

Trace metal release induced by chemo-lithotrophic denitrification in deeper aquifers of the Lower Rhine Embayment, Germany

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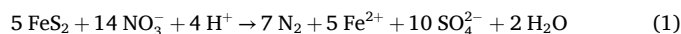
ABSTRACT

Chemo-lithotrophic denitrification is a crucial process that mitigates high nitrate fluxes in suboxic aquifers; however, it bears the risk of increasing sulfate and trace metal concentrations, which are generally attributed to the pyrite oxidation involved. To assess trace metal release induced by this reaction, we link mineralogical-geochemical analyses to hydrochemical data. As an example, we investigate an area in the Lower Rhine Embayment, a Cenozoic sedimentary basin that hosts important groundwater resources in Western Germany. Geochemical analysis reveals that pyrite in the sediments contains arsenic, cobalt, copper, nickel, and zinc. The trace metals show a highly heterogeneous distribution between pyrite grains but also within individual pyrites. Analysis of groundwater samples indicates that chemo-lithotrophic denitrification results in the release of the aforementioned elements, except for copper. Subsequent oxidation and precipitation of a large proportion of the released iron produces protons, which are partly buffered by carbonate dissolution. Carbonate dissolution may be an additional trace metals source, especially for zinc. At the same time, precipitated iron(oxyhydr)oxides act as a sink for trace metals, particularly arsenic. The study demonstrates that trace metal release induced by chemo-lithotrophic denitrification depends on the trace metal content of pyrites, the extent of pyrite oxidation, the abundance and composition of additional mineral phases (e.g., carbonates), and the sorption and cation exchange capacity of the aquifer sediment.

1. Introduction

Groundwater pollution with nitrate is a common problem worldwide (Abascal et al., 2022). High nitrate concentrations in groundwater mainly originate from the excessive use of nitrogen-containing fertilizers and manure, applied to maximize agricultural yields (Böhlke, 2002). Consequently, a vast body of scientific literature addresses nitrate attenuation in groundwater systems, for example, reviewed by Rivett et al. (2008). One of the main processes that decreases nitrate concentrations in groundwater systems is denitrification. It is a microbially mediated process in which nitrate is reduced stepwise to elemental nitrogen ($\text{NO}_3^- \rightarrow \text{NO}_2^- \rightarrow \text{NO} \rightarrow \text{N}_2\text{O} \rightarrow \text{N}_2$) (Jørgensen et al., 2009; Knowles, 1982; Korom, 1992; Rivett et al., 2008). These reduction steps require electrons, provided by a suitable electron donor. In natural aquifers, electron donors for denitrification include organic carbon and reduced sulfur compounds such as pyrite (FeS_2) (Appelo and Postma, 2005;

Korom, 1992; Rivett et al., 2008). In the latter case, nitrate is reduced by denitrifying microorganisms, while dissolutive pyrite oxidation supplies the electrons required for nitrate reduction and produces sulfate and ferrous iron. Kölle et al. (1983, 1985) first identified nitrate reduction coupled to pyrite oxidation in the Fuhrberg Feld aquifer (Germany). The stoichiometry of this so-called chemo-lithotrophic denitrification is described by (Appelo and Postma, 2005; Korom, 1992; Rivett et al., 2008):



The process of nitrate reduction coupled to pyrite oxidation was studied in different aquifers e.g., in the Netherlands (van Beek et al., 1989; Zhang et al., 2009, 2012), Denmark (Jessen et al., 2017; Jørgensen et al., 2009; Postma et al., 1991), Germany (Böttcher et al., 1990; Houben et al., 2021; Kölle et al., 1983, 1985), and North America (Böhlke et al., 2002; Tesoriero et al., 2000). It was found to be a key

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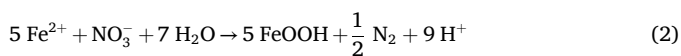
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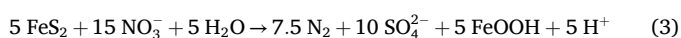
process for naturally lowering high nitrate concentrations in groundwater systems affected by intensive agriculture.

Most of the past studies focused on major groundwater hydrochemistry, isotopic signatures, and reaction pathways; only a few included trace metals in their analysis (e.g., Cremer, 2002; Cremer et al., 2003; van Beek et al., 1989; Zhang et al., 2009). On the other hand, a vast body of literature documents that natural pyrite is a sink for trace metals such as arsenic, cadmium, cobalt, nickel, and zinc (Abratis et al., 2004; Huerta-Diaz et al., 1998; Huerta-Diaz and Morse, 1992). Trace elements in pyrite can occur in several forms. They may be incorporated into the pyrite crystal lattice through substitution for Fe or S, may be adsorbed onto mineral surfaces, or be present as nano-to micro-scale inclusions of other sulfide minerals (e.g., ZnS) or native elements (e.g., Au) (e.g., Atienza et al., 2023; Deditius et al., 2011; Gregory et al., 2019, 2022; Large et al., 2009). During oxidative dissolution of pyrite, these trace elements can be mobilized as the mineral structure breaks down and mineral surfaces are progressively destroyed. In addition, sulfide inclusions may themselves undergo oxidation and thereby contribute to the release of associated trace metals. Consequently, nitrate-induced pyrite oxidation may effectively attenuate nitrate but bears the risk of releasing iron, sulfate, and pyrite-bound trace metals, eventually exceeding guideline values and recommended thresholds (Filter et al., 2024; Houben et al., 2017; Larsen and Postma, 1997; Riedel et al., 2022; Stuyfzand and Bonte, 2023; van Beek et al., 1989; Zhang et al., 2009). The European Union Drinking Water Directive currently specifies the following parametric values for the indicator parameters iron, and sulfate, as well as arsenic, cadmium, copper, and nickel, respectively: 0.2 mg/L, 250 mg/L, 10 µg/L, 5 µg/L, 2000 µg/L, and 20 µg/L. For example, van Beek et al. (1989) and Zhang et al. (2009), who both studied chemo-lithotrophic denitrification in sandy aquifers of the Netherlands, found nickel concentrations up to 600 µg/L (van Beek et al., 1989) and 200 µg/L (Zhang et al., 2009), respectively. Additionally, van Beek et al. (1989) reported a maximum arsenic concentration of 100 µg/L, while Zhang et al. (2009) observed zinc and cobalt concentrations up to 800 µg/L and 300 µg/L, respectively. Both examples highlight the potential role of chemo-lithotrophic denitrification for high trace metal concentrations in groundwater.

The fate of trace metals in groundwater systems strongly depends on geochemical and hydrochemical conditions such as redox state and pH. The pH-dependence of trace metal mobility is mainly attributed to the adsorption of trace metals on mineral surfaces, which restricts their mobility (Fest et al., 2005; Kjeller et al., 2004). Sorption of trace metals is known to be highly pH-dependent as variable-charged mineral surfaces become increasingly protonated at low pH, being feasible for anion adsorption, and deprotonate at higher pH, which favors the adsorption of cations (Appelo and Postma, 2005). The nitrate-induced oxidation of pyrite consumes protons, increasing pH and consequently increasing cationic trace metal adsorption. However, if pyrite oxidation does not consume the entire available nitrate, the released ferrous iron may also act as an electron donor for further nitrate reduction. In the pH range of natural groundwater, the resulting ferric iron undergoes hydrolysis and subsequently precipitates e.g., as iron(oxyhydr)oxides. This reaction can be expressed as (Appelo and Postma, 2005; Korom, 1992; Rivett et al., 2008):



Hydrolysis associated with this reaction releases protons, thereby decreasing pH. Combining equations (1) and (2) yields the following net reaction, which releases five protons:



While a decreasing pH favors the unspecific adsorption of anionic trace metal species such as arsenate, adsorption of cationic trace metal species such as Co^{2+} , Ni^{2+} , or Zn^{2+} is lowered. On the other hand, precipitation of iron(oxyhydr)oxides creates new adsorption sites,

which further restrict the mobility of anionic trace metals such as arsenate but may also counter the decrease in adsorption of cationic trace metals.

A pH decrease may be buffered by the dissolution of carbonate minerals, if present. Such a buffering is beneficial for the adsorption of cationic trace metals. For example, 20 % of total zinc is adsorbed onto ferrihydrite at pH 6, whereas rising the pH to 7 increases adsorption to about 80 % (Appelo and Postma, 2005). However, carbonate dissolution may also release trace metals that are adsorbed onto or incorporated within carbonate minerals (Cremer, 2002; Cremer et al., 2003).

If groundwater in a closed system is in equilibrium with respect to calcite, re-equilibration after acid addition will generally result in a pH lower than the initial value, causing a net release of cationic trace metals, either by desorption, as a direct release from trace metal containing carbonates, or both. In contrast, if groundwater is undersaturated with respect to calcite, carbonate dissolution occurs even without additional proton input, and increases alkalinity and pH until equilibrium is approached, potentially enhancing sorption of trace metals released during dissolution. Additional proton input to such calcite-undersaturated groundwater will intensify carbonate dissolution; however, the resulting change in pH and the net effect on trace metal mobility depends on groundwater composition as well as on the abundance, reactivity, and trace metal content of carbonate minerals. A quantitative assessment of these coupled processes is beyond the scope of this study.

