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Reactive fronts in chemically heterogeneous porous media: Experimental and modeling investigation of pyrite oxidation

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Abstract

The spatial distribution of reactive minerals in subsurface porous media is an important control for groundwater quality. In this study we investigate pyrite oxidation reactive fronts in chemically heterogeneous porous media by combining laboratory experiments and reactive transport modeling. We performed experiments in different setups including batch, 1-D column, and 2-D flow-through systems. The flow-through experiments were performed in physically homogenous but chemically heterogeneous domains with embedded reactive pyrite inclusions at different spatial locations and with different concentrations. The setups were initially maintained under anoxic conditions and subsequently flushed with an inflowing oxic solution. A non-invasive optode technique was used for high-resolution monitoring of oxygen. This allowed us to capture the dynamics of the reactive oxygen fronts in the 1-D columns and in the 2-D flow-through chamber. Water quality analyses of

the products of pyrite oxidation, iron (Fe) and sulfur (S), were also carried out in the different setups. The concentration of these species released in the 1-D columns (up to 6.2×10^{-5} mol/L Fe and 13.7×10^{-5} mol/L S) and in the 2-D setup (up to 3×10^{-6} mol/L Fe and 9×10^{-6} mol/L S) could be quantitatively related to the consumption of oxygen (up to 1.9×10^{-4} mol/L consumed in the 1-D and 2-D setups). The reaction rates were found to be different between the setups and dependent on the spatial location and concentration of the pyrite inclusions.

A modeling approach coupling 1-D and 2-D transport codes with the geochemical simulator PHREEQC is proposed to simulate the spatial and temporal dynamics of oxygen transport, the kinetics of pyrite oxidative dissolution, and the changes in water quality in the chemically heterogeneous flow-through setups. The model allowed the quantitative interpretation of the experimental results and represents a valuable tool to capture the coupling between multidimensional transport and geochemical reactions both in laboratory and in field scale applications.

1 Introduction

Geochemical heterogeneities in subsurface formations exert a primary control on the chemistry of water bodies (Appelo and Postma, 2005; Battistel et al., 2016; Zhu and Schwartz, 2011). The presence of reactive minerals and their spatial distribution affect important biogeochemical processes such as dissolution and precipitation reactions (Li et al., 2014; Manaka and Takeda, 2016; Salehikhoo and Li, 2015; Shi et al., 2013; Soltanian et al., 2015; Wen and Li, 2018) as well as the fate and transport of toxic elements in groundwater (Englert et al., 2009; Li et al., 2011; Steefel et al., 2005). The impact of reactive minerals on groundwater quality is critical in areas where redox conditions may be altered due to both natural processes, subsurface contamination, and engineering applications. For instance in aquifers where managed aquifer recharge is used as a strategy to

improve drinking water supply, the injection of oxidizing water into an anoxic groundwater system triggers a series of geochemical reactions that are responsible for changes in the chemical conditions and composition in the subsurface (Descourvières et al., 2010b; Prommer and Stuyfzand, 2005). Also groundwater pumping and subsequent dewatering (e.g., during groundwater supply or mining activity) can lead to a change in the subsurface redox conditions. The decrease of piezometric levels allows the atmospheric oxygen to penetrate into sediments layers containing reactive minerals and thus promotes the mobilization of heavy metals and metalloids (Andersen et al., 2001; Kinniburgh et al., 1994; Larsen and Postma, 1997). As shown in comparative studies on intact core sediments, pyrite oxidation plays a predominant role in oxygen consumption and can be a faster process than microbially-mediated organic matter degradation and siderite oxidation (Descourvières et al., 2010a; Hartog et al., 2002). The oxidation of pyrite is indeed a crucial reaction for the chemistry of water resources, and often the oxidative dissolution of pyrite can have adverse effects on water quality. The release of trace elements in groundwater aquifers (Neil et al., 2014; Walker et al., 2006; Ziegler et al., 2017), and the acidification of surface and groundwater, are two major adverse impacts of pyrite oxidation (Gerke et al., 2001, 1998). Activities, such as mining and ore processing, can exacerbate the problems related to the oxidative dissolution of pyrite, producing acid drainage often heavily enriched with high concentration of metals and metalloids (Blowes et al., 2003; Galán et al., 2003; Sánchez España et al., 2005; Stollenwerk, 1994). The oxidation of pyrite can also play a role in nitrate migration in sandy aquifers (Jessen et al., 2017; Postma et al., 1991) and in nickel mobilization (Larsen and Postma, 1997). Furthermore, the oxidative dissolution of arsenic-bearing pyrite has been identified as one of the main causes of arsenic release in natural and managed aquifers (Appelo and Postma, 2005; Jones and Pichler, 2007; Kocar et al., 2008; Lazareva et al., 2015; Price and Pichler, 2006; Prommer and Stuyfzand, 2005; Schreiber et al., 2000; Wallis et al., 2010).

This study aims to investigate the role of chemical heterogeneity on reactive transport in porous media and to provide a high-resolution dataset, obtained under well-controlled conditions, which can be used as a benchmark for validation of reactive transport simulators. The latter are fundamental tools to understand complex geochemical reactions in subsurface porous media and for the quantitative upscaling of important biogeochemical processes such as mineral precipitation and dissolution in field scale reactive transport scenarios (e.g., Jung and Navarre-Sitchler, 2018; Wen and Li, 2018). We performed a detailed investigation of pyrite oxidation in saturated porous media by carrying out laboratory experiments in different setups including batch, 1-D column, and 2-D flow-through systems. We focused on the impact of geochemical heterogeneities and, in a number of flow-through experiments, we embedded reactive pyrite inclusions in a sandy matrix with identical grain size, thus creating physically homogeneous but chemically heterogeneous media. Oxidic water was flushed through the initially anoxic media and the transport of oxygen, its consumption due to the oxidative dissolution of pyrite, and the impact of the reaction on the quality of the pore water solution were monitored at high-spatial and temporal resolution. A reactive transport modeling approach coupling 1-D and 2-D transport codes with the geochemical simulator PHREEQC (Parkhurst and Appelo, 2013) was used to quantitatively interpret the experimental observations. Advection, dispersion and kinetic gas partitioning of oxygen with residual entrapped gas were the main physical processes described in the transport codes, whereas the reaction network, including a kinetic description of pyrite oxidation, was implemented in PHREEQC.

2 Material and Methods

2.1 Experimental setups

In this work, the oxidative dissolution of pyrite was experimentally investigated in batch, 1-D and 2-D setups. A schematic overview of the three setups is given in Fig. 1. All the experiments were performed in a temperature controlled room at 20°C.

Fig. 1. Experimental laboratory setups for the investigation of pyrite oxidation: (a) batch experiments, (b) 1-D column experiments, (c) 2-D flow-through experiments. Different colors of the inclusions represent their different composition, dark gray: pure pyrite inclusion, light gray: pyrite mixed with sand.

