nukleonika,* vol. 47, no. Supplement 1, p. S67–S68, 2002.

[77] I. Pluta, "Pochodzenie siarczanów w wodach Górnośląskiego i Zagłębia Węglowego w świetle badań izotopowych [Origin of sulfates in Uppersilesian Coal Basin waters in the light of isotopic research - in Polish]," *Przegląd Górniczy,* vol. 58, no. 3, pp. 36-43, 2002.

[78] IAEA/WMO, "Global Network of Isotopes in Precipitation. The GNIP Database," 2019.

[79] S. Nelson, "A simple, practical methodology for routine VSMOW/SLAP normalization of water samples analyzed by continuous flow methods," *Rapid Communications in Mass Spectrometry,* vol. 14, no. 12, p. 1044–1046, 2000.

[80] T. Donnelly, S. Waldron, A. Tait, J. Dougans and S. Bearhop, "Hydrogen isotope analysis of natural abundance and deuterium-enriched waters by reduction over chromium on-line to a dynamic dual inlet isotope-ratio mass spectrometer," *Rapid Communications in Mass Spectrometry,* vol. 15, no. 15, pp. 1297-1303, 2001.

[81] R. Carmody, L. Plummer, E. Busenberg and T. Coplen, "Methods for collection of dissolved sulfate and sulfide and analysis of their sulfur isotopic composition. USGS Open-File Report 97-234," United States Geological Survey, Reston, Virginia, USA, 1998.

[82] M. Coleman and M. Moore, "Direct reduction of sulfates to sulfur dioxide for isotopic analysis," *Analytical Chemistry,* vol. 50, no. 11, p. 199–260, 1978.

[83] Lenntech, "Composition of seawater," Lenntech, 2005. [Online]. Available: https://www.lenntech.com/composition-seawater.htm. [Accessed 14 11 2019].

[84] Lenntech, "Lithium and water: reaction mechanisms, environmental impact and health effects," Lenntech, [Online]. Available:

https://www.lenntech.com/periodic/water/lithium/lithium-and-water.htm. [Accessed 14 11 2019].

[85] Stanford University, "Mineral makeup of seawater," [Online]. Available: https://web.stanford.edu/group/Urchin/mineral.html. [Accessed 14 11 2019].

[86] D. Banks, N. Burnside, A. Boyce, E. Janson and N. Roqueñi Gutierrez, "Stable isotopic and hydrochemical composition of selected European minewaters. LoCAL dataset," 2020.

[87] S. Davis, D. Whittemore and F.-M. J., "Uses of chloride/bromide ratios in studies of potable water," *Ground Water,* vol. 36, no. 2, pp. 338-350, 1998.

[88] G. Gzyl and D. Banks, "Verification of the “first flush” phenomenon in mine water from coal mines in the Upper Silesian Coal Basin, Poland," *Journal of Contaminant Hydrology,* vol. 92, pp. 66-86, 2007.

[89] P. Younger, "Predicting temporal changes in total iron concentrations in groundwaters flowing from abandoned deep mines: a first approximation," *Journal of Contaminant Hydrology,* vol. 44, pp. 47-69, 2000.

[90] P. Krzywiec, T. Peryt, H. Kiersnowski, P. Pomianowski, G. Czapowski and K. Kwolek, "Chapter 11 - Permo-Triassic evaporites of the Polish Basin and their bearing on the tectonic evolution and hydrocarbon system, an overview," in *Permo-Triassic salt provinces of Europe, North Africa and the Atlantic margins - tectonics and hydrocarbon potential*, Amsterdam, Elsevier, 2017, pp. 243-261.

[91] J. Szulc, M. Gradziński, A. Lewandowska and C. Heunisch, "The Upper Triassic crenogenic limestones in Upper Silesia (southern Poland) and their paleoenvironmental context," in *Paleoenvironmental record and applications of calcretes and palustrine carbonates. Geological Society of America Special Papers Volume 416*, Geological Society of Amercia, 2006, pp. 133-151.

[92] P. I. G. -. P. I. Badawczy, "Mapy geologiczne (Geological maps) - Mapa geologiczna Polski 1:500,000," [Online]. Available: http://geologia.pgi.gov.pl/arcgis/apps/MapSeries/index.htm. [Accessed 25 9 2019].

