The Impact of Temperature and Oxygen on Water-Rock Interactions in Siliciclastic Rocks and Implications for Aquifer Thermal Energy Storage Systems

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For my grandfather, Dr. Günter Lehmann.

Abstract

Water-rock interactions are sorption-, dissolution-, precipitation-, and redox reactions at the interface between rock matrix and water. In aquifer thermal energy storage (ATES) systems, certain water-rock interactions can have undesired consequences, such as clogging of aquifer pores or contaminant release, and are therefore geochemical risks. Their prediction and prevention requires site-specific knowledge about water-rock interactions at specific operational conditions.

This study investigates the reactivity of two pyrite-bearing siliciclastic rocks from the Hettangian and Lower Sinemurian stages of the Lower Jurassic. They are associated with the heat storage aquifer of the ATES system at the German parliament buildings in the city of Berlin, which is located in the south-eastern part of the Northeast German Basin. The study presents a workflow to (a) describe mineralogy and sorption reactions at the rock surface, (b) quantify the maximum of potentially critical (mineralforming/contaminant) elements that can be released from the rocks, (c) determine their phase association and release mechanisms, and (d) identify the most important control parameters and process interactions during heat storage. The bulk mineralogy was identified by X-ray diffraction, X-ray fluorescence and scanning electron microscopy. Potentially critical mobile elements and easily soluble crystalline and amorphous solid phases, such as hydroxides and sulfides, were quantified with a specifically developed sequential extraction. This method allows the partition of mobile elements by association with specific rock fractions with the help of appropriate solvents. These fractions are (1) exchangeable (2) associated with acid-soluble phases (carbonates), (3) associated with reducible phases (oxides/hydroxides), and (4) associated with oxidizable phases (organic matter/sulfides). Heat storage, defined by temperatures of up to 90 °C and potential intrusion of oxygen into the aquifer, was investigated by steady-state leaching experiments with simplified synthetic groundwater (0.42 M NaCl solution) by varying the control parameters temperature (25, 50, 70, 90 °C), solute oxygen (oxic/anoxic) and leaching time (1, 2, 4, 7 days). The influence of different control parameters and process interactions was analyzed by numerical simulations and statistics, using experimental data for parameterization and validation. The following results and implications for ATES operation in the originally oxygen-depleted aquifer were found for the potentially critical (contaminant/mineral-forming) mobile elements Al, As, Ba, Ca, Cu, Fe, Mn, Ni, Pb, and Si:

• The total leachable quantity of each element, i.e. the leached sum over all sequential extraction steps, is very small in the aquifer sandstone (<0.1 mg/g), and significantly higher in the siltstone of the topset aquitard (up to ca. 4 mg/g for Ca).

- The iron system is the main risk factor. At oxic conditions, pyrite (FeS₂) dissolves. If no suitable buffers are present, the solution is acidified, which facilitates the mobilization of several other elements. At anoxic conditions, the dissolution of iron hydroxides is the process mainly controlling element mobilization. Ferric iron re-precipitates readily, and is the main mineral-forming species in the investigated system.
- Calcium is predominantly adsorbed, and can be mobilized by pH reduction. In case the solute concentration decreases due to mineral precipitation, Ca can be desorbed quickly to regain thermodynamic equilibrium between rock matrix and groundwater.
- Small amounts of aluminum and silicon can be released rapidly from amorphous (hydr)oxides, which were their main source during leaching experiments of up to seven days. Kinetically slow dissolution of crystalline silicates prevails during longer leaching periods.
- Arsenic is nearly immobile in the aquifer sandstone. During the experiments, it was released only in the reduction step of the sequential extraction (ca. 0.02 µg/g), and represents no critical risk.
- Barium, copper, nickel, and lead have no single phase association. They are probably mainly present as solid solutions or co-precipitates, and their mobility seems to be primarily controlled by iron phase dissolution/precipitation. Copper was also found in elementary form.

For the investigated heat storage at the German parliament buildings, these findings indicate no critical risk factors, which could lead to groundwater contamination or porosity reduction in dimensions that would prohibit ATES operation. However, constant nitrogen pressurization of the system is imperative to prevent oxygen intrusion, which could eventually lead to pyrite dissolution, groundwater acidification once its buffering capacity is exceeded, and critical element mobilization.

Keywords:

Aquifer thermal energy storage, rock reactivity, siliciclastic rocks, pyrite, element mobilization, sequential extraction, leaching test, numerical simulation

Kurzfassung

Wasser-Gesteins-Wechselwirkungen umfassen Sorptions-, Lösungs-, Fällungs- und Redox-Reaktionen zwischen Gesteinsmatrix und Wasser. In thermischen Aquiferspeichern (ATES: Aquifer Thermal Energy Storage) können bestimmte Wasser-Gesteins-Wechselwirkungen unerwünschte Folgen haben, etwa das Zusetzen von Gesteinsporen durch Ausfällungen oder die Freisetzung von Schadstoffen. Sie müssen daher als geochemische Risiken betrachtet werden. Ihre Prognose und Vermeidung erfordert standortspezifische Informationen über Wasser-Gesteins-Wechselwirkungen

Die vorliegende Arbeit untersucht die Reaktivität von zwei pyritführenden siliziklastischen Gesteinen aus den unterjurassischen Stufen des Hettangium und des unteren Sinemurium. Sie bilden den Wärmespeicher des ATES-Systems der deutschen Parlamentsbauten in Berlin, gelegen im südöstlichen Teil des Nordostdeutschen Beckens. Die Arbeit stellt ein Verfahren dar, das (a) Mineralogie und Sorptionsreaktionen an der Gesteinsoberfläche beschreibt, (b) die maximal aus einem freisetzbare Gestein Menge potentiell kritischen Elementen an (Schadstoffe/Mineralbildner) quantifiziert, (c) ihre Phasenbindung und Freisetzungsmechanismen bestimmt und (d) die wichtigsten Kontrollparameter und Prozesswechselwirkungen bei der Wärmespeicherung identifiziert. Die Mineralogie wurde mit Hilfe von Röntgendiffraktometrie, Röntgenfluoreszenzanalyse und Rasterelektronenmikroskopie bestimmt. Potentiell kritische mobile Elemente und leichtlösliche kristalline und amorphe Festphasen, z.B. Hydroxide und Sulfide, wurden mit Hilfe einer speziell entwickelten sequentiellen Extraktion quantifiziert. Diese Methode ermöglicht die Unterscheidung mobiler Elemente anhand ihrer Assoziation mit bestimmten Gesteinsfraktionen mithilfe geeigneter Lösungsmittel. Diese Fraktionen sind (1) austauschbar, (2) mit säurelöslichen Phasen assoziiert (Karbonate), (3) mit reduzierbaren Phasen assoziiert (Oxide/Hydroxide), und (4) mit oxidierbaren Phasen assoziiert (Organik/Sulfide). Die Wärmespeicherung, definiert durch Temperaturen von bis zu 90 °C und möglichen Sauerstoffeintrag in das Grundwasser, wurde durch stationäre Laugungsversuche mit vereinfachtem synthetischen Grundwasser (0.42 M NaCl-Lösung) untersucht, indem die Kontrollparameter Temperatur (25, 50, 70, 90 °C), gelöster Sauerstoff (oxisch/anoxisch) und Extraktionsdauer (1, 2, 4, 7 Tage) variiert wurden. Der Einfluss verschiedener Kontrollparameter und Prozessinteraktionen wurde mithilfe numerischer Simulationen und statistischer Methoden bestimmt. Versuchsdaten wurden hierbei zur Parametrisierung und Validierung herangezogen. Die folgenden Resultate und Implikationen für den Speicherbetrieb in dem ursprünglich sauerstoffarmen Grundwasserleiter wurden für die potentiell kritischen mobilen Elemente (Schadstoffe/Mineralbildner) Al, As, Ba, Ca, Cu, Fe, Mn, Ni, Pb und Si bestimmt:

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- Die insgesamt, d.h. aufsummiert über alle Schritte der sequentiellen Extraktion, aus dem Aquifersandstein extrahierbaren Mengen der einzelnen Elemente sind sehr niedrig (<0.1 mg/g), und liegen für den Siltstein des hangenden Geringleiters deutlich höher (bis zu ca. 4 mg/g für Ca).
- Das Eisensystem ist der Hauptrisikofaktor. Bei oxischen Bedingungen wird Pyrit (FeS₂) gelöst. Liegt kein geeigneter Puffer in Lösung vor, sinkt der pH-Wert, was die Mobilisierung weiterer Elemente unterstützt. Bei anoxischen Bedingungen wird die Elementmobilisierung vorwiegend durch die Lösung von Eisenhydroxiden kontrolliert. Freigesetztes dreiwertiges Eisen neigt zu rascher Wiederausfällung, und stellt im untersuchten System den wichtigsten Mineralbildner dar.
- Calcium ist vorwiegend adsorbiert, und kann durch pH-Wert-Absenkung freigesetzt werden. Falls die Ca-Konzentration durch Mineralausfällungen sinkt, kann das thermodynamische Gleichgewicht zwischen Gestein und Grundwasser durch Desorption rasch wiederhergestellt werden.
- Kleine Mengen Aluminium und Silizium konnten in Laugungsversuchen über bis zu sieben Tage rasch aus amorphen (Hydr)oxiden mobilisiert werden. Die kinetisch langsamere Lösung kristalliner Silikatminerale spielt bei langfristigen Lösungsprozessen allerdings die wichtigere Rolle.
- Arsen kann aus dem Aquifersandstein kaum freigesetzt werden. Im Labor wurde eine Mobilisierung nur im Reduktionsschritt der sequentiellen Extraktion beobachtet (ca. $0.02 \mu g/g$), sodass keine kritische Gefährdung befürchtet werden muss.
- Barium, Kupfer, Nickel und Blei zeigen keine eindeutige Fraktionierung. Sie liegen vermutlich vorwiegend als feste Lösung oder Kopräzipitat vor, und ihre Mobilität scheint hauptsächlich durch Lösung und Fällung von Eisenphasen bestimmt zu werden. Kupfer wurde in gediegener Form nachgewiesen.

Für den untersuchten Wärmespeicher an den deutschen Parlamentsbauten wurden keine kritischen Risikofaktoren gefunden, die zu Grundwasserkontamination oder Porenraumverkleinerung in einem Umfang führen würden, der den Speicherbetrieb verhindert. Es muss allerdings eine durchgängige Stickstoffbeaufschlagung des Systems sichergestellt werden, um Sauerstoffintrusion mit folgender Pyritlösung, Grundwasserversauerung bei Überschreiten der Pufferkapazität und Freisetzung kritischer Elemente zu verhindern.

Schlüsselbegriffe:

Thermische Aquiferspeicher, Gesteinsreaktivität, Siliziklastika, Pyrit, Elementmobilisierung, Sequentielle Extraktion, Laugungsversuch, Numerische Simulation

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1 Introduction

1.1 Background

Groundwater has been used as a drinking water supply for thousands of years, and shallow aquifers are a major source for public, agricultural and industrial fresh water nowadays. Over the last decades, aquifers have additionally been used for purposes other than fresh water supply, such as wastewater disposal (Tsang et al. 2008) or natural gas storage (Evans et al. 2009). With the advancement of renewable energies, aquifers will also be increasingly needed for energy production and storage techniques such as geothermal energy production (Bayer et al. 2012, Blum et al. 2010, Huenges 2011), compressed air energy storage (Chen et al. 2013), hydrogen underground storage (Pudlo et al. 2013) or seasonal thermal energy storage (e.g. Andersson et al. 2013, Kranz & Frick 2013, Seibt & Kabus 2006). In these geotechnical systems, chemical interactions between the rock matrix of the aquifer and the groundwater occur because system operation rapidly shifts natural equilibria, which are the result of reaction and transport processes over geological timescales (e.g. Hochella & White 1990). Determining and avoiding critical processes requires a thorough understanding of the site-specific chemical properties of the rock, and failure to do so can result in the clogging of pores or release of contaminants, making expensive cleaning operations or even the shut-down of wellbores necessary (e.g. Bonte 2013, Regenspurg et al. 2015, Wagner et al. 2005). Consequently, avoiding undesired water-rock interactions which would diminish groundwater quality, disturb safety and efficiency of the facility or interfere with other nearby facilities is an important operational aspect of geotechnical systems. This thesis will present an approach to determine the reactivity of a specific rock, focusing on predicting the geochemical risks due to water-rock interactions which are associated with the operation of a seasonal aquifer heat storage system (aquifer thermal energy storage, ATES).

1.2 Water-rock interactions

Interactions at the interface between water and rock are a combination of transport processes and surface chemical reactions (Hochella & White 1990, Lasaga 1990). They comprise a part or all of several individual steps: transport to the rock- or mineral surface, attachment to or detachment from the surface, surface diffusion, and attachment to or detachment from edges or kinks on the surface (Lasaga 1990). These individual steps in turn consist of one or multiple chemical reactions (ibid.). Depending on the types of steps and reactions occurring, water-rock interactions can be separated into the following processes, which will be described briefly in the referenced chapters (Hochella & White 1990):

- Adsorption and desorption (chapter 1.2.1)
- Dissolution and precipitation (chapter 1.2.2)
- Redox reactions and microbial catalysis (chapter 1.2.3).

Water-rock interactions depend on the surface composition and surface structure of the rock, which does not have the same properties as the bulk structure, and on the composition and distribution of aqueous species near the water-rock interface (Hochella 1990, Merkel & Planer-Friedrich 2005). In natural rocks, only part of the rock surface is accessible by water, because some pores or cracks are blocked and inaccessible to liquids (Vafai 2005). The reactivity of a rock is thus defined by the following surface properties of the minerals found at its water-accessible surface (Hochella 1990, Lasaga 1998):

- Mineral composition
- Atomic structure
- Surface topography

The surface mineral properties can be described by its bulk composition and its reaction history, i.e. past interactions between mineral and water, gases or solids which add, remove or exchange surface atoms (Hochella 1990). These surface reactions affect at least the outermost layer of the mineral structure, but can reach up to several thousands of Ångstrom (0.1 nm) deep into the crystal lattice (ibid.). The atomic structure in the layers near the surface may be warped because atoms shift laterally or perpendicular to the surface to optimize their energetic state relative to the other constituents of the crystal lattice (ibid.). The surface topography is modified by its reaction history, and reactions do not occur evenly distributed, but prefer charged or energetically favorable sites (e.g. Lasaga 1990, Lasaga 1998, Lasaga & Blum 1986). Examples are lattice disturbances due to missing or substituted atoms, and steps, edges or kinks on the surface due to attached or missing atoms (Figure 1.1) (Langmuir 1997, Lasaga & Blum 1986). The result is a complex topography of the mineral surface, where disturbances on atomic or microscopic scales represent seeds for water-mineral interactions that modify the surface even further (Lasaga 1990). As the topography is individually different for each mineral grain, it is nearly impossible to predict what percentage of a given mineral surface will be reactive, unless material-specific tests are performed (Hochella 1990, Lasaga & Blum 1986, Lasaga 1998).



Figure 1.1: Simplified mineral surface topography on the atomic scale. Missing atoms which were removed during dissolution form holes, while adsorbed atoms ("adatoms") can diffuse toward edges or kinks, which form during the precipitation of a new mineral layer or the formation of a hole during dissolution. Image taken from Lasaga (1990).

As an example, Figure 1.2 shows a scanning electron microscopic (SEM) image of a quartz (SiO₂) grain with a magnification of 1120 as an example for natural mineral grain topography. The surface of the quartz grain has several "etch pits", which are large holes resulting from highly located mineral dissolution at disturbed surface sites (Lasaga & Blum 1986). On the left side, element distribution scans performed with energy-dispersive X-ray spectroscopy (EDX) show an iron-titanium accumulation, which has been identified as an iron-titanium oxide (Fe-Ti oxide) with the help of a binocular microscope. Sodium (Na) and potassium (K) were found to be preferentially sorbed to the Fe-Ti oxide, because its surface is large compared to quartz, and its charged surface facilitates the adsorption of solute components (see chapter 1.2.1).



Figure 1.2: Scanning electron microscope (SEM) image of a quartz grain with 1120x magnification (top). Pseudo-colored element distribution scans by energy-dispersive X-ray spectroscopy (EDX) show the distribution of iron (Fe), titanium (Ti), potassium (K), and sodium (Na).

1.2.1 Adsorption and desorption

Adsorption and desorption describe the attachment and detachment of solute components on solid surfaces (Stumm & Morgan 1996). Sorption is a fundamental process in water-rock interactions, and the first or last reaction step in other surface processes, including dissolution, precipitation, and surface redox reactions (Hochella & White 1990). Two types of sorption reactions can be distinguished (Parks 1990):

- Non-specific adsorption or physisorption, where solute components adsorb onto surfaces of opposite charge by electrostatic attraction and London-van der Waals forces (Langmuir 1997, Parks 1990).
- Specific adsorption or chemisorption, where chemical bonds between the adsorbed component and the charged surface are formed; this mechanism is independent of polarity, because the force of the chemical bond exceeds electrostatic repulsion (Parks 1990).

Surface charge can be the result of lattice disturbances, which cause permanent surface charges onto which charged solute components can adsorb, and of broken or unsatisfied bonds at mineral surfaces (Langmuir 1997). Lattice disturbances commonly occur in clay minerals, while broken or unsatisfied surface bonds are the most important mechanism in oxides and hydroxides (ibid.). When water molecules dissociate into H⁺ and OH⁻ groups at mineral surfaces, they can react rapidly with mineral surface ions of opposite charge (Parks 1990). This hydroxylation of the mineral surface results in the formation of ionizable functional surface groups, which can protonate or deprotonate in dependence of the pH, form bonds with metal ions, or be exchanged for another ligand (Parks 1990, Stumm & Morgan 1996). Positively charged surfaces at low pH allow the adsorption of anions, negatively charged surfaces at high pH adsorb cations (Langmuir 1997, Merkel & Planer-Friedrich 2005). Adsorption of metal ions onto functional hydroxyl surface groups comprises the formation of a surface complex by coordination of the ions with surface oxygen, and the release of protons into solution (Stumm & Morgan 1996). Surface complexes formed by non-specific adsorption are called outer-sphere complexes, which are separated from the surface by one or more water molecules, while inner-sphere complexes formed by specific adsorption are sorbed directly to the surface (ibid.). In common sorption models, the distribution of charge near the surface is idealized as an electric double layer, where the inner layer has a fixed charge and comprises the surface and any kind of adsorbed particles, while the charge of the outer layer decreases with distance from the surface, and contains a diffuse ion swarm which is weakly attracted to the surface by electrostatic forces (Parks 1990, Stumm & Morgan 1996). Adsorbed ions are exchangeable; the sorption strength or sorption affinity depends on the properties of the surface and of the adsorbed ion, particularly ion valence and ion radius, so that adsorbed ions can be replaced by other ions with higher sorption affinity (Langmuir 1997, Stumm & Morgan 1996). Figure 1.3

illustrates the position of ions in the electric double layer, and the described adsorption mechanisms on a mineral surface, differentiating between functional hydroxyl surface groups, inner sphere complexes (specific adsorption), outer sphere complexes (non-specific adsorption), and the diffuse ion swarm.



Figure 1.3: (a) Position of ions in an idealized electric double layer: diffuse ion in the outer layer, outer sphere complex, and inner sphere complex. (b) Interface between solution (right) and mineral (left) with functional hydroxyl surface groups and adsorbed particles in four different planes close to the mineral surface: s = hydroxyl surface groups, a = inner sphere complexes, $\beta = outer$ sphere complexes, d = diffuse ions. Image taken from Stumm & Morgan (1996).

1.2.2 Dissolution and precipitation

Dissolution reactions can be described as two-step reaction sequences at the mineralwater interface: first, the bond of the central ion in the crystal lattice is destabilized, second, the destabilized bond is broken and the ion can be detached from the crystal lattice (Casey & Bunker 1990). Mechanisms can be separated into ion-exchange followed by hydration of the exchanged ion, and hydrolysis (ibid.). Destabilization in hydrolysis reactions occurs by at least one of the following reaction mechanisms between lattice ion and adsorbed components: (1) formation of a surface complex, (2) protonation of hydroxyl groups attached to the central ion, and (3) change of the redox state of the central ion or an attached ligand (ibid.). Following destabilization, the central ion-ligand bond can be dissociated and the central ion gets detached from the crystal lattice (Casey & Bunker 1990, Hering & Stumm 1990). It should be noted that the first two destabilization mechanisms depend on pH, or rather the presence of H⁺ and OH⁻ groups in solution, and dissolution kinetics differ significantly in acidic, neutral, and basic environments (Hering & Stumm 1990). The third destabilization mechanism can occur if a mineral has reducible or oxidizable components, and the change of the redox state by a reductant or oxidant can accelerate the dissociation of a crystal bond greatly (ibid.). This mechanism is discussed further in chapter 1.2.3.

Figure 1.4 illustrates the dissolution process on the example of quartz (SiO₂) hydrolysis, where a water molecule is first adsorbed onto the central Si atom, subsequently forms a surface complex, and finally dissociates the Si-O bond. Once all four Si-O bonds are dissociated in this manner, the resulting H₄SiO₄ molecule can be detached from the mineral surface (Lasaga 1990).



Figure 1.4: Reaction sequence of quartz dissolution. *(a)* Adsorption of a water molecule onto the central Si ion, *(b)* surface complex formation, *(c)* dissociation of the Si-O bond by hydrolysis. Image taken from Lasaga (1990).

Precipitation of a solid phase from solution depends on its saturation state: the solid phase is undersaturated until its solubility is exceeded, in which case it first becomes metastable, and then oversaturated (Stumm & Morgan 1996). Precipitation is often delayed until strong oversaturation is reached, and the first phase to precipitate is the thermodynamically least stable polymorph in a disordered (amorphous) form (Parks 1990, Stumm & Morgan 1996). This first phase then proceeds to age and convert into a more stable polymorph, e.g. Fe(III) first forms amorphous hydroxide (simplified formula: Fe(OH)₃) when oversaturated, which subsequently converts into the stable polymorphs goethite (FeOOH) or hematite (Fe₂O₃) (Cornell & Schwertmann 1996, Parks 1990, Stumm & Morgan 1996). Precipitation often occurs on existing surfaces, because they facilitate nucleation of the solid phase in the metastable state (Zhang & Nancollas 1990). Growth on mineral surfaces involves transport to the surface, adsorption, surface diffusion, and adsorption to kink sites or edges, as described before (compare Figure 1.1). Minerals precipitated in natural environments are rarely pure, but commonly contain foreign components, which in turn affect their solubility (Merkel & Planer-

Friedrich 2005). Impurities can be incorporated into crystals as they grow and thus coprecipitate, which commonly occurs with metals and iron hydroxides, or two components can form a solid solution, where one phase is dissolved in a solid-state solvent, which often occurs when uncommon carbonates, such as strontianite (SrCO₃) or otavite (CdCO₃), are incorporated into calcite (CaCO₃) (Merkel & Planer-Friedrich 2005, Stumm & Morgan 1996).

