The Legacy of Hard Coal Mining Revealed by Isotopic Fingerprinting of Mine Waters, Ruhr Area, Germany

B.M.A. Teichert[1], H. Jasnowski-Peters[1], S.E. Nikutta[1], H. Strauss[2], S. Schlömer[3], S. Westermann[1]

[1]Research Center of Post-Mining, Technische Hochschule Georg Agricola University, Herner Str. 45, Bochum, Germany, ORCID 0000-0003-1729-9064

[2]University Münster, Institute for Geology and Paleontology, Corrensstr. 24, Münster, Germany, ORCID 0000-0003-2639-1225

[3]Federal Institute for Geosciences and Natural Resources, Stilleweg 2, Hanover, Germany, ORCID 0000-0002-7706-4235

Abstract

Hard coal mining ended in Germany in the Ruhr Area in December 2018. The cessation of mining activities and the associated changes in mine water management lead to a controlled mine water rebound. The geochemical composition of mine water is fundamentally influenced by sulfur cycling. Research results enable a deeper understanding of the sulfur and carbon cycles in mine water, and thus provide important information about ongoing biogeochemical processes in the now inaccessible underground mine workings. This in turn allows projecting expected biogeochemical changes into the future which is important for risk assessment.

Keywords: Ruhr Area, mine water, sulfate, methane, bacterial sulfate reduction, isotopic composition, iron sulfide oxidation

Introduction

The carbon and sulfur cycle in mine waters of shallow to deep mine workings in the Ruhr Area is mainly controlled by the presence of iron sulfide in hard coal deposits. Iron sulfide, mostly as pyrite, is oxidized under aerobic conditions in a complex hydrobiogeochemical process, often catalyzed by bacterial species such as *Acidithiobacillus ferrooxidans* and *Leptospirillum* sp.. Pyrite can be oxidized either by dissolved molecular oxygen (eq. [1]) or by ferric iron (eq. [2]; Singer & Stumm 1970). Oxygen in water ensures consistently high reaction rates (eq. [3]) as it accelerates the oxidation of ferrous iron (Fe^{2+}) to ferric iron (Fe^{3+}). This reaction may be catalyzed by microorganisms:

$$[1]\ FeS_2 + 3.5O_2 + H_2O \rightarrow Fe^{2+} + 2SO_4^{2-} + 2H^+$$

$$[2]\ FeS_2 + 14Fe^{3+} + 8H_2O \rightarrow 2SO_4^{2-} + 16H^+$$

$$[3]\ Fe^{2+} + 0.25O_2 + H^+ \rightarrow Fe^{3+} + 0.5H_2O$$

The sulfate formed during iron sulfide oxidation shows a diagnostic isotopic fingerprint because practically no fractionation occurs during oxidation. Therefore, the sulfur isotopic composition of the resulting dissolved sulfate reflects the signature of the original iron sulfide.

Bacterial sulfate reduction is an important process in which organic matter is mineralized under anaerobic conditions. Sulfate acts as an electron acceptor in this metabolic pathway. The following equation [4] illustrates organotrophic sulfate reduction, assuming a simple organic compound (CH_2O):

$$[4]\ SO_4^{2-} + 2\ CH_2O \rightarrow H_2S + 2\ HCO_3^-$$

Continued sulfate reduction leads to sulfate depletion if sulfate is not sufficiently replenished. The reaction product, hydrogen sulfide (H_2S), can precipitate as iron sulfide in the presence of reactive Fe^{2+}-species. Bacterial sulfate reduction is associated with a kinetic fractionation of the sulfur and oxygen isotopes of the dissolved sulfate. Bacteria preferentially use the lighter isotope. As a result, the reaction product (H_2S) is enriched in the lighter sulfur isotope ^{32}S, while the remaining dissolved sulfate becomes enriched in the heavier sulfur isotope ^{34}S. In natural environments, a sulfur isotope fractionation range of 20 ‰ to 40 ‰ is commonly observed between the sulfate and the resulting hydrogen sulfide during bacterial sulfate reduction (e.g., Canfield 2001). However, even larger fractionations have been observed (Sim *et al.* 2011).

In the presence of methane (CH_4), bacterial sulfate reduction can also be coupled to the anaerobic oxidation of methane (AOM, eq. [5]):

$$[5]\ CH_4 + SO_4^{2-} \rightarrow HCO_3^- + HS^- + H_2O$$

Terrestrial environments, especially in anaerobic groundwaters or mine waters, have been studied to a much lesser extent than marine environments (e.g. Banks & Boyce 2023, Dockins *et al.* 1980, Jakobsen & Postma 1994, Malik *et al.* 2023, Schulte *et al.* 1997). The goal of this project is to characterize the sulfur turnover using isotope analyses and to identify the influence of microbially controlled processes during the interaction between hard coal deposits and mine water.