All of these considerations highlight that assessing trace metal release from nitrate-induced pyrite oxidation, and the effects of potential secondary reactions, requires both an estimation of the potentially releasable trace metal inventory of pyrite and measurements of the trace metal concentrations actually occurring in groundwater. However, only a few studies have directly linked the trace metal inventory of pyrite-bearing sediments with trace metal concentrations observed in groundwater (e.g., Cremer, 2002; Cremer et al., 2003; Houben et al., 2017). Consequently, the extent to which pyrite oxidation associated with chemo-lithotrophic denitrification contributes to trace metal mobilization in groundwater systems, and the importance of subsequent reactions remain insufficiently constrained. To address this gap, we combine sediment geochemistry, trace metal analyses of individual pyrite crystals, and groundwater hydrochemistry to evaluate the potential for trace metal release during nitrate-driven pyrite oxidation and its manifestation in groundwater. The study focuses on a deeper aquifer within a multi-layer aquifer system affected by high nitrate influx, where nitrate reduction is coupled to oxidative pyrite dissolution (chemo-lithotrophic denitrification), potentially releasing pyrite-bound trace metals.

We hypothesize that nitrate-driven pyrite oxidation represents a relevant source of trace metals to groundwater in this aquifer. Specifically, we expect that (i) pyrite occurring in the aquifer sediments contains measurable contents of trace metals that can be mobilized during oxidation, and (ii) groundwater affected by nitrate reduction shows trace metal concentrations that are consistent with the trace metal inventory of pyrite.

To test this hypothesis, we (i) quantify sulfur and trace metal contents in aquifer sediments from two stratigraphic units using aqua regia digestion, (ii) determine trace metal contents in individual pyrite crystals by electron microprobe analysis to assess the trace metal inventory, (iii) analyze trace metal concentrations in groundwater from the affected aquifer, and (iv) compare the trace metal inventory of sediments and pyrite with groundwater concentrations to identify the geochemical processes controlling trace metal release and mobility following nitrate reduction.

2. Materials and methods

2.1. Study area

We investigated an area in the German federal state of North Rhine-Westphalia. Fig. 1a and b show the location of the study area. The area is part of the Lower Rhine Embayment (LRE), a Cenozoic rift basin. Its subsidence has begun during the Oligocene and has occurred along large, predominantly NW-SE-striking faults that divide the basin into tectonic blocks (Schäfer et al., 2004, 2005; Schäfer and Siehl, 2002). The study area is located on the Venlo Block.

The LRE is mainly filled with unconsolidated Cenozoic sediments. Marine conditions dominated during the Oligocene and Miocene, resulting in the deposition of marine sands and peats, which turned into lignite with burial. Regression of the North Sea since the Miocene-Pliocene transition shifted sedimentation towards predominantly fluvial and lacustrine environments (Klett et al., 2002; Prinz et al., 2017; Schäfer et al., 2004, 2005; Schäfer and Siehl, 2002; Schäfer and Utescher, 2014). Fig. 1c shows the hydrostratigraphic column relevant to this study based on DIN 21919-3 (2001).

This study focuses on two sedimentary units that represent contrasting depositional environments. The Miocene Neurath Sand (Horizon 6D, hereafter Hz. 6D) consists of marine sediments, whereas the Miocene/Pliocene Hauptkies Formation (Horizon 8, hereafter Hz. 8) comprises sands and gravels deposited in a fluvial system (Prinz et al., 2017; Schäfer et al., 2004, 2005; Schäfer and Utescher, 2014). Both units represent important aquifers in the Lower Rhine Embayment.

The sandy to gravelly sediments of the Hauptkies Formation (Hz. 8) exhibit a relatively high permeability. Because the clay layers of the Rotton Formation (Hz. 9) are only partly developed in the study area, the Hauptkies Formation is largely hydraulically connected to the overlying Middle and Lower Reuver Sands (Hz. 11B/10), together forming the local third aquifer (Hz. 11B–8). In contrast, the Neurath Sand (Hz. 6D) has a distinctly lower permeability and is therefore considered a separate aquifer. Fig. 1d and e show the subsurface structure of the study area along two cross sections.

Agricultural land use dominates within the study area and results in nitrate concentrations up to 200–300 mg/L in the first two aquifers, which are in an oxic state. Because deeper aquifers are under reducing conditions and are known to contain pyrite, which can provide electrons for denitrification, local water supply companies use deeper aquifers to extract nitrate-free groundwater. In the study area, the local third aquifer (Hz. 11B–8) is the most important one for groundwater extraction. Influx of nitrate into deeper aquifers happens through areas where confining units are missing, e.g., through river erosion, so-called hydraulic windows (Cremer, 2015; Cremer et al., 2003; Greven et al., 2019; Mäurer and Wisotzky, 2008; Meyer et al., 2018).

2.2. Sediment sampling and analysis

In this study, we analyzed sediment samples from three boreholes. From the first borehole, we obtained samples from the fluvial Hauptkies Formation (Hz. 8). From boreholes two and three, we collected samples from the marine Neurath Sand (Hz. 6D). Seven samples were taken from different depths from each borehole.

The location of borehole one is indicated in Fig. 1b. Drilling was performed in 2016 to 75 m below surface ordered by the public water supplier NEW NiederrheinWasser GmbH. During drilling, cored samples were obtained at different depths using the cone penetration technique. Using this technique, undisturbed sediment cores (1 m in length, 100 mm in diameter) were retrieved in transparent liners. To prevent pyrite oxidation, the liners were quickly capped in the field; liners that were not completely filled with sediment were purged with nitrogen before capping. The closed liners were then stored in gas-tight foil bags filled with nitrogen and frozen at -12°C to prevent further reactions. For this study, we selected samples from 68.3 to 74.6 m depth below

surface.

Boreholes two and three are horizontal boreholes, drilled by the mining company RWE Power at the open-pit mine Garzweiler II, located approximately 20 km south-east of the study area (see Fig. 1b). The boreholes were drilled horizontally 10 m deep into the mine slope section which was at the level of the Neurath Sand (Hz. 6D). Samples from every 0.2 m section were collected in small plastic round containers. The samples were also frozen at -12°C . For this study, we selected samples from the 7–10 m section of each of the two boreholes.

To prevent pyrite oxidation, we prepared the sediment samples for further analysis in a glove box filled with argon 5.0. First, the frozen sediment samples were thawed and dried. Then, the sediment was sieved through a 500 μm mesh.

From the sieved material, approximately 150 g aliquots were taken for aqua regia digestion. This digestion, involving a 1:3 ratio of concentrated nitric (9–10 M) and hydrochloric (11–12 M) acids, is a partial digestion method that dissolves metal sulfides, most sulfates, carbonates, phosphates, organically bound metals, gold, platinum, palladium, tellurides, selenides, and arsenides, while silicate minerals remain mostly untouched. The solution obtained from aqua regia digestion is analyzed for trace metal concentrations by inductively coupled plasma atomic emission spectroscopy (ICP-OES) and/or mass spectrometry (ICP-MS). For this study, aqua regia digestions and subsequent ICP-OES and ICP-MS analyses (Agilent ICP-OES 5110, Agilent ICP-MS 7900) were performed at the ALS Geochemistry geochemical laboratory (Ireland). At the laboratory, the 150 g aliquots were pulverized (85 % passing 75 μm). For aqua regia digestion, 0.5 g of the pulverized samples was used. The laboratory inserted its own geological quality control sample MRGeo08 for overall quality control as well as an aliquot of the certified reference material OREAS-46.

To gain deeper insights into minor to trace metal contents of individual pyrite grains, we applied electron microprobe analysis using a JEOL JXA-iSP100. Before analysis, five samples (two from Hz. 8 and three from Hz. 6D) were further separated with a magnetic separator (Frantz Isodynamic Separator). Pyrite was thereby accumulated in the diamagnetic fractions. These fractions were used to create polished thin sections for electron microprobe analysis at the ABC A Head thin section laboratory (Poland). After carbon coating, the samples were examined using backscattered electron (BSE) images. Element concentrations were determined applying an acceleration voltage of 15 kV, a probe current of 2.5×10^{-8} A, and using signals of S (K α), Fe (K α), Co (K α), Ni (K α), Cu (L α), Zn (L α), As (L α), Cd (L α), and Pb (M α). Quantification was based on calibration with certified reference materials of pyrite (S, Fe), metal cobalt (Co), nickeline (Ni), chalcocite (Cu), sphalerite (Zn), arsenopyrite (As), metal cadmium (Cd), and galena (Pb). Peak and background counting times were 60 and 30 s, respectively, for Co, Ni, Cu, Zn, As, Cd, Pb, and 20 and 10 s for S and Fe.

2.3. Groundwater sampling and analysis

We sampled a total of 29 observation wells, all screened within the third aquifer, composed of fluvial sediments from the Middle/Lower Reuver Sands and the Hauptkies Formation (Hz. 11B–8). The locations are shown in Fig. 1b. Before groundwater sampling, each well was purged until the volume of the stagnant water column had been replaced three times, and on-site parameters (especially electrical conductivity, pH, and temperature) stabilized. These parameters, along with the dissolved oxygen concentration and the redox potential Eh (calculated from field oxidation-reduction potential), were measured using electrodes (WTW-Xylem) installed in a closed flow-through cell. Observation wells with a diameter of 2" were purged using a Grundfos MP1 pump (Q ~15 L/min); wells larger than 2" in diameter were purged with a Grundfos SQ 3-65 pump (Q ~60 L/min). For groundwater sampling, we used a Grundfos MP1 pump along with PVC riser pipes in all observation wells.