1.2.3 Redox reactions

Redox reactions in water-rock interactions primarily facilitate the dissolution or precipitation of minerals by changing the redox state of elements at crystal surfaces or in solution (Hering & Stumm 1990). While O₂/H₂O is the most important redox couple in geochemical environments, due to the abundance and reactivity of O_2 , most redox processes are catalyzed by microbial communities, which harvest part of the released energy for sustenance and growth (Bethke 2007, Hering & Stumm 1990, Stumm & Morgan 1996). Their composition depends on the temperature and the geochemical environment, as microbes need a specific substrate to grow, e.g. the sulfur-oxidizing bacteria of the genus Thiobacillus require substrate having reduced sulfur, such as pyrite (FeS₂) (Baker & Banfield 2003, Bethke 2007). Since the focus of this thesis will be on abiotic water-rock interactions, microbial catalysis will only be discussed briefly where necessary. An example for an important abiotic redox process, which plays a central role in this thesis, is the dissolution of pyrite. This process corresponds to the third destabilization mechanism described in chapter 1.2.2, and involves the destabilization of a pyrite crystal by oxidation of sulfidic sulfur S(-I) to sulfatic sulfur S(VI) by O₂ or Fe^{3+} , according to the following equations (Nordstrom 1982):

$$FeS_2 + 3.5O_2 + H_2O \leftrightarrow Fe^{2+} + 2SO_4^{2-} + 2H^+$$

$$(1.1)$$

$$FeS_2 + 14Fe^{3+} + 8H_2O \leftrightarrow 15Fe^{2+} + 2SO_4^{2-} + 16H^+$$
 (1.2).

The electron transfer is a step-by-step mechanism (McKibben & Barnes 1986, Rimstidt & Vaughan 2003):

- 1. An electron is transferred from a Fe^{2+} ion on the mineral surface to the oxidant, i.e. Fe^{3+} or O₂, so that it becomes Fe^{3+} .
- 2. The missing electron is replaced by an electron from a sulfur ligand, so that the iron is reduced back to Fe²⁺.
- 3. The sulfur ligand that is now missing an electron reacts with a water molecule by attaching an OH⁻ group, which releases a proton into solution.

On condition that the supply of oxidant is sufficient, this procedure can be repeated up to seven times, so that an SO_4^{2-} molecule forms, which is subsequently released into solution (ibid.).

1.3 Water-rock interactions in geotechnical systems

1.3.1 Geochemical risks

In geotechnical systems which use aquifers for water supply or storage purposes, geochemical processes can compromise groundwater quality and long-term efficiency and safety of the facility (e.g. Bonte 2013, Frick et al. 2011). Depending on the type of facility, the main geochemical risks are the release of contaminants into drinking water, adverse effects on the groundwater ecosystem and microbial growth, the corrosion of well piping or surface facilities, the clogging of aquifer pores, and the clogging of pipes ("scaling") (Bonte 2013, Frick et al. 2011, Griebler et al. 2014, Weber 2000). The critical processes controlling these risks are water mixing, temperature changes, and gas pressure changes, which affect microbial activity, chemical equilibria in water-rock-interactions, and groundwater pH, salinity, and redox conditions (Hartog et al. 2013). These processes will be discussed further in chapter 1.3.2.

To give a few examples of geochemical risks and critical processes in different types of facilities, the mixing of oxic and anoxic water during aquifer storage and recovery (ASR) of drinking water was found to release contaminants and clog pores, involving mainly redox-sensitive iron minerals such as pyrite or iron hydroxides (Brown & Misut 2010, Bustos Medina et al. 2013, Dillon et al. 2006, Prommer & Stuyfzand 2005, Wallis et al. 2011). The precipitation of carbonate minerals is a desired process in CO_2 storage facilities, and extensive experimental and numerical work has been performed to identify mineral precipitation timescales and other interactions between rocks and the CO₂-saturated injection water (Beyer et al. 2012, De Lucia et al. 2012, Pudlo et al. 2012, Sell et al. 2013). In geothermal systems, high temperatures and aggressive fluids often lead to corrosion and scaling (Frick et al. 2011, Regenspurg et al. 2010). Corrosion of equipment is usually caused by oxidation or electrochemical processes involving acidic or highly saline water and gases such as hydrogen sulfide (H₂S) or solute oxygen (O₂) (Frick et al. 2011). Scaling is the formation of precipitates in the pipes, which reduces the attainable volumetric flow (Huenges 2011, Regenspurg et al. 2010). Aquifer thermal energy storage (ATES) systems store hot or cold water in aquifers, and exchange the stored energy in surface facilities during seasonal storage and recovery cycles: surplus heat is stored in summer and withdrawn for heating in winter (Figure 1.5) (Allen et al. 1984). Cold storage systems work vice versa, with cold storage in winter and withdrawal of cooling energy in summer (ibid.). ATES system use shallow aquifers (approx. < 400 m depth; Hähnlein et al. 2010) for thermal energy storage purposes, and geochemical risks are similar to geothermal and ASR systems. The impact on groundwater quality due to the release of contaminants is an environmental issue, which is mainly important when aquifers are utilized for both drinking water production and thermal energy storage (Bonte et al. 2013a, Zuurbier et al. 2013). Increased temperatures do not only shift

chemical equilibria, but also favor the growth of specific microbial communities, and legal limitations restrict thermal utilization of groundwater in many countries to avoid adverse effects on drinking water quality (Griebler et al. 2014, Hähnlein et al. 2010). Clogging of aquifer pores, pipes and heat exchangers by precipitated solids has been an issue in several systems: operation has been impaired by incrustations, predominantly salts such as calcite (CaCO₃), and various oxides and hydroxides of iron and manganese (Weber 2000). Depending on the geochemistry of the site, other solid phases such as iron sulfides may also precipitate, and microbial activity can be an important factor in these reactions (Huenges 2011, Würdemann et al. 2014). When solids precipitate in aquifer pores, porosity does not necessarily correlate with permeability, as the mass redistribution by dissolution and re-precipitation may fill small pores or pore throats and consequently block flow pathways (Schepers 2012, Tenthorey et al. 1998).



Figure 1.5: Storage and recovery operation cycles in aquifer thermal energy storage (ATES) heat storage systems. In summer (left), groundwater is produced from the cold well (blue), heated up with surplus energy, and reinjected into the aquifer through the hot well (red). In winter (right), the stored hot water is withdrawn, pumped through heat exchangers, and reinjected into the cold well. A cold water bubble forms around the cold well, and a hot water bubble around the hot well.

1.3.2 Critical processes and control parameters

Water mixing, temperature changes, and gas pressure changes are the critical processes that affect the control parameters of hydrogeochemical reactions, e.g. temperature, pH, redox, or solute concentrations, which can ultimately lead to negative impacts on facility operation and groundwater quality (Hartog et al. 2013). Mixing induces redox-, pH-, salinity- or concentration gradients in the groundwater, temperature directly affects thermodynamic equilibria and reaction kinetics, and gas pressure affects carbonate precipitation (CO₂), corrosion (e.g. O₂, H₂S), and redox

processes (O₂) (Frick et al. 2011, Hartog et al. 2013). Microbial communities can be affected by all of these processes if they change the hydrogeochemical environment significantly, but the most important control parameter is temperature (Griebler et al. 2014, Hartog et al. 2013).

The control parameters for water-rock interactions in ATES systems, which the present thesis focuses on, have been studied at different sites, and both universally valid and site-specific issues which have been found in these studies will be discussed briefly in the following paragraphs. A study of quarternary sands from northwest Germany identified minor dissolution of silicates and precipitation of carbonates as major processes at up to 50 °C, but found no significant porosity changes (Arning et al. 2006). In another study, tertiary lignite sands from northern Germany were extracted in laboratory experiments with tap water at up to 70 °C (Jesußek et al. 2013). A shift in desorption behavior of cations and organic acids at 70 °C was postulated based on changes in pH, solute potassium, and solute magnesium, but no distinct effects were found at temperatures below 40 °C (ibid.). An exhaustive study on the impact of geothermal energy systems on shallow aquifers in the Netherlands showed temperature-induced effects on redox conditions, pH, solute cation concentrations and dissolved organic carbon (DOC) at 60 °C, but only small changes in groundwater quality were observed below 25 °C (Bonte et al. 2013a, 2013b, 2013c). The most significant issue was the mobilization of arsenic, which can be a major environmental problem (Bonte et al. 2013c). In these three examples, significantly elevated temperatures were required for a detectable increase in water-rock interactions, although "threshold" temperatures and induced processes depended on the site-specific mineralogy and geochemistry. Concerning the sensitivity of chemical equilibria, sorption reactions are particularly dependent on temperature changes, and several observed water quality changes were attributed to desorption (Bonte et al. 2013c, Jesußek et al. 2013). In addition to temperature, water mixing was identified as a major contributing process (Bonte et al. 2013a). Hydrogeochemical reactions caused by the reinjection of chemically altered groundwater after water treatment or operationally induced chemical processes were also reported by other authors (e.g. Holm et al. 1987, Perlinger et al. 1987). Since shifts in redox conditions were observed in some studies (Bonte et al. 2013b, Jesußek et al. 2013), or directly introduced into the aquifer by water mixing or atmospheric oxygen intrusion, e.g. when the nitrogen pressurization of the system failed (Huenges 2011), the dissolution of redox-sensitive minerals such as sulfides can become an important secondary process. As shown in chapter 1.2.3, the dissolution of (iron-bearing) sulfides acidifies the groundwater, potentially inducing further water-rock interactions. This phenomenon has been addressed by countless studies, as iron sulfide is very common and reactive (e.g. Nordstrom 1982, Possemiers et al. 2016, Prommer & Stuyfzand 2005, Wallis et al. 2011).

1.4 Site of investigation

The research in this study was performed with two types of siliciclastic rocks from the Lower Jurassic series of the North German Basin. Both rock types, one sandstone and one siltstone, had been sampled during the drilling of the wellbore "Am Reichstag 2/98". The well is part of an active ATES system located at the German parliament buildings in the city of Berlin. During the installation and initial operation of the ATES system, extensive research work had been performed, and the results were made available in a comprehensive project report (Huenges 2011). The Lower Jurassic series, found at a depth of approximately 300 m, consists of interbedded sequences of weakly cemented sand-, silt-, and claystones that had been formed during eustatic progression and regression of the coastline (Göthel 2006). At the wellbore location, Cretaceous, Upper Jurassic and Middle Jurassic sediments are eroded, so that the Lower Jurassic rocks are found directly below the Tertiary sediments (Rockel et al. 1999) (Figure 1.6).



Figure 1.6: Map of the deep boreholes and the solid rocks located directly below Quarternary / Tertiary sediments in Berlin (Germany). The ATES wellbore "Am Reichstag 2/98" is situated in the city centre (marked within the black frame). Map taken from Kahnt et al. (2011), modified.

The sandstone had been cored from an aquifer of the Hettangian stage in a depth of 310 m, which is being used as the heat storage aquifer of the ATES system. The siltstone stems from a Lower Sinemurian horizon in a depth of 297 m, which forms the topset aquitard of the Hettangian aquifer.

The natural groundwater found in the Hettangian aquifer is weakly saline (ca. 28 g/L), and 97 % of its ion concentration consists of sodium (Na⁺) and chloride (Cl⁻). The water is poor in oxygen (0 to 0.25 mg/L), has a neutral pH between 7 and 7.3, and has a density of 1018 kg/m³ (Huenges 2011).

1.5 Scope of the thesis

This thesis seeks to comprehensively determine the reactivity of siliciclastic rocks with respect to the specific use case of ATES systems. This comprises an understanding of the water-rock interactions that mobilize contaminants or potentially mineralforming elements in a worst case scenario and in the ATES scenario. The ATES scenario was defined to have elevated temperatures of up to 90 °C and possible changes of the groundwater redox potential by intrusion of oxygen. The latter is important to observe the dissolution of redox-sensitive minerals such as sulfides, and assess potentially triggered reactions due to pH reduction.

The aim is to perform a workflow that allows the description of geochemical risks related to the reactivity of the analyzed rock, and compile a reference that provides a qualitative and quantitative list of critical (contaminant/mineral-forming) mobile elements that will be released under specific operational conditions. The following issues shall be addressed:

- 1. Quantify the bulk mineral composition and the surface composition of the rock.
- 2. Quantify the maximal amount of potentially critical mobile elements that can be leached from a defined mass of rock material.
- 3. Identify the chemical bond or phase association of the leached mobile elements, e.g. adsorbed, carbonatic, sulfidic, to understand the release mechanism.
- 4. Quantify the amount of potentially critical mobile elements that are leached from a defined mass of rock in the use case scenario. Identify governing factors, interactions and potential feedback effects.

Concerning the methodology, items 2 and 3 require a selective leaching procedure with strong solvents, for which the sequential extraction, a method originally from soil science, may be suitable. However, the method has to be adapted for the small leachable element amounts of rocks, compared to soils, and for a complete dissolution of common soluble rock components, such as sulfides. For item 4, a combination of leaching experiments, statistical methods and numerical simulations will be applicable. In the following chapter 1.6, an overview over the chapters, in which these issues are addressed in detail, is given.

1.6 Outline of the thesis and included publications

The thesis is structured into three main chapters, each of which corresponds to an article published in an international peer-reviewed scientific journal. All articles included in this thesis are postprint versions. Its contents correspond to the published articles. Layout and pagination have been modified for the thesis. Due to the different guidelines of the publishing journals, chapter 3 is written in British English, and all other chapters in American English. References for all chapters are provided at the end of the thesis. The cited articles and contents of the chapters are as follows.

Chapter 2: "Geochemical characterization of the Lower Jurassic aquifer in Berlin (Germany) for Aquifer Thermal Energy Storage applications".

Originally published as:

Müller D, Regenspurg S. Geochemical characterization of the Lower Jurassic Aquifer in Berlin (Germany) for aquifer thermal energy storage applications. Energy Procedia 2014; 59:285–92. <u>https://doi.org/10.1016/j.egypro.2014.10.379</u>.

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This chapter investigates the geologic setting, the bulk mineral composition, and the reactivity at 90 °C of the two sampled rock types. Several common mineralogical methods (X-ray diffraction, X-ray fluorescence, scanning electron microscopy) were performed to determine the bulk mineralogy of the rocks. Long-term leaching tests with 90 °C hot synthetic brine (25 g/L NaCl solution) over one month were carried out to investigate element mobilization, secondary precipitates and potentially critical rock components. A hydrogeochemical model using the software PHREEQC was built to help understand the observed processes.

Chapter 3: "An improved sequential extraction method to determine element mobility in pyrite-bearing siliciclastic rocks".

Originally published as:

Müller DR, Friedland G, Regenspurg S. An improved sequential extraction method to determine element mobility in pyrite-bearing siliciclastic rocks. Int J Environ Anal Chem 2017; 97(2):168–88. <u>https://doi.org/10.1080/03067319.2017.1294166</u>.

This is an Accepted Manuscript of an article published by Taylor & Francis Group in the International Journal of Environmental Analytical Chemistry on 20/02/2017, available online: <u>https://www.tandfonline.com/doi/abs/10.1080/03067319.2017.1294166</u>.

In this chapter, the adaptation of the sequential extraction method to siliciclastic rocks with a focus on pyrite is described. This leaching method is capable of discerning the phase association of mobile elements into (1) an exchangeable/adsorbed fraction, (2) an acid-soluble fraction (carbonates), (3) a reducible fraction (oxides and hydroxides), and (4) an oxidizable fraction (sulfides and organic matter). Since strong solvents are applied to the material, the amount of leached elements corresponds to a worst case scenario, which means that a complete mobilization of elements susceptible to a specific solvent can be assumed. Furthermore, the results of the method allow a quantitative estimation of minor surface phases, such as hydroxides, which cannot be quantified by common mineralogical methods (compare chapter 2).

Chapter 4: "The element-release mechanisms of two pyrite-bearing siliciclastic rocks from the North German Basin at temperatures up to 90 °C under oxic and anoxic conditions".

Originally published as:

Müller DR, Regenspurg S. The element-release mechanisms of two pyrite-bearing siliciclastic rocks from the North German Basin at temperatures up to 90 °C under oxic and anoxic conditions. Geothermal Energy 2017; 5(25). <u>https://doi.org/10.1186/s40517-017-0080-1</u>.

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In chapter 4, the release mechanisms of the potentially critical elements aluminum, arsenic, barium, calcium, copper, iron, manganese, nickel, silicium and lead in dependence of temperature and solute oxygen are investigated. The mechanisms are studied using oxic and anoxic leaching tests with synthetic brine (25 g/L NaCl) at 25 °C, 50 °C, 70 °C and 90 °C. With the results of the leaching tests and additional input from the sequential extraction (chapter 3), numerical simulations with the software PHREEQC and various statistical analyses are performed to identify important control parameters and interactions between the involved release mechanisms.

2 Geochemical characterization of the Lower Jurassic aquifer in Berlin (Germany) for Aquifer Thermal Energy Storage applications

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2.1 Abstract

Hydrogeochemical processes associated with the potential seasonal storage of 90 °C hot water in a Lower Jurassic aquifer (Lower Sinemurian / Hettangian stages) in the city of Berlin, Germany, are characterized and evaluated to determine possible sources of mineral precipitation resulting in aquifer damage (clogging). Laboratory leaching tests with material from the sandstone aquifer and the pelitic hanging aquiclude obtained from the wellbore "Am Reichstag 2/98" were conducted over a period of 28 days under anoxic conditions. A hydrogeochemical batch reaction simulation of the leaching test was set up with the commercial software PHREEQC and matched to the experimental results. Laboratory experiments show a strong pH decrease and sulfur mobilization as well as precipitation of reddish-brown iron hydroxides. This is most likely the consequence of pyrite oxidation. PHREEQC simulations can reproduce acidification and hematite precipitation if a minor diffusion of oxygen into the system is assumed.

Keywords:

Aquifer Thermal Energy Storage, hydrogeochemistry, geochemical modeling

2.2 Introduction

Aquifer Thermal Energy Storage (ATES) systems are a specific type of Underground Thermal Energy Storage (UTES) systems, in which shallow or intermediate aquifers are utilized for seasonal storage of large amounts of thermal energy. To that end, aquifer water is produced, heated up and reinjected into the aquifer. One of the most important issues regarding the reliability and the long-term efficiency of these systems is the effect of elevated temperatures and pressures caused by the production-injection cycles on the hydraulic properties of the storage aquifer (e.g. Lee 2010, Seibt et al. 2010). Generally, porosity and permeability in ATES systems can diminish as a result of mobilization and deposition of fine particles, dissolution or precipitation of minerals, clay swelling or gas trapping (e.g. Ochi & Vernoux 1998, Seibt & Wolfgramm 2008, Ungemach 2003). In addition to aquifer clogging, geochemical interactions between pore fluid and matrix can affect pH and redox conditions of the groundwater, resulting in undesirable environmental consequences (Palmer & Cherry 1984).

In this study, the Lower Jurassic aquifer in the city of Berlin (Germany) is investigated with respect to hydrogeochemical processes associated with hot water storage of up to 90 °C. The geochemical characterization is required to simulate the long-term aquifer storage behavior with a coupled hydraulic-thermal-chemical (HTC) aquifer model.

Nomenclature

A _{surf}	surface area (m²)
E	activation energy (J/mol)
Κ	equilibrium constant
Q	activity product
R	universal gas constant (J/kg/mol)
Т	temperature (K)
a _{H+}	activity of H⁺
$k_{\rm m}^{298.15K}$	rate constant at 25 $^\circ\mathrm{C}$ and pH 0 for a mechanism m
ni	reaction order
pi, qi	empirical constants
Ω	mineral saturation index ($\Omega=Q/K$)

2.3 Materials

2.3.1 Geology

The German capital Berlin is located in the south-eastern part of the Northeast German Basin. Its deep geologic structure is mainly influenced by tectonic movements of the Permian Zechstein salt in the Late Jurassic and Cretaceous periods. The uplifted Mesozoic sediments were subsequently eroded and are missing on top of salt diapirs (Kahnt et al. 2011, Rockel et al. 1999, Sippel et al. 2013). Cenozoic sediments are undisturbed by salt tectonics and are mainly composed of unconsolidated sands. In the Berlin area, Quarternary and Tertiary sediments contain two to four main freshwater aquifers, which are separated from deeper saline aquifers by the Oligocenian Rupelian clay (Limberg & Thierbach 2002).

The target horizon for the aquifer storage is the Lower Jurassic aquifer (Hettangian and Lower Sinemurian stage), which is the shallowest saltwater horizon in central Berlin. Core samples for mineralogical analysis and hydrogeochemical experiments were obtained from the wellbore "Am Reichstag 2/98" from depths of 310 m ("Sample I") and 287 m ("Sample II") below surface. The formation consists of poorly cemented well-sorted greyish fine sandstones with weakly rounded grains (Rockel et al. 1999). Figure 2.1 shows the wellbore profile and the sampling depth. Sample I represents the aquifer material, sample II was taken from the hanging aquiclude located in the transition zone between Lower Sinemurian and Upper Sinemurian sediments. Before analysis, the cored sections had been stored for several years in the core repository of the Berlin geological survey.



Figure 2.1: Profile of the wellbore "Am Reichstag 2/98". The sampling depths of sample I (Hettangian / Lower Sinemurian aquifer) and sample II (Sinemurian aquiclude) are marked by black boxes. Profile from Rockel et al. 1999, modified.

2.3.2 Groundwater composition

The groundwater chemistry of the Hettangian and Lower Sinemurian aquifer in the Berlin area was described by Huenges using samples from the well "Am Reichstag 2/98" (Huenges 2011). The average total salinity of the fluid is about 28 g/L, its main ions being sodium (Na) and chloride (Cl) (97 %), and minor ions being magnesium (Mg), calcium (Ca), potassium (K), strontium (Sr), ammonium (NH₄⁺), sulfate (SO₄²⁻), iron (Fe) and manganese (Mn) (Figure 2.2). Small concentrations of carbon dioxide (CO₂) (20 mg/L) and oxygen (O₂) (0 – 0.25 mg/L) are dissolved in the fluid. The dissolved organic carbon (DOC) content is about 3 mg/L. Concentrations of chromium (Cr), nickel (Ni) and copper (Cu) are below 5 µg/L, and of arsenic (As) below 10 µg/L. The average fluid density is 1.018 g/cm³. The pH is neutral, measured values are between 7 and 7.3.