The pyrite used in these experiments was provided from Mexico by Ward's Science. The mineral was prepared for the experiments following the procedure described in Walker et al. (2006) for arsenopyrite. Pyrite was crushed in a mortar and sieved to obtain a grain size between 125 μm and 250 μm . After sieving, the pyrite was rinsed five times with ethanol 50% (v/v) with sonication cycles of three minutes each and the supernatant was removed by decantation. After the sonication cycles, the pyrite was dried under N_2 . The mineral was then treated with HCl (37%) for five minutes, rinsed three times with distilled water for three minutes and with ethanol 50% (v/v) for one minute. Finally, the pyrite was dried under a constant N_2 flow and preserved under anoxic conditions until used in the experiments. To avoid microbial contamination, all glassware and materials that contacted the minerals were autoclaved. The average chemical formula of the mineral was determined to be $\text{Fe}_{1.72}\text{S}_{1.72}$, based on X-ray fluorescence (XRF) analysis (Spectro XRF-XEPOS X-ray fluorescence spectrometer). Iron K-edge extended X-ray absorption fine structure (EXAFS) spectroscopy was conducted at Stanford Synchrotron Radiation Lightsource, (SSRL) and revealed that Fe exists entirely as pyrite and no iron oxides were detected onto the mineral surface (Fig. S1; Supporting Information). The sand used for packing the flow-through setups (Euroquartz GmbH) was washed four times with HCl (37%), rinsed with water, and then dried for > 24 h at 100°C.

During the experiments the oxygen consumption and the propagation of conservative and reactive oxygen fronts were monitored using a sensor-based non-invasive approach. The sensors used in this study allowed us to measure oxygen concentrations in the three different setups at high spatial and temporal resolution. O_2 measurements could be taken directly inside the porous media by applying a non-invasive optode technique (PreSens GmbH, Germany; e.g., Haberer et al., 2011). Spots and strips of a luminophore oxygen sensitive polymer were glued into the inner walls of the experimental setups. The sensor was excited by a modulated light via an optic fiber from the outside of the walls, and since the molecular oxygen has the property of quenching the luminescence

emitted by the excited luminophore, O₂ content was estimated by measuring the luminescence intensity and lifetime (Klimant and Wolfbeis, 1995). This technique has been applied in porous media to investigate the exchange of O₂ across the capillary fringe (Haberer et al., 2015b, 2012), transverse mixing (Rolle et al., 2012, 2010), aerobic degradation of organic contaminants and oxygen dynamics in the hyporheic zone (Bauer et al., 2009; Jost et al., 2011; Vieweg et al., 2013). The technique allows to quantify oxygen concentrations with an accuracy ranging between ± 0.002 mg/L and ± 0.16 mg/L depending on the oxygen concentration, and has a detection limit of 0.015 mg/L. Further details on the measurement technique and an illustration of the O₂ sensors and the optic fiber in the 2-D flow-through setup is provided in the Supplementary Material (Figure S2).

The products of pyrite oxidation, total iron (Fe), total sulfur (S) and pH, were analyzed in the different experimental setups. The samples for the measurements of total Fe and S were filtered through a 0.2 μ m filter and acidified with 3% HNO₃, and the analyses were performed with Inductively Coupled Plasma - Optical Emission Spectroscopy (ICP-OES) (Perkin Elmer AvioTm 200). The pH was measured in the non-acidified samples with a Hach electrode PHC28101 (HACH Denmark).

2.1.1 Batch experiments

Batch experiments were performed to characterize the kinetics of the oxidative dissolution of pyrite by monitoring the consumption of oxygen and the formation of the reaction products. Two sets of batch experiments (Batch 1 and Batch 2) were prepared using glass bottles with a volume of 26.8 mL each. At the inner wall of each bottle an O₂-sensitive sensor spot (PreSens GmbH) was attached. The bottles were filled with 20.0 mL of oxic solution of NaCl (5 mM) in deionized water and 1.0 g of pyrite. The remaining headspace (6.8 mL) was initially filled with atmospheric air. At the beginning of the experiment the bottles were hermetically sealed with butyl/PTFE 20 mm caps.

Each batch experiment consists of an array of 15 bottles and during the experiment all the bottles were stirred continuously with a magnetic stirrer at two different velocities: 300 rpm (Batch 1) and 100 rpm (Batch 2). Oxygen concentrations were measured every 24 hours with the non-invasive optode technique described above. A blank replicate, consisting of a bottle with the same volume of solution but with no pyrite was used to monitor the oxygen concentration in absence of reaction throughout the entire experiments. For each batch experiment, two bottles were sampled and sacrificed at different times (every 24 h for Batch 1 and at larger time intervals for Batch 2) and measurements of O₂, Fe, and S were performed; pH was measured at the beginning and at the end of each experiment. Figure 1a schematically illustrates the setup of the batch experiments.

2.1.2 Column experiments

Glass columns (length: 14.5 cm; inner diameter: 1.7 cm) were used to study pyrite oxidation in 1-D flow-through setups. Prior to the investigation of reactive transport, 1-D flow-through experiments were conducted to characterize O₂ transport under conservative conditions (i.e., with no pyrite present in the system). A 10 cm × 0.5 cm O₂ sensitive strip (SF-PSt3-NAU, PreSens GmbH) was glued into the inner wall of each column and the columns were then packed with fine silica sand (125-250 μm) in the column previously filled with anoxic water, always keeping the water table above the porous media to minimize air entrapment (Haberer et al., 2012).

The reactive transport experiments were performed in three columns, in which different pyrite inclusions were embedded in the porous media. The grain size of the pyrite was the same of the surrounding sandy matrix (125-250 μm), thus the column setups consisted of physically homogeneous but chemically heterogeneous porous media. In Column 1, a 4-cm inclusion of pure pyrite was located in the middle of the column. In Column 2, two 2-cm inclusions of pure pyrite were placed in the middle of the column at a distance of 2 cm from each other. Column 3 was

packed with a single 6-cm inclusion of pyrite mixed with sand (1:1 in mass) placed in the middle of the column. The initial bulk concentration of pyrite in Column 1 and Column 2 was 25.70 mol/L_{bulk} while in Column 3 was 12.85 mol/L_{bulk} (Table 1). The columns were sealed with two screw caps with silicon-polytetrafluoroethylene septa. Steady-state flow-through conditions were established in the three columns with a high-precision multi-channel peristaltic pump (Ismatec IPC-24, Ismatec, Glattburg, Switzerland). The initial anoxic conditions were reached inside the columns by flushing the porous media with an anoxic solution (O₂ concentration < 0.1 mg/L), prepared using an anoxic gas generation sachet (Oxoid AnaeroGen 2.5L, Thermo Scientific). The experiment consisted in flushing oxic water through the initially anoxic reactive columns and was started by connecting the pump tubings with the oxic solution, a 5 mM NaCl solution equilibrated with atmospheric oxygen. The average seepage velocity was maintained at 1.5 m/day in all three columns. The propagation of the oxygen fronts in the different porous media was monitored by measuring high-resolution spatial profiles along the columns (2.5 mm spacing) as well as breakthrough near the outlet of each column ($x = 11.75$ cm), with three fiber optic cables recording oxygen concentrations every five minutes throughout the duration of the experiments. Conventional sampling was also performed at the columns' outlets and effluents were collected for the measurement of total Fe, S and pH.

