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Reactive transport modelling to investigate multi-scale waste rock weathering processes

N. Seigneur^{1,2}, B. Vriens^{3,2}, R.D. Beckie², K.U. Mayer²

Abstract

Prediction of drainage quantity and quality is critical to reduce the environmental risks associated with weathering mine waste rock. Reactive transport models can be effective tools to understand and disentangle the processes underlying waste-rock weathering and drainage, but their validity and applicability can be impaired by poor parametrization and the non-uniqueness conundrum. Here, a process-based multicomponent reactive transport model is presented to interpret and quantify the processes affecting drainage quantity and quality from 15 waste-rock experiments from the Antamina mine, Peru. The deployed uniform flow formulation and consistent set of geochemical rate equations could be calibrated almost exclusively with measured bulk waste-rock properties in experiments ranging from 2kg to 6500 tons in size. The quantitative agreement between simulated dynamics and the observed drainage records, for systems with a variety of rock lithologies and over a wide range of pH, supports the proposed selection of processes. The controls of important physicochemical processes and feedbacks such as secondary mineral precipitation, surface passivation, oxygen limitations, were confirmed through sensitivity analyses. Our work shows that reactive transport models with a consistent formulation and evidence-based parametrization can be used to explain waste-rock drainage dynamics across laboratory to field scales.

Keywords:

Reactive Transport Modelling, acid rock drainage, water quality, coupled processes

1. Introduction

Mining operations around the world produce millions of tons of waste materials every year, including waste rock that is stored on-site in tall piles

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(Hudson-Edwards and Dold, 2015). Waste-rock piles require effective management to reduce environmental risks associated with the oxidation of minerals that can mobilize contaminants and lead to deterioration of downstream water quality, e.g., acid rock drainage (Akcil and Koldas, 2006; Lindsay et al., 2009; Amos et al., 2015). A quantitative understanding of the processes controlling waste-rock weathering and drainage rates is required to develop predictive models for strategic waste management planning. Similar to the so-called "5P" rule of economics, it can be said that *Proper Prediction Prevents Poor Performance*, for which reactive transport models constitute an attractive tool to disentangle the strongly coupled hydrogeochemical processes. Hence, a growing number of reactive transport modelling studies is dedicated to waste-rock piles (Linklater et al., 2005; Molson et al., 2012; Demers et al., 2013; Shokri et al., 2016; Lahmira et al., 2017; Pabst et al., 2017; Wilson et al., 2018). Additionally, reactive transport simulations offer the possibility to examine future reclamation scenarios, e.g., the effectiveness of cover systems or co-disposal techniques (Haug and Pauls, 2002; Aubertin et al., 2009; Martin et al., 2017; Raymond et al., 2020b).

Various coupled physicochemical processes control the overall drainage dynamics of an exposed waste-rock pile (Amos et al., 2015). Principal geochemical reactions include primary sulfide, carbonate and silicate mineral dissolution and secondary mineral precipitation. Geochemical reaction rates are controlled by mineral abundance and particle size, i.e., reactive surface area (Erguler and Erguler, 2015), often aggregated to describe waste-rock reactivity (Lawrence and Wang, 1996; Blowes et al., 2003; Price, 2009; Elghali et al., 2019), and local geochemical conditions such as pH, oxygen concentration and temperature. Relevant physical transport processes include gas, heat and water transport through the unsaturated waste rock. Water infiltration is typically non-uniform in waste rock-piles that have a wide range of particle sizes; orders-of-magnitude discrepancies may exist between the transport times of drainage fronts and thus dissolved solutes. In addition, mineral dissolution and precipitation can impact reactive surface area and porosity and thereby associated physical transport parameters (Seigneur et al., 2019). Gas reactions, O_2 consumption and CO_2 production, induce concentration gradients that trigger diffusive gas transport, respectively: oxygen ingress has been shown to limit weathering rates in large systems with reactive materials (Vriens et al., 2019c). Furthermore, heat production from sulfide oxidation in large waste-rock piles can result in temperatures as high as 70C (Lefebvre et al., 2001) and induce thermal gas convection and im-

