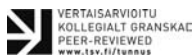


# Predicting potential pollutant release from waste rock at the abandoned Beck mine (Karelia, Russia) by equilibrium kinetic modeling



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## Abstract

The Beck mine, located in the Republic of Karelia, Russia, is an abandoned mining site with significant potential for environmental contamination due to the presence of potential pollutants in its waste rocks. In this study, we investigated the chemical composition of mine waters and waste rocks and developed a theoretical model to understand water-rock interactions and the release of potential pollutants. Water samples collected from various locations on the Beck mine property were analyzed for chemical composition and showed low concentrations of total dissolved solids with pH values ranging from 6.42 to 7.74. The chemical composition of natural waters was determined by ICP-MS, ICP-AES, ion chromatography, potentiometric titration, and spectrophotometry.

Equilibrium kinetic modeling was used to simulate water-rock interactions. The model predicted the concentrations of major and trace elements, demonstrating that dissolution-precipitation and complexation are the primary mechanisms shaping the chemical composition of mine waters. The dynamics of dissolution-precipitation of Fe-containing minerals highlighted the importance of the duration of water-rock interaction, with stagnant mine waters exhibiting higher concentrations of heavy metals. In addition, the presence of dissolved organic matter played a critical role in the accumulation of iron and arsenic in the studied mine waters.

Overall, this study highlights the utility of equilibrium kinetic modeling in understanding the behavior of heavy metals during water-rock interactions and provides valuable insights into the potential environmental impacts of abandoned mine sites such as the Beck mine.

Keywords: abandoned mine, ore-rich area, heavy metal contamination, contaminant transport, transport of toxic elements, geochemical modeling, historic mining site

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# 1. Introduction

A thorough understanding of the behavior of potential pollutants and their impact on natural water systems is important for assessing the environmental sustainability of ore-mineral rich areas (Angelo et al. 2007; Appleton et al. 2001; Cortada et al. 2021; Esteller et al. 2015; Torrance et al. 2021). The mining industry exacts a significant toll on the environment, leaving permanent scars that persist long after mining operations have ceased. Abandoned mines, particularly in areas where systematic environmental monitoring is lacking, are of particular concern. The negative environmental impacts of abandoned mines have been extensively documented across different types of mineral deposits worldwide (Bao et al. 2023; Hudson-Edwards & Edwards 2005; Liu et al. 2019; Mhlongo et al. 2016; Matlock et al. 2002; Navarro et al. 2008; Tabelin et al. 2022; Verbuyst et al. 2024). The greatest attention is attracted to ore deposits where acid mine drainage forms (Campbell et al. 2020; Murray et al. 2021; Nordstrom 2020). However, despite the obvious less attention from researchers, we should not forget that neutral mine drainage is capable of forming high concentrations of pollutants in natural waters (Jarvis et al. 2023; Hällström et al. 2018; Pope & Trumm 2015).

Recent advancements in analytical precision have enabled us to conduct highly detailed assessments of water conditions in abandoned mines. However, unraveling the complex processes that shape the chemical composition of these waters requires a deep understanding of geochemical mechanisms and other factors influencing water-rock systems. This challenge is addressed by numerical geochemical modeling.

Our study focuses specifically on near-surface conditions characterized by low temperature, low pressure, active water exchange, and exposure to the atmosphere. Geochemical modeling based on equilibrium principles is inadequate for some situations because it assumes complete equilibrium in the system, which is unachievable, for example, under the conditions considered in the current

research. To develop accurate models of water-rock interactions in such environments, it is critical to consider the kinetics governing the interactions between system components. In our case, such kinetic aspects depend primarily on the dissolution rate of minerals that are not in equilibrium with the studied waters.

In contrast to equilibrium systems, where all components including primary minerals maintain equilibrium, our approach accounts for the important kinetic factors that govern rates of primary mineral dissolution. To illustrate our approach to modeling long-term water-rock interactions, we refer to the modeling study of lateritic weathering clast formation in Hawaiian basalt tuffs, a model rigorously validated using published data (Mironenko & Cherkasova 2015).

The approach outlined above has proven effective in projecting the chemical composition of mine stockpile water and acid drainage in ore deposits slated for future development (Sidkina et al. 2020; Cherkasova et al. 2021). However, validating such projections is a significant challenge, especially in the case of newly developed deposits that lack a comprehensive exploration history. A more reliable validation opportunity arises when studying abandoned mines. A previous study (Sidkina et al. 2022) successfully used a similar approach to model the chemical composition of stagnant water within the Lupikko I mine. This research was the first attempt to investigate the behavior of ore elements during prolonged water-rock interactions in this region. In the present study, the focus shifts to the Beck mine, characterized by a dynamic water exchange pattern, simulated as water drainage through the waste rock.

Compared to other mines in the Pitkäranta ore district (Cherkasova et al. 2021; Konyshev et al. 2020; Sidkina et al. 2022), the Beck mine waste rocks show a lower degree of mineralogical diversity. However, understanding the ongoing evolution of water chemistry at the Beck mine is important because of the presence of toxic metals in waste rocks that are gradually leached from the rocks under atmospheric precipitation. The drainage network

in the study area consists of a system of small lakes connected by streams and rivers. Consequently, potential pollutants from the waste rocks can enter the drainage network through surface runoff and potentially spread throughout the region surrounding Lake Ladoga, the largest freshwater lake in Europe. Therefore, the objective of the current research is to assess the potential for toxic element leaching from the Beck mine waste rocks as a result of atmospheric precipitation.