For sampling, approximately 1 L of fresh groundwater was collected

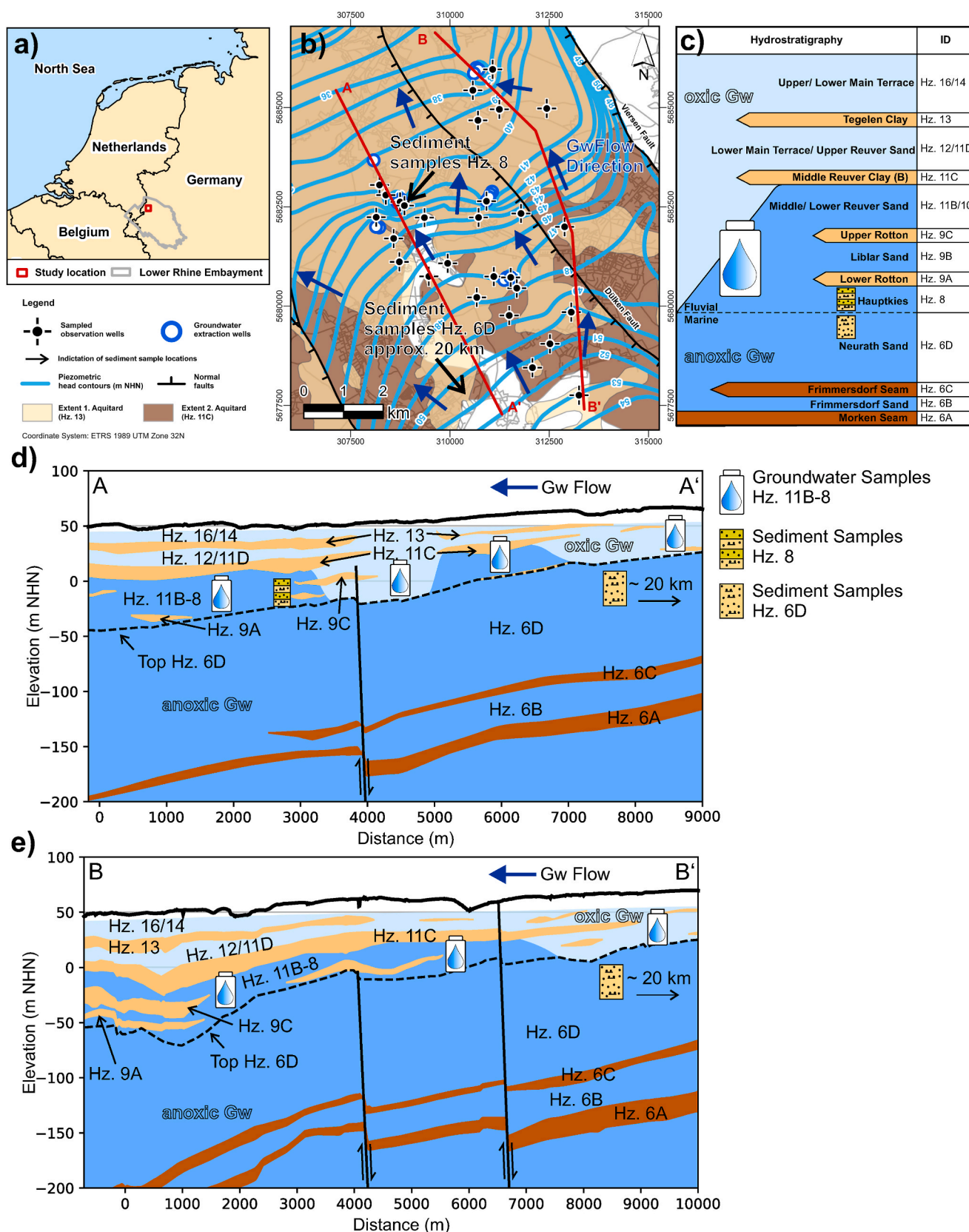


Fig. 1. a) Map of the study area, b) sampling locations, c) hydrostratigraphy, d) cross-section A-A', and e) cross-section B-B' (lightblue = oxic aquifers, darkblue = anoxic aquifers, light brown = aquitards, dark brown = lignite). Extent of the two aquitards according to the current geological model from the Geological Survey North Rhine-Westphalia (GD NRW, 2025). Hydrostratigraphy based on DIN 21919-3 (2001). Layer IDs according to Schneider and Thiele (1965). (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

through a bypass mounted to the riser pipes. The bypass included a flow-regulating valve, allowing groundwater sampling at a flow rate of 1–2 L/min. Aliquots for cation and dissolved trace metal analysis were filtered (0.45 µm) into 100 mL HDPE bottles in the field. The 100 mL HDPE bottles were prepared with 1 mL of 65 % nitric acid (suprapur) to ensure that the sample pH was <2. For anion analyses, unfiltered aliquots were collected in 500 mL HDPE bottles. For transportation, all samples were stored in a portable cooling box and then kept in a refrigerator at approximately 6 °C until further laboratory analysis at the Federal Institute for Geosciences and Natural Resources (BGR).

Major cation concentrations were measured using inductively coupled plasma – optical emission spectroscopy (ICP-OES; Spectro Arcos MV). Chloride, nitrate, and sulfate concentrations were determined through ion chromatography (Thermo Scientific Dionex ICS-5000+, Dionex IonPac AS19 column). Bicarbonate concentrations were analyzed via alkalinity titration (Mettler Toledo Titration Excellence T9). Dissolved trace metal concentrations were determined by inductively coupled plasma – mass spectrometry (quadrupole ICP-MS; Agilent 7900). Drift correction and quality control were maintained by using rhodium and bismuth as internal standards for every sample and by measuring an external standard (TMDA 62.2) every tenth to fifteenth sample.

The plausibility of the hydrochemical analyses was verified by calculating the ion balance. The relative errors for all samples are within ±2 %.

2.4. Hydrochemical calculations

To assess whether the ferrous iron released by chemo-lithotrophic denitrification is further oxidized by nitrate and precipitates according to equation (2), we calculated theoretical iron release concentrations. This calculation requires to distinguish excess sulfate, which is the sulfate resulting from pyrite oxidation, from other sulfate source such as fertilizer inputs or gypsum dissolution. In the LRE, under agricultural areas, sulfate and chloride typically leach into the groundwater at a fixed ratio. Analysis of time-series data from near-surface groundwater in the study area yields an average molar sulfate to chloride ratio of 0.74 ± 0.05 ($n = 56$, $\alpha = 0.05$). In a regional context, Cremer (2015) reports – from approximately 1000 pumping and observation wells – that this ratio is approximately 0.7 in the LRE, consistent with the locally derived value. Sulfate to chloride ratios exceeding 0.74 serve as an indicator of sulfate mobilization from the sediment due to the oxidation of pyrite. Pyrite oxidation can occur by either oxygen or nitrate reduction. Because we study deeper aquifers, where nitrate influx happens through hydraulic windows, oxygen concentrations are low compared to the inflowing nitrate concentrations, and pyrite oxidation by oxygen can be neglected. Furthermore, no gypsum is present in the studied sediments, eliminating the need to account for gypsum dissolution. Sulfate reduction following pyrite oxidation might reduce sulfate concentrations, which would lead to underestimates of excess sulfate. However, our hydrochemical data (e.g., Eh 120–484 mV) do not indicate sulfate reduction.

The molar concentration of iron released by chemo-lithotrophic denitrification [$Fe_{released}$] is calculated using molar sulfate [SO_4^{2-}] and chloride [Cl^-] concentrations as follows:

$$[Fe_{released}] = 0.5([SO_4^{2-}] - 0.74[Cl^-]) \quad (4)$$

The term in brackets indicates the amount of sulfate released during chemo-lithotrophic denitrification (excess sulfate). To verify this method for calculating excess sulfate, we compared it with a mass balance approach, using two groundwater samples located along a groundwater flow line. For the calculations the reader is referred to the Supplementary Material (SM1). Both methods yield similar results, confirming the validity of the chosen calculation approach.

The quantities of released iron are only determined for samples in

which the sulfate to chloride ratio suggests ongoing chemo-lithotrophic denitrification ($SO_4^{2-}/Cl^- > 0.74$). The amount of precipitated iron can be calculated by subtracting the observed iron from the released iron. This calculation is carried out only for samples where the released iron exceeds the observed iron.

We used the hydrogeochemical code PHREEQC (Version 3.7.3; Parkhurst and Appelo, 2013) to calculate total inorganic carbon (TIC), calcite saturation, and trace metal speciation in the groundwater samples. The “minteq.v4” thermodynamic database was employed for these calculations.

2.5. Statistical methods

We applied standard statistical measures (minimum, maximum, mean, median, etc.) to describe the distributions of the geochemical and hydrochemical data obtained. The data are presented using standard graphical methods (scatter plots, box-whisker plots). To assess correlations between two variables, we used the non-parametric Spearman's rank correlation coefficient; to compare two groups, we used the non-parametric Wilcoxon rank-sum test. Rank-based methods are usually more robust than their parametric alternatives (Helsel et al., 2020).