2.1.3 2-D flow-through experiments

The setup consists of a quasi two-dimensional flow-through chamber with inner dimensions of 80 cm × 40 cm × 0.5 cm (length×height×width). The walls of the chamber are made of transparent acrylic glass and were equipped with four O₂ sensitive strips (SF-PSt3-NAU, PreSens GmbH) with dimensions of 20 cm by 1 cm, glued in the inner-side of the chamber wall. The sensors strips were located at 16 cm, 32 cm, 48 cm and 64 cm from the inlet perpendicular to the flow direction. The chamber was filled with fine sand (125-250 μm), following the wet-packing procedure described

for the column setups. A rectangular reactive pyrite inclusion, with the same grain size of the surrounding sandy matrix, was embedded in the chamber. The pyrite inclusion was created by mixing pure pyrite and sand (1:1 in mass) and had a length of 16 cm and a height of 4 cm. The inclusion was placed at 5 cm from the inlet and at 10 cm from the bottom of the flow-through chamber. Two high-precision multichannel peristaltic pumps (Ismatec IPC-N24) connected to 19 ports (1.2 cm spacing) at the inlet and at the outlet of the chamber (Fig. 1c) were used to create steady flow conditions throughout the duration of the experiment.

Similarly to the column experiments, the system was initially maintained under anoxic conditions (background O_2 concentration < 0.1 mg/L) obtained by flushing the system with an anoxic solution. At the beginning of the experiment, an inflowing oxic solution (5 mM NaCl aqueous solution equilibrated with the atmospheric oxygen) was continuously injected into the chamber at a seepage velocity of 1.5 m/day.

High-resolution vertical O_2 profiles were measured along the four sensor strips, located at different cross-sections. Measurements were repeated at various time intervals to monitor the dynamics of oxygen transport and consumption in the 2-D setup. When the oxygen concentrations approached steady state, effluent samples were also collected from the dense network of outlet ports and measurements of pH, iron and sulfur were performed.

The physical properties, the initial, and the inlet concentrations of the solutions in the different laboratory experiments are listed in Table 1.

Table 1. Overview of the laboratory experiments including both initial and inlet concentrations of aqueous species and the physical properties for the laboratory setups.

Parameter	Batch	1-D columns			2-D chamber
	1-2	1	2	3	
Physical properties					
Experiment duration [hours]	170 - 333	100	100	100	98
Seepage velocity [m/day]	-	1.5	1.5	1.5	1.5
Grain size [mm]	0.125-0.250	0.125-0.250	0.125-0.250	0.125-0.250	0.125-0.250
Porosity [-]	-	0.38	0.38	0.38	0.38

Initial aqueous concentrations

pH	6.0	5.8	5.8	5.8	6.77
O ₂ [mol/L]	2.6×10 ⁻⁴	3.0×10 ⁻⁵	3.0×10 ⁻⁵	3.0×10 ⁻⁵	3.0×10 ⁻⁵
Na ⁺ [mol/L]	5.0×10 ⁻³	5.0×10 ⁻³	5.0×10 ⁻³	5.0×10 ⁻³	5.0×10 ⁻³
Cl ⁻ [mol/L]	5.0×10 ⁻³	5.0×10 ⁻³	5.0×10 ⁻³	5.0×10 ⁻³	5.0×10 ⁻³

Solid phase

Concentration of pyrite [mol/L _{bulk}]	0.45*	25.70	25.70	12.85	12.85
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Inlet aqueous concentrations

pH	-	5.8	5.8	5.8	5.2
O ₂ [mol/L]	-	2.5×10 ⁻⁴	2.5×10 ⁻⁴	2.5×10 ⁻⁴	2.5×10 ⁻⁴
Na ⁺ [mol/L]	-	5.0×10 ⁻³	5.0×10 ⁻³	5.0×10 ⁻³	5.0×10 ⁻³
Cl ⁻ [mol/L]	-	5.0×10 ⁻³	5.0×10 ⁻³	5.0×10 ⁻³	5.0×10 ⁻³

*concentration in mol/L, corresponding to 1 g in 20 mL of solution for each bottle of the batch experiments.

2.2 Modeling approach**2.2.1 Chemical reaction framework**

To quantitatively evaluate the results obtained from the experiments, chemical reactions including pyrite oxidation, the subsequent iron (hydr)oxides precipitation and the aqueous speciation were considered in the model. The oxidation of pyrite in the presence of oxygen releases iron and sulfate as main reaction products, and implies the consumption of O₂ and the generation of acid (e.g., Appelo and Postma, 2005; Prommer and Stuyfzand, 2005; Rimstidt and Vaughan, 2003; Williamson and Rimstidt, 1994) according to the following chemical reaction:

Upon the persistence of oxidizing condition, the released Fe(II) is further oxidized to Fe(III) and can subsequently precipitate as described by the following reactions:

227 Note that FeOOH(s) represents the precipitation of a solid Fe(III) phases. Both pyrite oxidation and
 228 FeOOH precipitation were simulated as kinetically-controlled reactions. For the oxidative
 229 dissolution of pyrite, we used the rate law proposed by Williamson and Rimstidt (1994), which is
 230 widely accepted in the literature and has been adopted by different authors investigating pyrite
 231 oxidation both in experimental and modeling studies (Fakhreddine et al., 2016; Jørgensen et al.,
 232 2008; Prommer and Stuyfzand, 2005; Vaclavkova et al., 2015) :

$$R_{pyr} = \left(k [O_2]^{0.50} [H^+]^{-0.11} \right) \left(\frac{A_{pyr}}{V_w} \right) \left(\frac{m}{m_0} \right)^{0.67} (1 - \Omega_{pyr}) \quad [4]$$

233 where R_{pyr} [mol/L/s] is the overall rate of reaction, k [mol/m²/s] the rate constant, and $[O_2]$ and
 234 $[H^+]$ [mol/L] are the aqueous concentration of oxygen and protons. The last term represents the
 235 distance from equilibrium and $\Omega_{pyr} = IAP/K$ is the ratio of the ion activity product and the
 236 thermodynamic equilibrium constant. The term A_{pyr}/V_w [m²/L] specifies the ratio of reactive surface
 237 area to the volume of solution, and the term $(m/m_0)^{0.67}$ accounts for the change in surface area
 238 resulting from the dissolution of pyrite being m [mol] the unreacted pyrite content and m_0 [mol] the
 239 initial mineral content. We consider the surface area of the mineral and the volume of solution
 240 surrounding it as:

$$\frac{A_{pyr}}{V_w} = \frac{A_e}{V_w} m_0 \quad [5]$$

241 where A_e [m²/g] is the reactive surface area, considered as the specific surface area that effectively
 242 reacts (Li et al., 2014), which is typically defined as the total surface area per unit mass of the
 243 mineral. In this study, we used the same value of the rate coefficient ($k = 10^{-8.19}$ mol/m²/s) as
 244 reported by Williamson and Rimstidt (1994), whereas the ratio A_e/V_w was considered as a fitting
 245 parameter.