[93] J. Szulc, G. Racki and K. Jewuła, "Key aspects of the stratigraphy of the Upper Silesian middle Keuper, southern Poland," *Annales Societatis Geologorum Poloniae,* vol. 85, no. 4, pp. 557-586, 2015.

[94] K. Jewuła, M. Matysik, M. Paszkowski and J. Szulc, "The late Triassic development of playa, gilgai floodplain, and fluvial environments from Upper Silesia, southern Poland," *Sedimentary Geology,* vol. 379, pp. 25-45, 2019.

[95] J. Szulc, "Middle Triassic evolution of the northern Peri-Tethys area as influenced by early opening of the Tethys Ocean," *Annates Societatis Geologorum Poloniae,* vol. 70, pp. 1-48, 2000.

[96] W. Heijlen, P. Muchez, D. Banks, J. Schneider, H. Kucha and E. Keppens, "Carbonate-hosted Zn-Pb deposits in Upper Silesia, Poland: origin and evolution of mineralizing fluids and constraints on genetic models," *Economic Geology,* vol. 98, no. 5, pp. 911-932, 2003.

[97] I. Pluta, "Influence of salt bed of the Zawada Basin on mine waters in the Upper Silesian Coal Basin (Poland)," in *Proceedings of the 10th Congress of the International Association of Mine Water, "Mine Water and the Environment", Karlsbad, Czech Republic*, Karlsbad, Czech Republic, 2008.

[98] A. Kasprzyk, "Oxygen and sulphur isotope composition of Badenian (Middle Miocene) gypsum deposits in southern Poland: a preliminary study," *Geological Quarterly (Polish Geological Institute),* vol. 41, no. 1, pp. 53-60, 1997.

[99] S. Biernat, S. Wilanowski and J. Lewandowski, Szczegółowa Mapa Geologiczna Polski 1:50,000 (Geological Map of Poland 1:50,000). Sheet 910 Bytom M-34-50-D, Warszawa, Poland: Państwowy Instytut Geologiczny - Państwowy Instytut Badawczy, 2016.

[100] I. Pluta, "Powstawanie I neutralizacja kwaoenych wód w kopalni Niwka-Modrzejów na Górnym Śląsku [Generation and neutralization of acid waters in the Niwka-Modrzejów coal mine (Upper Silesia) – in Polish]," *Biuletyn Państwowego Instytutu Geologicznego,* vol. 436, pp. 361-366, 2009.

[101] J. López-Gómez, F. Martín-González, N. Heredia, R. de la Horra, J. Barrenechea, P. Cadenas, M. Juncal, J. Diez, V. Borruel-Abadía, D. Pedreira, J. García-Sansegundo, P. Farias, C. Galé, M. Lago, T. Ubide, G. Fernández-Viejo and G. Gand, "New lithostratigraphy for the Cantabrian Mountains: A common tectono-stratigraphic evolution for the onset of the Alpine cycle in the W Pyrenean realm, N Spain," *Earth-Science Reviews,* vol. 188, pp. 249-271, 2018.

[102] F. Martín-González, M. Freudenthal, N. Heredia, E. Martín-Suárez and R. Rodríguez-Fernández, "Palaeontological age and correlations of the Tertiary deposits of the NW Iberian Peninsula: the tectonic evolution of a broken foreland basin," *Geological Journal,* vol. 49, no. 1, pp. 15-27, 2014.

[103] J. Truyols, J. García Ramos, M. Casanovas-Cladellas and J. Santafé-Llopis, "El Terciario de los alrededores de Oviedo," *Acta Geológica Hispánica,* vol. 26, p. 229–233, 1991.

[104] W. Anderson, "On the chloride waters of Great Britain," *Geological Magazine,* vol. 82, no. 6, pp. 267-273, 1945.

[105] P. Bedson, "On the composition of certain colliery waters," *Journal of the Society of Chemical Industry,* vol. 6, p. 712–715, 1887.

[106] P. Shand, R. Tyler-Whittle, M. Morton, E. Simpson, A. Lawrence, J. Pacey and R. Hargreaves, "Baseline Report Series 1: The Permo-Triassic Sandstones of the Vale of York," British Geological Survey Commissioned Report No. CR/02/102N, Keyworth, UK, 2002.