## 2. Study area

### 2.1. History of exploration at the Beck mine

The Beck mine, located within the broader Hopunvaara mine field, is part of the deserted Pitkäranta magnetite ore province. Ore extraction using traditional mining methods started there in 1896, but was eventually discontinued due to the lack of economic viability. While the ore quality was satisfactory, the ore body's thickness proved to be

insufficient (Trüstedt 1907). Today, the Beck mine has historical significance as a 19th century mining site.

Early surveys by Trüstedt in 1907 mentioned only one mine within the Beck mine field. However, subsequent field research by the North Ladoga Regional Museum from 1997 to 2010, and by the Karelian Regional Public Organization for Speleological Research from 2008 to 2011, led to the discovery of two mine shafts (eastern – Fig. 1a and western – Fig. 1b). It was determined that the western shaft was the historical mine, while the eastern shaft was created during the Soviet era (Mining Road 2014).

Both shafts are lined with wooden timbers. In addition to the mine shafts, there is a small pond filled with blue-green water, probably a flooded open pit, as well as waste rock stockpiles and a water-filled drainage channel that crosses the waste rock stockpiles (see Figure 2). Both mines are currently flooded. The waste rock material is exposed to the atmosphere, resulting in interactions with atmospheric precipitation and surface runoff.



Figure 1. Photographs of the flooded eastern (a) and western (b) mines in the Beck mine field, captured by the authors during field campaigns in 2021 and 2022.

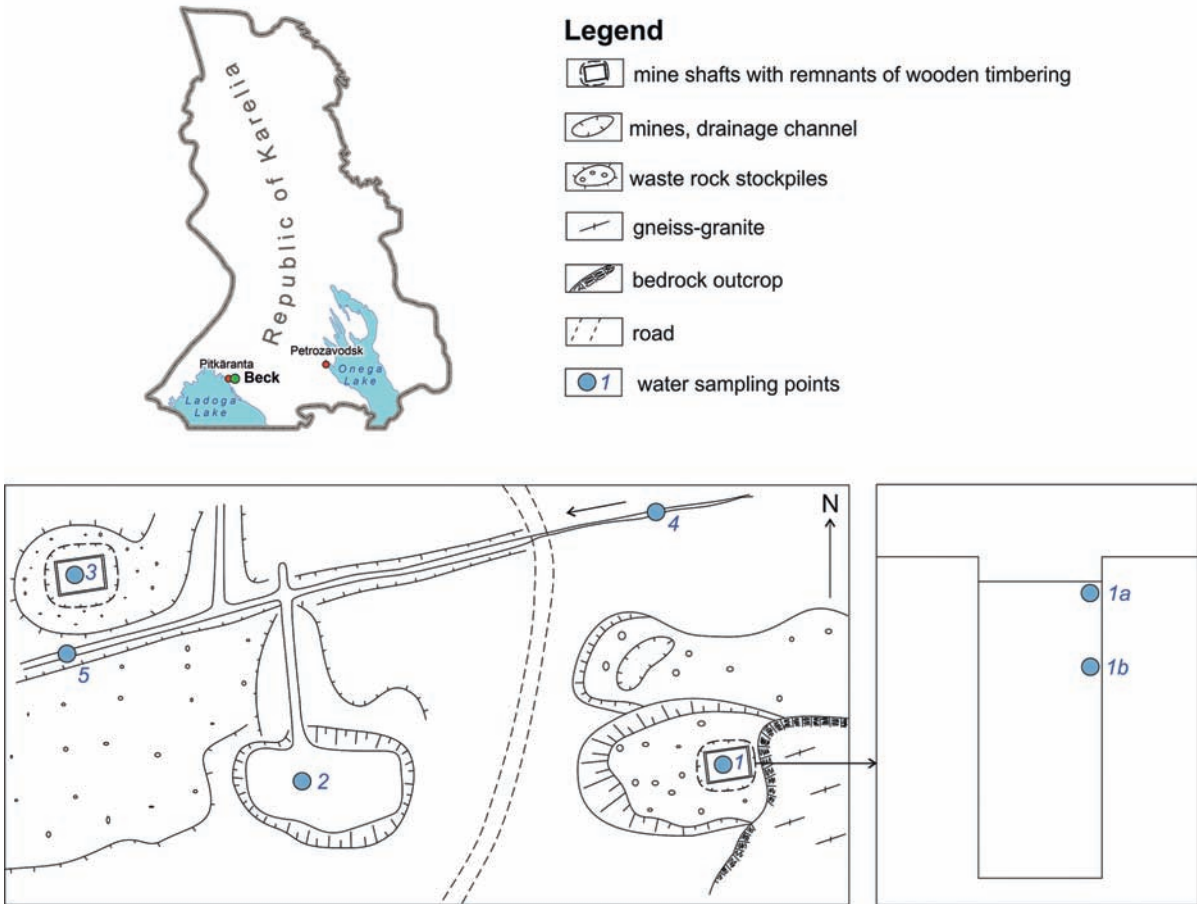


Figure 2. Location of the study area in the Republic of Karelia (Russia) and the schematic representation of the Beck mine field created by the authors, incorporating the information from Borisov (2007). Water sampling points: (1a) eastern mine shaft (surface), (1b) eastern mine shaft (2 m depth), (2) pond, (3) western mine (surface), (4) drainage channel upstream of the waste rock stockpiles, (5) drainage channel near the waste rock stockpiles.