The precipitation of FeOOH was modeled with a simple rate law with an effective rate constant and a term accounting for the distance from equilibrium:

$$R_{\text{FeOOH}} = k_{\text{eff}} (1 - \Omega_{\text{FeOOH}}) \quad [6]$$

2.2.2 Reactive transport

A reactive transport description was implemented to simulate the propagation of oxygen fronts in the chemically heterogeneous flow-through porous media. The governing equations include the main physical and chemical processes occurring in the experimental setups. The considered transport processes include advection and dispersion, as well as the kinetic partitioning of oxygen between the aqueous and an entrapped gas phase. The latter process was found to be important to interpret the experimental results; in fact, although good care was taken to minimize air entrapment it was not possible to completely avoid it and a minor fraction of the pore space was occupied by entrapped gas. The gas phase influenced the oxygen transient transport behavior and led to the delay of the oxygen fronts compared to a conservative, non-partitioning solute. Such phenomena was observed in all the reactive flow-through experiments (both 1-D and 2-D) and additional column experiments without pyrite inclusions were run to further characterize oxygen partitioning. This process has been studied also by other authors who found that even a very small amount of entrapped gas causes a remarkable impact on oxygen transport and breakthrough (e.g., Donaldson et al., 1997). For the cases of reactive transport, the chemical reactions were implemented according to the framework described in the previous section and applied to evaluate the results of the batch setups. The governing mass conservation equations for reactive transport in multidimensional flow-through systems can be expressed as:

$$\theta_w \frac{\partial c_{w,i}}{\partial t} + \theta_g \frac{\partial c_{g,i}}{\partial t} + \mathbf{q} \cdot (\nabla c_{w,i}) - \nabla \cdot (\theta_w \mathbf{D}_i \nabla c_{w,i}) = - \sum_{j=1}^{N_j} v_{ij} R_j \quad [7]$$

$$\theta_g \frac{\partial c_{g,i}}{\partial t} = \lambda (H c_{w,i} - c_{g,i}) \quad [8]$$

where Eq. [7] refers to reactive solute transport and partitioning of a volatile species within the mobile aqueous phase and Eq. [8] describes the mass transfer of the species between the immobile gas phase and mobile water phase, $c_{w,i}$ and $c_{g,i}$ [mol/L] are the aqueous and gas phase concentrations of species i , respectively; whereas θ_w and θ_g [-] represent the volumetric water and gas content, respectively. R_j [mol/L/s] and v_{ij} [-] represent the reaction rate and the corresponding stoichiometric coefficient of species i for the j^{th} reaction; λ [s^{-1}] is the kinetic water-gas mass transfer coefficient; H [-] is the dimensionless Henry's law coefficient, and t [s] is the time. For transport in the aqueous phase (Eq. 7), $\mathbf{q}$ [m/s] denotes the specific discharge vector and $\mathbf{D}$ [m^2/s] is the hydrodynamic dispersion tensor, which, in a 2-D coordinate system aligned in the principal flow directions, can be expressed as:

$$\mathbf{D} = \begin{bmatrix} D_L & 0 \\ 0 & D_T \end{bmatrix} \quad [9]$$

To parameterize the entries of the dispersion tensor, we used the empirical expressions developed in detailed experimental and pore-scale modeling studies in granular porous media: a linear parameterization for the longitudinal component (Guedes de Carvalho and Delgado, 2005), and a non-linear, compound-specific parameterization for transverse dispersion (Chiogna et al., 2010; Hochstetler et al., 2013; Rolle et al., 2013a):

$$D_L = D_p + 0.5dv \quad [10]$$

$$D_T = D_p + D_{aq} \left(\frac{Pe^2}{Pe + 2 + 4\delta^2} \right)^\beta \quad [11]$$

where D_{aq} [m^2/s] is the aqueous diffusion coefficient, D_p [m^2/s] is the pore diffusion coefficient, Pe [-] ($= v d/D_{aq}$ with v and d being the seepage velocity and the grain size diameter, respectively) is the grain Péclet number, δ [-] denotes the ratio between the length of a pore channel to its hydraulic radius, and β [-] is an empirical exponent that accounts for the effects of incomplete mixing in the pore channels. The values of $\delta = 5.37$ and $\beta = 0.5$, determined in laboratory experiments performed with different grain sizes and seepage velocities in both 2-D and fully 3-D porous media (Ye et al., 2015a), were adopted in this study.

In the transport simulations of the conservative and the reactive flow-through experiments, the gas partitioning parameters (θ_g and λ) were considered as fitting parameters and determined based on the measured oxygen concentrations.

2.2.3 Numerical simulations

The batch experiments were simulated using the widely used geochemical code PHREEQC (Parkhurst and Appelo, 2013), considering a closed system and implementing the kinetically controlled pyrite oxidation reaction and the chemical framework presented above. The considered stoichiometry is described in Eq. [1-2] and the kinetics of the oxidative dissolution of pyrite by oxygen was implemented according to Eq. [4]. The outcomes from the model calculations were compared with the experimentally measured consumption of O_2 and the evolution of the water chemistry parameters in the solution. In particular, these reactants and products concentrations were determined in order to obtain the best-fit specific surface area to solution volume ratio (A_e/V_w) in Eq. [4] for our reactive system. The optimization procedure was performed by following the approach described in Haberer et al., (2015), which involves using the MATLAB[®] function *lsqnonlin*, and by coupling the PHREEQC reaction calculations with MATLAB[®] utilizing the

IPhreeqcCOM module (Charlton and Parkhurst, 2011). This especially designed PHREEQC module allows all the native features of PHREEQC to be effectively used in other software programs or programming languages (e.g., Charlton and Parkhurst, 2011; Wissmeier and Barry, 2011).

For reactive transport in flow-through systems a convenient approach consists in coupling transport codes with PHREEQC as geochemical engine to simulate complex subsurface problems (e.g., Appelo and Rolle, 2010; Nardi et al., 2014; Prommer et al., 2003; Rolle et al., 2018). In this study we adopted, both for the 1-D and 2-D setups, a coupling procedure based on a sequential non-iterative operator splitting approach utilizing the IPhreeqcCOM module (Muniruzzaman and Rolle, 2016). In such a way, the solution of the physical transport processes is carried out for a given time step and, subsequently, the calculated species/components concentrations are passed to IPhreeqc to perform the reaction calculations. We used a finite volume method to solve the 1-D and the 2-D transport problems. In the simulations of 1-D column setup, we used the Crank-Nicholson scheme for the spatial discretization and temporal integration of the transport equations. For the 2-D flow-through chamber we used the method presented by (Cirpka et al., 1999), with an upwind differentiation scheme for the spatial discretization, the explicit Euler method for the advection (with Courant number, $Cr = 1$) and the gas partitioning problems, and the implicit Euler method for the computation of the 2-D dispersion problem. In both 1-D and 2-D simulations, the system of discretized algebraic transport equations was solved with the direct matrix solver UMFPACK (Davis and Duff, 1997) and the whole reactive transport simulator was implemented in MATLAB®. Within the reaction step, all the aqueous and mineral reactions were simulated by considering a batch reactor in each cell of the simulation domain. Further details regarding the IPhreeqc coupling and the relevant solution steps can be found in Muniruzzaman and Rolle (2016).