[107] P. Smedley, P. Shand and A. Butcher, "Age and quality stratification of groundwater in the Triassic SherwoodSandstone aquifer of South Yorkshire and the East Midlands, UK," *Applied Geochemistry,* vol. 97, pp. 109-122, 2018.

[108] S. Bottrell, L. West and K. Yoshida, "Combined isotopic and modelling approach to determine the source of saline groundwaters in the Selby Triassic sandstone aquifer, UK," *Barker, R.D. & Tellam, J.H. (eds) "Fluid Flow and Solute Movement in Sandstones: The Onshore UK Permo-Triassic Red Bed Sequence", Geological Society of London Special Publication,* vol. 263, pp. 325-338., 2006.

[109] T. McKie, "Chapter 7. Paleogeographic evolution of latest Permian and Triassic salt basins in Northwest Europe," in *Permo-Triassic salt provinces of Europe, North Africa and the Atlantic margins. Tectonics and hydrocarbon potential*, Amsterdam, Elsevier, 2017, pp. 159-173.

[110] T. McKie and B. Williams, "Triassic palaeogeography and fluvial dispersal across the northwest European Basins," *Geological Journal,* vol. 44, p. 711–741, 2009.

[111] M. Benton, E. Cook and P. Turner, Permian and Triassic Red Beds and the Penarth Group of Great Britain, Geological Conservation Review Series, No. 24, Peterborough, UK: Joint Nature Conservation Committee, 2002, p. 337.

[112] British Geological Survey Earthwise, "Bedrock Geology UK South: Permian," British Geological Survey, 28 7 2015. [Online]. Available: http://earthwise.bgs.ac.uk/index.php/Bedrock_Geology_UK_South:_Permian. [Accessed 12 6 2019].

[113] S. Bottrell and R. Newton, "Reconstruction of changes in global sulfur cycling from marine sulfate isotopes," *Earth-Science Reviews,* vol. 75, p. 59– 83, 2006.

[114] B. Frengstad and D. Banks, "Evolution of high-pH Na-HCO3 groundwaters in anorthosites: silicate weathering or cation exchange?," in *"Groundwater: Past Achievements and Future Challenges", Proc. XXXIInd Congress of the International Association of Hydrogeologists*, Cape Town, South Africa, 2000.

[115] D. Banks and F. Frengstad, "Evolution of groundwater chemical composition by plagioclase hydrolysis in Norwegian anorthosites," *Geochimica et Cosmochimica Acta,* vol. 70, p. 1337–1355, 2006.

[116] I. Pluta and S. Hałas, "Skład izotopowy siarki i tlenu siarczanów wód z utworów mezozoiku [Sulphur and oxygen isotopic composition in sulphates from Mesozoic formations - in Polish]," *Przegląd Geologiczny,* vol. 50, no. 7, pp. 634-638, 2002.

[117] GeoMatic Ventures Ltd., "Sentinel-1 Relative Land Motion Map of the UK 2015-2017," 2018. [Online]. Available: https://www.geomaticventures.com/uk-map. [Accessed 12 6 2019].

[118] A. Sowter, L. Bateson, P. Strange, K. Ambrose and M. Syafiudin, "(2013) DInSAR estimation of land motion using intermittent coherence with application to the South Derbyshire and Leicestershire coalfields," *Remote Sensing Letters,* vol. 4, no. 10, pp. 979-987, 2013.

[119] D. Gee, L. Bateson, A. Sowter, S. Grebby, A. Novellino, F. Cigna, S. Marsh, C. Banton and L. Wyatt, "Ground Motion in Areas of Abandoned Mining: Application of the Intermittent SBAS (ISBAS) to the Northumberland and Durham Coalfield, UK," *Geosciences,* vol. 7, no. 3, Article 85, 2017.

[120] C. Rees, "Sulphur isotope measurements using SO2 and SF6," *Geochimica et Cosmochimica Acta,* vol. 42, no. 4, pp. 383-389, 1978.

[121] N. Balci, W. Shanks, B. Mayer and K. Mandernack, "Oxygen and sulfur isotope systematics of sulfate produced by bacterial and abiotic oxidation of pyrite," *Geochimica et Cosmochimica Acta,* vol. 71, no. 15, pp. 3796-3811, 2007.

[122] S. Brennan, T. Lowenstein and J. Horita, "Seawater chemistry and the advent of biocalcification," *Geology,* vol. 32, no. 6, p. 473–476, 2004.