49 pact geochemical equilibria and reaction rates. All of the above processes
 50 are subject to vary with significant heterogeneity, from small-scale mineral
 51 impurities and textural variability to macroscale material heterogeneity, e.g.,
 52 as a result of rock blending and structural features such as traffic surfaces
 53 (Atherton, 2017; Wilson et al., 2018; Raymond et al., 2020a). The predictive
 54 success of a mechanistic model relies on identifying and taking into account
 55 the relevant processes and heterogeneities.

56 It is unpractical and unrealistic to quantify all these processes, feedbacks,
 57 and heterogeneities existing in waste-rock piles. Reactive transport models
 58 are often constructed *as simple as possible, as complicated as necessary*, and
 59 incorporate only a select number of processes known or assumed to be rel-
 60 evant in the studied systems. This selection will change with the goal of
 61 the model (fit-for-purpose) and availability of field data to parameterize the
 62 considered processes, which complicates the deployment and cross-validation
 63 of reactive transport models between sites. Only in few cases is the exclu-
 64 sion of certain processes justified by actual field data, *e.g.* in-situ temper-
 65 ature measurements to estimate thermal convection Lefebvre et al. (2001).
 66 The number of model parameters increases with the number of considered
 67 processes, and over-parametrization for the sake of fitting is a valid con-
 68 cern when field data is limited and physical parameters are challenging to
 69 quantify, such as gas permeability, preferential flow in piles with boulder-
 70 sized waste rock. As a result, non-uniqueness, the multiple combinations of
 71 parametrized processes can be used to reproduce data Carrera and Neuman
 72 (1986); Bethke (2007), is of particular concern when interpreting reactive
 73 transport simulations of waste-rock systems. Finally, waste rock models are
 74 often parameterized with physicochemical properties from small-scale static
 75 and kinetic laboratory tests, but the values of model parameters determined
 76 at small scales often differ from those needed in models at larger spatiotem-
 77 poral scales, i.e. hundreds of meters tall piles. Certain processes irrelevant
 78 to weathering rates in laboratory tests will gain significance at increasing
 79 scale (thermal gradients and gas-transport limitations, preferential flow phe-
 80 nomena). Scaling factors have been proposed to facilitate the extrapolation
 81 of laboratory parameters onto practice-relevant dimensions (Strömberg and
 82 Banwart, 1999; Malmström et al., 2000; Plante et al., 2014), but these are
 83 typically semi-empirical correction factors based on limited mechanistic evi-
 84 dence. Process-based reactive transport simulations constitute an alternative
 85 tool for waste-rock drainage prediction, provided that the critical processes
 86 and feedbacks are identified, and reliable data are available to characterize

these.

To this end, we developed a process-based reactive transport framework and use data from a long-term multiscale research program at the Antamina mine in Peru to investigate physicochemical processes in the weathering of waste rock. At Antamina, multiple types of waste rock have been extensively characterized (hydraulically, mineralogically and physically) and weathered at different spatiotemporal scales, providing a unique opportunity to quantify the relevance of individual weathering processes. We focus on processes that could be well-constrained experimentally (i.e. grain size, porosity, hydraulic parameters and mineralogy) and deploy a consistent model formulation across all experiments and waste-rock types. The adopted consistent model formulation is built on a one-dimensional uniform flow description for all investigated experiments, offering the opportunity for evidence-based parametrization. The limitations and scale dependence of the adopted model framework for larger-scale heterogeneous systems is the focus of an associated article (Vriens et al., 2020). This work uses the same model framework to examine individual processes underlying drainage dynamics across these experimental scales.

This work is structured as follows: section 2 describes the reactive transport formulation, parametrization and calibration; section 3 presents the observed drainage dynamics and simulation results and the overall implications of this work are discussed in section 4.