3. Results and discussion

3.1. Sediment geochemistry

3.1.1. Aqua regia digestion

Fig. 2 shows the measured total sulfur and iron contents for both geological formations – the fluvial Hauptkies Formation (Hz. 8) and the marine Neurath Sand (Hz. 6D). In both, total sulfur content strongly correlates with iron content. The data points lie parallel to the pyrite reference line, which is defined by the Fe:S₂ mass ratio of pure, stoichiometric pyrite (FeS₂), i.e. 55.85 g/mol Fe to 64.12 g/mol S₂. For Hz. 8, total sulfur content ranges from 0.26 wt-% to 3.0 wt-%, with a mean of 1.23 wt-% and a median of 0.71 wt-%. For Hz. 6D, contents range from 0.53 wt-% to 1.08 wt-%, with a mean and a median of 0.79 wt-%. Using pyrite stoichiometry, these values suggest iron contents between

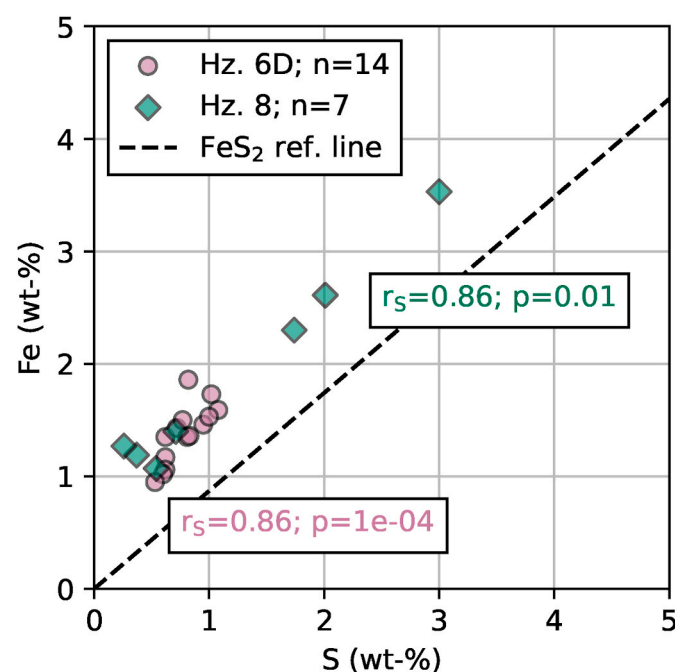


Fig. 2. Correlation between total sulfur and iron together against the pyrite reference line. r_s : Spearman's rank correlation coefficient, p : p-value for rank correlation.

0.23 wt-% and 2.61 wt-% for Hz. 8, and between 0.46 wt-% and 0.94 wt-% for Hz. 6D. The actual iron contents exceed these ranges, with minimum, mean, median, and maximum values of 1.07 wt-%, 1.91 wt-%, 1.4 wt-%, and 3.53 wt-%, respectively, for Hz. 8, and 0.95 wt-%, 1.38 wt-%, 1.40 wt-%, and 1.86 wt-%, respectively, for Hz. 6D.

The strong, significant correlation between total sulfur and iron contents, together with the fact that the data plot parallel to the pyrite reference line, indicates that iron(di)sulfides, such as pyrite, are the primary sulfur source. Both formations are known to contain pyrite. For example, Cremer (2002) and Meyer et al. (2018) determined a mean pyrite content of 0.14 wt-% and 0.2 wt-% as $\text{FeS}_2\text{-S}$, respectively, for the Hauptkies Formation (Hz. 8). The sediments of the Neurath Sand (Hz. 6D) have pyrite contents between 0.01 and 0.9 wt-% (Schulte et al., 1997), 0.01–1.1 wt-% (Friedrich et al., 1999), and 0.6–0.9 wt-% as $\text{FeS}_2\text{-S}$ (Cremer, 2002). Previous studies found that sulfur-free sediments of the LRE were also pyrite-free, and that, overall, total sulfur contents are in good agreement with pyritic sulfur contents (Cremer, 2002; Meyer et al., 2018; Schulte et al., 1997). Therefore, total sulfur is a suitable indicator for pyrite content in the studied sediments.

The samples from Hz. 8 exhibit a wider range of total sulfur and iron contents than the samples from Hz. 6D. Bulk geochemical analyses of sediment samples from the same borehole, carried out by Meyer et al. (2018), yielded considerably lower total sulfur and iron contents, with values ranging from 0.14 to 1.20 wt-% S and from 0.17 to 1.51 wt-% Fe, respectively (see Supplementary Material, Table S1). Cremer (2002) also reported conspicuously high sulfur values up to 2.2 wt-% in sediments from the Hauptkies Formation (Hz. 8) and attributed them to finer-grained sediment fractions. We therefore infer that the conspicuously high values do not represent the typical chemical composition of the Hauptkies Formation, but rather reflect a highly heterogeneous sediment composition. The difference between the two investigated formations may be attributed to their different depositional environments. While a high-energy, dynamic braided-river system deposited the sediments of the Hauptkies Formation (Hz. 8), the sediments of the Neurath Sand (Hz. 6D) represent shallow-marine deposits (Klett et al., 2002; Prinz et al., 2017; Utescher et al., 2002). Braided-river systems typically deposit sediments with highly variable and heterogeneous characteristics, whereas marine sediments generally show less compositional variation and are more homogeneous (e.g., Boggs, 2013).

Iron contents are higher than expected from the pyrite stoichiometry, indicating additional iron sources. In Hz. 8, excess iron accounts for 26–82 % of the total iron; in Hz. 6D, it contributes 41–61 %. In both formations, the mean contribution is about 50 %. Possible additional iron sources include iron(oxyhydr)oxides, e.g., as coatings on sand grains, and iron-containing carbonates, e.g., siderite or ferrous dolomite. The presence of both phases in the investigated aquifers was described by Cremer (2002) and Cremer et al. (2003). Especially iron(oxyhydr)oxides are known to be an additional source of trace metals.

Fig. 3 shows correlations between total sulfur and trace metal contents, grouped by geological unit. For the fluvial Hauptkies Formation (Hz. 8), no statistically significant correlation is found at a significance level of 0.05. However, Spearman's rank correlation coefficients for the correlations between total sulfur and nickel, and between total sulfur and arsenic, are relatively high, with corresponding p-values close to 0.05. For the marine Neurath Sand (Hz. 6D), total sulfur significantly correlates with all the trace metals considered.

Given that total sulfur is derived from pyrite, the significant correlations between total sulfur and trace metal contents, together with the small intercepts, indicate that trace metals in Hz. 6D are primarily bound to pyrite. In contrast, for Hz. 8, the non-significant correlations, together with large intercepts, suggest that a considerable proportion of trace metals are not pyrite-bound. Therefore, electron microprobe analyses were performed on individual pyrite grains to quantify the amount of trace metals potentially released by chemo-lithotrophic denitrification.

The results will be discussed in the following.

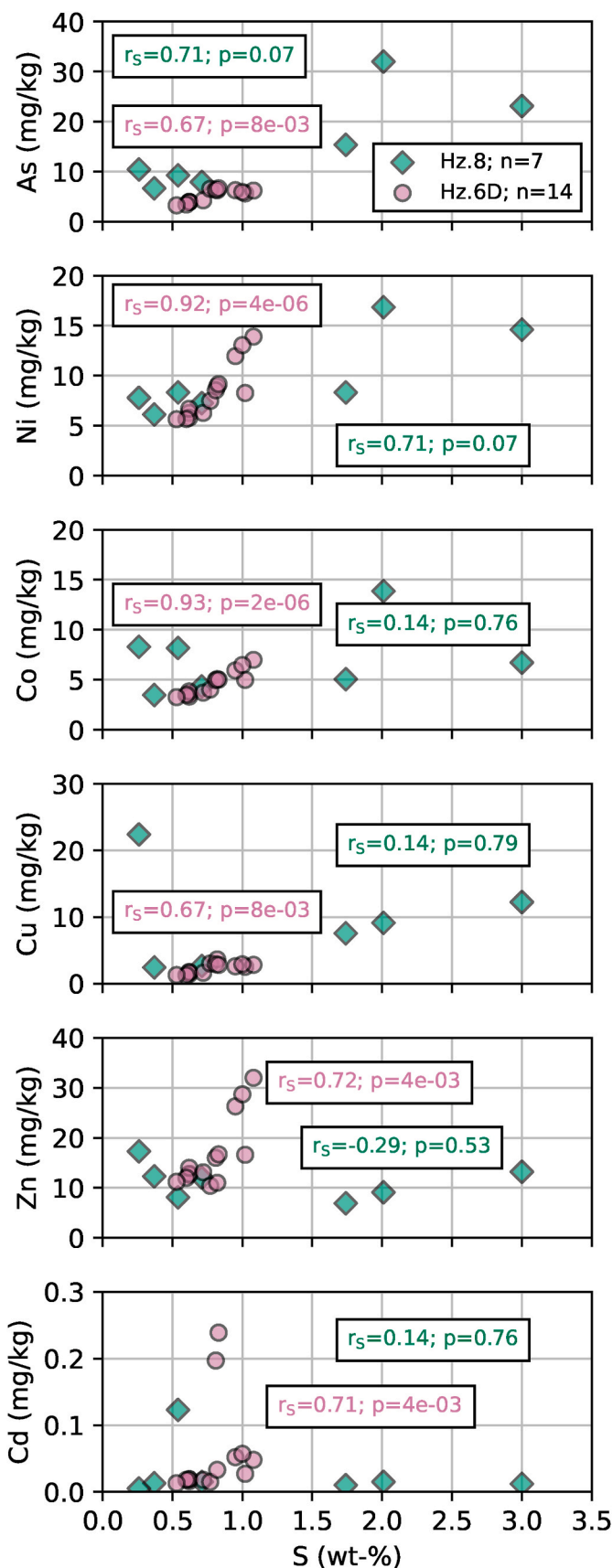


Fig. 3. Correlations between total sulfur and trace metals. r_s : Spearman's rank correlation coefficient, p : p-value for rank correlation. For Hz. 8, one of the measured Cu values is considered as an outlier ($\text{Cu} = 78 \text{ mg/kg}$, $\text{S} = 0.54 \text{ wt-%}$).