Study area

The Carboniferous geology in the Ruhr Area is defined by hard coal-bearing strata that was formed in extensive swampy environments. These layers, rich in terrestrial plant material, were later buried (resulting in coal formation) and deformed by tectonic activity. Over time, they became unconformably overlain by Permian, Mesozoic and Cenozoic successions, reflecting a dynamic geological history of subsidence, sedimentation, and uplift. Today, Carboniferous rocks are only exposed in the southern part of the Ruhr Area. The strata are dipping to the northwest and mostly found beneath thick overburden.

Methods

Sampling

Since 2021, mine water was sampled every two months at nine different mine water pumping stations in the Ruhr Area (WA: Walsum, CO: Concordia, AM: Amalie, ZV: Zollverein, STI: Stinnes, CG: Carolinenglueck, RM: Robert Mueser, FN: Friedlicher Nachbar, HN: Heinrich). Due to the mine water rebound and the involved changes in mine water management, five mine water pumping locations were closed during 2022 and 2023. Therefore, only four locations (WA, HN, FN, RM) are being sampled since 2023.

***Figure 1** Mine water sampling locations since 2021 (yellow: until 2022/2023, red: ongoing).*

Isotope analysis

For sulfate sulfur and oxygen isotope analyses, dissolved sulfate was precipitated as barium sulfate at pH ≤ 2 and sub-boiling conditions using an 8.5% $BaCl_2$ solution following Dogramaci *et al.* (2001). Sulfur isotope measurements ($\delta^{34}S$) were performed in continuous-flow mode via EA-IRMS using a Flash EA Isolink elemental analyzer interfaced to a ThermoScientific Delta V Advantage isotope ratio mass spectrometer. Results are reported in the standard delta notation as per mil difference to the V-CDT standard. Reproducibility as determined through replicate measurements was generally better than 0.3 ‰. Analytical performance was monitored using international reference materials IAEA S1, S2, S3, NBS 127 and lab reference materials Ag_2S and CdS. Oxygen isotope measurements were carried out in continuous-flow mode using a high-temperature combustion unit (TC/EA) interfaced to a ThermoScientific Delta V Plus. Results are reported in the standard delta notation as per mil difference to V-SMOW. Reproducibility as determined through replicate measurements was generally better than 0.5 ‰. International reference materials IAEA SO-5, SO-6, NBS 127 and a lab $BaSO_4$ reference material were measured to monitor analytical performance.

Sulfide sulfur, stabilized during sampling with zinc acetate solution as zinc sulfide, was transferred to silver sulfide following Canfield *et al.* (1986). Sulfur isotope measurements were performed via EA-IRMS as described above. Results are reported in the standard delta notation ($\delta^{34}S$) as per mil difference to the Vienna Canyon Diablo Troilite (V-CDT) standard.

Carbon isotope signatures of methane were determined after injecting into a continuous flow GC-IRMS system (Agilent GC coupled to a Thermo Fisher Scientific MAT 253 via a GC-Combustion interface II/III). The different compounds were separated on a 25 m Porapak column and methane was combusted to CO_2 at a temperature of 960 °C. The reproducibility for $\delta^{13}C$ is ± 0.3‰. $^{13}C/^{12}C$ are presented in the standard δ-notation versus the reference standard V-PDB.

Compositional gas analysis

Sampling and analysis of dissolved hydrocarbon has followed the internal standard operation procedures. In short, 100 mL serum flasks were filled air-free, stabilized with 1 mL HCl (molarity 9 mol/L) and immediately crimped with Teflon-coated butyl-rubber seals. The dissolved gas concentrations were determined applying a headspace equilibration method as described in Schloemer *et al.* (2018). Hydrocarbon composition was determined by means of a Trace 1310 GC (Thermo Fischer Scientific, USA) equipped with a heated valve system and column switching. Pre-separation of hydrocarbons (C1 through C6) from a 500 µL sample was performed on a non-polar polysiloxane polymer column (Restek MX-1, 15 m, 0.28 mm ID, film thickness 3 µm). Molecular weight components >C7 were back-flushed. Full separation was performed on the main 50 m Al_2O_3 capillary column (0.32 mm ID, film thickness 5 µm). Both columns were operated non-isothermally. All components were detected on a Flame Ionization Detector (FID) with helium (He) as carrier gas. The quantification limit for dissolved methane is ~20 nL/L, with a duplicate error of ±10%. The ethane/propane quantification/detection limits are 10 nL/L and 3 nL/L, respectively.