3 Results and discussion

3.1 Batch experiments

Two series of batch experiments, stirred at different velocities, were performed to study the kinetics of pyrite oxidation. The main water chemistry parameters that were measured to characterize the pyrite oxidation kinetics were the consumption of oxygen due to the reaction with the pyrite mineral and the total iron and sulfur concentration produced by the redox reaction.

The trends of observed O_2 , Fe and S concentrations for the two batch experiments are plotted in Fig. 2. The oxygen concentrations were determined with the non-invasive optode technique, whereas the concentrations of iron and sulfur were measured with ICP-OES and the data points in the figure represent the average of two replicates. The batch experiment stirred at 300 rpm (Batch 1) reached anoxic conditions after 100 h of experiment (Fig. 2a), while the one stirred more gently (at 100 rpm, Batch 2) did not reach anoxic conditions within the total duration of the experiment (333 h, Fig 2b). In Batch 1, the concentration of Fe and S in solution increased due to the oxidative dissolution of pyrite and reached concentrations of $\sim 1 \times 10^{-3}$ mol/L and $\sim 1.4 \times 10^{-3}$ mol/L for Fe and S respectively, once the oxygen was entirely consumed. Fe and S in Batch 2 also increased accordingly with the partial depletion of O_2 (from 2.6×10^{-4} mol/L to 1.5×10^{-4} mol/L), reaching values of 4.5×10^{-4} mol/L for Fe and 6.7×10^{-4} mol/L for S at the end of the experiment.

The batch experiments were modeled considering a volume of 20 mL of aerobic solution, 1 g of pyrite and a gas phase volume of 6.8 mL, representing the headspace in the bottles and having an oxygen partial pressure of 0.21 atm. The volume of the aqueous and gas phases was not changed throughout the simulations. The fitting parameter for the pyrite oxidation kinetic, A_e/V_w , was adjusted in order to simultaneously fit the experimentally measured reactant (O_2) and products (Fe and S). As best-fit results, we obtained values of A_e/V_w equal to $47 \text{ m}^2/\text{mol/L}_w$ and $3.3 \text{ m}^2/\text{mol/L}_w$ for Batch 1 and Batch 2, respectively. The reduction in stirring velocity caused a significant

350 decrease in the reaction rate (Eq. [2]), by reducing the effectiveness of the contact between the
 351 solution and the reactive surface of the mineral. The model reproduced the experimental data
 352 obtained in both Batch 1 and Batch 2. The oxygen consumption and the production of iron are
 353 captured very well, whereas the simulated sulfur concentrations appeared to be slightly
 354 overestimated compared to the measured values.

355

356 *Fig. 2. Observed (symbols) and simulated (lines) concentrations of reactants and products in the*
 357 *two series of batch experiments performed with different agitation.*

358 3.2 Column experiments

359 1-D column experiments with no pyrite inclusions were performed to track the propagation of non-
 360 reactive oxygen fronts in porous media under flow-through conditions. The experiments lasted 15
 361 hours and the O_2 concentration were measured inside the porous medium with two fiber optic
 362 cables located at 7.5 cm and close to the outlet of the column (12.5 cm). Measurements of oxygen
 363 breakthrough were recorded at high temporal resolution (5 min).

364 The experimental results show a characteristic mass-transfer limited behavior of oxygen in the
365 column, resulting in the retardation and tailing of the breakthrough curves. A conservative transport
366 model, including kinetic partitioning of oxygen between the pore water and a residual trapped gas
367 phase, allowed us to capture the observed breakthrough behavior (Fig. 3). The parameters θ_g and λ
368 in Eq. [8] were obtained by fitting the experimental data. We obtained values of 0.0163 for the
369 volumetric gas content and $1.27 \times 10^{-5} \text{ s}^{-1}$ for the mass transfer coefficient. Although the volume of
370 the entrapped gas phase is minimal, it considerably impacts the propagation of the oxygen front, as
371 also reported in a previous study (Donaldson et al., 1997). The extent of retardation and tailing of
372 the oxygen breakthrough curves becomes evident when the trends are compared to the breakthrough
373 of a non-partitioning dissolved tracer. The simulations of the tracer behavior show curves that are
374 considerably steeper and less spread compared to the observed behavior of oxygen. For instance,
375 the oxygen breakthrough at $x=12.5 \text{ cm}$ shows that the concentrations reach steady state after 10 h,
376 whereas the prediction for the non-partitioning tracer at the same location indicates that steady-state
377 conditions are already reached after approximately 2 h.

Fig. 3. Observed (symbols) and simulated (lines) breakthrough curves of O_2 in the conservative column experiment at two different locations: $x=7.5$ cm and $x=12.5$ cm. The dotted lines represent the simulated O_2 breakthrough with no gas partitioning.

Reactive column experiments were performed to investigate the propagation of O_2 fronts in porous media in the presence of pyrite. Fig. 4 shows the high-resolution measurements of oxygen concentrations obtained with the optode sensor technique. The spatial profiles were taken at different times for all three columns, in which different inclusions of reactive pyrite were embedded.

Fig. 4. Spatial profiles of oxygen concentrations measured during the reactive experiments in the three chemically heterogeneous column setups (the grey areas show the reactive pyrite inclusions; the different colors of the inclusions represent their different concentration, dark gray: pure pyrite inclusion, light gray: pyrite mixed with sand).

The measurements show the evolution of the reactive systems with initial anoxic conditions that are progressively impacted by the injection of oxic water at the columns' inlets and the reaction with the pyrite mineral. The effect of the geochemical heterogeneity clearly affects the transport of oxygen: as soon as the O_2 fronts reach the reactive mineral inclusions, oxygen is depleted due to the oxidative dissolution of pyrite (Eq. 1). At late time, the systems approach steady-state conditions