For experiments conducted within this study, a synthetic groundwater was prepared from purified water and 25 g/L > 99 % pure NaCl.


Figure 2.2: Main element concentrations (g/L) in the Hettangian and Lower Sinemurian aquifer water. The samples were taken in the well "Am Reichstag 2/98" (Huenges 2011).

2.4 Methods

2.4.1 Mineralogical analysis

The mineralogical composition of the rocks was determined by X-ray diffraction (XRD), X-ray fluorescence spectrometry (XRF) and scanning electron microscopy coupled with energy-dispersive X-ray spectroscopy (SEM-EDX). In addition, the specific surface area was measured by Brunauer-Emmett-Teller surface area analysis (BET).

XRD was carried out with a Bruker-axs D8 X-ray Microdiffractometer with GADDS after grinding the grains to a size of 32 µm. Minerals were identified with the software DIFFRAC.EVA, version 2.1. XRF was performed with a PANalytical AXIOS Advanced spectrometer. From the resulting oxide distribution, a set of normed standard minerals was determined using a modified CIPW analysis (Cross et al. 1902), which was adapted to include the mineral phases identified by XRD and EDX. SEM and EDX were realized utilizing a Carl Zeiss SMT Ultra 55 Plus with a tungsten-zircon field emission cathode. The samples were covered with gold for the measurements. Sample I was partitioned by gravitational separation with bromoform (density 2.82 g/cm³) to identify heavy minerals. Minerals were additionally identified by interpreting the EDX spectrograms utilizing reference data from Reed (2010). BET measurements were performed according

to DIN-ISO 9277 as a 5-point nitrogen adsorption isotherme by Quantachrome, Odelzhausen (Germany) with a Quantachrome Quadrasorb surface area and pore size analyzer.

2.4.2 Leaching tests

Laboratory leaching tests were conducted under anoxic conditions with homogeneously ground rock material and synthetic groundwater in PTFE autoclaves ("Bola Hydrolyzing and Digestion Vessels") manufactured by Bohlender. The synthetic groundwater was flushed with nitrogen (N₂) before the experiments to remove dissolved oxygen. A glovebox with argon protective atmosphere was utilized to load the autoclaves under anoxic conditions. Mortared rock from both samples was leached in solid-liquid-ratios (SLR) of 89 g/L and 178 g/L, respectively. The tests were conducted in duplicates. Leaching time was 672 hours (28 days) and the leaching temperature 90 °C. Afterwards, the eluate was filtered (2 μ m) and analyzed by inductively coupled plasma optical emission spectroscopy (ICP-OES) for the cations and ion chromatography (IC) for the anions. Electrical conductivity was determined with a WTW TetraCon 325 sensor connected to a WTW Multi 340i data acquisition unit, and pH was measured with a VWR pHenomenal pH 1000L measuring device.

2.4.3 PHREEQC simulation

The numerical simulation of the leaching tests was conducted with the hydrogeochemical batch reaction code PHREEQC, version 3.1.2. Thermodynamic data was provided by the built-in database file lnll.dat, which had been compiled by the Lawrence Livermore National Laboratory for the geochemical codes EQ3/6 and Geochemist's Workbench (Parkhurst & Appelo 2013). The data therein is based on an extended Debye-Hückel activity formalism and valid in a temperature range between 0 and 300 °C (Wolery 1992). Additionally, the mass action balance equation for schwertmannite was added to the database from Regenspurg et al. (2004).

Reaction kinetics were calculated according to Palandri & Kharaka (2004). The rate equation given there integrates neutral, acid and base mechanisms for mineral dissolution. Precipitation can be estimated by reversing the equation or by calculating saturation indices and assuming thermodynamic equilibrium. The rate equation is

$$\frac{dm}{dt} = -A_{surf} \begin{bmatrix} k_{acid}^{298.15K} e^{\frac{-E_{acid}}{R} \left(\frac{1}{T} \frac{1}{298.15 K}\right)} a_{H^+}^{n_1} (1 - \Omega^{p_1})^{q_1} \\ + k_{neut}^{298.15K} e^{\frac{-E_{neut}}{R} \left(\frac{1}{T} \frac{1}{298.15 K}\right)} (1 - \Omega^{p_2})^{q_2} \\ + k_{base}^{298.15K} e^{\frac{-E_{base}}{R} \left(\frac{1}{T} \frac{1}{298.15 K}\right)} a_{H^+}^{n_3} (1 - \Omega^{p_3})^{q_3} \end{bmatrix}$$
(2.1).

Reaction rate constants, activation energies, reaction orders and empirical constants were taken from Palandri & Kharaka (2004) and the references therein. The reactive surface area is a key parameter for rate calculation in mineral dissolution kinetics since it determines the effective amount of minerals involved in reactions. However, a precise value is often difficult to determine for several reasons (Cantucci et al. 2009). First, specific surface areas of different mineral phases vary by several orders of magnitude. Unless ground and mineral-separated samples are measured, laboratory methods such as BET determine the surface area of the whole rock, which is a combined value of all mineral phases found in the rock. Second, depending on grain packing, mineral paragenesis, coating, and other factors, only part of the mineral surface is exposed to the pore fluid and thus available for reactions. In addition, reactions between pore fluid and mineral surfaces usually occur at selective sites, where etch pits may form (Gautier et al. 2001, Xu et al. 2005, Xu et al. 2007). Consequently, BET surface analysis overestimates the reactive surface area (Xu et al. 2007). Third, the morphologies of the mineral surfaces change during reactions, which alters the specific surface area (Cantucci et al. 2009). It is unclear if this affects the actual rate of dissolution, however (Gautier et al. 2001).

In this study, the specific surface area of the rock samples was measured by BET. These values serve as upper boundaries. To determine initial values for the individual mineral phases, literature values from Cantucci et al. (2009), Steefel & Lichtner (1998) and Xu et al. (2005) were used. These initial values were subsequently tuned to the experimental results to get a best match for the actual reactive surface areas. The resulting values for the modeled minerals are given in Table 2.1, in combination with all other required kinetic parameters.

For the simulation, the mineral composition was taken from the XRD, XRF and SEM-EDX measurements, and the fluid composition corresponds to the synthetic groundwater used in the experiments. Initial pH was set to 7, initial pe to -3. Reaction temperature was 90 °C. The reaction was modeled over 672 hours in 28 steps of 24 hours each. All dissolution reactions were modeled using equation (1), while precipitation reactions were modeled assuming thermodynamic equilibrium. Two simulations were conducted to account for possible air leaks in the autoclaves. In simulation 1, 400 µmol of oxygen were assumed to diffuse into the autoclave over 28 days. In simulation 2, no oxygen was allowed to be present in the system.

Mineral	A _{surf}	Acid m	echanism		Neutral mechar	l 1ism	Base m	echanism	
	(m²/g)	log k	E (kJ/mol)	n ₁	log k	E (kJ/mol)	log k	E (kJ/mol)	n ₃
Quartz	0.02				-13.4	90.9	-16.29	108.366	-0.5
K-Feldspar	0.01	-10.06	51.7	0.5	-12.41	38.0	-21.2	94.1	-0.823
Albite	0.01	-10.16	65.0	0.457	-12.56	69.8	-15.6	71.0	-0.572
Anorthite	0.01	-3.5	16.6	1.411	-9.12	17.8			
Muscovite	0.10	-11.85	22.0	0.37	-13.55	22.0	-14.55	22.0	-0.22
Kaolinite	2.32	-11.31	65.9	0.777	-13.18	22.2	-17.05	17.9	-0.472
Illite	0.20	-11.31	23.6	0.78	-13.18	35.0	-17.05	58.9	-0.47
Montmorill.	0.20	-12.71	48.0	0.22	-14.41	48.0	-14.41	48.0	-0.13
Ilmenite	0.02	-8.35	37.9	0.421	-11.16	37.9			
Pyrite	0.02	-7.52	56.9	0.5	-4.55	56.9			

Table 2.1: Mineral kinetic rate parameters required for equation (1). Kinetic data is from Palandri & Kharaka (2004).

2.5 Results

2.5.1 Mineralogy

The average mineral composition calculated from XRD and XRF data is shown in Figure 2.3 for both samples. Sample I is a sublithic arenite according to the classification of sandstones by Dott & Folk, and mainly consists of quartz, feldspars, mica and kaolinite. Trace minerals constitute less than one percent of the total mass. Rutile and Ilmenite were identified by SEM-EDX. The XRF detected 0.035% carbon (C) and 0.06% sulfur (S) in the samples, which could not be attributed to any mineral phase identified by SEM-EDX or XRD. The carbon originates either from unidentified carbonates or from organic matter. In addition to these trace minerals, gravitational separation of the sample yielded 0.03% heavy minerals with a density above 2.82 g/cm³, which consist of zircon, tourmaline, staurolite, aluminosilicates and elemental copper.

Sample II is a pelitic rock mainly composed of quartz, k-feldspars, plagioclase, mica and clay minerals. A precise mass distribution of kaolinite, illite and montmorillonite could not be realized with the available data, therefore all clay minerals were merged into a single category. Ilmenite and rutile were identified with SEM-EDX. The XRF spectroscopy detected 1.47 % carbon and 0.76 % sulfur. All sulfur was assumed to be bound in pyrite, as verified by SEM-EDX. Carbon content was associated to calcite, which had been detected by SEM-EDX, and presumably other unidentified carbonates as well as organic matter.



Figure 2.3: Mineral distribution estimated from XRD, XRF and SEM-EDX, (a) sample I (b) sample II.

2.5.2 Ion mobilization

A thin layer of reddish to brown precipitates formed on the inner walls of all autoclaves or was suspended in the liquid. The precipitates were of orange-red (sample I) and muddy-brown (sample II) color (Figure 2.4). In all cases, fluid conductivity increased, and the pH values decreased. For sample I, pH values dropped from an initial value of 7 to 3 (SLR 178 g/L) and 3.3 (SLR 89 g/L), and electrical conductivity increased from 40.4 mS/cm to 42.0 (SLR 178 g/L) and 40.7 mS/cm (SLR 89 g/L), respectively. Main cations in the liquid were Ca, Si, Mg, Fe, Al and K, and the dominant anion was sulfate with only traces of carbonate, phosphate and bromide (Table 2.2). The specific surface area measured by BET decreased from 0.5 m^2/g to 0.42 m^2/g .



Figure 2.4: Precipitates on the inner autoclave walls and in the liquids, *(a)* sample I *(b)* sample II.

In the sample II extracts, the pH values dropped from an initial value of 7 to 4.1 (SLR 178 g/L) and 4.7 (SLR 89 g/L), and electrical conductivity increased from 40.4 mS/cm to 43.2 (SLR 178 g/L) and 41.8 mS/cm (SLR 89 g/L), respectively. Again, Fe, Si, K, Ca and Mg were the dominant cations in the fluid, but the Al concentration was below the detection limit of the ICP-OES. Sulfur was the main anion, with traces of carbonate, phosphate and bromide (Table 2.2). The specific surface area increased from 13.2 m²/g to 16.5 m²/g.

2.5.3 PHREEQC simulation

The best fit for the simulations was obtained by assuming pyrite oxidation to occur. This explains the decreased pH value, the release of sulfuric acid, the increased amounts of iron and sulfate in solution and the precipitation of iron bearing minerals as indicated by the reddish color.

Precipitates from sample I were calculated to be hematite, when oxygen was included in the autoclave reaction. In this case, the pyrite oxidation rate was accelerated and more iron and sulfur were dissolved. Sodium and magnesium were not mobilized at all, and potassium was underestimated by one order of magnitude. Silicium and aluminium concentrations matched the order of magnitude of the experiments. The pH decreased to 2.3 (SLR 178 g/L) and 2.6 (SLR 89 g/L), respectively. If no oxygen was present during the reaction, hematite did not become oversaturated and the pH value decreased to slightly acidic values of 6.1 (SLR 178 g/L) and 6.2 (SLR 89 g/L), respectively (Table 2.2).

In sample II, calculations did not show iron mineral precipitation, regardless of the presence or absence of oxygen. The concentration of dissolved iron was two orders of magnitude higher than measured in the experiments. The concentrations of sodium and potassium were underestimated by one order of magnitude, the concentration of magnesium by two orders of magnitude. Silicium matched the experimental results. The pH decreased to 3.5 (SLR 178 g/L) and 3.2 (SLR 89 g/L), respectively. Without oxygen addition, the pH increased to slightly alkaline values of 8.4 (SLR 178 g/L) and 8.1 (SLR 89 g/L) (Table 2.2).

simulatio EXP marl condition due to on Sample,	ns. Sample ks experimen s. For the exp ly one sample	s are diff. tal results, SI/ eriments, com e being availa.	erentiated L M +O2 marks centrations ar ble for measu	simulation re e given as arit rements. C	thmetic mean.	ng/L)			Conductivity	Hd
SLR (g/L)		Ca	Fe	Mg	Si	×	АІ	S(6)	—(mS/cm)	
l, 178	EXP	15.5±0.7	3.15±0.35	9.00±0.28	15.0±0.0	6.90±1.70	3.10±0.28	42.6	42.0±0.1	3.0±0.0
	SIM +O2	0	2.80E-03	0	11	0.94	4.73	148	n.a.	2.3
	SIM	0	0.11	0	12.9	0.06	0.21	2.40E-04	n.a.	6.2
l, 89	EXP	7.25±0.21	0.76±0.20	4.50±0.14	8.40±0.71	3.50±0.00	1.30±0.28	22.3	40.7±0.4	3.3±0.1
	SIM +O2	0	5.10E-04	0	6.09	0.59	2.54	74.1	n.a.	2.6
	SIM	0	0.06	0	8.95	0.04	0.2	1.70E-04	n.a.	6.1
II, 178	EXP	738±14	1.90±0.28	76.5±2.1	18.5±0.7	38.5±0.7	v	536	43.2	4.7
	SIM +O2	82.8	156.8	0.13	7.74	1.123	0.46	170	n.a.	3.5
	SIM	15.6	4.30E-04	1.50E-05	28.4	1.68	0.63	1.60E-04	n.a.	8.4
II, 89	EXP	407	5.3	44	18	23	1.4	328	41.8	4.4
	SIM +O2	70	153	0.07	6.62	0.65	2.94	169	n.a.	3.2
	SIM	7.84	1.30E-03	2.40E-04	19.1	0.76	0.41	1.60E-04	п.а.	8.1

2.6 Discussion

The major part of both rock samples consists of weakly reactive minerals, such as quartz, feldspars and mica. The mass fraction of minerals or amorphous phases that are highly reactive is as low as 1 % for sample I and 2 % for sample II. Comparison of data from XRF spectroscopy and fluid analysis of the eluate show a strong mobilization of sulfur. From both samples, approximately 40 % of the sulfur contained in the rock material was mobilized. Additional sulfur may be contained in the precipitates. In a first approximation, the sulfur-bearing mineral of the rock is assumed to be pyrite, which was identified by SEM-EDX in sample II. Since pyrite oxidation is a highly acidifying process, its presence could explain the measured decrease of the pH during the experiments. However, it cannot be excluded that there are other sulfur-bearing minerals, such as Greigite (Fe₃S₄) or amorphous phases, present in the samples.

The precipitates found on the inner walls of the autoclaves are most likely ferrous oxides or hydroxides. Fe³⁺ ions in aqueous solutions can precipitate as goethite (FeOOH) or hematite (Fe₂O₃), releasing protons (Cornell & Schwertmann 1996)

$$Fe^{3+}+2H_2O \Leftrightarrow FeOOH+3H^+$$
 (2.2)

$$2Fe^{3+}+3H_2O \Leftrightarrow Fe_2O_3+6H^+$$
(2.3).

The formation of goethite and hematite is considered to be preceded by the formation of amorphous ferrihydrites. The rates of transformation and the ratio of resulting goethite and hematite depend on reaction kinetics. Precipitation of hematite is favored by high temperatures, high ionic strength of the water, and neutral or very low pH (Cornell & Schwertmann 1996). Consequently, the elevated experimental temperatures favor a rapid formation of crystalline goethite and hematite. In terms of pH, sample I favors the formation of hematite over goethite, while sample II provides favorable conditions for goethite precipitation. Furthermore, the presence of secondary ions facilitates the formation of metastable minerals which transform to hematite or goethite over time. In the presence of sulfate, the iron(III)-oxyhydroxysulfate Schwertmannite (Fe₈O₈(OH)₆SO₄) precipitates (Regenspurg et al. 2004)

$$8Fe^{3+} + ySO_4^{2-} + (12-y+0.5x)H_2O \Leftrightarrow Fe_8O_8(OH)_x(SO_4)_y + (24-2y)H^+$$
(2.4).

The numerical simulations show that pyrite dissolution is strongly dependent on the availability of oxygen. Assuming a perfectly closed system, no ferrous oxides or hydroxides precipitate. However, even the diffusion of small amounts of O_2 into the system accelerates pyrite oxidation notably. In sample I, this results in the precipitation of iron minerals and an acidification of the solution. In sample II, no precipitation of iron minerals is calculated, regardless of the oxygen content. However, the concentration of sulfur is slightly underestimated while the concentration of iron is

overestimated by two orders of magnitude. This suggests that iron was removed from the solution during the experiments, which is supported by the coating found inside the autoclaves. Since the llnl database includes only the reaction of pyrite with water (Parkhurst & Appelo 2013)

$$FeS_2 + H_2O \Leftrightarrow 0.25H^+ + 0.25SO_4^{2-} + Fe^{3+} + 1.75HS^-$$
 (2.5),

other scenarios that do not involve the diffusion of air into the system are possible. Pyrite may be oxidized by Fe³⁺, or the reaction may be microbially catalyzed by ironand sulfur-oxidizing bacteria such as *Thiobacillus ferrooxidans* (e.g. Nordstrom & Alpers 1999). Schwertmannite is undersaturated in both samples, because the sulfur concentration is too low. Acceleration of pyrite oxidation could result in oversaturation and precipitation of this mineral.

2.7 Conclusions and outlook

Although the investigated rock samples consist of mainly inert minerals, less than 1% of highly reactive sulfur-bearing minerals, presumably pyrite, generate precipitations of ferrous oxides and hydroxides that may lead to aquifer clogging. In addition, those reactions release protons, which will decrease the pH of the aquifer water. Oxygen is a key parameter in this process, and preventing O_2 diffusion into the system is required to avoid aquifer damage by chemically clogging the pores of the rock.

An approximate reproduction of the laboratory leaching tests with PHREEQC is possible, but requires further refinement. Particularly, oxidization of pyrite and precipitation of ferrous oxides and hydroxides are complex processes which are difficult to model and quickly become computationally expensive. For coupled reactive flow simulations however, complexity needs to be kept to a minimum to maintain reasonable computation times.

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3 An improved sequential extraction method to determine element mobility in pyrite-bearing siliciclastic rocks

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3.1 Abstract

A sequential extraction method was developed for pyrite-bearing (FeS₂) siliciclastic rocks. The focus of this study was to enhance the procedure by an improved oxidation step to completely dissolve not only organic matter but also microcrystalline pyrite. In the first experiment, four oxidation procedures were compared for pure pyrite at extraction temperatures of 25°C and 85°C with hydrogen peroxide (H_2O_2) as the main oxidant. It was found that pyrite dissolution was most effective by using a mixture of H₂O₂, ammonium acetate (NH₄OAc) and nitric acid (HNO₃) at 25°C. This procedure dissolved >90% pyrite, and detected >75% using solute iron measurements. The difference between these two results was explained by reprecipitation of secondary iron minerals. The procedure worked best at 25°C, since solvent evaporation at 85°C amplified iron oversaturation and precipitation. For the pyrite-bearing siliciclastic rocks, two sequential extraction schemes were compared to optimise solid-solvent ratio, extraction step order and type of solvent. Eventually, the most effective step order identified for siliciclastic rocks containing pyrite and little organic matter was to first (1) remove the exchangeable fraction, followed by (2) dissolution with acid and afterwards (3) with a reducing agent. The (4) oxidation step was performed last.

Keywords

Sequential extraction, siliciclastic rocks, pyrite, element mobilization, solid phase quantification

3.2 Introduction

Over the last decades, aquifers have been increasingly used for large-scale storage applications and energy production (Zuurbier et al. 2013). Significant techniques are storage and recovery of freshwater (Dillon et al. 2006, Wallis et al. 2011), CO₂ storage (Förster et al. 2006), waste water injection (Tsang et al. 2008), shallow and deep geothermal energy production (Bayer et al. 2012, Blum et al. 2010, Huenges 2011) and seasonal thermal energy storage (Kranz & Frick 2013, Possemiers et al. 2014). The efficiency and operational safety of these systems are heavily influenced by hydrogeochemical processes in the aquifer. Changes in temperature, oxygen input and fluid mixing are the most important parameters potentially causing aquifer damage (Griebler et al. 2014, Hartog et al. 2013), such as pore clogging by mineral precipitation (Allen et al. 1984, Palmer et al. 1992) and degradation of groundwater quality by contaminant release (Bonte et al. 2013c, Possemiers et al. 2014). The release of mobile elements responsible for contamination and pore clogging is mainly associated with highly reactive solid phases, such as organic matter, carbonates, sulphides, oxides and hydroxides (Bonte et al. 2013c, Jesußek et al. 2013).

The phase fractionation of contaminants in soils, sediments or solid waste materials can be quantified by sequential extraction, a leaching procedure in which a sediment is treated successively with solvents of increasing aggressivity. Tessier et al. (1979) were the first to propose a four-step extraction scheme to differentiate between the exchangeable, acid-soluble (carbonates), reducible (metal oxides and hydroxides) and oxidisable fraction (organic matter and sulphide minerals), which was complemented by the analysis of the insoluble residual fraction. The Tessier scheme has been applied to numerous environmental materials (Arunachalam et al. 1996, Förstner et al. 1981, López-Sánchez et al. 1993, Schultz et al. 1998, Wisotzky & Cremer 2003), and modified to address specific research aims. Major modifications concerned solvent choice, step order and control of resorption and reprecipitation (Gleyzes et al. 2002, Sahuquillo et al. 2003). To improve reliability and allow comparability, the Community Bureau of Reference of the Commission of the European Communities (BCR) proposed a harmonised reference extraction scheme (Ure et al. 1993), which was improved later on (Rauret et al. 1999). The BCR scheme comprises a three-step sequence with the step order: (1) ion exchange/acid dissolution, (2) dissolution by reducing agent, (3) dissolution by oxidation, leaving behind the insoluble residual fraction. It differs from the Tessier scheme by combination of the exchange and acid solution steps, and specifies minor changes to extraction time and solvent choice.