## 2.2. Geological setting of the Hopunvaara mine field and the Beck mine

The Pitkäranta ore province is located in the southeastern part of the Fennoscandian shield, at the convergence of significant geological features: the Svecofennian orogen and the Karelian craton. Stretching approximately 50 km along the northwestern border of the Salmi batholith (Larin 2011), this province predominantly hosts skarn deposits and ore occurrences featuring diverse

iron-polymetallic-tin, rare metal, and fluorite mineralization (Valkama et al. 2016; Ivashchenko 2021). These skarn bodies are primarily associated with the Ludicovian metacarbonate strata, Sortavala Series (Pitkäranta Formation). Most of the ore deposits associated with metacarbonates are localized within the flat downwarping of top of Salmi batholith igneous rocks along its northwestern boundary.

One of the mine fields within the Pitkäranta ore province is the Hopunvaara. This mine field includes the Beck mine which is confined to the



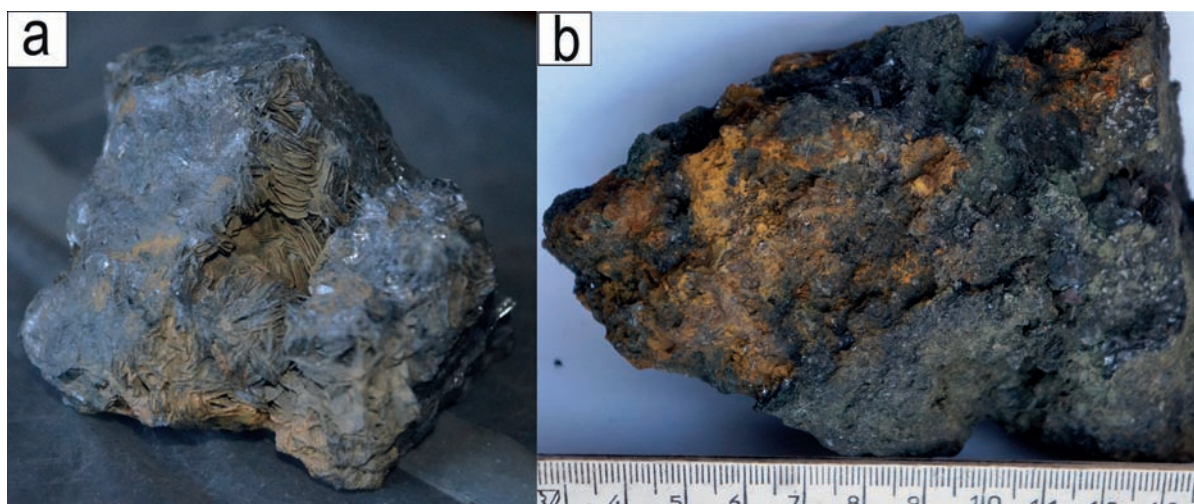


Figure 3. Samples collected from the Beck waste rocks: a) “mushketovite” pseudomorphs of magnetite after hematite; b) iron-oxides and hydroxides in skarn.

lower metacarbonate horizon framing the gneiss-granite dome of Lupikko. As described by Trüstedt (1907), the Beck mine consists of extensive magnetite ore deposits with coarsely disseminated chalcopyrite and sphalerite, accompanied by a minor presence of various sulfide minerals. Notable among the minor minerals are phlogopite, fluorite, scheelite, and calcite, while sporadic discoveries of vesuvian have also been documented.

The western shaft reaches a depth of 7 meters and contains a 1-meter-thick magnetite ore body (Trüstedt 1907). Within this shaft, the dominant rock type is skarn with pseudomorphs of “mushketovite” in which magnetite has replaced hematite (Fig. 3a). In addition, sporadic occurrences of sphalerite, quartz, and fluorite are observed in irregularly shaped ore bodies, although these mineral occurrences have no significant commercial value. The surrounding gneiss-granite rocks have undergone significant alteration to a depth of several tens of centimeters. This alteration is characterized by an enrichment of chlorite aggregates, which have replaced feldspars, and the presence of phlogopite, accompanied by a minor amount of fluorite.

### 3. Materials and methods

#### 3.1. Sampling and analytical methods

In 2021, samples of waste rocks and natural water were collected from both mines, the pond, and the drainage channel to investigate the chemical composition, abundance, and mobility of potential pollutants, as well as to determine their sources.

During the fieldwork, a total of six water samples were collected (see Fig. 2): samples 1a and 1b represented water from the eastern mine, sampled from the surface and at a depth of 2 meters, respectively; sample 2 represented water from the pond; sample 3 was taken from the surface of the western mine; and samples 4 and 5 were collected from the drainage channel, one upstream of the waste rock stockpiles and the other near the stockpiles. In addition to the water samples, three typical types of waste rocks were also collected: pyroxene-bearing skarn with ore mineralization, magnetite ore containing “mushketovite” pseudomorphs, and altered gneiss-granite.

*In-situ* measurements included the determination of pH and Eh values, temperature, and

dissolved oxygen content using a PH200 meter (HM Digital), ORP-200 meter (HM Digital), and portable DO meter (AZ Instruments). Water samples intended for elemental analysis were passed through acetate-cellulose membranes with a 0.45  $\mu\text{m}$  pore size and transferred to 15-mL sterile polypropylene vials, followed by acidification with 0.45 mL of  $\text{HNO}_3$ . For the analysis of carbonate system components, chloride, and sulfate ions, the samples were collected in 300-mL plastic bottles that had been thoroughly washed three times with water from the study area.