2. Materials and methods

2.1. Overview of the experimental program

Since 2005, an experimental program has been conducted at the Antamina mine ($9^{\circ} 32' 14.6''$ S, $77^{\circ} 02' 51.8''$ W), a large polymetallic (Cu, Zn, Mo) open-pit mine located at ~ 4400 m altitude in the Peruvian Andes. Love et al. (2004) describe the geological setting of Antamina, one of the largest skarn deposits in the world, hosted by Cretaceous sedimentary rocks. Harrison et al. (2012) and Beckie et al. (2011) describe Antamina's waste-rock research program. This paper focuses on 15 experiments, grouped into four levels of increasing scale and complexity:

- Humidity test cells: 5 tests each consisting of 2 kg crushed waste rock (2.5 cm maximum particle size) weathered for 20-40 weeks in laboratory controlled conditions (Hirsche et al. (2017)). 1 liter of water was added at every weekly cycle, generating leachates with neutral pH.

- 123 • Field barrels: 6 kinetic tests each consisting of 350 kg of waste rock
124 (max particle size 15cm) weathered for ≥ 10 years in field conditions
125 (Vriens et al., 2019b; St-Arnault et al., 2020). Approximately 1500
126 liters of water were added over 10 years exhibiting a wide range of
127 leachate quality.
- 128 • Composite laboratory column: 170 kg of mixed-composition waste rock
129 (max particle size: 8 cm), weathered for one year in laboratory con-
130 ditions; (Blackmore et al., 2014, 2018b).180 liters of water were added
131 over one cycle, corresponding to the field barrel condition, generating
132 a low-pH and low-quality drainage.
- 133 • Mesoscale instrumented waste-rock piles: 20 000 tons of mixed-composition
134 waste rock (max particle size ≈ 1 m), weathered for over 10 years in
135 the field (Vriens et al., 2019a), (Vriens et al., 2019c). Only the frontal
136 tipping phases of these piles (described in prior publications as lysime-
137 ters C) were considered for modelling efforts. These experiments can
138 be conceived of as 2 m x 2 m x 11 m columns ($\sim 100,000$ kg of rock)
139 embedded within the 36 m x 36 m x 11 m high experimental piles
140 (Blackmore et al., 2014; Vriens et al., 2019a). Neutral and low qual-
141 ity leachates were observed depending on the waste rock lithology and
142 mineral composition.

143 The particularly wide range of waste-rock lithologies produced at An-
144 tamina is divided into reactivity classes based on sulfide and metal content
145 (Bay et al., 2009). We examine reactive (Antamina type A) **i**ntrusive (I)
146 and **s**karn (S) rocks and slightly reactive (Antamina type B) **h**ornfels (H)
147 and **m**arble (M) (see Tables S2 and S3 for particle size distribution and min-
148 eral contents). For this work, experiments were selected such that all major
149 waste-rock lithologies were included in the analyses. Nomenclature of the
150 investigated experiments is adopted from the works cited above. Measured
151 bulk waste-rock properties in the investigated experiments include hydraulic
152 parameters (porosity, hydraulic conductivity and van Genuchten parameters,
153 Table S1; particle size distribution, Table S2), mineralogical data (Table S3)
154 and elemental composition (Table S4). Drainage outflow and chemistry sam-
155 ples were collected on a weekly to monthly basis for the various experimental
156 scales (Blackmore et al., 2018b; Vriens et al., 2019a,b,c).

157 2.2. Reactive transport modelling

158 2.2.1. Formulation

Reactive transport models were built in MIN3P-HPC (Mayer et al., 2002; Mayer and MacQuarrie, 2010; Su et al., 2017), which has been used for several studies involving mine waste drainage simulations (Mayer et al., 1999; Brookfield et al., 2006; Bea et al., 2012; Wilson et al., 2018). The code is used to model transient unsaturated flow, advective-diffusive-dispersive solute transport, gaseous diffusion, as well as the solid-liquid-gas equilibrium and kinetic reactions. Formulation of transient unsaturated flow follows Richards equation, in the form given in (Mayer et al., 2002):

$$S^l S_s \frac{\partial h}{\partial t} + \phi \frac{\partial S^l}{\partial t} - \vec{\nabla} \cdot [k_r^l K \vec{\nabla} h] = 0, \quad (1)$$