In this study, the improved BCR scheme was used as reference, and modified for the application to siliciclastic rocks with small quantities of mobile elements compared to soils and solid waste materials commonly analysed by this technique. To that end, the most common reactive phases in siliciclastic rocks need to be dissolved, including microcrystalline pyrite (FeS₂). Pyrite is the most frequently occurring sulphide, found as primary and secondary minerals in both sedimentary and igneous rocks (Deer et al. 1992). Sulphide oxidation plays an important role in water acidification and the release of heavy metals, sulphate and iron, which affects water quality and may facilitate the formation of secondary iron minerals (Nordstrom 1982). To dissolve pyrite, the oxidation step originally designed for quantifying solely the organic fraction had to be improved. The sequential extraction has already been utilised for the quantification of mobile elements associated with pyrite by applying concentrated nitric acid or acidified chromium chloride as solvents (Canfield et al. 1986, Claff et al. 2010, Poulton & Canfield 2005). However, the use of acidified hydrogen peroxide (H_2O_2) allows dissolving both organic matter and pyrite in one extraction step, which preserves the number of steps originally proposed by Tessier et al. (1979). On aquifer sediments, the sequential extraction technique has been mainly applied to determine the mobility of individual contaminants, such as chromium, lead or arsenic (Asikainen & Nikolaidis 1994, Fuller et al. 1996, Guo et al. 2008), and occasionally on other tasks such as groundwater decontamination supervision (Fox et al. 2005) or trace metal fractionation (Škvarla 1998). Wisotzky and Cremer (2003) proposed a flow-through sequential extraction for

porous aquifer samples which successfully detected minor reactive phases such as carbonates, but required a large amount of rock samples. The aim of the present study was to optimise the sequential extraction procedure for siliciclastic rocks and to quantify very small fractions of mobile elements and soluble solid phases, by modifying step order, extraction time and solvent choice, while preserving the general usability of the original Tessier scheme.

3.3 Experimental

3.3.1 Materials

The sequential extraction was investigated with two siliciclastic rocks from the Lower Jurassic series, which had been cored in the aquifer thermal energy storage well 'Am Reichstag 2/98' in the city of Berlin (Germany), situated in the south-eastern part of the Northeast German Basin. Sample I, a weakly cemented sandstone from the Hettangian aquifer, is from 310 m depth, and sample II is from the overlaying Sinemurian clay-bearing siltstone at 297 m depth, which forms the hanging aquiclude of the Hettangian aquifer. The mineralogical composition of both rocks was already discussed by Müller & Regenspurg (2014), based on data from X-ray diffraction analysis (XRD), X-ray fluorescence (XRF) and scanning electron microscopy coupled with energy dispersive X-ray spectroscopy (SEM-EDX). It was found that the sandstone mainly consists of quartz (ca. 85%), with some feldspar, mica, clay minerals and traces of heavy minerals. The siltstone contains approximately 40% quartz, and 15-25% feldspar, mica and clay minerals each. In this study, these measurements were complemented with feldspar, clay mineral and trace mineral analyses performed with SEM-EDX, and with transmitted-light microscopy, reflected-light microscopy and electron microprobe analysis (EMPA) measured on thin sections. SEM-EDX was performed at high vacuum utilising a Carl Zeiss SMT Ultra 55 Plus microscope with a Thermo Fisher Scientific UltraDry SDD EDX detector. For EMPA, a JEOL Hyperprobe JXA-8500 F with thermal field-emission cathode was used. Total carbon (TC) was determined with a EuroVector EA 3030 elemental analyzer. For the sequential extraction, the consolidated rock samples were ground in a mortar to a homogeneous powder, keeping the original grains intact.

The pyrite (FeS₂) utilised for dissolution experiments had been collected in Italy (Elba; Tanelli et al. 2001). XRD confirmed the absence of trace minerals. Before the dissolution experiments, the pyrite crystals were powdered in an agate disc mill for 25 min to a grain size $<50 \mu$ m, which was verified by SEM. The effect of inhomogeneous grain size distribution was tested in a separate batch, where pyrite crystals were ground manually for 10–15 min in an agate mortar, resulting in a range of grain sizes between 1 and 1000 μ m.

The masses of sedimentary rock and pyrite were determined with Kern ABJ lab scales having a reproducibility of 0.1 mg and a linearity of ± 0.2 mg.

All reagents utilised were of analytical grade, except acetic acid and hydrogen peroxide, which were available as 'pure' and pharmaceutical grade (Ph. Eur.) reagents, respectively. Aqueous solutions were prepared with ultrapure water.

3.3.2 Pyrite dissolution

Four methods for pyrite dissolution were tested by varying reagents, extraction time and temperature (Table 3.1). In all of them, pyrite was oxidised by hydrogen peroxide (H_2O_2) (McKibben & Barnes 1986):

$$FeS_2 + 7.5H_2O_2 \leftrightarrow Fe^{3+} + 2SO_4^{2-} + H^+ + 7H_2O$$
 (3.1).

Method 1 corresponds to the oxidation procedure utilised in the improved BCR scheme (Rauret et al. 1999), and method 2 doubles the solvent volume proposed therein. For method 3, the oxidation procedure from the original Tessier scheme was applied (Gupta & Chen 1975, Tessier et al. 1979), but using an extraction temperature of 25° C instead of 85° C to avoid solvent evaporation. Method 4 corresponds to method 3, with ammonium acetate (NH₄OAc) added for iron complexation, and nitric acid (HNO₃) for pH control and improved pyrite oxidation. The oxidation of pyrite by nitric acid can be described by (Cho et al. 1983):

$$FeS_2 + 5NO_3^- + 4H^+ \leftrightarrow Fe^{3+} + 2SO_4^{2-} + 5NO(g) + 2H_2O$$
 (3.2).

Solvent	Complexing agent	Temp.	Procedure	Reference
30% H2O2, pH 2 (HNO3, 1.4 mmol/L)	1 M NH4OAc, pH 2	85 °C	10 mL solvent, 1 h 25 °C + 1 h 85 °C 10 mL solvent, 1 h 85 °C 30 mL complexing agent, 16 h 25 °C	Rauret et al. 1999
30% H ₂ O ₂ , pH 2 (HNO3, 1.4 mmol/L)	1 M NH₄OAc, pH 2	85 °C	10 mL solvent, 1 h 25 °C + 1 h 85 °C 3 x 10 mL solvent, 3 x 1 h 85 °C 30 mL complexing agent, 16 h 25 °C	
30% H2O2, pH 2 (HNO3, 1.4 mmol/L)	None	25 °C	30 mL, 16 h	Gupta & Chen 1975 mod.
30% H2O2, 1 M NH4OAc, pH 4 (HNO3, 170 mmol/L)	Added to solvent	25 °C	30 mL, 16 h	

Table 3.1: Comparison of the four pyrite dissolution methods.

All experiments were performed in duplicates with 5, 25, 50, 250 and 500 mg of powdered pyrite with 30 mL of solvent, corresponding to pyrite-solvent ratios of 0.167, 0.833, 1.67, 8.33 and 16.7 g/L. Pretests on the effect of inhomogeneous grain size distribution with a separate batch of manually ground pyrite were performed in duplicates for 0.167, 1.67 and 16.7 g/L utilising the oxidation methods 1, 2 and 3. In methods 1 and 2, the solvent evaporates, and the pyrite-solvent-ratio refers to the 30 mL of complexing agent added to the solid residue after evaporation. The extraction was performed in glass beakers sealed with Parafilm, which were placed on heating plates. After extraction, the solid residue was separated from the solution by filtration, and dried overnight at 70°C. Precipitated crust remaining in the filters after drying was separated gravimetrically from the undissolved pyrite grains. The undissolved pyrite was weighed and the precipitates discarded. In the 8.33 g/L experiments, the precipitated quantities from both samples were large enough (>1 mg) for composition analysis by mid-infrared Fourier Transform Infrared Spectroscopy (FTIR), performed with a Bruker Tensor 27. Samples were measured as potassium bromide (KBr) pellets (sample to KBr ratio of 1:450) in absorbance at wave numbers between 4000 and 400 cm⁻¹. Data for the identification of precipitated solids were taken from Estep et al. (1969), Kong et al. (2011), Laurikenas et al. (2016), Miller & Wilkins (1952), Ruan et al. (2002), Saberi et al. (2008), and Villacís-García et al. (2015). The amount of dissolved pyrite was determined by both weighing the undissolved pyrite residue and by measuring the solute iron concentration and multiplying it with the reciprocal of the pyrite iron mass fraction of 0.4655. Solute iron was determined spectrophotometrically with phenanthroline (Deutsches Institut für Normung 2011), which forms complexes with Fe²⁺ after reducing all iron with hydroxylamine hydrochloride (NH₂OH·HCl). The iron-phenanthroline complex concentration was measured at a wavelength of 500 nm utilising a WTW PhotoLab S 12 spectrometer.

3.3.3 Sequential extraction

Two sequential extraction procedures were designed as permutations of an exchange step (X), an acid solution step (A), a reduction step (R) and an oxidation step (O). The residual fractions were analysed after both procedures. Each extraction step was performed by treating powdered rock with different solvents at various solid– solvent ratios (SSRs), contact times and extraction temperatures. Samples were heated to the desired temperatures on heating plates and agitated with a platform shaker. After each extraction step, the undissolved residue was separated from the eluate by filtration, washed carefully with deionised water and dried overnight at 70°C.

Exchange-oxidation-reduction (XOR) sequence

The first sequential extraction scheme was designed as a three-step exchangeoxidation– reduction (XOR) sequence (Table 3.2), a modification of the scheme proposed by Schultz et al. (1998), but without the acid dissolution step. The acid dissolution was omitted because of low carbon contents, as determined previously for both rock types (Müller & Regenspurg 2014). All extraction steps were carried out in quintuplicates with 50 mL of solvent and 4 g of sediment, resulting in a SSR of 80 g/L. Solvents used were 0.4 M magnesium chloride (MgCl₂) in the X step, 6% sodium hypochlorite (NaOCl) in the O step and acidified (HNO₃) 0.04 M hydroxylamine hydrochloride (NH₂OH·HCl) in the R step. The exchange step was performed at room temperature in 60 mL PP bottles shaken at 115 rpm for 1 h. For the O step, sediment and solvent were filled into glass beakers and heated up to 96°C for 0.5 h under occasional manual shaking. The reduction step was performed in glass beakers at room temperature for 5.5 h.

	Mobilization	Solvent	Time	Procedure
1. Exchange	Adsorbed species (specific and unspecific)	0.4 M MgCl ₂	1 hour	Shaking at room temperature
2. Oxidation	Organic matter and sulfides	6% NaOCI, pH 7.5	0.5 hours	Heating to 96 ° C, manual shaking
3. Reduction	(Hydr)oxides of manganese and iron	0.04 M NH2OH•HCl, pH < 2 (HNO3)	5.5 hours	Shaking at room temperature

Table 3.2: Three-step sequential extraction scheme XOR (exchange-oxidation-reduction).

Exchange-acid solution-reduction-oxidation (XARO) sequence

The second extraction scheme was designed as a four-step exchange–acid solution-reduction–oxidation (XARO) sequence, based on the schemes of Förstner et al. (1981) and Rauret et al. (1999). It is described in Table 3.3. Two set-ups with different SSRs (33.3 g/L and 66.7 g/L) were performed in triplets with two additional blanks. The applied solvents were 0.4 M MgCl₂ in the X step, 25% acetic acid (HOAc) buffered with 1 M ammonium acetate (NH₄OAc) in the A step, acidified (HNO₃) 0.5 M NH₂OH·HCl in the R step and a mixture of 30% H₂O₂, 1 M NH₄OAc and HNO₃ (pH 4) in the O step. The O step was optimised for pyrite dissolution, and corresponds to pyrite dissolution method 4 (see Table 3.1), which was found to be most efficient (see item 3.3.2). All extraction steps were performed at room temperature. For the X, A and R steps, solvent and rock powder were filled into 60 mL PP bottles and shaken at 150 rpm for 1 h, 2 h and 16 h, respectively. For the O step, open glass beakers were used and sealed with Parafilm to avoid spattering due to fierce reactions. The extraction time was set to 16 h, samples were occasionally shaken manually.

	Mobilization	Solvent	Time	Procedure
1. Exchange	Adsorbed species (specific and unspecific)	0.4 M MgCl ₂	1 hour	Shaking at room temperature
2. Acid solution	Carbonates and remaining adsorbed species	1 M NH₄OAc in 25 % HOAc, pH 4	2 hours	Shaking at room temperature
3. Reduction	(Hydr)oxides of manganese and iron	0.5 M NH2OH•HCl, pH < 2 (HNO3)	16 hours	Shaking at room temperature
4. Oxidation	Organic matter and sulfides	30 % H2O2 with 1 M NH4OAc, pH 4 (HNO3)	16 hours	Room temp., manual shaking

Table 3.3: Four-step sequential extraction scheme XARO (exchange-acid dissolution-reduction-oxidation).

Analysis

Solute metals in the eluates were determined by inductively coupled plasma optical emission spectrometry (ICP-OES) for aluminium (Al), arsenic (As), barium (Ba), calcium (Ca), iron (Fe), potassium (K), nickel (Ni) and lead (Pb), and with ICP mass spectrometry (ICP-MS) for copper (Cu) and manganese (Mn). Utilised instruments were Thermo Scientific iCAP 6300 Duo (ICP-OES) and Thermo Fisher Scientific Neptune (ICP-MS). Elemental composition of the solid residue after the final extraction step was analysed by XRF, utilising a PANalytical AXIOS Advanced spectrometer, for Al, Ca, Fe, K and Mn. Arsenic, Cu, Ni and Pb were quantified with ICP-MS after full digestion with aqua regia, hydrofluoric acid and perchloric acid. In the XOR sequence, XRF measurements were conducted for each of the five extracted samples, while in the XARO sequence, the measurement was conducted on one residue. The grain surfaces of the powdered rocks before and after the extraction procedure were investigated with SEM-EDX in the XOR sequence. Carbon-nitrogen-sulphur (CNS) analyses were performed as part of the XARO sequence on untreated rock samples, on the residue after the reduction step and on the residue after the oxidation step. The CNS analyses were performed in triplets on samples from the 66.7 g/L extraction, using a Vario EL III element analyzer.

Calculation of solid phase mass fractions

The fractionation of TC and total sulphur was quantified from CNS sediment analysis on untreated and extracted sediment. To estimate total inorganic carbon (TIC) and total organic carbon (TOC), TC was measured on the untreated sample before extraction, after the reduction step before organic matter was removed and after the oxidation step. TIC was calculated by TIC = $TC_{untreated}$ - $TC_{reduced}$, and TOC corresponds to $TC_{reduced}$, where $TC_{(untreated, reduced)}$ is the TC in the untreated rock, and in the rock after the reduction step. For these estimates, the residual carbon was assigned to TOC, because

the acid solution step dissolves calcite and dolomite without residue (Pickering 1986, Tessier et al. 1979), while organic matter dissolution may be incomplete and leave paraffinic and non-humified residues (Tessier et al. 1979). The quantification of these residues allows an estimate of the effectiveness of the oxidation procedure for organic matter by calculating the dissolved TOC fraction in per cent by $TOC_{dissolved} =$ (TC_{reduced}-TC_{residue}/TC_{reduced}), where TC_{(reduced, residue}) is the total carbon after the reduction step, and in the insoluble residue after the oxidation step. Organic matter was quantified by multiplying the TOC content with the conventional Van Bemmelen conversion factor of 1.724. Total sulphur (S) can be attributed to adsorbed S, easily soluble sulphates (e.g. gypsum $CaSO_4 \cdot 2H_2O$), oxidisable fractions such as sulphides or organic matter or hardly soluble sulphates (e.g. barite BaSO₄). These fractions were calculated according to S_{sorbed}, gypsum = S_{untreated}-S_{reduced}, S_{org}, sulphide = Sreduced-Soxidised, and Sbarite = Soxidised, where S(untreated, reduced, oxidised) corresponds to the total sulphur measured in the untreated rock, in the rock after the reduction step and in the residuum after the oxidation step, respectively. To calculate the sedimentary mass (m) fractions of C and S by $w_{(C/S)} = m_{(C/S)}/m_{\text{sediment}}$, the sediment mass m_{sediment} was assumed to be constant, neglecting the mass removed during the sequential extraction. The quantification of minor minerals and amorphous phases contained in the sediment was performed under the assumption that all mineral-forming cations (Ca, Fe, Mn) were released from their respective solid phases in the corresponding extraction steps. Calcite $(CaCO_3)$ was calculated from Ca released in the acid solution step, pyrite from the iron released in the oxidation step. Fe and Mn (hydr)oxides were calculated from the respective cations released in the reduction step. To calculate (hydr)oxide mass fractions, $Fe(OH)_3$ and MnO_2 were chosen as simplified representative phases.

3.4 Results

3.4.1 Mineralogical composition

The Hettangian sandstone contains 95% quartz, and is thus a quartz arenite (Dott 1964). Secondary minerals comprise potassium feldspar, mica and kaolinite. Approximately 1% consists of organic matter, minor and trace minerals. The trace mineral fraction consists mainly of microcrystalline (1 μ m) pyrite, ilmenite (FeTiO₃) and rutile (TiO₂), while TC is <0.1%. The Sinemurian siltstone contains 39% quartz, approximately 10% feldspar and mica each, and 37% clay minerals (kaolinite with traces of illite and chlorite). Organic matter, minor and trace minerals form 4% of the rock, and comprise mainly microcrystalline and framboidic pyrite (1–5 μ m), ilmenite, rutile and calcite (CaCO₃). TC is 1.2%. Scattered heavy minerals, such as zircon (ZrSiO₄), aluminosilicates (Al₂SiO₅) and native copper were detected in both rock types. The mineralogical compositions of both rocks are shown in Figure 3.1.



Figure 3.1: Mineralogical composition of the Hettangian sandstone and the Sinemurian siltstone, determined by XRD, XRF, SEM-EDX and EMPA.

3.4.2 Comparison of pyrite dissolution methods

The pretests on the influence of grain size distribution conducted with a separate batch of manually ground pyrite indicated that an increasing SSR decreased the amount of dissolved pyrite (Figure 3.2). However, method 3 dissolved a larger pyrite fraction at 16.7 g/L than at 1.67 g/L, which contradicts the general trend. Furthermore, pyrite dissolution with method 1 at 0.167 g/L partially demonstrated unsatisfactory repeatability (Figure 3.2). Analysis of the pyrite grains by SEM after the dissolution experiments showed incomplete dissolution of the largest pyrite grains.



Figure 3.2: Mass fractions of dissolved pyrite in experiments performed with manually ground pyrite. Dissolved pyrite was determined by weighing. Not all error bars are visible due to small error size.

In contrast, the test series with powdered pyrite ($<50 \mu$ m) gave more precise results with coefficients of variance below 5%, and with consistent trends (Figure 3.3a). In all four dissolution methods, increasing SSR decreased the mass fraction of dissolved pyrite. While all solvents oxidised nearly all of the initial pyrite at 0.167 g/L, their efficiency diverged at higher ratios. Method 4 was most efficient, with more than 85% dissolved pyrite at all SSRs. Methods 1 and 2, which oxidise pyrite at 85°C, dissolved between 40% and 50% at the highest SSR. Method 3 was least efficient, with less than 40% of the initial pyrite dissolved at 16.7 g/L. Measured solute iron was highest in the room temperature oxidation experiments, especially in method 4 (Figure 3.3b).



Figure 3.3: (a) Mass fractions of dissolved pyrite determined by weighing, *(b)* and by solute iron measurements for all four oxidation methods. Error bars represent standard deviations. Not all error bars are visible due to small error size.

Between 75% and 80% of the initially available pyrite was detected by solute iron measurements. In method 3, solute iron measurements detected nearly as much pyrite as weighing, with the exception of the 0.167 g/L experiment, where only 30% of the initial pyrite could be detected, and orange-red precipitates were observed. Pyrite

detection in the experiments performed at 85°C (1 and 2) was generally below 60%. In both methods, an iron recovery of less than 10% was observed at 0.833 g/L and at 8.33 g/L, where light brown and dark brown precipitates were formed. FTIR spectroscopy of the 8.33 g/L filter residues identified ammonium nitrate (NH₄NO₃), hydrated ferrous sulphate (FeSO₄·nH₂O) and small quantities of goethite (FeOOH) in the precipitates from both methods. Only in method 1, copiapite (Fe₄(SO₄)₆(OH)₂·20H₂O) was identified, while in method 2 ferric acetate ([Fe₃O(OAc)₆(H₂O)₃]OAc) had precipitated, giving the filter residues a characteristic brown colour (Figure 3.4).



Figure 3.4: FTIR spectra of the secondary precipitates from pyrite dissolution experiments (8.33 g/L pyrite) at 85°C (methods 1 and 2). The most likely candidates and element group assignments for the peaks are marked: AN = ammonium nitrate, C = copiapite, FA = ferrous acetate, FS = hydrated ferrous sulphate, G = goethite; b = bending, d = deformation, o = out of plane, s = stretching (a = asymmetric, s = symmetric), $\vartheta =$ sulphate vibration.

3.4.3 Results of the sequential extraction

Leaching of elements

In the XOR sequence, the eluates and the solid residuum were analysed for the main elements Al, Ca and Fe (Figure 3.5). Calcium was the most mobile element of the Hettangian sandstone. It was mainly released from exchangers, but also by oxidation. The total mobile mass fraction was in the same order of magnitude as the immobile mass fraction. Iron was mainly released from oxidisable and reducible phases, and the immobile fraction was two orders of magnitude higher than the total mobile mass fraction (Figure 3.5). Aluminium release was consistently low (<0.003 mg/g) in all

extraction steps. The residue was three orders of magnitude higher than the cumulated mobile fraction. In the Sinemurian siltstone, mobile element fractions were up to two orders of magnitude higher than in the sandstone. Calcium was mainly released from exchangers, and the total mobile Ca fraction was higher than the residual fraction. Reductive release of Fe was one order of magnitude higher than oxidative release, indicating a considerable amount of Fe (hydr)oxides in the sediment. Aluminium was nearly immobile, and the largest part of the mobile fraction was released by oxidation.



Figure 3.5: Mean values and standard deviations of the main elements released during the extraction sequences, given in mg/g of rock. X = exchange, A = acid solution, R = reduction, O = oxidation, Res = residual phase.