The concentrations of Ca, Mg, Na, K, Fe, and Al were determined by ICP-AES (iCAP 6500 DUO, Thermo Scientific), while the concentrations of Ni, Cu, Zn, Cd, Pb, As, and other trace elements (Electronic Appendix A) were analyzed by ICP-MS (X-series 2, Thermo Scientific). The contents of  $\text{CO}_2$ ,  $\text{HCO}_3^-$ , and  $\text{CO}_3^{2-}$  were determined by potentiometric titration using Expert-001 (Econix-Expert). In addition, the concentrations of  $\text{Cl}^-$  and  $\text{SO}_4^{2-}$  were quantified by ionic chromatography (ICS-3000, Thermo Scientific). Dissolved organic carbon (DOC) was measured by the bichromate method coupled with spectrophotometry (Shimadzu 1900i).

The rock samples collected from the Beck waste rocks were carefully stored in plastic zip lock bags. Mineralogical composition was determined by scanning electron microscopy (SEM) using a Mira3 instrument (Tescan) coupled to an X-ray microanalysis spectrometer (X-MAX, Oxford Instruments). The rock samples were crushed, quartered, and reduced to powder in a planetary mill using alund ceramic vessels. The chemical composition of the powdered samples was analyzed by X-ray fluorescence (Axios mAX, Malvern PANalytical) according to (Methodology No. 439-RS, 2010). The quality control of the analytical results was performed using standard rock samples from the US Geological Survey (Denver, CO, USA). The Fe content of the samples was reported as  $\text{Fe}_2\text{O}_3$  (total).

### 3.2. Equilibrium kinetic modelling

The equilibrium kinetic model is based on the partial equilibrium assumption (Barton et al. 1963; Helgeson 1968; Helgeson et al. 1970). To simulate water-rock interactions over time, a series of sequential equilibria were calculated for each time step. To calculate each equilibrium, input data were necessary, including the overall composition of the aqueous solution from the previous time step and the chemical composition of the minerals that dissolved during the current time step, considering the current values of mineral dissolution rates. The result of each calculation provided the current equilibrium composition of the aqueous solution and any masses of newly precipitated minerals. Minerals precipitated in previous steps were considered primary and could potentially dissolve if they were not in equilibrium with the current composition of the aqueous solution.

Notably, the time step  $\Delta t_k$  was variable and self-regulating; it was chosen so as to ensure that the mass of the most rapidly soluble mineral dissolved during this step did not exceed  $1 \times 10^{-5}$  mol/kg  $\text{H}_2\text{O}$ . This approach prevented abrupt changes in the pH of the aqueous solution, which could significantly affect mineral dissolution rates. Consequently, mineral dissolution rates were assumed to remain constant throughout each modeling step.

The approach described above has been implemented in the GEOCHEQ\_M software package (Mironenko et al. 2008). This comprehensive package includes a thermodynamic and kinetic database as well as an equilibrium calculation program with a module for kinetic parameters associated with congruent dissolution reactions of minerals. To improve the accuracy of mineral dissolution kinetics, the GEOCHEQ\_M database has been significantly enhanced. This included the incorporation of kinetic parameters derived from a comprehensive review by Palandri and Kharaka (2004). Their work compiled experimental data on bulk congruent dissolution kinetics of minerals. The modified database now

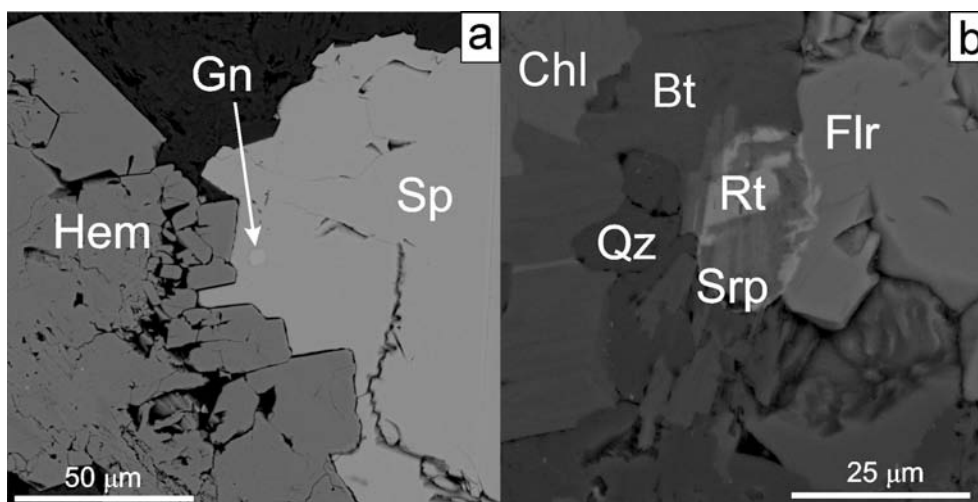


Figure 4. Back-scattered electron images: a) Contact between large crystals of hematite (Hem) and sphalerite (Sp) with inclusions of small grains of galena (Gn); b) Intergrowth of large fluorite (Flr) crystals with rutile (Rt) and scaly biotite (Bt). Secondary alteration is chloritization. Chl - chlorite group mineral, Srp - serpentine group mineral, Qz - quartz.

includes individual activation energies for mineral dissolution reactions under acidic, neutral, and alkaline conditions.