3.1.2. Electron microprobe analysis

Backscattered electron (BSE) images were used for a preliminary visual screening of pyrite grains. Those images show that in the fluvial Hauptkies Formation (Hz. 8), pyrite occurs in a variety of textures. We observed framboids as well as framboidal structures within individual, non-framboidal pyrite grains (see Fig. 4a and b). The latter represents a typical intermediate stage in the formation of euhedral pyrite recrystallizing from initially formed framboids. A framboidal core surrounded by an overgrowth of pyrite characterizes a so-called sunflower texture (Chang et al., 2022; Merinero et al., 2008, 2017; Sawlowicz, 1993; Schoonen, 2004). In our case, these overgrowths exhibit a layered texture and slight changes in the BSE grey scale that may reflect impurities.

In the marine Neurath Sand (Hz. 6D), pyrite grains are considerably smaller than those in Hz. 8. We also observed pyrite framboids and framboidal structures within individual pyrites (see Fig. 4c and d). However, the small grain size impedes textural analysis. Pyrites were frequently found attached to (see Fig. 4c) or embedded in silicates. Furthermore, we observed pyrite associated with titanium-containing domains (see Supplementary Material, Fig. S1). In these domains, titanium, iron, sulfur, and oxygen were detected. Friedrich et al. (1999) also observed these structures and described them as ilmenite exsolution lamellae that had been replaced by rutile. Within these structures, the magnetite proportion is fully or partially replaced by pyrite.

Based on the visual screening, pyrite grains were chosen for point measurements of elemental contents. The grains were selected to cover the full range of observed textures, grain sizes, and crystal morphologies. Within each category, individual pyrite grains were picked randomly. Overall, we analyzed 31 individual pyrite grains by electron microprobe, 15 from the fluvial Hauptkies Formation (Hz. 8) and 16 from the marine Neurath Sand (Hz. 6D). The small grain size of pyrite observed in Hz. 6D influences electron microprobe analysis because sub-crystals might be smaller than the electron beam's interaction volume. The existence of “empty” pore space between the sub-crystals thus negatively affects the yield of fluorescence radiation. In four cases, this resulted in total masses below 90 % (minimum 69.7 %).

Fig. 5 summarizes the trace metal contents of the pyrites measured. Statistical measures are provided in Tables S2 and S3 for Hz. 8 and Hz. 6D, respectively. Fig. 5, and Tables S2 and S3 are based only on values above the respective limit of quantification. As this approach leads to a bias to higher values, this study looks at a “worst-case” scenario.

Among the elements determined in pyrite, cadmium and lead are not further discussed as they fall almost entirely below the limits of quantification of the electron microprobe analysis.

The results of the aqua regia digestions indicate that the fluvial deposits of the Hauptkies Formation (Hz. 8) are more heterogeneous than the marine sediments of the Neurath Sand (Hz. 6D) in terms of total sulfur and iron, as well as trace metal content and the trace metal bounding forms. It therefore stands to reason that the pyrites in both formations also differ in their trace metal contents. Comparing the trace

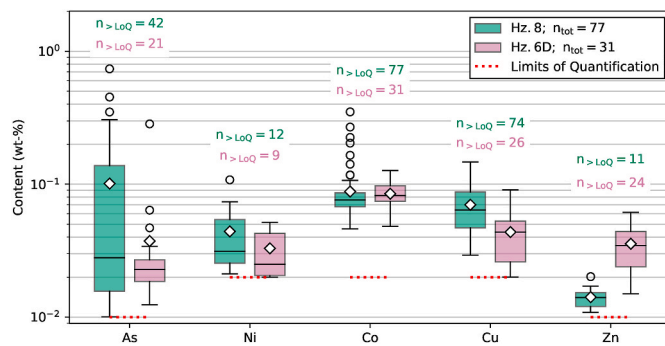


Fig. 5. Box-whisker plots of trace metal contents of pyrite measured by electron microprobe analysis. Only values above the respective limit of quantification are shown. The boxes extend from the 25th to the 75th percentiles; the whiskers extend from the box edges to 1.5 times the interquartile range. All data points outside the whiskers are considered outliers (shown as closed circles). The solid lines within the boxes indicate medians, whereas diamonds indicate means. n_{tot} : total number of point measurements, $n > \text{LoQ}$: number of point measurements above the limit of quantification.

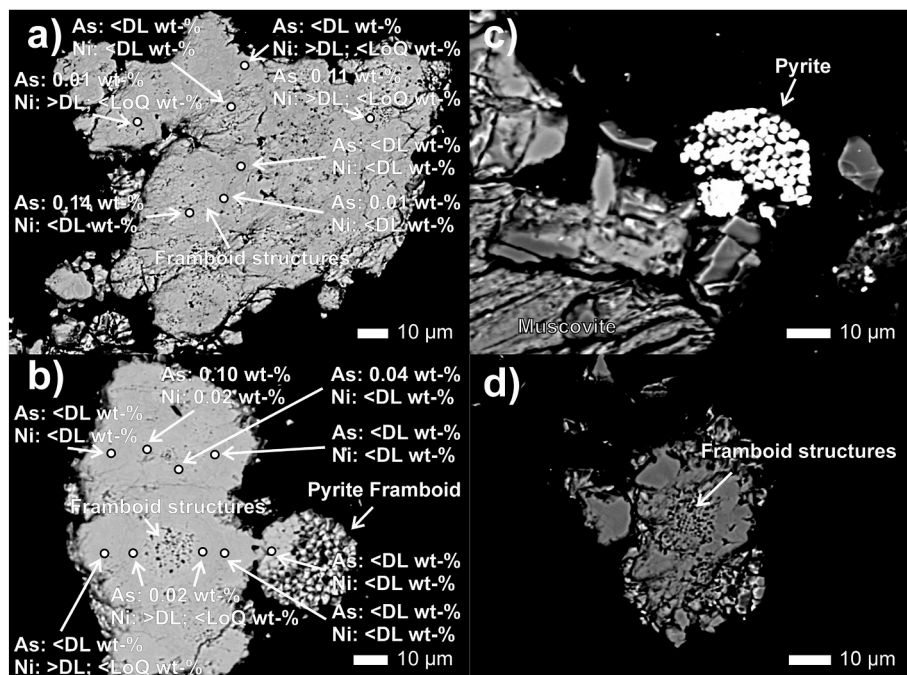


Fig. 4. Backscattered electron (BSE) images obtained from electron microprobe analysis. a) Pyrite with framboid structures, sunflower texture – sample from Hz. 8. b) Pyrite framboid and pyrite with framboid structures – sample from Hz. 8. c) Pyrite framboid attached to muscovite – sample from Hz. 6D. d) Framboidal structures within pyrite – sample from Hz. 6D. In panels a) and b), the results of point measurements are shown for arsenic (As) and nickel (Ni). DL: detection limit, LoQ: limit of quantification.

metal contents of both units reveals both similarities and differences. For arsenic, the median contents are similar; however, in Hz. 8, we observed a much greater spread, particularly toward higher values. The same holds for cobalt. The nickel and copper contents are of the same order of magnitude and show a similar spread in both formations; for both metals, the contents in Hz. 6D are only slightly lower than Hz. 8. The zinc contents of pyrite differ between the two formations with Hz. 6D showing higher contents. Overall, the depositional environment may influence pyrite formation and trace metal incorporation; however, our data indicate that such differences are less pronounced between the investigated marine and fluvial units than expected from the aqua regia digestions.

The observed nickel contents are in good agreement with the results published by Friedrich et al. (1999), who also studied trace metal contents of pyrite in the Neurath Sand (Hz. 6D). They reported arsenic values ranging from 0.1 wt-% to 0.38 wt-%, which are considerably higher than those found in the present study. However, the arsenic contents reported in the present study fall within the same range as those observed by Houben et al. (2017) for sedimentary pyrite from the Emsland (northern Germany). Friedrich et al. (1999) observed that cobalt, copper, and zinc contents were below the detection limits of 0.01 wt-%, 0.01 wt-%, and 0.06 wt-%, respectively. Houben et al. (2017) also conclude that cobalt, copper, and zinc are only minor constituents within the investigated pyrite. In contrast, Cremer (2002) and Cremer et al. (2003) found considerable amounts of cobalt and zinc incorporated in sulfide minerals, with cobalt contents sometimes even exceeding nickel contents. Their results are based on a sequential extraction technique applied to sediment columns, rather than on electron microprobe analysis of individual pyrite grains. For cobalt, our results are in good agreement with those reported by Cremer (2002) and Cremer et al. (2003), while the zinc contents observed by the aforementioned authors are higher than those found in our study. The zinc contents observed in the present study are mostly below the detection limit given by Friedrich et al. (1999). As far as we know, copper was not reported as a considerable trace metal incorporated in the pyrite of the Hauptkies Formation (Hz. 8) and Neurath Sand (Hz. 6D) so far. In our analysis, copper was almost consistently above the limit of quantification. Literature values for the copper content in pyrite, reviewed by Abraitis et al. (2004), range from 0.00025 wt-% to 4.52 wt-%.