In the eluates obtained from the XARO extraction sequence, Ca was again the most mobile element in the Hettangian sandstone, and was mainly found in the exchangeable fraction (Figure 3.5). In contrast to the XOR extraction, little Ca was released during the oxidation step, but considerable amounts in the reduction and in the acid solution step. The fractionation of Fe was comparable to the XOR sequence, with mainly reducible, oxidisable and acid-soluble Fe. Mobile Al was low compared with residual Al. In the Sinemurian siltstone, the high concentration of released Ca from the exchangers corresponds to the results of the XOR sequence. Similar to the sandstone, Ca release in the reduction and oxidation steps was reversed. Iron release was significantly higher than in the XOR sequence, with the largest release in the reduction and oxidation steps. Aluminium release in the exchange and oxidation steps were comparable to the XOR sequence, but significantly higher in the reduction step (Figure 3.5). In addition to the main elements Al, Ca and Fe, the minor and trace elements As, Ba, Cu, Mn, Ni and Pb were measured in the XARO sequence (Figure 3.6). Copper, Mn and Ni were the most mobile minor elements in both rock samples, showing a relatively uniform phase distribution. Arsenic and Pb were released primarily during reduction and oxidation, Ba during acid dissolution. All three elements were hardly mobile.



Figure 3.6: Mean values and standard deviations of the minor and trace elements released during the XARO extraction sequences, given in mg/g of rock. X = exchange, A = acid solution, R = reduction, O = oxidation, Res = residual phase.

Solid phase analysis

A comparison of SEM pictures of the rock material before and after the XOR extraction evidenced that secondary minerals and amorphous phases coating the surfaces of quartz and feldspar grains were removed by the sequential extraction (Figure 3.7a, Figure 3.7b). EDX measurements performed on the few remaining surface coatings detected only hardly soluble heavy minerals, such as ilmenite (FeTiO₃) or rutile (TiO₂) (data not shown). SEM scans of pyrite framboids identified in the untreated Sinemurian siltstone revealed a widespread coating with amorphous phases. EDX measurements detected mainly Fe, O and S in the coated framboids, indicating the presence of iron hydroxides and probably also iron sulphates in the coating (Figure 3.7c). Some coated

framboids were still detectable after extraction, which suggests that pyrite was protected against dissolution by the hydroxide coatings.



Figure 3.7: SEM images of quartz grains found in the Hettangian sandstone (a) before and (b) after the XOR sequential extraction. (c) Pyrite framboids present in the untreated Sinemurian siltstone were commonly covered with amorphous hydroxide coatings. The EDX spectrogram indicates the presence of pyrite (Fe, S), iron hydroxides (Fe, O) and possibly iron sulphates (Fe, O, S).

The TC measured in the Hettangian sandstone was $0.077 \pm 0.007\%$, and in the Sinemurian siltstone $1.25 \pm 0.01\%$ (Figure 3.8). The estimated TOC was $0.023 \pm 0.001\%$ (TIC $0.055 \pm 0.009\%$) in the sandstone and $1.04 \pm 0.23\%$ (TIC $0.20 \pm 0.24\%$) in the siltstone. The resulting TIC/TOC ratio of the sandstone is 2.4, and of the siltstone 0.2. The calculated percentage of dissolved organic matter in the oxidation step is 30% for the sandstone and 83% for the siltstone. In the sandstone, the estimated quantity of the adsorbed or easily soluble sulphatic sulphur was $0.13 \pm 0.04 \text{ mg/g}$ (52% of total sulphur), of the sulphur associated with organic matter and sulphides $0.06 \pm 0.02 \text{ mg/g}$ (26%), and of the sulphur associated with hardly soluble sulphates $0.05 \pm 0.01 \text{ mg/g}$ (22%). In the siltstone, the respective values were 0.49 ± 1.69 (9%), 4.97 ± 1.47 (87%) and $0.26 \pm 0.01 \text{ mg/g}$ (4%). Both carbon and sulphur were thus mainly associated with oxidisable phases in the siltstone, that is, with organic matter and sulphides, while the

sandstone predominantly contained inorganic carbon and sorbed or easily soluble sulphatic sulphur (Figure 3.8).



Figure 3.8: Total carbon and sulphur mass fractions in the solid residue after certain steps of the XARO extraction sequence, determined by CNS analysis.

Solid phase quantifications

The result of the solid phase quantification calculated as described in item 3.3.3 is depicted in Figure 3.9 for both tested rock types. Data for calcite, Mn (hydr)oxides and organic matter are only available for the XARO sequences, because the XOR sequence did not include the acid dissolution step (calcite), solute Mn measurements (Mn (hydr)oxides) and solid TOC analysis (organic matter). While the mass fractions of all phases are approximately two orders of magnitude higher in the siltstone than in the sandstone, their distribution is similar. Organic matter is the main component, followed by Fe phases, while there are nearly no Mn (hydr)oxides. The siltstone contains more pyrite than Fe (hydr)oxides, which is reversed in the sandstone.



Figure 3.9: Mass fractions of the solid trace phases contained in the two tested rocks, calculated from the results of both XARO sequence and the XOR sequence.

3.5 Discussion

3.5.1 Pyrite dissolution methods

Results of the pyrite dissolution experiments in dependence of grain size (Figure 3.2) indicate that an inhomogeneous grain size distribution decreases the repeatability of the proposed oxidation procedure. Consequently, the method is only reliable after verifying the pyrite grain size distribution in the rock. Sieving of the rock is often not possible to separate microcrystalline pyrite particles, as they may adhere to the surfaces of larger grains, but it was found that determining the grain size by SEM (<50 μ m after milling) yielded repeatable results in the following extraction procedure (Figure 3.3). Both rock types investigated for the sequential extraction contain pyrite with diameters of <5 μ m, as determined by SEM, which implies that the pyrite dissolution procedure was applicable.

The efficiency of pyrite dissolution decreases with the SSR. The smallest tested pyrite content of 0.167 g/L is close to the real pyrite mass fractions in both investigated rock types, corresponding to 0.5% or 0.25% sedimentary pyrite for an SSR of 33.3 g/L or 66.7 g/L, respectively. At this ratio, all tested extraction methods dissolved approximately 100% of the pyrite (Figure 3.3), while pyrite dissolution at the highest SSR of 16.7 g/L was between 35% (method 3) and 86% (method 4). The good performance of method 4 can be explained with the addition of 170 mmol/L HNO₃, while all other

methods only contained 1.4 mmol/L HNO₃. Nitric acid is an efficient oxidising agent for pyrite (Lord 1982), and has already been utilised in iron-specific sequential extraction schemes (Claff et al. 2010, Huerta-Diaz & Morse 1990). The pH needs to be reduced to <4 to avoid the rapid reprecipitation of iron oxide coatings onto the pyrite surface, which would inhibit pyrite oxidation otherwise (Zhang & Evangeliou 1996).

Reprecipitation and re-adsorption of the mobilised Fe were prevented best in the dissolution methods conducted at room temperature (methods 3 and 4, Figure 3.3). This can be explained by solvent evaporation in the methods performed at 85°C, resulting in the oversaturation of hardly soluble iron phases that were identified by FTIR as hydrated ferrous sulphate, copiapite, goethite and ferric acetate. Goethite frequently precipitates from iron-rich solutions over a wide range of pH (Cornell & Schwertmann 1996). Hydrated ferrous sulphates form during solvent evaporation after dissolving pyrite according to Equation (1), because the oxidation of ferrous to ferric iron is slower than the oxidation of sulphidic sulphur to sulphate (Rimstidt & Vaughan 2003). Copiapite might form when Fe contained in hydrated ferrous sulphates is oxidised, and precipitates from warm acidic solutions after several hours (Nordstrom 1982). Precipitates collected after the application of method 2 (Table 3.1) contained ferric acetate instead of copiapite. This may be explained with quick ferric iron formation by faster pyrite oxidation and the abundance of oxidising agent, which led to the oversaturation of solid ferric acetate. The removal of ferric iron from the solution prevented copiapite formation. The precipitation of hydrous iron sulphates (Figure 3.4) indicates that solvent evaporation should be avoided, that is, methods 1 and 2 are not suitable for pyrite quantification. Method 4 performed better than method 3 in both dissolving pyrite and avoiding iron reprecipitation, and is therefore suited best for pyrite quantification.

3.5.2 Sequential extraction schemes

Order of the dissolution steps

The comparison of the XOR and XARO sequences allows the assessment of the acid dissolution, reduction and oxidation steps. The exchange step was conducted similarly in both sequences. MgCl₂ solutions displace weakly sorbed cations from particle surfaces, while strongly sorbed ions are retained. The mobilisation is governed by sorption affinity, site specificity and complexation (Pickering 1986).

During the acid dissolution step of the XARO sequence, Ca was released from both rocks, although SEM-EDX did not reveal any calcite in the sandstone, and only a few grains in the siltstone. The Ca release of the XOR sequence, where the acid dissolution step was omitted, was significantly higher in the oxidation step, which was not the case for any of the other elements (Figure 3.5). Since the sodium hypochlorite used for the

XOR oxidation step hardly dissolves calcite (Pingitore et al. 1993), Ca was probably released by desorption or dissolution of oxidisable phases. Any undissolved calcite in the XOR sequence should have been attacked in the reduction step, because it was performed at low pH (<2). Since Ca released in the XOR reduction step was significantly lower than in the XARO reduction step, it can be assumed that Ca was released during the acid dissolution step by desorption, although small quantities of calcite might also be present in the sample. Conclusively, the acid dissolution step should not be omitted, even if no calcite is detected by mineralogical analyses. It should be noted that no efforts were made to separately extract sulphate minerals. Easily soluble sulphates, such as gypsum (CaSO4•2H₂O), would therefore partially dissolve in the first step (Dold 2003, Cappuyns et al. 2007), inducing effects similar to the discussed Ca carry-over.

The position of the oxidation step within the sequential extraction order controls the accessibility of solid phases and can therefore strongly influence the results of the procedure. Performing the oxidation step as last step may prevent the dissolution of solid phases underlying organic coatings in the previous steps (Schultz et al. 1998). On the other hand, performing that step earlier, Mn(II) oxides can be dissolved by the oxidising agent H_2O_2 at pH <5, which requires their removal before the oxidation step (Jenne 1968). Furthermore, performing the oxidation before the reduction could lead to the reprecipitation of oxidatively released metal cations as hydroxides, which would erroneously increase the reducible fraction. The pyrite dissolution experiments demonstrated that even oxidation methods relying on both complexation and acidification as means to keep mobilised elements in solution cannot entirely prevent reprecipitation. Finally, SEM image analysis of the untreated sediment showed that pyrite concretions were often covered with amorphous hydroxide coatings (Figure 3.7), which have to be removed before the pyrite can be dissolved. In conclusion, performing the reduction before the oxidation step is recommended for optimal pyrite and iron (hydr)oxide quantification in sediments, as long as the organic matter content is low.

Solvent efficiency and solid phase quantification

The quantification of TC/TIC/TOC and organic matter requires the measurement of TC on the solid residue after certain extraction steps, and depends mainly on the selectivity of the applied reagents and the precision of the sedimentary carbon measurements. The dissolution of organic matter by the improved pyrite oxidation method integrated into the XARO sequence was more efficient in the siltstone than in the sandstone, suggesting a higher percentage of insoluble humified and paraffinic substances in the sandstone (Tessier et al. 1979). Sulphur quantification has the same dependencies as carbon, and allows the differentiation of oxidisable (sulphidic, organic-bound), non-oxidisable (easily soluble sulphatic, adsorbed) and insoluble (hardly soluble

sulphates) fractions. Further differentiation of the non-oxidisable fraction requires an additional water solution step (Dold 2003).

The quantification of calcite, pyrite and the (hydr)oxides of manganese and iron was made under the assumption that these solid phases are the sole sources of their respective cations in the corresponding extraction steps, and that their dissolution is complete. Buffered acetic acid, which was used in the acid solution step, dissolves calcite and other carbonates efficiently and with a high selectivity (Pickering 1986, Tessier et al. 1979). However, strongly adsorbed cations may not be desorbed completely in the first extraction step, but at decreased pH during acid dissolution (Tessier et al. 1979). The mobilisation of adsorbed Ca in the acid solution step, for example, from surfaces of clays, (hydr)oxides or organic matter, would therefore cause an overestimation of the calcite present in the sediment. As discussed in item 4.2.1, this was assumed to be the case for both tested rock types based on the comparison of XOR and XARO sequences. As this kind of solvent selectivity can only be identified by comparing multiple sequential extraction schemes, it was decided to omit corrections to the proposed calcite quantification, implying that calcite, as given in Figure 3.9, was overestimated. Furthermore, if other Ca-bearing carbonates, such as dolomite $(CaMg(CO_3)_2)$ are present in the sediment, their dissolution would also cause an overestimation of sedimentary calcite. The quantification of Mg release in the second step would be the obvious solution. However, this approach would facilitate the utilisation of a solvent other than MgCl₂ in the first extraction step.

The mobilisation of Fe in the oxidation step can originate from both pyrite and organic matter, and a differentiation with the method developed within this study is impossible. Therefore, the assumption was made that all oxidatively mobilised iron was bound in sulphides, which overestimates the total pyrite content. A differentiation should be possible by separating the extraction of pyrite and organic matter, for example with sodium pyrophosphate for easily soluble organic components and concentrated nitric acid for pyrite (Claff et al. 2010), or with an acidified chromium chloride solution for pyrite (Canfield et al. 1986) and hydrogen peroxide for organic matter. The results of the pyrite dissolution experiments showed furthermore that the extraction method applied in the XARO sequence (method 4, Table 3.1) detects approximately 75–80% of the pyrite (Figure 3.3), implying a slight underestimation. The degree of dissolution of amorphous hydroxides, crystallised hydroxides and crystalline oxides is hard to determine from the results obtained in the reduction step. While manganese oxides and hydroxides are easily dissolved by hydroxylamine hydrochloride (NH₂OH•HCl) solutions (Chao 1972), the dissolution of iron hydroxides and iron oxides depends on reductant concentration, extraction time and pH (Gleyzes et al. 2002). For example, only 5% of the initially available iron oxides dissolve in a 0.1 M NH₂OH·HCl in 0.01 M HNO₃ solution in 30 min, while goethite dissolves in a 0.1 M NH₂OH·HCl in

0.1 M HNO₃ within 2 h (Chao 1972, McCarty et al. 1998). The increase from 0.1 M to 0.5 M of the NH₂OH·HCl concentration and the reduction of the pH to <2 yields a higher mobilisation of trace metals and better reproducibility, due to the more effective dissolution of crystalline oxides and hydroxides (Rauret et al. 1999). This effect was confirmed in the present study, where the XARO reduction step (0.5 M NH₂OH·HCl in HNO₃, pH <2, 16 h) mobilised significantly more iron than the XOR reduction step (0.04 M NH₂OH·HCl in HNO₃, pH 2, 5.5 h).

Precision

Only the precision of the XARO sequence will be discussed, since it was shown previously that it performed significantly better than the XOR sequence. The empirical coefficient of variation (CV) averaged over all extraction steps and analysed elements was 45% at 33.3 g/L and 41% at 66.7 g/L for the Hettangian sandstone, and 24% at 33.3 g/L and 21% at 66.7 g/L for the Sinemurian siltstone (Figure 3.10). This large difference can be explained since most element concentrations measured in the sandstone eluates were near the instrumental detection limit of the ICP-OES, while the siltstone eluate concentrations were up to two orders of magnitude higher (Figures 3.5 and 3.6). These results confirm that precision is low when the extracted concentrations approach detection limit, but can be improved by selecting higher SSRs (Tessier et al. 1979). This was confirmed by the observation that the average CV was lower at the higher SSR in all individual extraction steps, with the exchange step of the sandstone as the only exception (Figure 3.10). However, since the siltstone's average CV was notably higher in the exchange step (33.3 g/L: 56 %, 66.7 g/L: 45 %) than in the other three steps (10-18%), this might have been due to a systematic error with the exchange step, such as insufficient adsorption control or dissolution of easily soluble salts. While these results are in favour of using the higher SSR, re-adsorption and reprecipitation effects also have to be considered, which are more likely to occur at higher SSRs (Sulkowski 2002). This effect would be indicated by higher element concentrations in the eluates of the lower SSR. The comparison between the 33.3 g/L and 66.7 g/L eluates shows that most concentrations were within standard deviation range, which suggests that readsorption and reprecipitation did not occur at significantly different levels (Figures 3.5 and 3.6). Based on these results, the higher SSR of 66.7 g/L was better suited for the investigated rocks. Nonetheless, no statements can be made for rocks with higher mobile element quantities than the siltstone, and potential reprecipitation and readsorption effects need to be considered when extracting such materials.

Concerning preparation, it is unlikely that significant inhomogeneities were introduced into the rock samples, because the siltstone required a more intense grinding than the sandstone, due to its stronger cementation. It is debatable if grinding increases element mobility in cemented rocks by breaking grain assemblages or by opening diagenetically closed pores. However, the use of unground rock pieces for sequential extraction would have a high chance of incomplete surface wetting, inducing low methodical reliability and repeatability.



Figure 3.10: The empirical coefficients of variance in the XARO sequence in per cent, averaged over all measured elements. The bar pairs show the arithmetic average of the complete sequence and of the individual extraction steps.

3.6 Conclusion

Two sequential extraction schemes were compared and optimised towards their applicability to quantify mobile elements and reactive phases of pyrite-bearing siliciclastic rocks with no or little organic matter (<1.2%). Experiments with two sedimentary rock types indicated that the step order 'exchange–acid dissolution–reduction–oxidation' is most effective to dissolve the respective fractions. To get optimal results for pyrite detection, the oxidation step should be performed at room temperature rather than at 85°C, because evaporation of the solvent facilitates the onset of secondary iron precipitates. Dissolution of pyrite was most efficient with a solvent composed of hydrogen peroxide, ammonium acetate and nitric acid, and showed good repeatability for pyrite grain sizes below 50 μ m. In the extraction sequence, the oxidation step should be placed after the reduction step, so that iron hydroxide coatings are removed from the surface of pyrite, iron (hydr)oxide and manganese (hydr)oxide were estimated based on the mobilisation of their respective main metals. Organic matter was quantified based on the oxidised carbon mass measured on solid residues.

The precision of the sequential extraction procedure was found to be directly related to mobile element quantities contained in the rock sample. While the average coefficient of variance of the siltstone extraction was approximately 20%, the extraction of the comparatively unreactive sandstone yielded relative errors of up to 45%. The comparison of two different SSRs (33.3 g/L and 66.7 g/L) showed slightly smaller errors at the higher SSR, while the extracted quantities were similar. Therefore, elevated SSRs should be chosen for siliciclastic rocks.

Conclusively, the proposed sequential extraction combined with solid phase carbon analysis is capable of quantifying minor solid phases with no or low crystallinity, including organic matter, pyrite and associated trace metals. The sequential extraction thus provides a detailed estimate of potential fluid–rock interactions in siliciclastic rocks, which allows a geochemical risk assessment for aquifer utilisation.

3.7 Acknowledgements

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4 The element-release mechanisms of two pyritebearing siliciclastic rocks from the North German Basin at temperatures up to 90 °C under oxic and anoxic conditions

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4.1 Abstract

Leaching tests with synthetic brines (25 g/L NaCl) between 25 °C and 90 °C were performed under oxic and anoxic conditions over 7 days on two pyrite-bearing siliciclastic rocks from the Lower Jurassic Hettangian and Sinemurian stages in the North German Basin. The release mechanisms of the mobile elements Al, As, Ba, Ca, Cu, Fe, Mn, Ni, Si, and Pb were studied and explained by means of numerical simulations of the leaching tests. The study was performed in the context of aquifer thermal energy storage (ATES) to improve the understanding of water-rock interactions during heat storage. Results showed that release patterns of Ba, Ca, Cu, Fe, Ni, and Pb were predominantly controlled by the dissolution of pyrite under oxic conditions and iron hydroxides under anoxic conditions. The mobilizations of Al and Mn could be explained by a combination of desorption and the dissolution of hydroxides. Si was mainly released from amorphous silica. The mobilization of Ca was governed by pH-sensitive desorption and calcite dissolution in one of the samples. Arsenic was immobile in both studied rocks. In general, elemental release was augmented by the presence of oxygen and the subsequent dissolution of pyrite and reduction of pH, which should therefore be avoided in ATES systems.

Keywords

Sandstone, pyrite oxidation, aquifer thermal energy storage, rock reactivity, PHREEQC, numerical simulation, leaching test

4.2 Background

Over the last few decades, shallow geothermal systems (< 400 m depth) have been increasingly utilized as renewable energy sources and storage systems for heating and cooling for domestic and public use (e.g., Bayer et al. 2012, Blum et al. 2010, Fridleifsson et al. 2009, Lund et al. 2011). Aquifer thermal energy storage (ATES) facilities directly use aquifers for seasonal storage of thermal energy. In summer, groundwater is produced from the storage aquifer, heated up with excess energy, and reinjected into the aquifer. In winter, the stored thermal energy is withdrawn from the water by reversing the process. That way, storage of cooling energy is possible as well (Hähnlein et al. 2010, Kranz & Bartels 2009, Kranz & Frick 2013). The reliability and efficiency of ATES systems can be affected by fluid mixing and changes in temperature and pressure in the storage aquifer during operation, which induces chemical reactions such as desorption and mineral dissolution or precipitation. Subsequently, physicochemical water properties like pH or redox potential may change, and mobilized elements may precipitate and clog the aquifer, block pipes, or form coatings that reduce the efficiency of the heat exchanger. If the ATES system is built in an aquifer that serves as drinking water supply as well, the release of toxic elements such as heavy metals need to be
avoided (Bonte et al. 2013c, Possemiers et al. 2014). Altered water properties may promote corrosion or induce subsequent fluid-rock interactions (Allen et al. 1984, Frick et al. 2011, Palmer et al. 1992). To avoid aquifer damage by clogging, corrosion or contamination, legal regulations in several countries limit the groundwater temperature change to a maximum of 3 to 11 K, as the effects of large temperature variations on dissolution, desorption and microbial communities are still poorly understood (Hähnlein et al. 2010). If deeper aquifers are used for ATES systems, either to avoid potential contamination of freshwater aquifers or to improve the heat recovery factor (Kranz & Bartels 2009), the impact of increased salinity needs to be considered as well. Several research projects investigated the feasibility of heat storage systems designed for up to 90 °C. Field monitoring campaigns over several years (e.g., Huenges 2011, Wolfgramm & Seibt 2006) were complemented by experiments in controlled environments, investigating both abiotic and microbially catalyzed hydrogeochemical reactions. Arning et al. (2006) investigated the reactivity of siliciclastic shallow aquifer sediments from the North German Basin at up to 50 °C, and observed increased solubility of silicates, particularly potassium feldspar. Jesußek et al. (2013) reported temperature-dependent redox shifts toward reducing conditions in column experiments with siliciclastic sediments from the North German Basin between 10 and 70 °C. Distinct cation release was only observed at 70 °C. Bonte et al. (2013c) performed column experiments with anoxic unconsolidated aquifer sands between 5 and 60 °C and reported significant increases in element solute concentrations at 60 °C, while the sediment remained only slightly reactive at lower temperatures. Consistent element release patterns were only partially observed, e.g., for silicium and potassium. Adaptations of the microbial communities to temperature changes in both composition and quantity were found in field-monitoring campaigns (Vetter et al. 2012, Würdemann et al. 2014) and in the laboratory (Bonte et al. 2013b). While these studies qualitatively interpret the fluid-rock interactions responsible for the observed changes in physicochemical water properties and ion release, the differentiation and quantification of the individual release mechanisms, such as mineral dissolution and desorption, remain difficult. Since knowledge of the release mechanisms is necessary to understand and predict reactions of the aquifer chemistry to changes in environmental parameters induced by ATES system operation, such as temperature or solute oxygen, this study utilizes extraction experiments and numerical simulations to quantify the reactivity of aquifer rocks under these conditions. It focuses on siliciclastic rocks at temperatures between 25 and 90 °C and under shifting redox conditions due to the introduction of dissolved oxygen into normally oxygen-depleted aquifers. In this context, pyrite (FeS₂) is the most important mineral, since it is ubiquitous and occurs in many sedimentary rocks used for ATES storage. It has a high sensitivity to changes under redox conditions and the potential to acidify the surrounding groundwater upon dissolution (Nordstrom 1982). The short-term reactivities of two siliciclastic rocks with synthetic, saline

groundwater under controlled laboratory conditions that mimic conditions in a thermal aquifer storage system were investigated to study their dependence on temperature. Experimental results were complemented by numerical simulations to help explain and quantify the observed release mechanisms.