In addition to modeling the congruent dissolution of aluminosilicates, oxides, and carbonates, the model also accounts for the oxidative dissolution rates of sulfides. In a first approximation, the dissolution rates of chalcopryrite, loellingite, galena, and sphalerite were approximated using the oxidative dissolution rate of pyrite as described by Williamson and Rimstidt (1994).

## 4. Results

### 4.2 Mineral composition of mine and waste rocks

Based on visual assessment, the eastern waste rock stockpile consists of approximately one-third altered gneiss-granite from the Lupikko dome and two-thirds skarn rock with a significant presence of sulfide mineralization, mainly sphalerite. In

contrast, the stockpile to the west of the flooded mine consists primarily of pyroxene-bearing skarns with mushketovite and a lesser amount of sulfide mineralization.

The Lupikko dome gneiss-granite in the Beck waste rock is a quartz-K-feldspar-albite-biotite rock that shows development of chlorite group minerals (Fig. 4b). Skarnified rock formations are ubiquitous throughout the study area. The silicate components of skarnified rocks include a mineral assemblage of serpentine, chlorite group minerals, and quartz. Ore minerals are predominantly composed of magnetite and sphalerite, alongside other sulfides such as chalcopryrite, pyrite, cobaltite, and galena (Fig. 4a). In addition, oxides such as cassiterite, scheelite, and magnetite are present, as well as phosphates (apatite), fluorides (fluorite), carbonates (calcite), and native metals (silver).

Based on the chemical and mineral analyses of waste rocks near the eastern mine shaft, we compiled a comprehensive summary of the mineral composition (Table 1), which served as the initial dataset for our modeling efforts.

Table 1. Simplified overview of mineral composition in the Beck waste rock

Mineral	%
Magnetite	25.2
Sphalerite	2.33
Chalcopyrite	0.01
Galena	0.01
Loellingite	0.002
Pyrite (0.002% Ni)	0.21
Fluorite	2.65
Calcite	0.05
Dolomite	0.05
Chrysotile	6
Clinochlore	2.1
Daphnite	4.38
Diopside	2
Quartz	32
Microcline	15
Albite	3
Phlogopite	3.69
Annite	1.32

## 4.2. Mine water chemistry

Water samples collected from various points (see Fig. 2) in the Beck mine property exhibited freshwater characteristics with low levels of total dissolved solids (TDS), all of which were less than 71 mg/L. The pH values of the samples ranged from 6.42 (in the surface water of the eastern mine shaft) to 7.71 and 7.74 (in the drainage channel and pond, respectively). The lowest pH recorded can be attributed to the prolonged interaction between water and sulfide mineralized rocks under oxidizing conditions (Eh 182 mV and O<sub>2</sub> (aq) 12 mg/L in the surface water of the eastern mine)

Chemically, the water samples from the mine shafts showed two distinct profiles: HCO<sub>3</sub><sup>-</sup>-SO<sub>4</sub><sup>2-</sup> and SO<sub>4</sub><sup>2-</sup>-HCO<sub>3</sub><sup>-</sup>-Mg-Ca. In contrast, the pond water contained mainly HCO<sub>3</sub><sup>-</sup> and Ca<sup>2+</sup> ions. Meanwhile, the drainage channel water was characterized by HCO<sub>3</sub><sup>-</sup> and Cl-HCO<sub>3</sub><sup>-</sup> ions, along with a mixture of cations including Mg, Na, and Ca.

In the surface water of the eastern mine (Fig. 5),

sulfate ions were the dominant anions, with their concentration reducing to 3.88 mg/L at a depth of 2 meters (Electronic Appendix A). While the surface water from the western mine had a lower sulfate ion concentration (6.85 mg/L), sulfate ions still made up a significant portion of the anion composition, especially considering the low TDS values (15 mg/L in the eastern mine water at a depth of 2 m and 33 mg/L in the western mine water). In addition, the surface water of the eastern mine had remarkably high concentrations of Zn and Cu compared to other sampling points, reaching 2661 µg/L and 6 µg/L, respectively (Fig. 5). Slightly elevated levels of Zn and Cu were also observed in other samples collected from the Beck mine property, with pond water containing 342 µg/L Zn and western mine water containing 2.7 µg/L Cu. While the pond water had a higher SO<sub>4</sub><sup>2-</sup> content (8.15 mg/L), its ratio to the TDS value of 71 mg/L was not as pronounced as that observed in the samples collected directly from the mine.

The behavior of trace elements, especially those considered toxic, in the water of the drainage channel passing through the stockpiles is a matter of great concern, since the drainage channel acts as a pathway for substances from the waste rock to enter the river network. In particular, the concentration of Zn increased from 6 to 41 µg/L in the drainage channel water in its course through the stockpiles (Fig. 5), and the As content nearly doubled in the drainage channel near the stockpile compared to the point upstream. While the concentrations of Pb and Cu also increased, the changes were less pronounced. These observations strongly suggest potential leaching of chemical elements from the Beck waste rocks.