Results and Discussion

The sampled locations show large differences in electrical conductivity (EC). The southern part of the Ruhr Area is characterised by a rather low EC with values between 2,000 µS/cm and 6,000 µS/cm (HN, FN, AM, RM) while medium EC values can be found at ZV and CG (19,500 µS/cm to 33,000 µS/cm). The highest conductivities have been measured at CO, WA and STI (63,800 µS/cm to 132,500 µS/cm).

The oxygen and sulfur isotopic composition of the dissolved sulfate (Figure 2) shows that each location has its characteristic isotopic signature. A positive correlation between $\delta^{18}O$ and $\delta^{34}S$ can be observed. This is indicative for the process of microbial sulfate reduction where microbes preferentially turn over the light sulfur and oxygen isotopes which results in an enrichment of the heavy

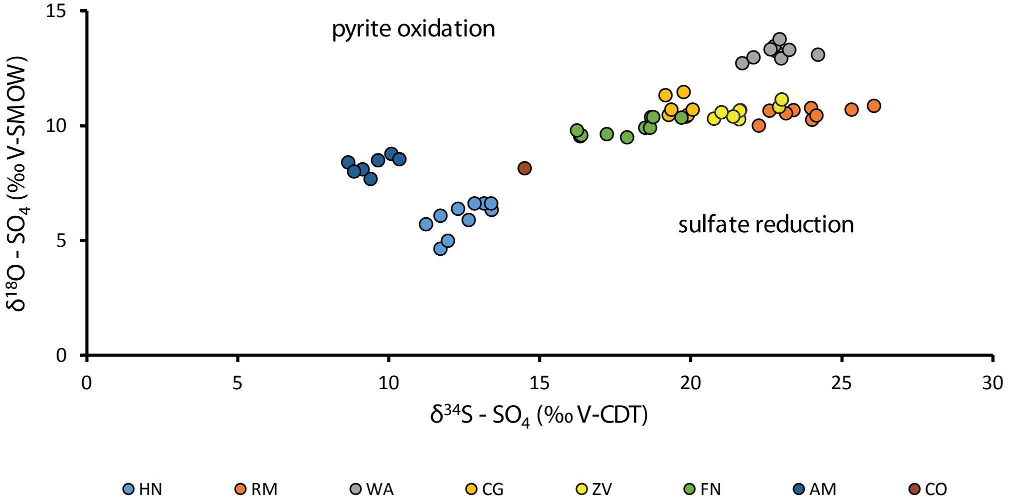

Figure 2 *δ^{18}O and δ^{34}S values of dissolved sulfate in mine waters from the Ruhr Area.*

sulfur and oxygen isotopes in the dissolved sulfate.

The sampled sites show different geochemical characteristics based on the geological history of the Ruhr Area. In the southern Ruhr Area, the Cretaceous overburden is either low or completely missing and allows the infiltration of meteoric waters into the underground mine workings (HN, FN, AM, RM). These locations are characterised by varying δ^{34}S values and relatively constant EC values. This can be interpreted as mine workings with a rather constant water source (Figure 3).

In the northwestern part of the Ruhr Area, the sampled mine waters (ZV, CG, CO, WA) have medium to high salinities (Figure 3). Here, the influence of lateral fluid flow or a contribution from deep-seated groundwater dominates the mine water composition. An aquitard in the overlying Cretaceous strata (Emscher Formation) of negligible to low thickness might limit the infiltration of meteoric waters locally. The saline, deep