4.3 Methods

4.3.1 Materials

Weakly consolidated rock material was sampled from two Lower Jurassic horizons in the North German Basin, which are used for aquifer thermal energy storage. The samples were collected in the ATES well "Am Reichstag 2/98," situated in the city of Berlin (Germany). Sample I was taken from the Hettangian aquifer in a depth of 310 m ("Hettangian sandstone"). It is a fine sandstone containing 95% quartz and 1-2% potassium feldspar, muscovite, and kaolinite each with minor and trace phases (< 1%) comprising rutile (TiO₂), ilmenite (FeTiO₃), pyrite (FeS₂), iron hydroxides, and 0.1% organic matter (Müller et al. 2017). Sample II was taken from the hanging Sinemurian aquiclude at a depth of 297 m ("Sinemurian siltstone"). It is a fine siltstone comprising 39% quartz, 37% clay minerals, 12% mica, and 8% potassium feldspar. Minor and trace phases (ca. 4%) contain the same minerals as sample I and 1.2% organic matter (ibid.). The mobilities and phase associations of several elements were determined by sequential extraction (ibid.), differentiating between exchangeable, acid-soluble (carbonates), reducible (oxides and hydroxides), and oxidizable (organic matter and sulfides) phases. The results of the extraction of 1 g rock with 30 mL of solvent are displayed in Figure 4.1.

The two rock samples were ground in a mortar to obtain a homogeneous powder with the original grains kept intact. After grinding, the material was washed carefully for 1 h with ultrapure water purged with nitrogen and dried overnight at 70 °C. The synthetic saline groundwater utilized in the extraction experiments was prepared from ultrapure water and 25 g/L analytic grade sodium chloride (NaCl), which corresponds to the salinity of the Hettangian aquifer. In addition to Na⁺ and Cl⁻, the natural groundwater contains 0.86 g/L of other solute species, mainly Ca²⁺ (0.29 g/L), SO4²⁻ (0.25 g/L), and Mg²⁺ (0.24 g/L) (Huenges 2011).



Figure 4.1: Mass fractions (mg/g sediment) and phase associations of mobile elements in the sampled rocks, as determined by sequential extraction with 1 g of rock and 30 mL of solvent. The phases are X, exchangeable; A, acid-soluble; R, reducible; O, oxidizable. Data taken from Müller et al. (2017).

4.3.2 Leaching experiments

Leaching tests were performed at room temperature (25 °C), 50, 70, and 90 °C, over 1, 2, 4, and 7 days under oxic and anoxic conditions. The experiments were carried out in triplicate with 1 g of rock material and 30 mL of synthetic groundwater. Manual shaking was applied every 24 h. The redox potential of the synthetic groundwater before leaching was 192 mV under oxic conditions and 105 mV after purging with nitrogen under anoxic conditions, as determined using a WTW SenTix 940 electrode connected to a WTW Multi 3420 multimeter. For tests under oxic conditions, the rock material and synthetic groundwater were filled into 60-ml PP bottles, which were placed in a lab

oven and heated up to the desired temperature. After leaching, rock material and eluate were separated by filtration using filter papers. The pH of the eluates was determined using WTW Sentix 81 electrodes connected to a WTW Multi 340i multimeter before acidizing the eluates to pH < 2 using 65% HNO₃.

To maintain anoxic conditions, all experiments were performed in an Ar $(5\% H_2)$ purged glovebox. The oxygen concentration in the gas phase was maintained at less than 10 ppm throughout the experiment. The synthetic groundwater was purged with nitrogen to < 0.1 mg/L solute oxygen, as determined using a WTW FDO 925 probe with a WTW Oxi 3310 acquisition unit. Inside the glovebox, ground rock samples and synthetic groundwater were filled into 50-mL centrifuge tubes, which were placed on heating plates equipped with stainless steel fittings to ensure a stable temperature distribution. After extraction, rock material and eluates were separated inside the glovebox by filtration using filter papers, and the eluates were decanted into 60-ml PP bottles, which were sealed against the atmosphere with Parafilm. The pH of the eluates was determined outside the glovebox by means of WTW Sentix 41 and 81 electrodes connected to a WTW Multi340i multimeter. Afterward, the eluates were acidized to pH < 2 with 65% HNO3. The solute concentrations of aluminum (Al), arsenic (As), barium (Ba), calcium (Ca), copper (Cu), iron (Fe), manganese (Mn), nickel (Ni), lead (Pb), and silicium (Si) were determined by inductively coupled plasma optical emission spectrometry (ICP-OES, Thermo Scientific iCAP 6300 Duo). For the results of the leaching experiments, correlation matrices were calculated utilizing Pearson's method to help identify possible relationships between the extracted concentrations, pH, time, and temperature. Calculations were performed using the library "Pandas" (McKinney 2010) for the high-level programming language, Python. The complete matrices are provided as Additional file 1. The correlation between the individual parameters was categorized into three groups: "strong correlation" for correlation coefficients (r) between 0.68 and 1; "modest" or "moderate correlation" for r between 0.36 and 0.67; and no correlation for $r \le 0.35$ (Taylor 1990).

4.3.3 Numerical simulation

Numerical simulations were performed using the software PHREEQC, version 3.3.7 (Parkhurst & Appelo 2013), for the release mechanisms of the main mineral-forming elements Al, Ca, Fe, Mn, and Si. For statistical analyses, the IPHREEQC module was accessed by Python scripts by means of the PhreeqPy interface (Müller 2013). Statistical analyses were performed by means of the Python libraries "Pandas" (McKinney 2010), "NumPy", and "SciPy" (van der Walt et al. 2011). The workflow comprised the following steps:

- 1. Defining the brine composition and the initial mineral content.
- 2. Compiling relevant thermodynamic and kinetic data and calibrating them with the results of the leaching experiments.
- 3. Conducting a sensitivity analysis to identify the influence of different release mechanisms to the final solute element concentrations.
- 4. Calculating the goodness-of-fit of the simulation to the experimental results and repeating steps 1 to 3 as required.

In the first step, the initial synthetic groundwater was modeled as a 25 g/L (0.44 M)NaCl solution with pH 7. The initial pe values obtained from measurements were 3.3 for the oxic brine, and 1.8 for the anoxic brine. The mineral composition data for both rocks were taken from Müller et al. (2017). Minerals considered were quartz, amorphous silica, potassium feldspar, kaolinite, muscovite, calcite, pyrite, amorphous ferrihydrite, amorphous aluminum hydroxide, and manganese oxohydroxide. Since the mass fraction of amorphous aluminum hydroxide had not been calculated before, the amount was estimated from the Al released during the acid-dissolution step of the sequential extraction (Müller et al. 2017), based on the assumption that the hydroxides would completely dissolve at pH 3.7 (Marion et al. 1976). The mass fraction of amorphous silica was unknown as well. The fast initial release of Si observed in the leaching tests (Figures 4.2-4.5) was attributed to amorphous silica dissolution, after calibrations found that crystalline silicate dissolution was too slow to explain it. This effect is common and has been described in other studies (e.g., Rimstidt & Barnes 1980). The mass fraction of amorphous silica was subsequently fitted to the experimental results using least squares regression. The final input mineral composition is shown in Table 4.1.

In the second step of the workflow, comprising reaction data compilation and calibration, thermodynamic data were taken primarily from the LLNL database integrated in PHREEQC. Amorphous ferrihydrite was modeled using the log K value from the SIT database, which is also included in the PHREEQC package, and the standard enthalpy of reaction (Δ H) from the LLNL database. Data for amorphous aluminum hydroxide were taken from Kittrick (1969). No Δ H values were available for amorphous aluminum hydroxide and manganese oxohydroxide, so no direct temperature dependence could be calculated for these two phases. The data for all considered reactions are compiled in Table 4.2.

Phase	Composition	Mass fractio	on, %	Reactive su	face, m²/g
		Sample I	Sample II	Sample I	Sample II
Quartz	SiO ₂	95	39	0.002	0.02
Amorphous silica	SiO ₂ (amorph)	0.0001	0.0009	300	300
Potassium feldspar	KAlSi ₃ O ₈	2	8	0.0023	0.023
Kaolinite	Al ₂ Si ₂ O ₅ (OH) ₄	1	37	3.6	3.6
Muscovite	KAl ₃ Si ₃ O ₁₀ (OH) ₂	1	12	1.2	1.2
Calcite	CaCO ₃	0	0.2	0	0.0001
Pyrite	FeS ₂	0.005	0.29	0.003	0.001
Ferrihydrite	Fe(OH)3 (amorph)	0.007	0.26	n.a.	n.a.
Aluminum hydroxide	Al(OH)3 (amorph)	0.0013	0.02	n.a.	n.a.
Manganese oxohydroxide	MnOOH	0.0007	0.0004	n.a.	n.a.
Al exchange	AIX ₃	7.3·10 ⁻⁵	2.6.10-4	n.a.	n.a.
Ca exchange	CaX ₂	3.8·10 ⁻³	0.3	n.a.	n.a.
Mn exchange	MnX ₂	8.4·10 ⁻⁵	6.4·10 ⁻⁴	n.a.	n.a.

Table 4.1: Minerals and exchangers considered in the model.

Phases printed in italics were excluded after sensitivity analysis or initial simulations. Mass fractions were taken from Müller et al. (2017), except amorphous aluminum hydroxide, which was calculated from sequential extraction data (ibid.). Reactive surfaces were calculated from specific surface values collected in the RES³T database.

Phase	Reaction	log K	∆H (KJ/mol)
Amorphous silica	$SiO_{2(am)} \leftrightarrow SiO_{2(aq)}$	-2.71	20.05
Kaolinite	$AI_{2}Si_{2}O_{5}(OH)_{4}+6H^{+}\leftrightarrow 2AI^{3+}+2SiO_{2(aq)}+5H_{2}O$	6.81	-151.8
Muscovite	$KAI_3Si_3O_{10}(OH)_2 + 10H^+ \leftrightarrow 3AI^{3+} + K^+ + 3SiO_{2(aq)} + 6H_2O$	13.6	-243.2
Calcite	$CaCO_3 + H^+ \leftrightarrow Ca^{2+} + HCO_3^-$	1.85	-25.71
Pyrite	$FeS_2+3.5O_2+H_2O \leftrightarrow Fe^{2+}+2SO_4^{2-}+2H^+$ $FeS_2+14Fe^{3+}+8H_2O \leftrightarrow 15Fe^{2+}+2SO_4^{2-}+16H^+$	217.4 98.5	-1412 -50.69
Ferrihydrite	$Fe(OH)_3^+3H^+ \leftrightarrow Fe^{3+}+3H_2O$	2.54	-84.08
Amorphous aluminum hydroxide	$AI(OH)_3 + 3H^+ \leftrightarrow AI^{3+} + 3H_2O$	9.7	-
Manganese oxohydroxide	$MnOOH+3H^+ \leftrightarrow Mn^{3+}+2H_2O$	-0.16	-

Table 4.2: Dissolution reactions considered in the model.

Data taken from the LLNL database, except log K of ferrihydrite (SIT database) and amorphous aluminum hydroxide (Kittrick 1969). Values for the standard enthalpy of formation ΔH for amorphous aluminum hydroxide and manganese oxohydroxide are not available in the databases.

Data for kinetic mineral dissolution were adopted from Palandri & Kharaka (2004). The formulation for the kinetic dissolution of minerals given therein is as follows:

$$\frac{dm}{dt} = -A_{surf} \begin{bmatrix} k_{acid}^{298,15K} e^{\frac{-E_{acid}}{R} \left(\frac{1}{T} \frac{1}{298,15K}\right)} a_{H^{+}}^{n_{1}} (1 - \Omega^{p_{1}})^{q_{1}} \\ + k_{neut}^{298,15K} e^{\frac{-E_{neut}}{R} \left(\frac{1}{T} \frac{1}{298,15K}\right)} (1 - \Omega^{p_{2}})^{q_{2}} \\ + k_{base}^{298,15K} e^{\frac{-E_{base}}{R} \left(\frac{1}{T} \frac{1}{298,15K}\right)} a_{H^{+}}^{n_{3}} (1 - \Omega^{p_{3}})^{q_{3}} \end{bmatrix}$$
(4.1).

In this formula, dm/dt is the mineral mass reduction over time (kg/s), A_{surf} is the reactive surface area (m²), km^{298.15 K} is a theoretical rate constant at 25 °C and pH 0 for a mechanism m; E_m is the activation energy for a mechanism m (J/mol); R is the universal gas constant (J/kg/mol); T is the temperature (K); a_{H^+} is the activity of H⁺; Ω is the mineral saturation index; and p_i and q_i are empirical constants. With the exception of the reactive surface area, which is an individual fraction of the specific surface area that depends on sample structure and texture (Lasaga 1998), these data were compiled from the article by Palandri & Kharaka (2004) for all minerals considered in the present study. Kinetically retarded dissolution was assumed for quartz, amorphous silica, potassium feldspar, kaolinite, muscovite, calcite, and pyrite. Thermodynamic equilibria were assumed for ferrihydrite, amorphous aluminum hydroxide, and manganese oxohydroxide. To obtain the reactive surface areas, first the specific surface areas Aspec were determined. For quartz and potassium feldspar, A_{spec} values were calculated geometrically assuming spheric shape with $A_{spec} = 3/(r \cdot \rho_m)$, where r is the average grain radius and ρ_m the grain density. The average grain radius was set to 50 μ m for sample I (fine sandstone), and to 5 µm (fine siltstone) for sample II. The grain radii had been determined by scanning electron microscopy (SEM) utilizing a Carl Zeiss SMT Ultra 55 Plus machine, coupled with energy-dispersive X-ray spectroscopy (EDX) using a Thermo Fisher Scientific UltraDry SDD EDX detector for mineral identification. Grain density is 2650 kg/m³ for quartz and 2600 kg/m³ for potassium feldspar (Deer et al. 1992). The average grain sizes and grain shapes of the other solid phases contained in the rock were unknown, and therefore, the median values of the specific surface values collected from numerous literature sources in the RES³T database (Brendler et al. 2003) were used as a reference. The specific surface values for each solid phase were multiplied with a factor of 3 to match the measured BET surface values of 0.5 m^2/g for sample I, and 13.2 m²/g for sample II, as reported by Müller & Regenspurg (2014). The resulting specific surface values were within the range of literature values compiled in the RES³T database. To account for the fact that only some of the grain surfaces are involved in dissolution reactions (Lasaga 1998), the reactive surfaces were estimated by reducing the specific surfaces stepwise to find the best fit to the data from the leaching tests. The specific surface was consequently reduced by one order of magnitude for all solid phases except pyrite and amorphous silica. For amorphous silica, half of the specific surface was assumed to be reactive. For pyrite, the reactive surface was fitted to the experimental data by matching the solute iron concentrations observed during dissolution under oxic conditions, assuming that reprecipitation and re-adsorption were negligible due to small solute concentrations (Sulkowski 2002). Fitting was performed with least squares regression (Table 4.1). Exchange reactions were calculated for Al, Ca, and Mn assuming unspecific bulk sorption, where the exchangeable amount per rock mass was taken from the exchange step of the sequential extraction performed by Müller et al. (2017).

In the third step of the workflow, a sensitivity analysis was performed to identify the contribution of various release mechanisms to solute Al, Si, and Fe concentrations. Ca and Mn have only one mineral contributing to their respective solute concentrations, and were thus not analyzed. As input parameters, all minerals and exchangers potentially releasing the investigated solute element were considered, as well as physicochemical water parameters. The mineral mass fractions and exchangeable amounts were varied between 0 and the fitted initial values displayed in Table 4.1, pe was varied between 1.8 (anoxic) and 3.3 (oxic), and oxygen was varied between 0 (anoxic) and "abundant supply" (oxic). Pyrite was selected as the controlling variable for pH. Temperature and reaction time were set to constant values. For Fe, only oxic mobilization was considered. The sensitivity analysis was performed by means of the Python library "SALib" (Herman et al. 2017). For each input parameter, seven samples within their respective boundaries were drawn and analyzed utilizing the quasi-Monte Carlo-type Sobol method (Sobol 2001, Saltelli 2002, Saltelli et al. 2010). As outputs, the total-order sensitivity indexes were calculated. They measure a combination of the firstorder sensitivity of an input parameter and the higher-order sensitivities which quantify synergetic effects between multiple input variables (Homma & Saltelli 1996).

In the fourth step of the workflow, the goodness-of-fit of the simulation was measured using the normalized root mean square error (NRMSE). The NRMSE was calculated for each solute element and temperature using the equation:

$$NRMSE = \frac{\sqrt{\sum_{tmin}^{tmax} (c_s - c_m)^2}}{\overline{c_m}}$$
(4.2)

where t_{min} and t_{max} are the first and last time steps, respectively, c_s is the simulated solute concentration, c_m is the measured solute concentration, and $\overline{c_m}$ is the arithmetic mean of all measured solute concentrations.

4.4 Results

4.4.1 Experimental study: leaching test

In both the Hettangian sandstone and the Sinemurian siltstone, the most mobile elements were Al, Ca, Fe, and Si, followed by Mn. Only traces of Ba, Cu, Ni, and Pb were mobilized. Arsenic was generally immobile.

During the leaching of samples of the Hettangian sandstone, the pH decreased over time, with the magnitude of the decrease depending on temperature and the presence of oxygen. The lowest pH under oxic conditions was 3.7, and 5.0 under anoxic conditions (Figures 4.2 and 4.3). The concentrations of Al, Ca, Fe, and Si released from samples of the Hettangian sandstone under oxic and anoxic conditions were in the order of magnitude of 1 mg/L, and the solute concentrations of all other elements were one or two orders of magnitude lower (Figures 4.2 and 4.3). In the oxic leaching tests, modest-to-strong positive correlations with temperature (0.48 < r < 0.88) and modestto-strong negative correlations with pH (-0.6 < r < -0.82) were observed for all elements except Ca and Cu. Under anoxic conditions, in contrast, strong positive correlations with pH were found only for Cu (0.83) and Ni (0.76). Strong positive correlations with temperature were observed for Ba (0.82), Fe (0.74), and Mn (0.95), and a moderate correlation for Si (0.52). Moderate correlations with extraction time were observed for a few elements under oxic conditions (Al, Fe, Si), but not under anoxic conditions. Calcium, Cu, and Pb were only released under oxic conditions (Figures 4.2 and 4.3). While the pH reduction induced moderately or strongly positive correlations between many elements under oxic conditions, only a few strong correlations were calculated under anoxic conditions: Al and Si (0.73), Ba and Mn (0.68), Cu and Ni (0.96), and Fe and Mn (0.86).

During the leaching of the Sinemurian siltstone, the pH decreased over time and with increasing temperature under oxic conditions, and remained nearly constant after 2 days with no temperature effects under anoxic conditions (Figures 4.4 and 4.5). Minimal oxic pH was 3.6 after 7 days at 90 °C, and 5.2 under anoxic conditions. The concentrations of elements released from the Sinemurian siltstone were usually one or two orders of magnitude higher than from the Hettangian sandstone (Figures 4.4 and 4.5). Under oxic conditions, strong negative correlations with pH (-0.68 < r < -0.99) were observed for all elements but Cu (- 0.28), and strong positive correlations with temperature for Ba (0.82), Ca (0.88), Mn (0.82), Ni (0.68), and Si (0.74). The other elements showed modest temperature correlations, with the exception of Cu, which had none. Similar to the Hettangian sandstone, pH dependencies vanished under anoxic conditions, and only Cu (0.61) and Ni (0.52) showed modest positive correlations. Moderate or strong positive correlations with temperature (0.41 < r < 0.93) were observed for all elements except Al (- 0.1), Cu (0.27), and Ni (0.32). The extraction time

correlated only moderately with a few elements under oxic conditions (Al, Fe, Ni), while solute concentrations under anoxic conditions did not have significant time trends. Oxic Fe mobilization started only after 2 days at 70 and 90 °C, and almost no Fe was released at lower temperatures (Figure 4.4). Aluminum was predominantly released under oxic conditions at 70 and 90 °C, and remained very low at lower temperatures and under anoxic conditions (Figures 4.4 and 4.5). Similar to the observations made in the leaching of the Hettangian sandstone, solute concentrations of most elements showed moderate or strong positive correlations under oxic conditions. Strong correlations under anoxic conditions were calculated for the releases of Fe, Mn, and Si (r > 0.85), and all three elements also had strong positive correlations with Ca (r > 0.8). The correlation coefficients between the other elements were mostly moderate.



Figure 4.2: Extracted elemental concentrations and changes of pH over time observed in the leaching of the Hettangian sandstone under oxic conditions.