with respect to the oxygen spatial profiles that become stable. This behavior results from the dynamic balance between the oxygen supplied from the inlet and its consumption due to the reaction with pyrite within the porous media. Column 1 shows a remarkable decrease of oxygen throughout the length of the reactive inclusion and steady-state O_2 concentration values at the outlet are approximately 15% compared to the inlet. The measurements of oxygen in Column 2 show patterns that are initially impacted only by the first pyrite inclusion, which effectively consumes the injected oxygen. Successively, the oxygen front reaches the second inclusion (at $t=8$ h) and a pattern with stepwise consumption of oxygen in the two reactive zones develops. Since the concentration of O_2 reaching the first inclusion is higher than the O_2 reaching the second inclusion, the reaction rate is faster in the first zone of geochemical heterogeneity compared to the reactive zone downgradient (the average reaction rates for the first and the second inclusions are 4.30×10^{-8} mol/L/s and 1.99×10^{-8} mol/L/s, respectively). This results in an oxygen concentration slope inside the first inclusion that is steeper than in the second inclusion and in a higher O_2 consumption within the first reactive zone. Similarly to Column 1, also in Column 2 the steady-state concentration of oxygen at the outlet of the columns reaches approximately 15% of the inlet. The trend observed in Column 3 is similar to the one observed in Column 1 with the decrease of oxygen in the reactive inclusion. However, the observed slopes are now less steep since the reactive mineral concentration in this setup was smaller compared to Column 1 and Column 2 (12.85 mol/L_{bulk} in Column 3 and 25.7 mol/L_{bulk} in Column 1 and Column 2). Consequently, slower consumption rates and a higher steady-state concentration of oxygen are observed at the outlet of Column 3 (approx. 27% of the inlet value). The average reaction rates calculated for the 1D-flow through experiments, and the consequent oxygen consumption, depends on the initial concentration of the pyrite inclusions: in Column 1 and 2 the average reaction rates are very close to each other, 3.13×10^{-8} mol/L/s and 3.12×10^{-8} mol/L/s (for Column 1 and the average of the two inclusions in Column 2, respectively) while

in Column 3 the average reaction rate is 1.88×10^{-8} mol/L/s. The reactive transport experiments were simulated with the modeling approach described in Section 2.2. Table 1 summarizes the parameters of the reactive transport simulations for both the 1-D column experiments and for the 2-D flow-through chamber. The kinetics of pyrite oxidative dissolution was simulated as in the batch setups by using the rate expression of Eq. 4. The best-fit value of the kinetic parameter A_e/V_w was $2.8 \text{ m}^2/\text{mol/L}_w$, which was closer to the gently stirred batch system (Batch 2). The obtained result is also consistent with the geometrically calculated value (for A_e) of $0.717 \text{ m}^2/\text{mol}$ (i.e., assuming spherical grains with $d = 200 \text{ }\mu\text{m}$ and $\rho_{s,\text{pyrite}} = 5.02 \text{ kg/L}$) and the value of $5.64 \text{ m}^2/\text{mol}$ reported by Williamson and Rimstidt (1994). The same value was also used to simulate the 2-D flow-through experiment. We accounted for the precipitation of an iron (hydr)oxide phase (FeOOH) considering a stability of the mineral intermediate between ferrihydrite and goethite ($\log K = 2.50$). FeOOH precipitation was described according to the stoichiometric reaction described in Eq. [3] and the effective rate constant was calculated according to Eq. [6].

Table 2. Geometry of the flow-through domains and parameters used in the reactive transport simulations.

Parameter	1-D columns	2-D setup
Domain size ($L \times W$) [cm]	14.5	80×24
Discretization ($\Delta x \times \Delta z$) [cm]	0.1	1×0.1
Time step, Δt [s]	58	576
Oxygen diffusion coefficient [m^2/s]	2×10^{-9}	2×10^{-9}
Porosity [-]	0.38	0.38
Volumetric water content, θ_w [-]	0.347	0.358
Volumetric gas content, θ_g [-]	0.033	0.022
Kinetic water-gas mass transfer coefficient, λ [s^{-1}]	1.95×10^{-6}	4.26×10^{-6}
Henry's coefficient for oxygen, H [-]	31.25	31.25
Reactive specific surface area, A_e/V_w [$\text{m}^2/\text{mol/L}_w$]	2.8	2.8
FeOOH effective rate constant, k_{eff} [mol/L/s]	5×10^{-15}	1.5×10^{-13}

The comparison between the measured oxygen concentrations and the outcomes of the reactive transport simulations is shown in Fig. 5 for selected spatial profiles in the different column setups.

439 The agreement between observed and simulated oxygen concentrations is very good, particularly
 440 after some time from the beginning of the flushing in the reactive columns. The model can
 441 reproduce both the shape of the profile and the magnitude of the oxygen concentrations measured
 442 within the chemically heterogeneous porous media. A small discrepancy between the model and the
 443 measured data is seen mainly in the profiles simulated at early time (after 4 hours of experiment),
 444 which show a simulated reactive O_2 front propagating faster than the experimental observation. This
 445 is probably due to the assumption of homogeneous distribution of the entrapped gas phase made in
 446 the model, whereas in the experiments the gas bubbles are more likely heterogeneously distributed
 447 within the porous media and their impact is more significant at early time.

448

449

450 *Fig. 5. Comparison between observed (symbols) and simulated (lines) O_2 spatial profiles in Column*
 451 *1 (a-d), Column 2 (e-h) and Column 3 (i-l) at different time steps. The gray areas show the location*
 452 *of the reactive pyrite inclusions; the different colors of the inclusions represent their different*
 453 *concentration, dark gray: pure pyrite inclusion, light gray: pyrite mixed with sand.*

454 The breakthrough of iron and sulfur were measured at the outlet of the column setups. The
455 concentrations of Fe and S remained close to the background content during the first 5 hours of
456 experiment and then increased until a steady-state value, which was reached after almost 24 hours.
457 The steady-state concentrations measured in the effluent of Columns 1 and 2 were close to 0.5×10^{-4}
458 mol/L for Fe and 1.3×10^{-4} mol/L for S, while in Column 3 they were slightly lower: 0.4×10^{-4} mol/L
459 for Fe and 1.1×10^{-4} mol/L for S (Fig. 6). pH was measured at the outlet of the columns at the end of
460 the experiments and ranged between 4.5 and 4.9, showing a decrease from the initial value of 5.8
461 due to the release of protons from the oxidation of pyrite, Eq. [1]. Similarly, in Column 1 and 2, the
462 reactive O_2 steady-state concentration was fluctuating between 0.2×10^{-4} mol/L and 0.3×10^{-4} mol/L,
463 lower than the concentration reached at steady state in Column 3, around 0.7×10^{-4} mol/L. The
464 stoichiometric ratio of the reaction products highlights the precipitation of a small amount of Fe as a
465 secondary phase mineral in the porous media. This is supported by the observation of a S/Fe ratio at
466 the outlet (2.2-2.5) that is higher than the stoichiometric ratio of the mineral used in the reactive
467 inclusions (1.72). The reactive transport simulations with the parameter values reported in the
468 second column of Table 2 allowed us to reproduce well also the trend of iron and sulfur observed in
469 the different experiments. The breakthrough curves of these dissolved species, produced during
470 pyrite oxidative dissolution, also show a tailing behavior that depends on the kinetic partitioning
471 and retardation of the oxygen front.