Comparing the results of the aqua regia digestion with those from the electron microprobe is beneficial to assess if pyrite is the primary source of trace metals and to identify heterogeneity in the trace metal distribution in pyrite. However, a direct comparison is not possible due to the methodological differences of both methods. Therefore, the median trace metals contents of individual pyrites (electron microprobe) were used to calculate theoretical, pyrite-bound trace metal contents corresponding to the sulfur contents obtained with the aqua regia digestion. This calculation is based on the assumption that all sulfur is present in form of pyrite-sulfur. The reader is referred to the [Supplementary Material \(SM2\)](#) for details about the calculation. A graphical comparison is shown in [Fig. S2](#). If the trace metal contents resulting from aqua regia digestion are in good agreement with those calculated from pyrite composition, pyrite is likely the primary trace metal source. This is approximately true for the arsenic contents found in the marine sediments (Hz. 6D) and the nickel contents found in the fluvial sediments (Hz. 8). If the aqua regia digestion results systematically exceed the values calculated from pyrite composition, further trace metal sources are likely to exist in the samples. This kind of deviation can be seen for arsenic (Hz. 8), nickel (Hz. 6D), and Zn (Hz. 8 and Hz. 6D). In both units, the calculated values for cobalt and copper exceed those resulting from aqua regia digestions. This indicates that the trace metals distribution in pyrite is highly heterogeneous, because besides the pyrites measured with the electron microprobe, which contain relatively high cobalt and copper contents, pyrites with low trace metal contents have to exist to explain the results of the aqua regia digestions.

In samples from the fluvial Hauptkies Formation (Hz. 8), we

observed a spatial zonation in the trace metal content. While arsenic and nickel were detectable near the framboidal cores, they were below detection limits at the edges of these pyrite grains (see [Fig. 4a](#) and [b](#)). This suggests that arsenic and nickel might be excluded from the pyrite crystal lattice during recrystallization or that geochemical conditions changed after the formation of the initial framboids. Gregory et al. (2022) also observed this kind of trace metal zonation. They found that the initially, quickly formed framboids are surrounded by a rim of pyrite that had formed during early diagenesis and is enriched in trace metals. During early diagenesis trace metal desorption from organic matter and/or further minerals such as iron oxides releases trace metals into the pore water solution. These metals are then included in pyrite surrounding the framboidal core. This observation has substantial implications because, in this case, trace metal release from pyrite oxidation depends on the extent of oxidation. Only small amounts would be released during the early stages of pyrite oxidation, whereas higher amounts would be released once the oxidation front within individual crystals reaches the framboidal cores. Oxidation may then be intensified because the framboidal structures have a higher specific surface area and are therefore more prone to oxidation.

3.2. Groundwater chemistry

[Fig. 6](#) illustrates the relationships between excess sulfate and trace metal concentrations in groundwater samples of the third aquifer, composed of fluvial sediments from the Middle/Lower Reuver Sands and the Hauptkies Formation (Hz. 11B–8). The figure also shows the trace metal concentrations expected for pyrite oxidation, assuming a pyrite composition defined by the median trace metal contents of Hz. 8. [Table S4](#) provides relevant statistical measures. Since trace metal mobility depends on pH, [Fig. 7](#) shows the correlations between pH and trace metal concentrations. [Table S4](#), [Fig. 6](#) and [Fig. 7](#) are based only on values above the respective limit of quantification. This approach introduces a bias toward higher values, which may influence correlation results.

For all trace metals except zinc the correlations between excess sulfate and trace metal concentrations are not statistically significant. However, for nickel, cobalt, arsenic, and zinc a tendency towards higher trace metal concentrations with increasing excess sulfate can be inferred. Arsenic, cobalt and copper concentrations are mostly below the concentrations expected from pyrite composition. For nickel the data points distribute above and below the expected concentrations, with a slight tendency towards values above the expected concentrations. The observed zinc concentrations are clearly above the concentrations expected from pyrite composition.

The calculation results of trace metal speciation are shown in the [Supplementary Material](#) (see [Fig. S3–S8](#)). Arsenic dominantly appears in its anionic oxidized state as H_2AsO_4^- and HAsO_4^{2-} in all samples, except one where the neutral reduced H_3AsO_3 species is dominant. The other trace metals are primarily present in their divalent cationic forms (M^{2+}). In some samples, the CuCO_3 -complex has to be considered.

The wide range of observed excess sulfate indicates that a variety of groundwater compositions were sampled, from samples showing no evidence of pyrite oxidation to those with strong indications of it. Based on previous studies (Cremer et al., 2003; Greven et al., 2019; Mäurer and Wisotzky, 2008; Meyer et al., 2018), pyrite oxidation primarily results from chemo-lithotrophic denitrification in the studied area. Consequently, an increase in trace metal concentrations accompanied with an increase of excess sulfate, as it can be inferred for arsenic, nickel, cobalt, and zinc, indicate that chemo-lithotrophic denitrification releases these metals into groundwater. This observation is consistent with the findings of the sediment analysis, which showed that pyrites contain the aforementioned trace metals. We also found that copper is consistently present in the pyrite. In contrast, the hydrochemical data do not indicate a significant release of copper through chemo-lithotrophic denitrification. Consistent with the low cadmium contents measured in the

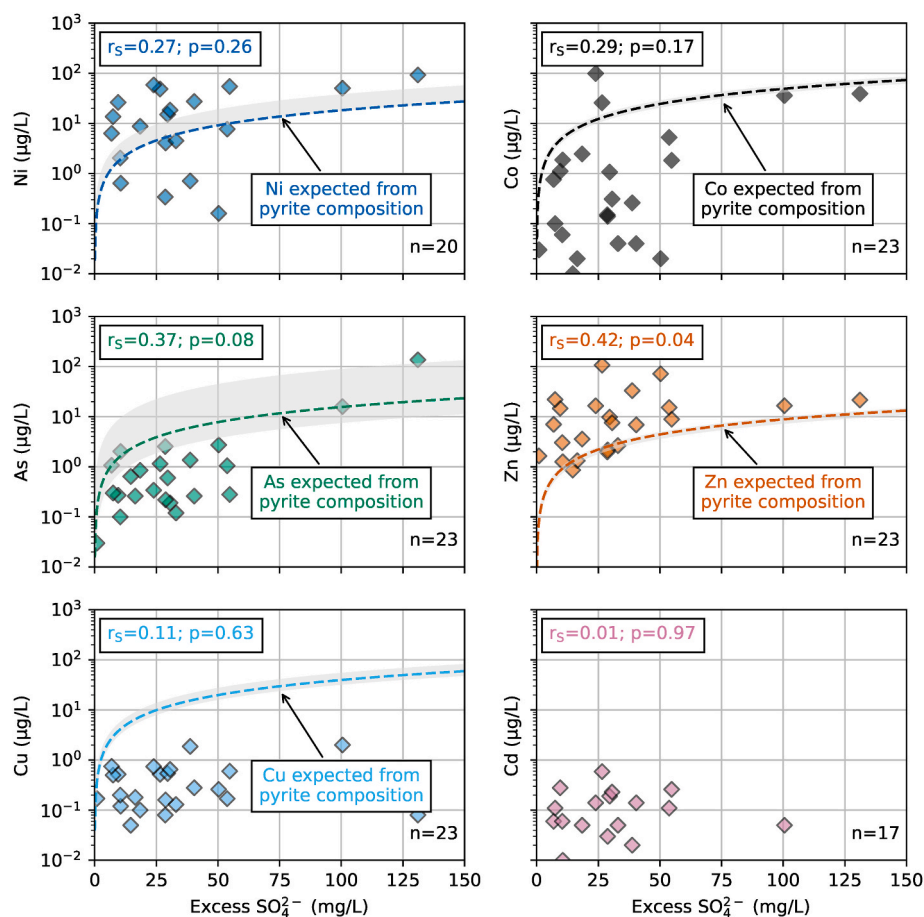


Fig. 6. Correlations between excess sulfate and trace metal concentrations in groundwater samples of Hz. 11B–8. Only values above the respective limit of quantification are shown. The dashed line represents the trace metal concentrations expected from pyrite oxidation, assuming trace metal to sulfur ratios equal to the median ratios measured in pyrites from Hz. 8. The grey band denotes the uncertainty in these predictions, spanning the range defined by the 1st and 3rd quartiles of the trace metal to sulfur ratios. r_s : Spearman's rank correlation coefficient, p : p-value for rank correlation.

investigated pyrite, no relationship between excess sulfate and cadmium concentrations is present.

For all trace metals there is negative correlation between pH and trace metal concentration, which is statistically significant at a confidence level of 0.05, except for cadmium. Because excess sulfate also shows a significant negative correlation with pH (see Supplementary Material, Fig. S9), we infer that chemo-lithotrophic denitrification lowers pH. While the nitrate-induced oxidation of pyrite consumes protons (see eqn. (1)), the subsequent oxidation, hydrolysis, and precipitation of the released ferrous iron releases protons (see eqn. (2)), resulting in a net production of one proton per mole pyrite oxidized or 0.33 mol per mole nitrate reduced (see eqn. (3)), if most of the released ferrous iron is oxidized. In Fig. 8, the observed iron concentrations are shown against the theoretical iron concentrations released by chemo-lithotrophic denitrification (according to eqn. (4)). For most samples, the calculated released iron concentration is higher than the observed concentrations, indicating a large portion of the released iron precipitates. Four samples are in good agreement with the 1:1 line, whereas in one sample the observed iron concentration exceeds the calculated released concentration. On average, 90 % of the released iron must have precipitated. These data indicate that chemo-lithotrophic denitrification leads to the release of protons.