Figure 4.3: Extracted elemental concentrations and changes of pH over time observed in the leaching of the Hettangian sandstone under anoxic conditions.

4.4.2 Numerical simulation

Simulation results

The NRMSE values (Eq. 2), which describe the difference between simulated and measured ion release, were calculated for Al, Ca, Fe, Mn, and Si. They show that the goodness-of-fit of the simulation tends to be better for oxic than for anoxic conditions, particularly for Fe (Figure 4.6). Ca and Mn errors are consistently <1 for all temperatures. No value was calculated for anoxic Ca mobilization from the Hettangian sandstone, because there was no release under these conditions, and simple temperature-dependent desorption models were not sufficient to explain the observed patterns. However, initial simulations showed that Ca would be released from calcite, if it were present, so it could be deduced that the Hettangian sandstone was calcite-free. NRMSE values for Al release are mostly around 1, although it should be noted that the time trends observed in the leaching of the Sinemurian siltstone could not be



Figure 4.4: Extracted elemental concentrations and changes of pH over time observed in the leaching of the Sinemurian siltstone under oxic conditions.

reproduced (Figures 4.4 and 4.5). It was found that increasing the reactive surfaces of kaolinite and muscovite within reasonable magnitudes could not explain this issue. The goodness-of-fit of solute Fe and Si concentrations varies with temperature, with the best fits at elevated temperatures (70 and 90 °C). The Fe release could be modeled with a higher precision for oxic than for anoxic conditions, where the observed Fe concentrations were generally strongly underestimated (Figure 4.6). In contrast, the solute concentrations and time trends of the oxic leaching tests could be reproduced well for both rocks by modeling only pyrite dissolution (Figure 4.7). Due to precipitation of iron hydroxides and consequent depletion of solute Fe during the 90 °C leaching of the Hettangian sandstone, this data point was excluded from fitting. For the Sinemurian siltstone, reproducing the experimental solute Fe trends required setting a threshold time point at which pyrite dissolution starts, and allow its reactive surface to increase linearly. Time thresholds were set to 50,000 s at 70 °C and 75,000 s at 90 °C. Pyrite



dissolution at lower temperatures was set to zero, resulting in large error values, as very small quantities of Fe were released in the leaching tests nevertheless (Figure 4.6).

Figure 4.5: Extracted elemental concentrations and changes of pH over time observed in the leaching of the Sinemurian siltstone under anoxic conditions.



Figure 4.6: The calculated normalized root mean square errors (NRMSE) over all time steps for a specific elements and temperature showing the goodness-of-fit of the simulations. Anoxic extraction of Ca from the Hettangian sandstone has no NRMSE values, because the extracted amount was zero.



Figure 4.7: Simulated (lines) and measured (dots) Fe concentrations released over time during oxic experiments from *(a)* Hettangian sandstone and *(b)* Sinemurian siltstone. The normalized root mean square errors for each temperature are shown in Figure 4.6.

Sensitivity analysis

The calculated values of total-order sensitivities for the release of Fe under oxic conditions show that pyrite dissolution is the main source of solute Fe, while the dissolution of ferrihydrite and changes in the redox potential (pe) are no important factors (Figure 4.8). An exception is the 25 °C extraction of the Sinemurian siltstone, where pyrite dissolution was manually disabled to match the experimental results (compare Figure 4.7). Under these conditions, pe is the most important input variable.

The calculated sensitivities for solute Si show that its mobilization depends primarily on the dissolution of amorphous silica. At 25 °C, kaolinite and, to a smaller extent muscovite also contribute significantly (Figure 4.9). The dissolution of quartz and potassium feldspar within a week is nearly zero. The reduction of pH by pyrite dissolution is insignificant, and direct influences of pe and oxygen availability cannot be observed.

For the mobilization of Al, the sensitivity analysis shows that its main release mechanism at low temperatures is cation exchange, and at elevated temperatures, the dissolution of amorphous aluminum hydroxides (Figure 4.10). The sensitivities to the presence of kaolinite and muscovite are minor, and potassium feldspar is insignificant. In contrast, the presence of pyrite is a significant parameter, as it affects dissolution and desorption mechanics of Al-bearing phases. Oxygen and pe have no direct effect.



Figure 4.8: Calculated total-order sensitivities for oxic Fe release depending on temperature after 1 and 7 days, respectively, from (a) the Hettangian sandstone and (b) the Sinemurian siltstone.



Figure 4.9: Calculated total-order sensitivities for Si release depending on temperature after 1 and 7 days, respectively, from *(a)* the Hettangian sandstone and *(b)* the Sinemurian siltstone.



Figure 4.10: Calculated total-order sensitivities for Al release depending on temperature after 1 and 7 days, respectively, from *(a)* the Hettangian sandstone and *(b)* the Sinemurian siltstone.

4.5 Discussion

4.5.1 Iron and manganese mobilizations

The release of Mn from both rock types increased with temperature and decreased with pH (Figures 4.2-4.5). Its mobilization patterns could be modeled precisely under oxic and anoxic conditions, taking ion exchange and the equilibrium dissolution of manganese oxohydroxides into account, although oxohydroxide dissolution was calculated with no value for the standard enthalpy of reaction (Figure 4.6). The release of Fe from both rock types under oxic conditions could be explained accurately with the oxidation of pyrite by oxygen and ferric iron (Table 4.2). Ferrihydrite did not contribute

significantly to oxic Fe release, as indicated by the sensitivity analysis (Figure 4.8). It was possible to fit the reactive surface of pyrite directly to the solute Fe concentration (Figure 4.7), which resulted in plausible reactive surface values of approximately three orders of magnitude lower than the median specific surface values obtained from the RES³T database of the literature values (Brendler et al. 2003). The observed retardation and temperature dependences of oxic Fe release from the Sinemurian siltstone can be explained with amorphous coatings blocking the surfaces of the pyrite crystals, which Müller et al. (2017) identified using SEM-EDX. These coatings had to be removed before pyrite dissolution could start. The release of Fe under anoxic conditions was fast and occurred almost entirely within the first day (Figures 4.3 and 4.5). A comparison of the leached concentrations of up to 1 mg/l (ca. 0.03 mg/g rock) from the Hettangian sandstone (Figure 4.3), and 21 mg/l (ca. 0.6 mg/g rock) from the Sinemurian siltstone (Figure 4.5) with the total amount of mobile Fe (Figure 4.1) shows that only the mobilization of the reducible fraction can explain the leached Fe concentration. This indicates iron (hydr)oxide dissolution. However, it was not possible to simulate the observed iron hydroxide dissolution, using ferrihydrite Fe(OH)₃ as a simplified representative phase, with acceptable precision. The released Fe concentrations were underestimated using thermodynamic data from the SIT database (Figure 4.6). Thermodynamic data from the LLNL database reproduced the observed anoxic Fe release, but overestimated oxic Fe release in turn. This result suggests that the simplified ferrihydrite phase is insufficient for a precise simulation of the dissolution of iron (hydr)oxides. Another possible explanation is that the hydroxides of Fe and Mn formed mixed amorphous layers in the investigated rocks (e.g., Mustafa et al. 2002), as suggested by the strong correlation of Fe and Mn release under anoxic conditions. In the Sinemurian siltstone, there is also a strong correlation of Si with Fe and Mn under anoxic conditions, suggesting that amorphous silica was also incorporated in these layers. It is also possible that microbial reduction of the iron (hydr) oxides occurred (e.g., Kappler et al. 2004), since biofilms were detected in the filters of the ATES well from which the studied rock material was sampled (Huenges 2011). Finally, oven-drying of the rock samples after washing during preparation might have dissolved some pyrite, leaving Fe loosely adsorbed to the grain surfaces of the rocks.

4.5.2 Aluminum and silicium mobilizations

The release of Si during the leaching experiments was initially too fast to be explained with the dissolution of crystalline silicates. In silicate dissolution experiments described in other studies (e.g., Rimstidt & Barnes 1980, Tester et al. 1994), the fast initial release of Si was explained by the highly reactive disturbed surfaces, such as amorphous coatings, edges, kinks, and micrograins, which dissolve quickly before the slower dissolution of the crystalline matrix starts. The sensitivity analysis performed in the present study confirmed this assumption, as it showed that Si release during the 7 days of the leaching experiments was mainly due to dissolution of amorphous silica (Figure 4.9). Its regularly incongruent dissolution might explain the poor goodness-of-fit values calculated for the numerical simulation of Si release (Figure 4.6). A second possible effect was suggested by the strong correlation of Si with Mn and Fe in the anoxic extraction of the Sinemurian siltstone, which might be explained by mixed layers of amorphous silica, iron (hydr)oxides and manganese hydroxides, potentially altering the dissolution kinetics of amorphous silica.

The mobilization of Al from the Hettangian sandstone could be explained well by combining ion exchange and the equilibrium dissolution of amorphous aluminum hydroxide, while the same explanation overestimated the Al release from the Sinemurian siltstone, and could not reproduce the observed time trends. A possible explanation is that Al hydroxides contained in the siltstone were partially crystalline, while those in the sandstone were entirely amorphous. The quantification of amorphous Al hydroxides applied in this study relies on Al hydroxide dissolution at pH 3.7 (see item 4.3.3), which will include part of the crystalline Al hydroxides as well (Marion et al. 1976). A second explanation could be the dissolution of highly reactive disturbed surface areas of the Al-bearing minerals kaolinite and muscovite, as already discussed above for Si. The strong correlation between anoxic Si and Al releases from the Hettangian sandstone suggests the dissolution of a solid phase containing both elements (Figure 4.3). However, this correlation was not observed for the Sinemurian siltstone, although it could have been masked by other processes such as the dissolution of amorphous silica.

4.5.3 Calcium and barium mobilizations

The release of Ca from the Sinemurian siltstone could be explained well by calcite dissolution and ion exchange (Figure 4.6). The strong correlation with Fe, Mn, and Si release under anoxic conditions suggests that Ca was sorbed to the surfaces of the respective hydroxides and amorphous silica. In contrast, Ca release from the Hettangian sandstone differed significantly under oxic and anoxic conditions: oxic release was up to 0.95 mg/L (0.05 mg/g sediment, Figure 4.2), indicating that nearly all available mobile Ca was released (Figure 4.1), while anoxic release was zero. This was due to sorption reactions, as initial simulations proved that the Hettangian sandstone contains no calcite. The zero release under anoxic conditions suggests that no competitive adsorptions of Na and Ca occurred. Instead, it is likely that Ca was desorbed under oxic conditions because the pH fell below the Ca adsorption edge due to pyrite dissolution (Davis & Kent 1990). Since no Ca was released under anoxic conditions despite the dissolution of Fe and Mn hydroxides, and no correlations between Ca and Fe or Mn were found, it is likely that Ca was sorbed to clay minerals or organic matter rather

than to hydroxides. This assumption was not tested by numerical simulations, because the sorbing surface was unknown.

Barium release from both rocks occurred mainly under oxic conditions (Figures 4.2-4.5). Since the released amounts were higher than the Ba associated with oxidizable phases (Figure 4.1), it can be assumed that Ba associated with acid-soluble phases, such as carbonates (Deer et al. 1992) and easily soluble hydroxides, was additionally mobilized by acidification caused by pyrite dissolution.

4.5.4 Mobilizations of other elements

Arsenic was immobile in both investigated rocks (Figures 4.2-4.5). The sequential extraction identified only small mobile quantities (Hettangian sandstone: $0.01 \mu g/g$, Sinemurian siltstone $2 \mu g/g$, Figure 4.1) in oxidizable and reducible phases, and it is likely that released As was below detection limit or re-adsorbed quickly.

Copper release was minor and significantly lower than the mobile fraction identified by the sequential extraction (Figure 4.1). No strong correlations with mineral-forming elements were found (compare Figures 4.2-4.5), so that the most likely source is native copper, which was identified in both rocks by Müller et al. (2017). The slightly higher oxic mobilization from both rocks may be explained by the presence of chalcopyrite (CuFeS₂), which is a common accessory in pyrite-bearing rocks (Deer et al. 1992).

The mobilization patterns of Ni and Pb were comparable for the Sinemurian siltstone. They increased with time and temperature under oxic conditions, and reached equilibrium within one day under anoxic conditions. In the Hettangian sandstone, Pb was associated with oxidizable phases (Figure 4.1), and was consequently released only under oxic conditions (Figures 4.2 and 4.3) while Ni showed no distinct release patterns. Both elements are commonly associated with reducible and oxidizable phases, especially with hydroxides, and with sulfides rather than organic matter (Cornell & Schwertmann 1996, Deer et al. 1992, Nissenbaum & Swaine 1976). In the present study, however, no strong correlations with other elements were found, and the exact release mechanisms remain unclear.

4.5.5 Implications for ATES systems

The fluid–rock interactions studied under controlled conditions allow a precise explanation and quantification of the release mechanisms responsible for element mobilization from the studied rocks at up to 90 °C. They help predict how the aquifer will react when specific parameters, such as solute oxygen, change, and if there are risks for aquifer clogging or contaminant mobilization. However, the chemistry of the aquifer during operation will be influenced by several other factors, and elemental mobilization

by fluid–rock interactions occurs alongside water mixing and microbial activity, which are the most important contributors to aquifer clogging (e.g., Griebler et al. 2014, Hartog et al. 2013).

The oxic and anoxic cases studied here are boundary cases, and solute oxygen concentration and distribution in the aquifer will be mainly close to the anoxic case $(O_{2(ac)}) = 0.25 \text{ mg/L}$, Huenges 2011). Conditions close to the oxic case may either occur in shallow aquifers, or close to the well in deeper aquifers if oxygen leaks into the groundwater during ATES operation. However, nitrogen pressurization, which is common in ATES systems (e.g., Frick et al. 2011, Seibt et al. 2010), should keep solute oxygen concentrations low. Oxygen leaking into the aquifer would furthermore be consumed by oxidizable solute species, e.g., Fe²⁺, thus reducing solute oxygen available for pyrite dissolution. The issue of groundwater acidification due to pyrite dissolution would be buffered in a natural system, reducing the magnitude of the pH-dependent processes observed in this study. Nitrogen pressurization, oxygen consumption by solute species and groundwater buffering are probably responsible that only minor pH variations between 7.3 and 6.9 were observed in the ATES system aquifer from which the samples of this study were collected (Huenges 2011). However, precipitated iron copper sulfides were found in the filters of the warm well of the system, which can be explained by pyrite dissolution. Severe precipitation of iron hydroxides after a phase of operation without nitrogen pressurization confirmed this assumption. Pyrite oxidation under anoxic conditions was probably catalyzed by iron-oxidizing microorganisms (Gallionella sp.), which were found in groundwater samples (ibid.), and oxidized iron in pH- and solute oxygen ranges in which abiotic pyrite oxidation cannot occur (Eggerichs et al. 2014). Other processes observed in the experiments will be less severe or nonexistent in the ATES system aquifer because of the difference in composition of natural groundwater and synthetic groundwater. For example, measured Ca concentrations in the groundwater during ATES operation ranged between 100 and 150 mg/L (ibid.). It is likely that sorption reactions are at least partially responsible for these shifts, but the exact magnitude is unknown. However, the workflow is capable of reliably excluding risk factors, such as contaminant release. For example, Bonte et al. (2013c) and Javed & Siddique (2016) reported the release of As from rock samples in experiments with elevated temperatures, and showed that the mobilized As had been sorbed to the rock matrix. This could be ruled out for both rocks studied in the present work, since they contained only reducible and oxidizable As, which remained immobile during leaching tests.

4.6 Conclusion

The element-release mechanisms of two pyrite-bearing siliciclastic rocks from oxygen-depleted aquifers were investigated with respect to ATES systems, varying temperature, and solute oxygen. A workflow consisting of time-resolved leaching experiments with synthetic groundwater, statistical analyses, and numerical simulations found that

- Oxygen availability controls Fe release from pyrite and iron hydroxides. Only pyrite is dissolved under oxic conditions, and only iron hydroxide is dissolved under anoxic conditions.
- The pH reduction induced by pyrite dissolution governs element mobilization under oxic conditions, e.g., Ca desorption. Under anoxic conditions, element mobilization depends mainly on hydroxide dissolution. Released concentrations are higher under oxic conditions.
- Temperature augments the dissolution of pyrite and hydroxides, and thus all subsequent processes.
- The mobilizations of Al and Si depend strongly on the dissolution of amorphous phases, which dissolve faster at low pH.

The results quantify the sensitivity of an ATES system aquifer to changes in environmental parameters, and can help quantify risks such as iron hydroxide clogging or contaminant release. In general, it was confirmed that the release of most potentially clogging elements and contaminants can be reduced or avoided by preventing oxygen from entering the aquifer, even at elevated temperatures.

4.7 Acknowledgements

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5 Synthesis

5.1 Summary

In this thesis, the reactivities of two siliciclastic rocks, a sandstone and a siltstone, were determined with multiple methods to address the main issues specified in chapter 1.5. The main issues are (1) the quantitative analysis of the bulk mineral composition and the surface composition, (2) the quantification of the maximal leachable amount of potentially critical mobile elements, (3) the identification of their chemical bond or phase association, and (4) the quantification of leachable critical mobile elements and the description of important control parameters and interactions in the ATES scenario. The workflow comprised mineralogical analyses, a sequential extraction, numerical simulations, statistical methods, and leaching experiments designed to mimic conditions of the ATES scenario.

In a first step, potential geochemical risks associated with the rock material were assessed by investigating the geologic setting, the bulk mineral composition and the reactivity of the material at 90 °C (chapter 2). The bulk mineralogy of the rocks was determined and quantified by X-ray diffraction analysis (XRD), X-ray fluorescence analysis (XRF), and scanning electron microscopy with energy-dispersive X-ray spectroscopy (SEM-EDX). The analyses identified quartz, potassium feldspar, mica, and clay minerals, which constituted more than 95 m-% of both analyzed rock types. Leaching tests conducted with synthetic groundwater (0.42 M NaCl solution) at 90 °C for 28 days resulted in pH decrease, the precipitation of secondary iron minerals, and the mobilization of several potentially critical elements, particularly calcium and sulfur, which suggested pyrite dissolution and an unknown calcium source. These results proved that solely characterizing the bulk mineralogy is insufficient for predicting geochemical risks of siliciclastic rocks, which shifted the analytical focus to the surface composition.

The quantification of the surface reactivity was realized by a sequential extraction procedure, which was specifically adapted for pyrite-bearing siliciclastic rocks, small mobile element amounts, and the quantification of soluble solid phases (chapter 3). The advantage of using the sequential extraction for solid phase quantification is the selective separation of the soluble solid phases from the insoluble silicate mineral grains they are attached to, which would not be possible with other separation techniques (compare Figure 1.2). The focus was consequently on quantifying the mobility of mineral-forming species, which requires effective mineral dissolution and prevention of re-precipitation. This was accomplished with the following modifications to previous sequential extraction references (e.g. Rauret et al. 1999, Tessier et al. 1979, Ure et al. 1993):

- Perform a sequence of an (1) exchange step (0.4 M magnesium chloride), an (2) acid-dissolution step (25% acetic acid buffered with 1 M ammonium acetate), a (3) reduction step (0.5 M hydroxylamine hydrochloride acidified with nitric acid to pH < 2), and an (4) oxidation step (30% hydrogen peroxide with 1 M ammonium acetate, acidified with nitric acid to pH 4). All of these steps should be performed in the given order.
- Perform the oxidation step at room temperature, not at 85 °C, to prevent solvent evaporation and iron phase re-precipitation. Added nitric acid improves pyrite oxidation, and ammonium acetate forms iron acetate complexes, which keeps iron in solution.

The precision of the sequential extraction was related to the leached element concentrations, with empirical coefficients of variance between 45 % for the sandstone with leachable element concentrations close to the instrumental detection limit, and 21 % for the siltstone with leachable concentrations between one and two magnitudes above the sandstone. Consequently, the precision improved slightly with increasing solid-solvent ratio, as tested with 33.3 g/L and 66.7 g/L. Re-precipitation and readsorption of the leached elements could not be observed. The sequential extraction yielded information about the total leachable amounts and bonding types of aluminum, arsenic, barium, calcium, copper, iron, lead, manganese, and nickel, and allowed the estimation of the quantities of calcite, manganese hydroxide, iron hydroxide, pyrite and organic matter. The solid phase quantification was based on the assumption that all released mineral-forming cations in a specific extraction step originated from a simplified reference solid phase: calcium in the acid-dissolution step from calcite, iron and manganese in the reduction step from iron- and manganese hydroxides, and iron in the oxidation step from pyrite. Organic matter was estimated from carbon measurements in the solid residuum before and after the oxidation step.

The ATES scenario was investigated with steady-state leaching experiments with synthetic groundwater, prepared as a 25 g/L (0.42 M) NaCl solution (chapter 4). This way, data points for 1 to 7 days of leaching time in dependence of temperature (25 to 90 °C) at oxic (air equilibrium) and anoxic (oxygen-free atmosphere and leachant) conditions were obtained. These results served as input and validation for further calculations. Correlation matrices compared leaching patterns of the potentially critical elements aluminum, arsenic, barium, calcium, copper, iron, manganese, nickel, lead, and silicium with each other and with leaching time, temperature and solute oxygen. A numerical model was optimized by fitting the reactive surfaces of the solid phases to

the experimental data points. The model was subsequently used to perform a sensitivity analysis to identify important reaction parameters and interactions. Combined with the information about bonding type and phase association from the sequential extraction, the following results were found for the investigated rock types:

- Solute oxygen governs the mobilization of most investigated elements due to the dissolution of iron phases. At anoxic conditions, iron hydroxides and associated elements are mobilized, at oxic conditions pyrite is dissolved, which decreases pH and induces further water-rock interactions.
- Temperature increases most leached concentrations. A temperature "threshold" was observed in the oxic leaching of the siltstone: pyrite dissolution occurred only at temperatures ≥ 70 °C, most likely due to the dissolution of iron-bearing coatings covering the pyrite crystals.
- Aluminum (Al), iron (Fe), manganese (Mn), and silicium (Si) were mobilized from their respective oxides and hydroxides in varying degrees of crystallinity. High correlations in mobilization patterns of Fe, Mn and Si from the siltstone suggested the presence of mixed amorphous hyr(oxide) coatings.
- Calcium (Ca) was mainly adsorbed, but sorption mechanisms in the investigated rocks differed from each other. While Ca was desorbed entirely during the leaching of the siltstone, only oxic leaching mobilized Ca from the sandstone, probably due to the pH falling below the Ca adsorption edge because of pyrite dissolution.
- Arsenic (As), barium (Ba), copper (Cu), lead (Pb), and nickel (Ni) showed no clear release patterns. While As was generally immobile, the other elements were likely present as solid solutions or co-precipitates. Copper was also found in elementary form.