Conversely, DOC concentrations in the eastern mine water and pond were relatively low at 5.3, 3.8, and 1.2 mg/L, respectively, compared to 16.5 mg/L in the western mine water and 38.2 mg/L in the drainage channel water upstream of the stockpiles and 50.4 mg/L in the vicinity of the stockpiles. Concentrations of Fe, As, and Ni, as well as the water color index, showed positive connection with DOC content. According to the modeling of metal



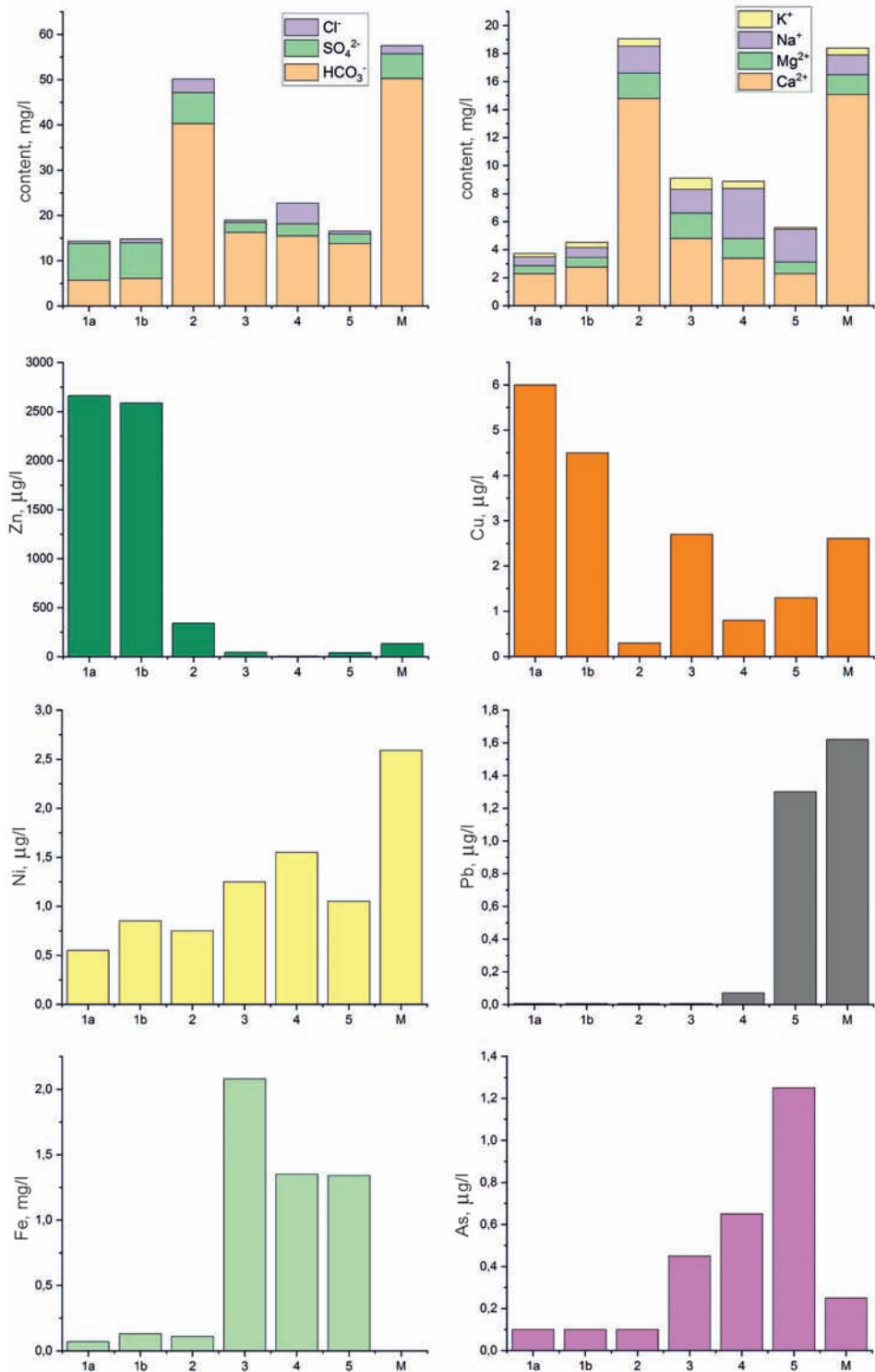


Figure 5. Content of major ions and other elements of concern in the natural waters of the Beck mine field and the model data. Legend: (1a) eastern mine shaft from the surface, (1b) eastern mine shaft from a depth of 2 m, (2) pond, (3) western mine from the surface, (4) drainage channel upstream of the waste rock stockpiles, (5) drainage channel near the waste rock stockpiles, (M) model data.

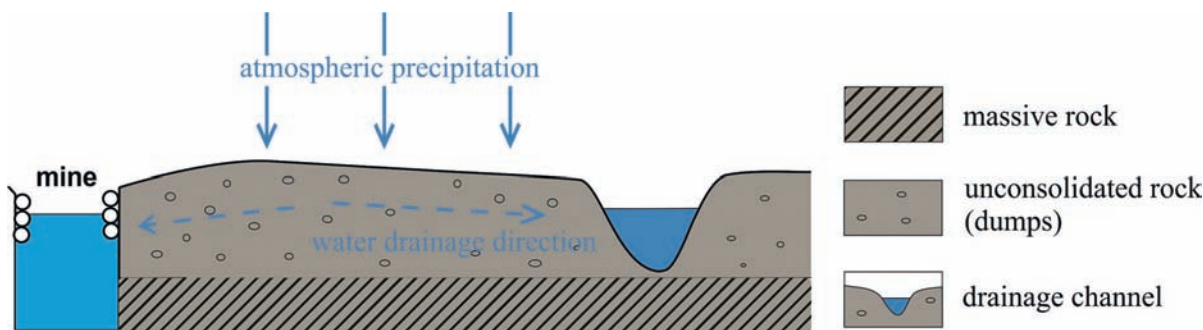


Figure 6. Modeling scheme

complexation with organic ligands at least Fe and As form complexes with dissolved organic matter (Sidkina et al. 2024).