Freshly precipitated iron(oxyhydr)oxides might form a sink for the released trace metals. However, the sorption of trace metals is highly pH-dependent. Because all trace metals, except arsenic, dominantly appear in their cationic form, sorption of these metals is expected to decrease with decreasing pH, as the variable-charged mineral surface

become more protonated, and the positively charged surfaces repel cations. This behavior is reflected in the negative correlations between pH and concentrations of the cationic trace metals (Ni, Co, Zn, Cu, Cd). For arsenic, dominantly appearing as oxyanion (H_2AsO_4^- or HAsO_4^{2-}), an opposite pattern would be expected, because when mineral surfaces become more protonated, a higher attraction of the oxyanions will occur. The observed negative correlation between pH and arsenic concentrations does not match this behavior. However, the correlation is strongly influenced by the samples at the distribution tails, while a plateau with relatively low arsenic concentrations (approximately 0.01–1 μg/L) for the pH range from 5.1 to 7 can be inferred. Most samples fall within this range. The correlation between excess sulfate and pH, suggest an increasing pyrite oxidation, and consequently an increasing trace metal release in this range. Because arsenic concentrations remain relatively stable in this range, we infer that sorption on iron(oxyhydr)oxides generally limits arsenic to concentrations approximately between 0.1 and 1 μg/L. Because pyrite samples from Hz. 8 show a wide range of arsenic contents, the high arsenic concentrations in groundwater samples might be linked to areas where pyrite with high arsenic contents predominates.

Because the observed pH values do not drop below 5, carbonate dissolution likely provides partial buffering, while all samples remain undersaturated with respect to calcite. Yet, the calcite content of the sediments is low. Schulte et al. (1997) reported a typical content of 0.04 wt-% total inorganic carbon (TIC) for Hz. 6 sediments, and Wisotzky and Obermann (2001) discussed a mean of 0.01 wt-% TIC for tertiary sediments in the LRE. Fig. 9 shows calculated precipitated iron

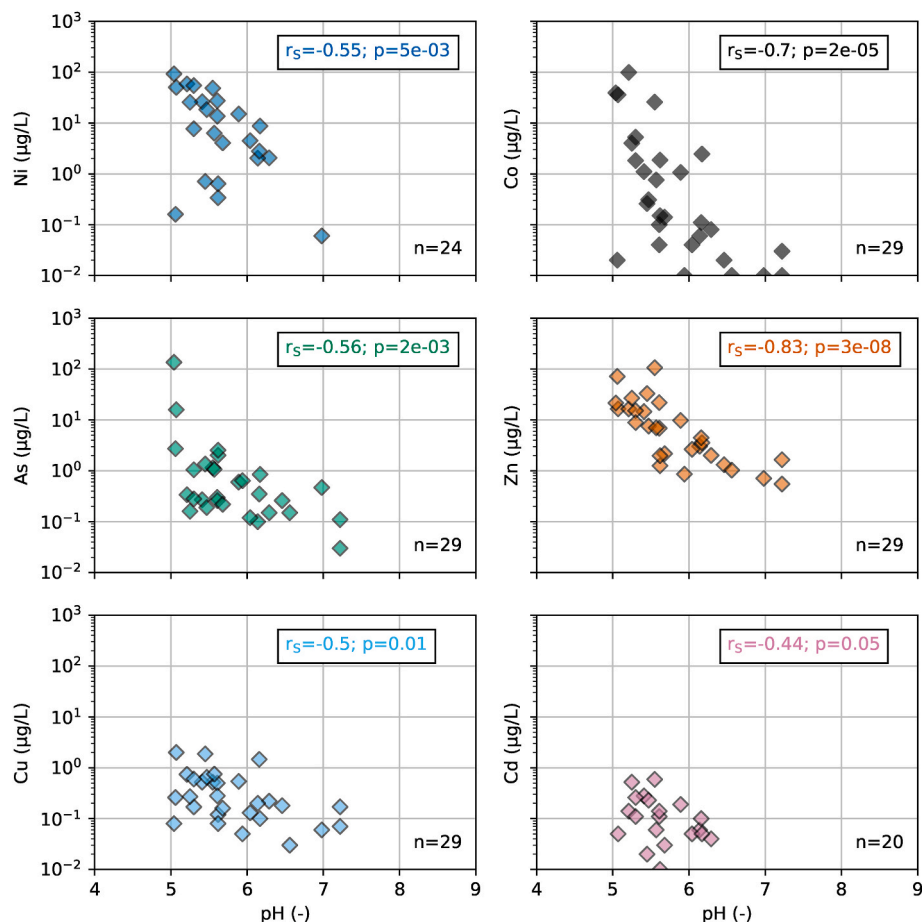


Fig. 7. Correlations between pH and trace metal concentrations in groundwater samples of Hz. 11B–8. Only values above the respective limit of quantification are shown. r_s : Spearman's rank correlation coefficient, p : p-value for rank correlation.

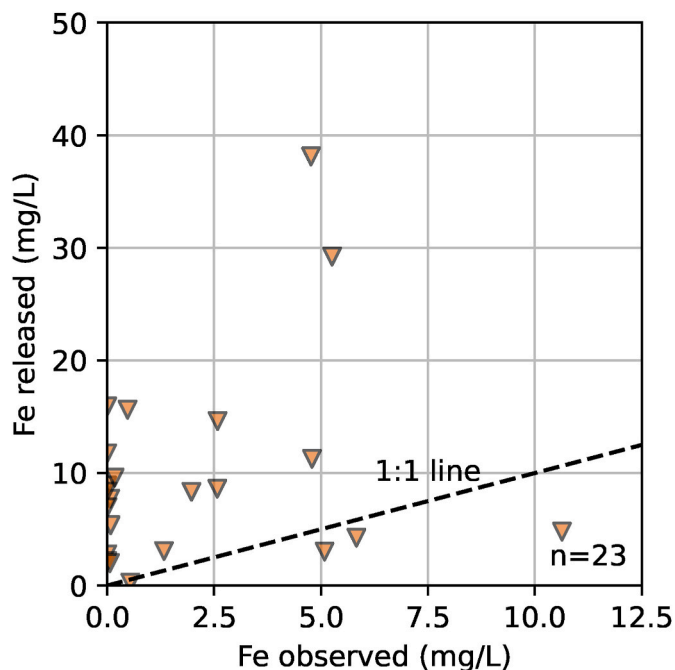


Fig. 8. Scatter plot of observed iron concentrations and theoretical iron concentrations released by complete chemo-lithotrophic denitrification according to eqn. (3) in groundwater samples of Hz. 11B–8. Only samples showing an indication of pyrite oxidation are shown.

concentrations against pH, calcium corrected for alkalinity, and alkalinity concentrations. While the correlation between precipitated iron and corrected calcium shows a strong and significant positive relationship, alkalinity remains approximately constant. This behavior is related to the pH range of the samples (~ 5 – 6), in which dissolved inorganic carbon is dominated by H_2CO_3^* ($\text{CO}_{2(\text{aq})} + \text{H}_2\text{CO}_3$). Under these acidic conditions, bicarbonate produced during carbonate buffering is readily protonated to H_2CO_3^* , so that alkalinity does not accumulate despite ongoing carbonate dissolution. The total inorganic carbon (TIC) show a general trend towards higher values with increasing iron precipitation, however, TIC is not solely influenced by carbonate dissolution. Therefore, the increase in corrected calcium concentrations is a better proxy for carbonate dissolution. Using an exemplary sample pair, which is well aligned on a groundwater flow line and shows little dispersive influences, the proton production from denitrification was compared with the proton consumption of carbonate dissolution (see Supplementary Material, SM3). Because proton production and consumption approximately balance, carbonate buffering triggered by iron precipitation is very likely. Cremer et al. (2003) observed the same effect within the Hauptkies Formation (Hz. 8) and Neurath Sand (Hz. 6D).

3.3. Comparison of sediment and groundwater chemistry

If pyrite is the sole source of trace metals and sulfur, and both would not be affected by subsequent reactions such as sorption or precipitation after their release, trace metal to sulfur ratios in groundwater should mimic those of pyrite. In natural systems, however, additional sulfur sources commonly contribute to groundwater sulfate, and subsequent reduction of sulfate released during pyrite oxidation might occur. To

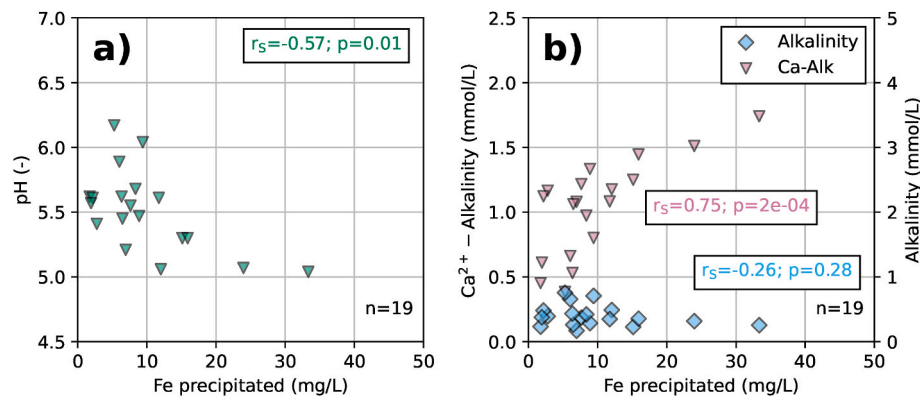


Fig. 9. Correlations between a) theoretically precipitated iron and pH. b) theoretically precipitated iron and observed calcium minus alkalinity, alkalinity in groundwater samples of Hz. 11B–8. Only samples showing indications of pyrite oxidation and iron precipitation are shown. r_s : Spearman's rank correlation coefficient, p : p-value for rank correlation.

enable a meaningful comparison between pyrite and groundwater, we calculated trace metal to sulfur ratios for the groundwater samples using only the excess sulfate fraction (as defined by the term in brackets in eqn. (3)). Because our groundwater samples do not show any indications of sulfate reduction, the calculated excess sulfate equals the sulfate released from pyrite oxidation. In cases where sulfate reduction occurs and parts of the released sulfate are reduced, the sum of excess sulfate and other dissolved sulfur components such as H_2S or HS^- could be a good estimator for sulfate released from pyrite oxidation. If these “corrected” trace metal to sulfur ratios of groundwater samples are compared with the ratios of pyrite crystals, any differences between the ratios, may indicate that the assumption that pyrite is the sole trace metal source and no subsequent reactions occur is not valid. Fig. 10 compares the trace metal to sulfur ratios in individual pyrites from the fluvial Hauptkies Formation (Hz. 8) with those in groundwater samples.