5.2 Methodological considerations

The workflow proved to be a suitable approach to characterize the mobile quantities, release mechanisms, and main control parameters of potentially critical mobile elements in the investigated siliciclastic rocks. The results expand on previous work on ATES geochemistry (e.g. Bonte 2013, Jesußek et al. 2013) by proposing approaches to define and quantify the reactive mineralogy of a rock, determine the dependence of element release mechanisms on temperature, and characterize possible responses to redox processes in the aquifer. They allow the assessment of risks posed by contaminants, such as arsenic, and can help to optimize strategies for remediation or attenuation, which are discussed elsewhere (Bonte 2013, Wallis et al. 2011). The mobilization of mineral-forming elements such as iron and manganese can be quantified, which allows an improved prediction of potential mineral precipitation and

pore clogging at specific operational conditions. However, precise release mechanisms of trace elements which are adsorbed, present in solid solutions, or co-precipitated, are difficult to determine, as observed with e.g. calcium, copper, and nickel, although mobile quantities in the respective sequential extraction steps can be measured precisely.

Since water-rock interactions are site-specific, risk assessments need to be performed individually for each system. Consequently, there is demand for rapid tests to predict geochemical risks for any site (e.g. Jesußek et al. 2013). A rapid test should include a basic assessment of reactive mineralogy and critical element mobility, so that a quick decision on the geochemical suitability of the site or potential issues and the need for further tests can be made. This can be achieved by bulk mineral analysis and sequential extraction, which only require a few grams of rock material and can be completed within one or two weeks. The results of the bulk mineral analyses performed in this work showed that they can be kept to a minimum (e.g. only XRD), because minor solid phases (< 3-5 m-%) need to be evaluated for their solubility and their water-accessible masses rather than their overall masses. The sequential extraction presented here allows a suitable estimation for calcite, Fe and Mn hydroxides, pyrite, and organic matter. Microscopy and spectroscopic methods (e.g. SEM-EDX) can prove the presence of specific minerals, which is recommended, because the sequential extraction associates leached elements with representative common solid phases, but does not prove their presence. The sequential extraction itself can be modified according to the focus of the study or available data on the investigated rocks. For example, the reduction step can be split to discern between amorphous and crystalline iron (hydr)oxides (Gleyzes et al. 2002), and a water extraction step can be inserted as a 0th step to remove easily soluble salts, such as halite (Dold 2003, Fanfani 1997). In a similar way, the differentiation of the oxidation step into a dedicated dissolution step for pyrite and one for organic matter would allow further differentiation of the respective phase associations (Claff et al. 2010). Leaching experiments with synthetic groundwater can determine reaction kinetics, control parameters, and process interactions, and help to set operational constraints and calibrate numerical simulations for long-term predictions or parameter studies. To minimize the initial effort, leaching experiments should not be part of a rapid risk assessment. They should rather be performed afterwards, either to get additional information on potential geochemical issues, or to determine operational constraints if the site has been deemed suitable for ATES operation. This results in a workflow comprising a general or rapid risk assessment, and an assessment of operational constraints (Figure 5.1).



Figure 5.1: Schematic of the workflow to quantify element release from siliciclastic rocks.

Leaching with synthetic groundwater containing only Na⁺ and Cl⁻ yields different results than leaching with natural groundwater containing other solute species, dissolved organic matter and microorganisms. The advantage of the synthetic NaCl solution is improved reaction control, because the masking of element mobilization by adsorption, precipitation, and any other interactions between solute components not mobilized from the rock will be avoided. Since water composition variables are minimized, the parameterization of dissolution kinetics for numerical simulations and the interaction of multiple dissolution processes can be observed. In leaching experiments with natural groundwater or with synthetic groundwater prepared to resemble the natural groundwater composition, chemical equilibrium between rock and water at the natural aquifer temperature can be assumed. Some reactions would not occur in this case. For example, the observed desorption of calcium from both investigated rocks (Figures 4.2, 4.4, 4.5) would be expected to be significantly smaller, and occur only due to temperature increases. Furthermore, solute water components may prevent, inhibit, or accelerate many water-rock interactions, and interact with released species. Solute components can act as complexing agents or pH buffers, they can be reductants and oxidants which interact with redox-active species, or they can provide nourishment to microbes that catalyze reactions in the aquifer (e.g. Langmuir 1997, Stumm & Morgan 1996). For example, pyrite dissolution can be accelerated by the presence of abiotic oxidants and microbes (chapter 1.2.3), released iron can be kept in solution by complexing agents which inhibit re-precipitation, and pH buffers can prevent water acidification and further reactions triggered by pH. Generally, leaching with natural groundwater provides direct information about water-rock interactions that can be expected in the field at the tested conditions (e.g. Arning 2006, Jesußek et al. 2013), while leaching with a NaCl solution provides specific information about the rock reactivity.

The timeframe of the leaching experiments can be adapted to the kinetics of specific reaction types. In the present work, the timeframe of the leaching experiments was set to between one and seven days to investigate fast exchange- and dissolution reactions. Extending the timeframe will provide additional information about the dissolution kinetics of hardly soluble minerals, such as quartz. This was limited in the present work, because initial Si mobilization was governed by the rapid dissolution of amorphous silica (Figure 4.9). However, extending the leaching time would facilitate the reprecipitation or re-adsorption of rapidly mobilized species, e.g. iron, and produce useless data for such elements (chapter 4.4.2 and Figure 4.7).

5.3 Implications for ATES operation and comparison with field data

The main geochemical risks related to element mobilization can be verified by comparison of the results of this work with field data from the ATES system at the German parliament buildings. Heat storage operation with temperatures of up to 50 °C was closely monitored for research and demonstration purposes for approximately six years (Huenges 2011). Since the investigated Hettangian sandstone forms the heat storage aquifer (chapter 1.4), field data can be linked directly to this rock type. The investigated siltstone was obtained from the topset aquitard of the heat storage aquifer, and while some contact between water and rock can be assumed, its influence on field measurements will be minor compared to the aquifer sandstone.

The comparison of the results of the present work to field data, taken from Huenges (2011) unless stated otherwise, is summarized in Table 5.1. It was found that in the aquifer sandstone, the overall leachable quantities of the investigated elements (sum of all sequential extraction steps) were small (<0.01 mg/g), and significantly larger in the siltstone (up to ~4 mg/g for calcium). These results suggest no major risks associated with the sandstone, which would prohibit ATES operation. Field observations confirmed this assessment, as heat storage did not result in problematic pore clogging or contaminant release.

The iron (Fe) system is the main risk factor, and solid iron phases were the primary constituent of particles found in the well's 0.45 µm thermal water filters and in a bailer sample. Prior work on the coupled iron-sulfur redox system investigated biotic and abiotic redox processes ultimately leading to iron mineral precipitation in the storage system (Opel et al. 2008, Opel 2012). A strong increase of solid particles accumulating in the thermal water filters was observed during a brief failure of the system's nitrogen pressurization, which allowed oxygen to infiltrate into the well. During this time, the filters retained 1270 mg/m³ of solids instead of the usual 20-170 mg/m³, which mainly consisted of iron hydroxides. It is unknown if pyrite oxidation occurred during this period, or if the oxidation of solute Fe(II) to Fe(III), which lead to iron hydroxide precipitation, consumed the infiltrated oxygen entirely. No pH decrease was measured, but due to the groundwater's buffering capacity (primarily hydrogen carbonate), no conclusions can be drawn from these measurements.

Calcium (Ca) was primarily adsorbed. Calcite particles were found regularly in the well filters, and since no calcite was detected in the aquifer sandstone, they were likely precipitates that formed during ATES operation due to the temperature-induced shift of the carbonate equilibrium (Weber 2000). The observed decrease of solute Ca during hot water storage confirms this assumption, and the subsequent concentration increase can be explained with rapid equilibration with adsorbed Ca. This answers an open issue, as Huenges (2011) found no significant correlations between temperature and calcite saturation or solute Ca, so that calcite precipitation could not be confirmed.

Aluminum and silicium were leached rapidly from amorphous (hydr)oxides during the experiments, but concentration measurements during ATES operation exhibited strong oscillations with peaks following weeks or months after hot water injection. This suggests kinetically slow mobilization from silicates as the main release mechanism.

Very small amounts of arsenic were leached from the sandstone, and solely during the reduction step of the sequential extraction (ca. 0.02 μ g/g). No mobilization was observed during the leaching experiments with synthetic groundwater in up to seven days. Groundwater monitoring in the ATES system showed that after hot water storage, the arsenic concentration increased from "below detection limit" (<0.02 μ g/L) to a peak of 23 μ g/L, and subsequently stabilized between 5 and 10 μ g/L. This arsenic could have been released from (hydr)oxides found in the sandstone due to temperature-induced or microbially catalyzed dissolution over extended time periods (>7 days).

Barium (Ba), copper (Cu), nickel (Ni), and lead (Pb) are associated with nearly all fractions differentiated by the sequential extraction, and are most likely present as solid solutions or co-precipitates. Groundwater concentrations increased slightly over time, but showed strong oscillations. This can be explained with the accumulation of Cu, Ni and Pb in the well filters, probably associated with iron hydroxides. No data on Ba accumulation was reported.

a ble 5.1: Comparis	on of the results with field data and implic	cations for ATES operation. Field da	ta were taken from Huenges (2011), unless stated
herwise.			
mponent	Experimental study (present work)	ATES field observations	Implications

Table 5.1: Comparison of th otherwise.	he re	sults with field data and implication	is for	ATES operation. Field data were	take	n from Huenges (2011), unless stated
Component	Expe	erimental study (present work)	ATES	S field observations	lmpl	ications
Leachable mass fractions	••	Sandstone: < 0.1 mg/g Siltstone: up to ~4 mg/g (Ca)	•	No problematic pore clogging or observed contaminant release	•	No major risks for ATES operation
Iron	•	Main risk, many element mobilization processes associated with Fe solids	• •	Fe hydroxide and Fe sulfide (FeS) most common solids in thermal water filter and bailer sample Failure of nitrogen pressurization: increased Fe hydroxide precipitation due to solute Fe(11) oxidation	• •	Complex iron-sulfur redox system responsible for iron mineral precipitation (Opel et al. 2008, Opel 2012). Pyrite oxidation during operation unknown, no pH decrease, consider groundwater buffering capacity
Calcium	•	Mainly adsorbed	• •	Concentration constant, except for shifts due to temperature increase Calcite particles common in filters	••	Equilibrium solute / adsorbed Ca Calcite is secondary precipitate due to temperature-induced carbonate equilibrium shift, as shown by decrease of solute Ca with temperature
Silicium, aluminum	•••	Rapid leaching from amorphous (hydr)oxides Slow leaching from silicates	•	Solute Si and Al increase slowly over time, oscillation peaks follow weeks or months after hot water storage cycles	•	Concentration peaks lagging behind hot water injection indicate mainly slow silicate dissolution
Arsenic	•	Sandstone: minuscule mobilization, only by reduction (ca. 0.02 µg/g), no release during synthetic GW leaching	•	Below detection limit (0.02 μg/L), after hot water injection peak of 23 μg/L, stabilization between 5 and 10 μg/L	•	Mobilization from (hydr)oxides possible due to elevated temperature or microbial activity, no major risk due to minuscule mobility
Barium, copper, nickel, lead	•	Associated with nearly all fractions, probably solid solutions or co-precipitates	• •	Concentrations increase slightly over time Accumulation of Cu, Ni, Pb in filters, likely associated with Fe hydroxides	•	Mobilization and retention probably mainly related to Fe solid phases, precise mechanisms unclear

5.4 Conclusion and outlook

The presented workflow characterizes the release mechanisms of several potentially critical mobile elements on the example of two siliciclastic rocks from the Lower Jurassic. It quantifies abiotic element mobilization from the rocks for a worst case scenario and for the ATES scenario, which was defined by temperatures of up to 90 °C and potential infiltration of solute oxygen. The results of the presented leaching experiments, numerical simulations, and statistical analyses could appropriately explain monitoring data of the ATES system at the German parliament buildings in the city of Berlin, which accesses the analyzed Lower Jurassic horizons for heat storage. As mobile element quantities are minor, groundwater contamination or porosity reduction in dimensions that would prohibit ATES operation are unlikely to occur. Since pyrite is present, the prolonged intrusion of oxygen into the aquifer has to be prevented by constant nitrogen pressurization of the system. However, a complex groundwater chemistry and microbial activity make accurate predictions of chemical processes in the aquifer challenging, and the transfer of the results to the field scale may be greatly assisted by integrating the numerical model of the rock reactivity into a hydraulicthermal-mechanical-chemical (HTMC) aquifer model. That way, the influence of flow conditions and groundwater chemistry can be integrated into the data. This allows the calculation of specific scenarios and interactions, e.g. the consumption of oxygen by solute redox-active species such as Fe(II)/Fe(III) in the well, and the remaining potential for pyrite oxidation. Based on the presented results for siliciclastic rocks, the extension of the workflow to other rock types, such as carbonates, may be possible. This would require adaptations to account for the solubility of these rock types, particularly in the acid-dissolution step of the sequential extraction. Generally, further work to integrate rates of microbial activity would be desirable, e.g. by adding suitable microorganisms to the leaching experiments.

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Appendix

Correlation matrices

Table A.1: Correlation matrix for the extracted element concentrations and pH changes over time at different temperatures, observed in the leaching of the Hettangian sandstone at oxic conditions.

	Al	As	Ba	Ca	Cu	Fe	Mn	Ni	Pb	Si	рН	Temp	Days
Al	1.00		0.55	0.19	0.15	0.68	0.55	0.45	0.52	0.66	-0.79	0.59	0.56
As													
Ba	0.55		1.00	0.10	0.35	0.62	0.76	0.51	0.84	0.63	-0.83	0.84	0.14
Ca	0.19		0.10	1.00	0.56	-0.05	0.30	0.20	-0.19	-0.32	-0.04	-0.06	0.07
Cu	0.15		0.35	0.56	1.00	0.11	0.57	0.42	0.37	-0.05	-0.30	0.39	-0.21
Fe	0.68		0.62	-0.05	0.11	1.00	0.38	0.30	0.57	0.44	-0.76	0.48	0.55
Mn	0.55		0.76	0.30	0.57	0.38	1.00	0.63	0.65	0.63	-0.82	0.88	0.04
Ni	0.45		0.51	0.20	0.42	0.30	0.63	1.00	0.50	0.33	-0.60	0.73	-0.14
Pb	0.52		0.84	-0.19	0.37	0.57	0.65	0.50	1.00	0.68	-0.80	0.85	0.10
Si	0.66		0.63	-0.32	-0.05	0.44	0.63	0.33	0.68	1.00	-0.80	0.78	0.39
рН	-0.79		-0.83	-0.04	-0.30	-0.76	-0.82	-0.60	-0.80	-0.80	1.00	-0.89	-0.42
Temp	0.59		0.84	-0.06	0.39	0.48	0.88	0.73	0.85	0.78	-0.89	1.00	0.00
Days	0.56		0.14	0.07	-0.21	0.55	0.04	-0.14	0.10	0.39	-0.42	0.00	1.00

Table A.2: Correlation matrix for the extracted element concentrations and pH changes over time at different temperatures, observed in the leaching of the Hettangian sandstone at anoxic conditions.

	Al	As	Ba	Ca	Cu	Fe	Mn	Ni	Pb	Si	рН	Temp	Days
Al	1.00		0.13		0.10	0.03	0.00	0.00	-0.16	0.73	0.03	-0.01	0.22
As													
Ba	0.13		1.00		0.20	0.39	0.68	0.17	0.41	0.50	0.08	0.82	-0.13
Ca													
Cu	0.10		0.20		1.00	0.18	0.17	0.96	-0.10	-0.13	0.83	0.09	-0.42
Fe	0.03		0.39		0.18	1.00	0.86	0.23	-0.07	0.39	-0.32	0.74	0.05
Mn	0.00		0.68		0.17	0.86	1.00	0.24	0.22	0.46	-0.22	0.95	-0.07
Ni	0.00		0.17		0.96	0.23	0.24	1.00	-0.19	-0.19	0.76	0.14	-0.50
Pb	-0.16		0.41		-0.10	-0.07	0.22	-0.19	1.00	0.13	0.01	0.30	0.05
Si	0.73		0.50		-0.13	0.39	0.46	-0.19	0.13	1.00	-0.32	0.52	0.51
рН	0.03		0.08		0.83	-0.32	-0.22	0.76	0.01	-0.32	1.00	-0.23	-0.46
Temp	-0.01		0.82		0.09	0.74	0.95	0.14	0.30	0.52	-0.23	1.00	0.00
Days	0.22		-0.13		-0.42	0.05	-0.07	-0.50	0.05	0.51	-0.46	0.00	1.00

Table A.3: Correlation matrix for the extracted element concentrations and pH changes over time at different temperatures, observed in the leaching of the Sinemurian siltstone at oxic conditions.

	Al	As	Ba	Ca	Cu	Fe	Mn	Ni	Pb	Si	рН	Temp	Days
Al	1.00		0.55	0.69	0.38	0.66	0.71	0.85	0.60	0.50	-0.79	0.41	0.55
As													
Ba	0.55		1.00	0.92	0.21	0.78	0.95	0.87	0.64	0.96	-0.90	0.82	0.38
Ca	0.69		0.92	1.00	0.23	0.72	0.98	0.92	0.63	0.86	-0.95	0.88	0.32
Cu	0.38		0.21	0.23	1.00	0.64	0.28	0.40	0.77	0.38	-0.28	0.04	0.12
Fe	0.66		0.78	0.72	0.64	1.00	0.78	0.85	0.90	0.88	-0.77	0.47	0.52
Mn	0.71		0.95	0.98	0.28	0.78	1.00	0.96	0.69	0.92	-0.99	0.82	0.42
Ni	0.85		0.87	0.92	0.40	0.85	0.96	1.00	0.75	0.85	-0.98	0.68	0.54
Pb	0.60		0.64	0.63	0.77	0.90	0.69	0.75	1.00	0.76	-0.68	0.35	0.33
Si	0.50		0.96	0.86	0.38	0.88	0.92	0.85	0.76	1.00	-0.86	0.74	0.38
рН	-0.79		-0.90	-0.95	-0.28	-0.77	-0.99	-0.98	-0.68	-0.86	1.00	-0.76	-0.50
Temp	0.41		0.82	0.88	0.04	0.47	0.82	0.68	0.35	0.74	-0.76	1.00	0.00
Days	0.55		0.38	0.32	0.12	0.52	0.42	0.54	0.33	0.38	-0.50	0.00	1.00

Table A.4: Correlation matrix for the extracted element concentrations and pH changes over time at different temperatures, observed in the leaching of the Sinemurian siltstone at anoxic conditions.

	Al	As	Ba	Ca	Cu	Fe	Mn	Ni	Pb	Si	pН	Temp	Days
Al	1.00		-0.36	-0.16	0.02	-0.04	-0.14	0.21	-0.33	-0.02	0.29	-0.10	0.23
As													
Ba	-0.36		1.00	0.63	0.56	0.44	0.57	0.14	0.60	0.40	-0.16	0.41	-0.11
Ca	-0.16		0.63	1.00	0.30	0.82	0.97	0.25	0.56	0.80	-0.29	0.83	-0.04
Cu	0.02		0.56	0.30	1.00	0.12	0.25	0.69	0.55	0.10	0.61	0.27	-0.45
Fe	-0.04		0.44	0.82	0.12	1.00	0.87	0.09	0.52	0.99	-0.27	0.93	0.23
Mn	-0.14		0.57	0.97	0.25	0.87	1.00	0.30	0.56	0.85	-0.29	0.91	0.01
Ni	0.21		0.14	0.25	0.69	0.09	0.30	1.00	0.34	0.04	0.52	0.32	-0.27
Pb	-0.33		0.60	0.56	0.55	0.52	0.56	0.34	1.00	0.48	0.09	0.67	-0.35
Si	-0.02		0.40	0.80	0.10	0.99	0.85	0.04	0.48	1.00	-0.29	0.91	0.26
рН	0.29		-0.16	-0.29	0.61	-0.27	-0.29	0.52	0.09	-0.29	1.00	-0.13	-0.56
Temp	-0.10		0.41	0.83	0.27	0.93	0.91	0.32	0.67	0.91	-0.13	1.00	0.00
Days	0.23		-0.11	-0.04	-0.45	0.23	0.01	-0.27	-0.35	0.26	-0.56	0.00	1.00

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List of Publications

Peer-reviewed journals

- Müller D, Regenspurg S. Geochemical characterization of the Lower Jurassic Aquifer in Berlin (Germany) for aquifer thermal energy storage applications. Energy Procedia. 2014; 59:285–92. <u>https://doi.org/10.1016/j.egypro.2014.10.379</u>.
- Müller DR, Friedland G, Regenspurg S. An improved sequential extraction method to determine element mobility in pyrite-bearing siliciclastic rocks. Int J Environ Anal Chem. 2017; 97(2):168–88. <u>http://dx.doi.org/10.1080/03067319.2017.1294166</u>.
- Müller DR, Regenspurg S. The element-release mechanisms of two pyrite-bearing siliciclastic rocks from the North German Basin at temperatures up to 90 °C under oxic and anoxic conditions. Geothermal Energy 2017; 5(25). https://doi.org/10.1186/s40517-017-0080-1.

Conference abstracts

Talks

- Müller D, Regenspurg S, Milsch H, Blöcher G, Kranz S, Saadat A. Predicting Formation Damage in Aquifer Thermal Energy Storage Systems Utilizing a Coupled Hydraulic-Thermal-Chemical Reservoir Model. In: Geophysical Research Abstracts 2014; 16, EGU2014-11962, EGU General Assembly, Vienna, Austria 2014.
- Müller D, Regenspurg S, Milsch H. Assessment of Potential Formation Damage in Aquifer Thermal Energy Storage (ATES) Systems Utilizing Reactive Transport Simulations. In: Proceedings of the 5th Workshop of the PhD Network on Reactive Transport, Tübingen, Germany, 2014.

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- Müller D, Francke H, Blöcher G, Shao H. Simulation of Reactive Transport in Porous Media: A Benchmark for a COMSOL-PHREEQC-Interface. In: Proceedings of the 2013 COMSOL Conference, Rotterdam, Netherlands, 2013.
- Müller D. Long-Term Effects of Aquifer Thermal Energy Storage: Characterization of Permeability Changes Due to Hydraulic-Thermal-Chemical Processes. In: Proceedings of the 5th European Geothermal PhD Day, Darmstadt, Germany, 2014.
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