### 4.3. Modeling scheme and results

According to *The Mining Road* (2014), the channel was initially dug for exploration, but now functions primarily as a drainage system. The water flows from sampling point 4 (upper drainage channel) to point 5 (near the waste rock area) and to the mine shafts, following the slope of the stockpile surface. The waste rocks are loosely consolidated. These observations formed the basis for the modeling scheme in which atmospheric precipitation drains through the waste rocks and into the drainage channel and mine shafts (Fig. 6).

The modeling was performed within a system consisting of 17 components, including H, O, Ca, Mg, Na, K, Al, Si, C, S, Cl, Fe, Ni, Cu, Zn, Pb, and As. A comprehensive list of minerals and aqueous complexes considered in the model can be found in Electronic Appendix B. To assess the leaching of potential pollutants, the interaction between atmospheric precipitation and the waste rock was simulated using equilibrium kinetic modeling. We used data on average quantity of atmospheric precipitation (60 mm per month, which is equal 0.6 L or 0.6 kg for freshwater) and average porosity of the stockpiles (40%) according to grain-size distribution to calculate volume of rock filled by water. The calculated volume of rock block with 40% porosity filled with 0.6 L of water was

1.5 dm<sup>3</sup>, pore volume filled with water was 0.6 dm<sup>3</sup>, rock skeletal volume was 0.9 dm<sup>3</sup>. Considering that waste rock contains 25% magnetite with density of 5.0 kg/dm<sup>3</sup> and remaining part of waste rock (75%) has density of 2.6 kg/dm<sup>3</sup>, resulting mass of rock skeletal was 2.88 kg. Thus, the water to rock ratio was accounted as 0.208.

The model used the atmospheric precipitation composition from the Roshydromet report (2017) as initial data, which included the following parameters: pH 6.1, Ca<sup>2+</sup> 1.2 mg/L, Mg<sup>2+</sup> 0.3 mg/L, Na<sup>+</sup> 1.4 mg/L, K<sup>+</sup> 0.5 mg/L, HCO<sub>3</sub><sup>-</sup> 4 mg/L, SO<sub>4</sub><sup>2-</sup> 2.4 mg/L, and Cl<sup>-</sup> 1.8 mg/L. Detailed information on the initial mineral composition can be found in the subsection 4.1. The system was considered open to atmospheric oxygen and carbon dioxide, and the simulation was conducted at a temperature of 10°C and a pressure of 1 bar.

The concentrations calculated after the atmospheric precipitation interacted with the initial rock are shown in Fig. 5. Notably, the concentrations of the major elements, as well as Zn, Cu, Ni, Pb, and As, showed a consistent increase over the specified time period. As mentioned in the equilibrium kinetic modeling description, the dissolution kinetics of minerals depend on pH, which remained relatively stable throughout the time period considered. It causes gradual increase in chemical elements concentrations. Typically, the dissolution of sulfide minerals leads to a decrease in pH, resulting in the generation of acid drainage and a significant increase of heavy metals in natural waters. However, several factors prevented this in our case. First, the waste rocks examined had a low concentration of sulfide

minerals. Second, neutralization processes occurred during the dissolution of carbonate minerals. Finally, rapid water exchange conditions prevented prolonged water-waste rock interactions.

## 5. Discussion

Modeling results demonstrated the increase in  $\text{SO}_4^{2-}$ , along with Ni, Zn, Cu, Pb, and As (Appendix B), in the model solution as a result of oxidative dissolution of sulfide minerals in the waste rocks. The increase was most pronounced in samples collected from the Beck mine shafts, which had higher sulfate concentrations, with the surface layer of water showing the most significant buildup. The elevated chemical element concentrations in this layer are logically consistent with the oxidative dissolution process, which depends on the greater abundance of atmospheric oxygen. Moreover, the limited water exchange in the mine shafts suggests prolonged interactions within the water-rock system, which favors the accumulation of chemical elements in the water.

The elevated Zn content in the water can be attributed to the dissolution of sphalerite, a mineral present in significant quantities in the waste rocks (Table 1). Likewise, Cu, Pb and As originate from chalcopyrite, galena, and sphalerite, respectively. Notably, pyrite serves as a source

of Ni, given its composition containing up to 0.002% Ni. Field observations are consistent with the simulation results, as the concentrations of almost all the examined elements increased in the water of the drainage channel near the stockpiles. However, it is worth noting that the model-derived concentrations generally exceeded those observed in the drainage channel. Our hypothesis is that the water in the drainage channel originates not only from the runoff through the waste rock stockpiles, but also from a mixture of atmospheric precipitation and surface runoff.

Special attention is warranted regarding the behavior of Fe and As in the system. Waters with elevated Fe and As concentrations, such as samples 3, 4, and 5, are also characterized by high DOC concentrations. It is widely known that Fe can form complexes with organic ligands (Zhang et al. 2022; Dinu and Baranov 2022; Moiseenko et al. 2020; Li et al. 2020; Kolpakova et al. 2018; etc.). We hypothesize that Fe enters the solution through the dissolution of Fe-containing minerals and, in the absence of organic matter, is subsequently reprecipitated in the form of Fe-(hydr)oxides. This phenomenon explains the low Fe concentrations observed in the mine water and in the model solution. According to our modeling results, the precipitation of goethite facilitates the removal of Fe from the solution (Fig.7).