For arsenic, cobalt, and copper, the trace metal to sulfur ratios in the groundwater samples are significantly lower than those in the sediment samples ($p < 0.05$). This indicates that subsequent processes, such as sorption or co-precipitation, may lower trace metal concentrations in groundwater. Precipitation of iron(oxyhydr)oxides is evident from the groundwater samples, and also from the aqua regia digestions. Furthermore, iron(oxyhydr)oxides precipitation might encapsulate partially oxidized pyrite grains, preventing further oxidation before the oxidation front reaches zones of higher trace metal contents within individual grains.

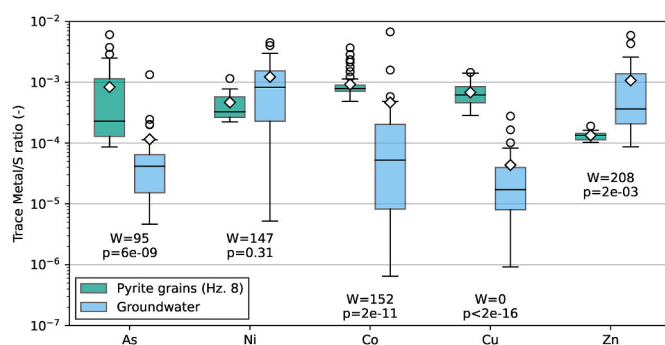


Fig. 10. Box-whisker plots of trace metal to sulfur ratios of sediment (Hz. 8) and groundwater samples (Hz. 11B–8). For the groundwater samples, only excess sulfate, released by pyrite oxidation, is used. Only values above the respective limit of quantification are shown. The boxes extend from the 25th to the 75th percentiles; the whiskers extend from the box ends to a distance of 1.5 times the interquartile range. All data points outside the whiskers are considered outliers (closed circles). The medians are shown as solid lines within the boxes; the diamonds indicate the means. W: test statistic from the Wilcoxon test, p: p-value from the Wilcoxon test.

Arsenic primarily occurs in its oxidized, negatively charged species, which sorb strongly on iron(oxyhydr)oxides under the observed pH conditions. Consequently, arsenic transport after release is likely affected by subsequent sorption processes, explaining the lower arsenic to sulfur ratios observed in groundwater samples. In contrast, cobalt and copper appear in their cationic forms. In particular, cobalt is less sorptive under the observed pH conditions, which may be reflected in the large spread of cobalt to sulfur ratios in the groundwater samples and the outliers toward higher ratios. This large spread might also be the result of a heterogeneous distribution of cobalt between and within pyrite grains, as indicated by the deviation of sediment cobalt contents calculated from pyrite composition and those actually observed by the aqua regia digestions (see section 3.1.2, and Fig. S2).

For nickel, the differences in ratios between groundwater samples and pyrite grains are not statistically significant ($p > 0.05$), indicating that pyrite could be the primary source of nickel, and that after its release the transport of nickel is not affected by subsequent process such as sorption. This interpretation is consistent with the observed pH values. Most samples fall in a pH range from 5 to 6; according to the ferrihydrite database established by Dzombak and Morel (1990), adsorption of nickel on ferrihydrite is $<20\%$ in this pH range. However, the spread of nickel to sulfur ratios in groundwater samples is larger than the ratios found in pyrite. This might be linked to a variable nickel distribution in pyrites or other secondary nickel sources, as indicated by the aqua regia digestions for Hz. 8.

The significantly ($p < 0.05$) elevated zinc to sulfur ratios in the groundwater samples compared to pyrite grains indicate an additional source of zinc besides pyrite. The findings of the aqua regia digestions also support this interpretation because no relationship between zinc and total sulfur was found for Hz. 8. Furthermore, the zinc contents from the aqua regia digestion exceed those predicted from pyrite compositions. As discussed above, carbonate dissolution buffers pH. Several authors have shown that carbonate minerals can incorporate zinc into their crystal lattice (Lamble et al., 1997; Reeder et al., 1999; Temmam et al., 2000). Therefore, carbonate minerals may be a source of zinc because their dissolution directly releases zinc that is adsorbed onto or incorporated within the mineral, while simultaneously buffering the pH decrease caused by proton release during iron precipitation after chemo-lithotrophic denitrification, which is beneficial for cationic trace metal sorption.

Cremer (2002) and Cremer et al. (2003) found that the carbonates present within the Hauptkies Formation (Hz. 8) and Neurath Sand (Hz. 6D) contain considerable amounts of nickel, cobalt, and zinc. Through geochemical modeling for Hz. 6D, they concluded that pyrite oxidation explains 50 % of the observed nickel concentrations (up to 200 $\mu\text{g/L}$), and 60–90 % of the observed cobalt concentrations (up to 170 $\mu\text{g/L}$), while the remaining percentages originate from the dissolution of trace

metal-containing carbonate phases. In contrast, our data suggest that nickel and cobalt concentrations in Hz. 8 may entirely result from pyrite oxidation. Combining the zinc content in carbonates from Hz. 8, provided by Cremer (2002), which is approximately 0.03 mol zinc per mol carbonate, with an estimated amount of carbonate required to buffer pH allows an estimation of the amount of zinc released through the buffering reaction. Following this approach, the resulting zinc concentrations are much greater than those observed in the groundwater samples. Consequently, we infer that some of the released zinc is also adsorbed.

4. Conclusions

Identifying, understanding, and quantifying relevant geochemical reactions and their effects on the groundwater quality of aquifers used for water supply is highly relevant. In this study, we evaluated whether nitrate-driven pyrite oxidation represents a relevant source of trace metals to groundwater by linking the trace metal inventory of pyrite-bearing sediments with groundwater hydrochemistry.

Pyrite in the investigated aquifer sediments contains measurable concentrations of the following trace metals: Co (0.08 wt-%), Cu (0.04–0.06 wt-%), As (0.02–0.03 wt-%), Ni (0.03 wt-%), and Zn (0.01–0.03 wt-%), supporting the hypothesis that nitrate-induced pyrite oxidation could result in the release of trace metals. However, the fate of released trace metals in groundwater was found to be governed by coupled processes: (i) pyrite oxidation and its extent, (ii) subsequent reactions such as iron(oxyhydr)oxide precipitation – on average 90 % of the iron released by pyrite oxidation precipitates – and carbonate dissolution buffering pH decrease, triggered by the release of protons during the hydrolysis involved in iron precipitation, to a minimal pH of 5, and (iii) sorption capacity of mineral phases. Specifically, subsequently formed iron(oxyhydr)oxides provide sorption sites, especially for arsenic, while cobalt and copper are only partially retained via sorption or co-precipitation. In contrast, nickel is poorly retained, with groundwater concentrations reflecting the heterogeneous distribution of nickel in pyrite or additional sources. Carbonate dissolution is likely an additional zinc source, because zinc concentrations in groundwater exceed those predicted by pyrite composition.

While our groundwater samples cover a large part of the study area, the sediment samples only represent punctual parts of the studied aquifer. Integrating these punctual information about sediment and pyrite composition into analyses on an aquifer-scale is challenging, because sediment and pyrite composition typically show a large spatial variability. This problem should be addressed in future research, e.g., by numerical, reactive transport modeling. Such modeling studies would also be beneficial to assess the future, long-term impacts of nitrate-induced pyrite oxidation if nitrate inputs remain high.

Overall, this study found that trace metal mobilization during nitrate-driven pyrite oxidation is controlled by the interplay of pyrite composition, the extent of pyrite oxidation and subsequent reactions, and the aquifer's sorption capacity.

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CRedit authorship contribution statement

Felix Fahrenbach: Conceptualization, Data curation, Formal analysis, Investigation, Methodology, Software, Visualization, Writing – original draft. **Thomas R. Rude:** Conceptualization, Data curation, Funding acquisition, Project administration, Resources, Supervision, Writing – review & editing. **Leonard Stoeckl:** Conceptualization, Data curation, Investigation, Writing – review & editing. **Georg J. Houben:**

Conceptualization, Funding acquisition, Project administration, Supervision, Writing – review & editing. **Sarah E. Wünsch:** Data curation, Formal analysis, Investigation. **Sven Sindern:** Conceptualization, Data curation, Investigation, Methodology, Project administration, Supervision, Writing – review & editing.

Declaration of competing interest

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

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.apgeochem.2026.106886>.

Data availability

The datasets, and *Python* and *R* scripts used for data analysis are available on HydroShare (Fahrenbach et al., 2026). The *Python* scripts depend on the following packages: *numpy* (Harris et al., 2020), *pandas* (McKinney, 2010), *matplotlib* (Hunter, 2007), and *scipy* (Virtanen et al., 2020). The *R* script depends on the *readxl* library (Wickham and Bryan, 2025).

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