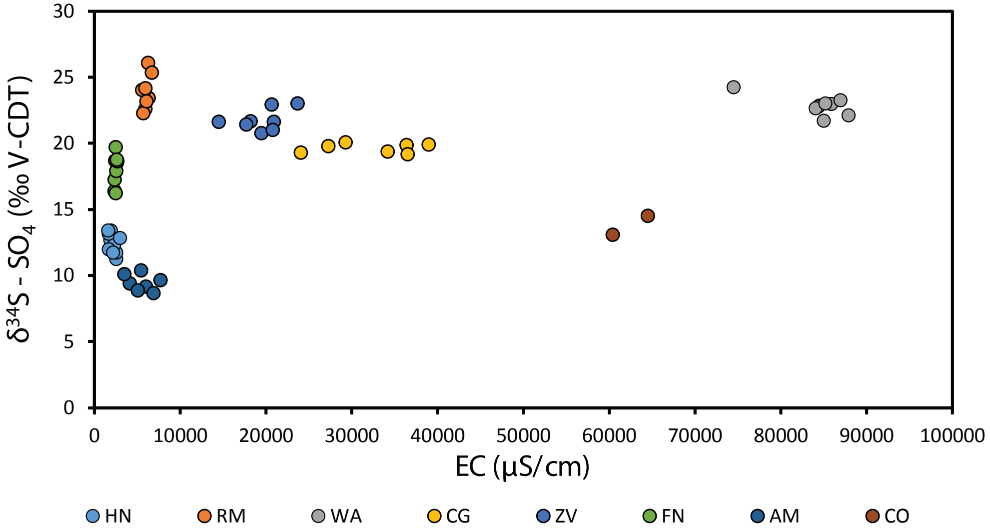

Figure 3 *Sulfur isotopic composition of sulfate versus electrical conductivity (EC) of mine waters.*

water mass is most probably derived from the dissolution of Permian evaporite deposits in the Lower Rhine region or from Cretaceous saline waters. Deep mine waters with high salt concentrations are found in many coal mining regions (e.g., England, Spain, Poland, China). Their origin is often unclear and remains a topic of discussion (Banks *et al.* 2020).

Geochemical characteristics of these saline mine waters is a variable EC, indicating changes in the composition of the supplied waters (Figure 3). The sulfur isotopic composition of the dissolved sulfate however shows no large variation. This indicates a rather homogenous sulfate source. Mainly high $\delta^{34}S$ values are typical for ongoing sulfate reduction.

The molecular as well as the isotopic composition of methane might provide some additional information on the main processes involving sulfate but also carbon in the mine waters of the Ruhr Area (Figure 4). Free methane, measured at combined heat and power plants (Teichert *et al.* in prep.), shows a mixture of microbial and thermogenic methane. Some of the sampled locations have an unambiguous microbial methane source. This observation has been previously made by Thielemann *et al.* (2004) and seems to be typical for the Ruhr Area. Some of the dissolved methane samples follow the same mixing trend as the free methane. However, most samples indicate a shift towards heavier $\delta^{13}C$ values with a consistent molecular composition (methane/ (ethane + propane)). This characteristic shift might be the result of anaerobe methane oxidation (AOM) where sulfate is bacterially reduced and methane anaerobically oxidized. While microbes preferentially oxidize the light carbon (^{12}C) isotope the remaining dissolved methane gets enriched in the heavier ^{13}C leading to increasingly heavier $\delta^{13}C$ values.

Conclusions

- If mine water contains oxygen through the infiltration of meteoric water (low EC), iron and sulfate are released through the process of iron sulfide oxidation. Iron will rapidly oxidize to FeOOH and may settle out. Sulfate has a typical light sulfur isotopic composition indicative of its origin from the oxidation of iron sulfide. This scenario can be observed at most sites in the southern Ruhr Area.

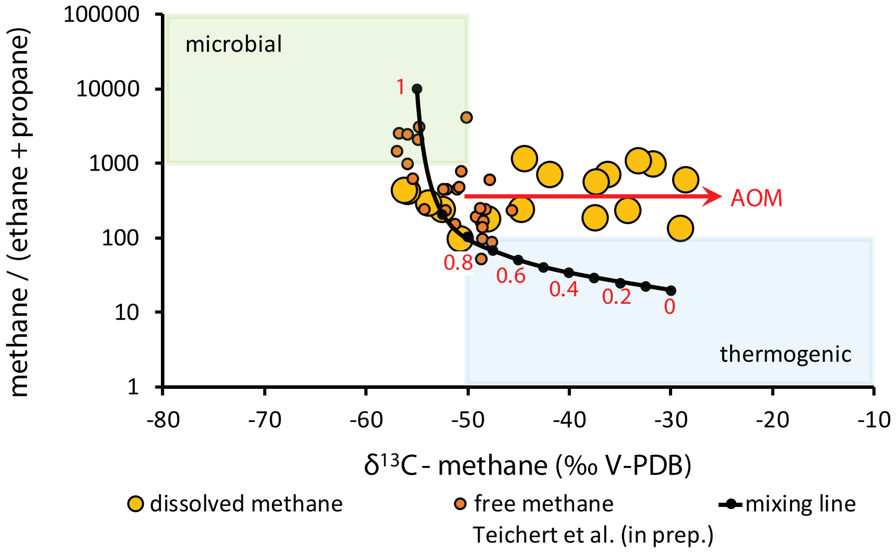

***Figure 4** Carbon isotopic composition of methane versus methane/(ethane + propane) ratio. The mixing line shows mixing between an assumed microbial (-55; 10,000) and thermogenic (-30; 20) methane endmember. Small, black circles show 10% intervals; red numbers give 20% intervals. Red arrow indicates direction of isotopic shift due to anaerobe methane oxidation (AOM).*