472 In the reactive experiments oxygen breakthrough was also continuously measured close to the outlet
473 ($x = 11.75$ cm) of the columns. The comparison between the O_2 concentration in the conservative
474 and reactive column experiments (circles and squares, respectively) is reported in Fig 6d-f. The
475 difference in oxygen breakthrough allows visualizing the effect of the pyrite reactivity in the
476 oxygen consumption, resulting in O_2 steady-state concentrations considerably lower in the reactive
477 rather than in the conservative experiments. The simulated breakthrough of oxygen is also reported

in Fig. 6d-f for both the conservative and the reactive cases. It is possible to calculate the mass of oxygen consumed by the reaction with pyrite in the different setups with the following mass balance:

$$M_{O_2} = \int_0^T (\dot{m}_{O_2,cons} - \dot{m}_{O_2,react}) dt \quad [12]$$

where M_{O_2} [g] is the mass of oxygen consumed and $\dot{m}_{O_2,cons}$ and $\dot{m}_{O_2,react}$ [g/s] are the mass fluxes of oxygen in the conservative and reactive experiments, respectively. The mass balance was calculated considering the outcomes of the simulations and a duration of all experiments of 100 h. The results show a similar mass of oxygen consumed in Column 1 and Columns 2 (4.01 mg and 4.03 mg), whereas the results for Column 3 show a smaller oxygen depletion (3.49 mg).

Fig. 6. Observed (symbols) and simulated (lines) breakthrough curves of Fe, S (a-c) and O₂ (d-f) for the column experiments: Column 1 (a,d), Column 2 (b,e), and Column 3 (c,f). Fe and S breakthrough curves were measured at the outlet of the column, whereas the oxygen breakthrough was measured at $x = 11.75$ cm.

3.3 2-D Flow-through experiments

In the 2-D flow-through chamber a rectangular inclusion of pyrite ($16\text{ cm} \times 4\text{ cm}$ with a concentration of $12.85\text{ mol/L}_{\text{bulk}}$) was embedded within the sandy porous matrix. The system was initially maintained under anoxic conditions and, at the beginning of the experiment, an inflowing oxic solution was injected into the chamber at the seepage velocity of 1.5 m/day . Vertical O_2 concentration profiles were measured at 16 cm , 32 cm , 48 cm and 64 cm from the inlet at different time intervals during the experiment. A visual illustration of the 2-D experiments is provided in Fig. 1 and the outcomes of the reactive transport simulations for that setup are reported in Fig. 7. The maps of Fig. 7 represent the results of the model at steady-state conditions with respect to oxygen and show: (a) the consumption of dissolved oxygen upon its contact with the pyrite and the formation of an oxygen-depleted plume in the center of the flow-through chamber, (b) the small consumption of the reactive pyrite mineral that was present in large stoichiometric excess, and (c) the precipitation of the FeOOH phase upon the contact of dissolved iron from the oxidation of pyrite with oxygen in the inclusion and at the lateral fringes, where the reactants can mix by transverse hydrodynamic dispersion. The 2-D simulations were performed with the approach based on coupling the two-dimensional transport code and IPhreeqc to solve the geochemical reaction network (section 2.2). The values of the kinetic and transport parameters used in the simulation are listed in the third column of Table 2.

509

510 *Fig. 7. Simulated spatial distributions of (a) O_2 concentration (b), pyrite content (b), and (c)*
 511 *FeOOH precipitate in the 2-D flow-through chamber after 98 hours.*

512 The spatially distributed measurements of oxygen concentrations at the four sensor strips allowed
 513 us to follow the dynamics of oxygen transport and consumption in the 2-D flow-through system.
 514 Fig. 8 shows measurements at different times from the beginning of the experiments and the
 515 comparison with the reactive transport simulation of the 2-D setup. The oxygen front advances in

the 2-D flow-through chamber and the consumption upon reaction with the embedded reactive pyrite is first recorded at the location of the first sensor strip ($x=16$ cm). The signature of oxygen depletion due to the reaction with pyrite becomes successively visible at the downgradient sensor measurement cross sections as the oxygen front moves through the domain. At late times the oxygen vertical profiles stabilize and approach steady-state conditions with a clear indication of an oxygen depleted plume in the central zone of the flow-through chamber. The reactive transport model captured the spatial and temporal dynamics of oxygen transport and consumption in the 2-D flow-through setup. The model reproduces well both the shapes and the spatially-distributed oxygen values measured during the flow-through experiments. The good agreement between measured and simulated oxygen concentrations show the capability of the model to reproduce the experimental data including the steep lateral gradients observed in the flow-through experiment. Similarly to the column experiments, the discrepancy between measurements and simulations is more pronounced at early times and the agreement progressively improves in the course of the experiment as the oxygen-depleted plume approaches steady state.

530

531 *Fig. 8. Experimental (symbols) and simulated (lines) O_2 concentration profiles at the four sensors*
 532 *strips locations (x=16, 32, 48, and 64 cm) in the 2-D flow-through chamber at different times.*

533 Iron, sulfur and pH were measured at the outlet of the flow-through chamber after 98 hours of
 534 experiment. In Fig. 9 the values of these dissolved species measured at each port (1.2 cm spacing) at
 535 the outlet of the chamber are plotted together with the results of the reactive transport simulations.
 536 The Fe concentration at the outlet of the chamber is close to zero since all the iron dissolved from
 537 the pyrite oxidation was precipitated as iron (hydr)oxides upon contact with dissolved oxygen
 538 through transverse mixing (Fig. 9a). Sulfur, instead, shows a distinct plume with the peak
 539 concentration aligned with the reactive mineral inclusion and with a width of approximately 7 cm.
 540 This behavior results from the oxidative dissolution of the pyrite, the downgradient advective
 541 transport, and the lateral dispersion and mixing of the dissolved products with the background
 542 solution. The reactive transport model, incorporating the measured stoichiometry of the mineral and

the kinetic and transport parameters described above and summarized in Table 2, successfully reproduces the experimental steady-state aqueous concentrations of sulfur and iron measured at the outlet of the flow-through chamber. The model appears to predict lower pH values compared to the measured ones. This discrepancy can be ascribed to the fact that the current version of the model does not include the complex surface/solution interaction of protons in silica porous media (e.g., McNeece and Hesse, 2017, 2016). The sorption of protons could explain the experimental observations in which this process appears to buffer the acidification due to pyrite oxidation and the difference compared to the reactive transport simulations in which these surface/solution interactions were not included.

Fig. 9. Measured (symbols) and simulated (lines) vertical profiles of Fe (a), S (b), pH (c) at the outlet of the 2-D flow-through chamber after $t = 98$ hours.

Breakthrough curves of oxygen at the outlet of the flow-through chamber were measured to characterize the transient transport of oxygen in the 2-D setup. Measurements were taken at two distinct locations along the most downgradient sensor strip ($x=64$ cm): outside of the O_2 plume, above the pyrite inclusion, and inside the oxygen-depleted plume where oxygen was significantly consumed (Fig. 10). As in the column setups, also in the 2-D flow-through experiment the oxygen breakthrough curves were affected by a retardation effect due to the small gas bubbles entrapped in the porous medium. The comparison between the two curves highlights the effect of pyrite

562 reactivity on the consumption of oxygen. The reactive transport simulations shown in Figs. 7-10
 563 were performed with $\theta_g = 0.022$ and $\lambda = 4.26 \times 10^{-6} \text{ s}^{-1}$, values that are similar to the ones obtained
 564 for the 1-D column setups.