This natural process is supported by field

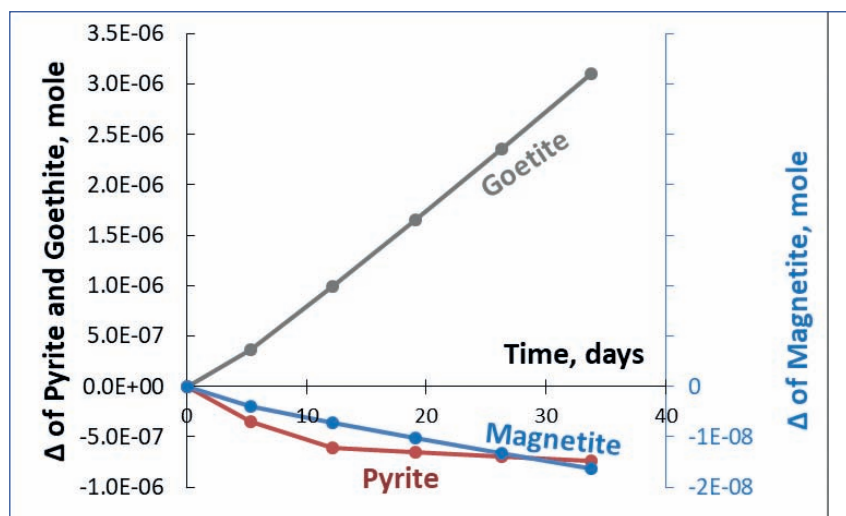


Figure 7. Dissolution and formation of Fe-containing minerals

Table 2. The Spearman correlation coefficients for the chemical composition of modeling solution and mining objects ( $p < 0.05$ )

	Eastern mine (surface)	Eastern mine (2 m)	Pond	Western mine	Drainage channel (upstream of the stockpiles)	Drainage channel (near the stockpiles)
Model solution	0.77	0.88	0.80	0.88	0.64	0.78

observations of the waste rocks (Fig. 3b). The presence of hydrogoethite in the Beck mine waste rocks suggests a likely supergene origin, similar to other ore-rich regions (Duuring et al. 2019; Yans et al. 2021). The observed correlation between elevated As and Fe concentrations is typical, as these elements tend to form Fe-As-OM complexes (Liu et al. 2011; Cai et al. 2020). This complexation phenomenon is often responsible for the accumulation of high As concentrations in natural waters (Xie et al. 2022). In addition, the slightly elevated Ni content in samples with elevated Fe concentrations can be attributed to a higher proportion of Ni-bearing pyrite in the waste rocks compared to the rocks in the mine walls.

Comparing the model results with the chemical composition of the study objects at the Beck property (Table 2), it is evident that the waters sampled from the eastern mine at a depth of 2 meters, the western mine, and the pond show the closest resemblance to the model solution. This suggests that the chemical composition of these waters is primarily shaped by water-rock interactions. Conversely, water from the drainage channel upstream of the stockpiles shows the most significant deviations from the model solution. This variance can be attributed to differences in compositional sources, primarily due to the prevalence of surface runoff originating outside the Beck waste rocks during recharge. The water in the drainage near the waste rock stockpile shows stronger correlations with the model data than the points upstream of the stockpiles. This supports the notion that the water in the drainage channel near the stockpiles results from a mixture of surface runoff originating outside the Beck waste rocks and runoff passing through the stockpiles themselves.

## 6. Conclusions

This research has facilitated the development of a theoretical model for understanding water-rock interactions using the Beck abandoned mine as an illustrative example. The model results for major and trace element concentrations closely match the observed values for the waters of both considered Beck mines (eastern and western), thus validating the accuracy of our calculations. Within this model, dissolution-precipitation and complexation processes emerge as the primary mechanisms shaping the chemical composition of the natural waters under consideration.

A key factor contributing significantly to the increase of elements of concern in solution is the duration of water-rock interaction. This aspect is supported by both model results and field observations: stagnant mine waters consistently exhibit high concentrations of heavy metals. In addition, the presence of dissolved organic matter plays a key role in the increase of iron and arsenic in the studied mine waters.

In conclusion, our research emphasizes that water-rock interaction is the dominant process controlling the chemical composition of water within the mine shafts and the pond. Conversely, the water chemistry within the drainage channel is a product of a mixture of surface runoff originating outside the Beck waste rock stockpiles and runoff passing through the stockpiles themselves.

This study demonstrates the effectiveness of equilibrium kinetic modeling as a valuable tool for understanding the behavior of heavy metals during water-rock interactions. In particular, it can be used to formulate predictive solutions for calculating the composition of drainage subdump waters, stagnant pond waters, and mine shafts



slated for future development. However, there are uncertainties associated with hydrogeological data (need to specify filtration coefficient and water-rock interaction time, absence of data on groundwater inflow to the mines).

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## Supplementary data

Electronic Appendices are available via Bulletin of the Geological Society of Finland web page.

Electronic Appendix A: Chemical composition of the Beck mine waters.

Electronic Appendix B: Aqueous species, minerals and gas phase accepted for the modeling.

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