- Anoxic, highly saline mine waters derive their sulfate not only from the oxidation of iron sulfide but also from the dissolution of evaporites and/or fossil seawater. In deep, anoxic mine workings (with the exception of CO), the sulfate is bacterially reduced, resulting in the formation of hydrogen sulfide and isotopically enriched sulfur and oxygen isotope values of sulfate. This scenario can be observed at the sites in the northwestern Ruhr Area.
- At some locations (RM, FN) with a rather low EC and sulfate primarily derived from iron sulfide oxidation, there is indication for bacterial sulfate reduction.
- Abandoned mines which undergo mine water rebound and show bacterial sulfate reduction (with sulfate derived from iron sulfide oxidation), will experience a declining hydrogen sulfide production in the future due to declining sulfate concentrations over time.
- The molecular and isotopic composition of dissolved methane in the mine water supports ongoing microbial sulfate reduction combined with anaerobe methane oxidation.

Acknowledgments

The authors would like to thank L. Rose and T. Genth for help with water sampling. A. Fugmann is thanked for assistance in the laboratory (Univ. Münster) and T. Trieb (RAG AG) during mine water sampling. We greatly appreciate the support and discussion with the RAG AG as well as the financial support of this project. The authors thank two anonymous reviewers for providing critical comments which helped to strengthen this text.

References

Banks D, Boyce AJ (2023) Dissolved sulfate δ^{34}S and the origin of sulfate in coal mine waters; NE England. Quarterly Journal of Engineering Geology and Hydrogeology 56: 1–12.

Banks D, Boyce AJ, Burnside NM, Janson E, Roqueñi Gutierrez N (2020) On the common occurrence of sulphate with elevated δ^{34}S in European mine waters: Sulphides, evaporites or seawater? Int. Journal of Coal Geology, 103619: 1–18.

Canfield DE (2001) Biogeochemistry of Sulfur Isotopes. Reviews in Mineralogy and Geochemistry 43(1): 607–636.

Canfield DE, Raiswell R, Westrich JT, Reaves CM, Berner RA (1986) The use of chromium reduction in the analysis of reduced inorganic sulfur in sediments and shales. Chem. Geol. 54: 149–155.

Dockins WS, Olson GJ, McFeters GA, Turbak SC (1980) Dissimilatory bacterial sulfate reduction in Montana groundwaters. Geomicrobiology J. 2(1): 83–98.

Dogramaci SS, Herczeg AL, Schiff SL, Bone Y (2001) Controls on δ^{34}S and δ^{18}O of dissolved SO_4 in aquifers of the Murray Basin, Australia and their use as indicators of flow processes. Appl. Geochem. 16: 475–488.

Jakobsen R, Postma D (1994) In situ rates of sulfate reduction in an aquifer (Rømø, Denmark) and implications for the reactivity of organic matter. Geology 22: 1103–1106.

Malik C, Böttcher ME, Jenner A–K, Schmiedinger I, Löffler S (2023) Akkumulation von Sulfat und Karbonat in nordostdeutschen Grundwässern – Eine Multi-Isotopen-Analyse. Grundwasser 28: 331–344.

Schloemer S, Oest J, Illing CJ, Elbracht J, Blumenberg M (2018) Spatial distribution and temporal variation of methane, ethane and propane background levels in shallow aquifers – A case study from Lower Saxony (Germany). Journal of Hydrology: Regional Studies 19: 57–79.

Schulte U, Strauß H, Bergmann A, Obermann P (1997) Isotopenverhältnisse der Schwefel – und Kohlenstoffspezies aus Sedimenten und tiefen Grundwässern der Niederrheinischen Bucht. Grundwasser 3: 103–110.

Sim MS, Bosak T, Ono S (2011) Large sulfur isotope fractionation does not require disproportionation. Science 333(6038): 74–77.

Singer PC, Stumm W (1970) Acidic mine drainage: the rate-determing step. Science 167: 1121–1123.

Teichert *et al.* (in prep.) Abandoned mine methane – defining methane sources in the Ruhr area and Saarland, Germany. – to be submitted to International Journal of Coal Geology.

Thielemann Th, Cramer B, Schippers A (2004) Coalbed methane in the Ruhr Basin, Germany: a renewable energy resource? Organic chemistry 35: 1537–1549.