565

566 *Fig. 10. Oxygen breakthrough curves measured on the last oxygen sensor strip ($x = 64 \text{ cm}$) in the 2-*
 567 *D flow-through chamber. The squares and the solid line represent measurements and simulation at*
 568 *the height of the pyrite inclusion, whereas the circles and the dashed line are the observation and*
 569 *simulation outside the inclusion.*

570 4 Conclusions

571 In this study, we investigated the impact of geochemical heterogeneities on the propagation of
 572 reactive fronts in porous media. We focused on pyrite oxidation that was studied in
 573 multidimensional systems. Experiments were performed in different laboratory setups including
 574 batch, 1-D columns, and a 2-D flow-through chamber.

575 The results of the batch experiments allowed us to characterize the kinetics of pyrite oxidative
 576 dissolution and to formulate and test a reaction module that was, successively, used to interpret the
 577 flow-through experiments. An approach based on spatially distributed sensor measurements was
 578 proposed to monitor oxygen transport and consumption upon reaction with pyrite in the flow-
 579 through setups. The outcomes of the flow-through experiments demonstrate the capability of the

proposed approach to capture the dynamics of oxygen reactive transport in porous media at high spatial and temporal resolution. The column experiments showed that both the distribution and concentration of the reactive mineral play a key role in the oxygen consumption, as indicated by the high-resolution spatial profiles measured within the porous media. Distributed spatial monitoring of oxygen concentrations, coupled with sampling and analysis of water chemistry parameters at a dense network of outlet ports, allowed us to investigate pyrite oxidation and its impact on the propagation of dissolved oxygen fronts also in the 2-D flow-through setup. In this system the results clearly show that the presence of a reactive pyrite inclusion generates an oxygen-depleted plume whose signature propagates downgradient due to the inherently poor mixing capability of subsurface porous media and, in particular, the limited extent of transverse mixing (Rolle et al., 2013b). The comparison of the experimental results in the 1-D and 2-D systems is also illustrative of the impact of dimensionality on reactive transport in porous media. In fact, although the systems in Column 3 and in the 2-D flow-through chamber were physically and chemically equivalent, the outcomes of the experiments show different results not only in the observed consumption and breakthrough of oxygen but also in the formation, transport and breakthrough of other products of pyrite oxidation. For instance, whereas the breakthrough of iron was clearly observed at the outlet of all column setups, mixing with the surrounding oxic water caused the precipitation of an iron (hydr)oxide phase and no breakthrough of iron could be observed at the outlet of the 2-D flow-through chamber. The effects of dimensionality are likely to be even more evident by considering reactive transport in fully 3-D setups in which the topology of flow, different mixing mechanisms and different mixing enhancement compared to 2-D cases (e.g., Chiogna et al., 2015; Ye et al., 2015b, 2015c) could considerably affect the reaction extents and the impact of chemical heterogeneity on water quality.

The reactive transport modeling presented in this study was instrumental for the quantitative interpretation of the propagation of the oxygen fronts in the different setups. The developed 1-D and 2-D models coupling the main physical transport processes and the chemical reactions allowed us to reproduce the spatial profiles and breakthrough curves of oxygen and the measurements of the other water chemistry parameters in the different experimental setups. In particular, the description of kinetic partitioning of oxygen with a small volume of entrapped gas phase within the porous medium was important to accurately describe the oxygen transport and retardation observed under conservative and reactive conditions in both the 1-D and 2-D setups.

This study represents one of the few experimental contributions focusing on the investigation of the effects of chemical heterogeneity in porous media and on the coupling between transport processes in multidimensional flow-through systems and geochemical reactions. We envision further work investigating the impact of spatially distributed chemical heterogeneity on the release of toxic metals and metalloids in flow-through porous media, as well as studies exploring the combined effect of physical (Muniruzzaman et al., 2014; Rolle et al., 2009) and chemical heterogeneity (Fakhreddine et al., 2016; Li et al., 2014; Salehikhoo and Li, 2015) on solute transport in subsurface porous media.

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Fig. 1. Experimental laboratory setups for the investigation of pyrite oxidation: (a) batch experiments, (b) 1-D column experiments, (c) 2-D flow-through experiments. Different colors of the inclusions represent their different composition, dark gray: pure pyrite inclusion, light gray: pyrite mixed with sand.

Fig. 2. Observed (symbols) and simulated (lines) concentrations of reactants and products in the two series of batch experiments performed with different agitation.

Fig. 3. Observed (symbols) and simulated (lines) breakthrough curves of O_2 in the conservative column experiment at two different locations: $x=7.5$ cm and $x=12.5$ cm. The dotted lines represent the simulated O_2 breakthrough with no gas partitioning.

Fig. 4. Spatial profiles of oxygen concentration measured during the reactive experiments in the three chemically heterogeneous column setups (the grey areas show the reactive pyrite inclusions; the different colors of the inclusions represent their different composition, dark gray: pure pyrite inclusion, light gray: pyrite mixed with sand).

Fig. 5. Comparison between observed (symbols) and simulated (lines) O_2 spatial profiles in Column 1 (a-d), Column 2 (e-h) and Column 3 (i-l) at different time steps. The gray areas show the location of the reactive pyrite inclusions; the different colors of the inclusions represent their different composition, dark gray: pure pyrite inclusion, light gray: pyrite mixed with sand.

Fig. 6. Observed (symbols) and simulated (lines) breakthrough curves of Fe, S (a-c) and O_2 (d-f) for the column experiments: Column 1 (a,d), Column 2 (b,e), and Column 3 (c,f). Fe and S breakthrough curves were measured at the outlet of the column, whereas the oxygen breakthrough was measured at $x = 11.75$ cm.

Fig. 7. Simulated spatial distributions of (a) O_2 concentration (b), pyrite content (b), and (c) $FeOOH$ precipitate in the 2-D flow-through chamber after 98 hours.

Fig. 8. Experimental (symbols) and simulated (lines) O_2 concentration profiles at the four sensors strips locations ($x=16, 32, 48$, and 64 cm) in the 2-D flow-through chamber at different times.

Fig. 9. Measured (symbols) and simulated (lines) vertical profiles of Fe (a), S (b), pH (c) at the outlet of the 2-D flow-through chamber after $t = 98$ hours.

Fig. 10. Oxygen breakthrough curves measured on the last oxygen sensor strip ($x = 64$ cm) in the 2-D flow-through chamber. The squares and the solid line represent measurements and simulation at the height of the pyrite inclusion, whereas the circles and the dashed line are the observation and simulation outside the inclusion.

Fig. 1. Observed (symbols) and simulated (lines) concentrations of reactants and products in the two series of batch experiments performed with different agitation: (a) Batch 1 and (b) Batch 2.

Highlights

- Pyrite oxidation investigated in multidimensional porous media
- Flow-through experiments in chemically heterogeneous setups
- High-resolution spatial and temporal monitoring of reactive fronts
- Quantitative, model-based interpretation of the pyrite oxidation experiments