159 where k_r^l is the liquid relative permeability [-], K is the hydraulic conductivity
160 [m·s⁻¹], h is the hydraulic head [m], S^l is the liquid saturation related to the
161 volumetric water content θ through the porosity ϕ and S_s is the specific stor-
162 age coefficient [m⁻¹]. Van Genuchten relations (Wösten and Van Genuchten,
163 1988) are used to compute the relative permeability and linkage between
164 liquid saturation and hydraulic head (see SI).

165 All experiments were simulated as uniform 1D vertical flow systems where
166 downward infiltration dominated the flow regime. Due to their limited het-
167 erogeneity and spatial scale (i.e. limited lateral flow dispersion), one-dimensional
168 vertical models are suited to describe the smaller-scale experiments (humid-
169 ity cells, field barrels and laboratory column), as was shown by previous
170 studies (Wilson et al., 2018; Pabst et al., 2017). As larger-scale piles usually
171 display more heterogeneous flow, dual-porosity and dual-permeability de-
172 scription might be more suited to capture preferential flow phenomena and
173 short-term drainage dynamics. However, dual-domain formulations require
174 additional parameters (e.g., inter-domain exchange terms) that are challeng-
175 ing to constrain experimentally (Arora et al., 2011; Moreira et al., 2016).
176 Additionally, the impact of dual-domain dynamics on mass loadings over a
177 yearly timescale is unclear. As will be shown below, a uniform flow formu-
178 lation was considered satisfactory for the purpose of this study, which is to
179 focus on the long-term trends in the drainage geochemistry. The mesoscale
180 experimental piles represent a possibility to assess the capability of simplified
181 model formulations to reproduce and predict long-term drainage dynamics
182 on larger scales (Vriens et al., 2020).

183 Initial conditions for the unsaturated flow problem are constrained by
 184 volumetric water contents that were measured in the composite laboratory
 185 column as well as in the experimental piles; representative average values were
 186 estimated for the field barrels. The transient infiltration rate (i.e. precipi-
 187 tation - evapotranspiration) at the top boundary and a constant volumetric
 188 water content at the bottom were selected to match observed outflow rates.
 189 The humidity-cell experimental wetting-drying cycles (complete saturation
 190 followed by gradual drying) were mimicked by an averaged "continuous flow"
 191 that produced the same total water flux.

192 Transport of solutes and gaseous species, and the solid-liquid-gas equilib-
 193 rium is modeled as:

$$\frac{\partial \phi S^l T_i^l}{\partial t} + \frac{\partial \phi S^g T_i^g}{\partial t} = \vec{\nabla} \cdot [\phi S^g \mathbf{D}^g \vec{\nabla} T_i^g + \phi S^l \mathbf{D}^l \vec{\nabla} T_i^l - T_i^l \vec{u}] + R_i^{\min}, \quad (2)$$

where S^g is the gas saturation, T_i^l and T_i^g respectively are the total concen-
 trations of basis species i in the aqueous [$\text{mol} \cdot \text{L}^{-1}$ of water] and gaseous [$\text{mol} \cdot \text{L}^{-1}$ of gas]
 phases, u is the Darcy-velocity [$\text{m} \cdot \text{s}^{-1}$]. $\mathbf{D}^l$ and $\mathbf{D}^g$ represent
 the liquid and gas diffusion-dispersion tensors [$\text{m}^2 \cdot \text{s}^{-1}$], assumed isotropic:

$$\begin{cases} \mathbf{D}^l &= \delta |\vec{u}| + D_0^l \\ \mathbf{D}^g &= D_0^g \end{cases}, \quad (3)$$

194 where δ is the dispersivity [m] and D_0^l , D_0^g are the pore diffusion coefficients
 195 [$\text{m}^2 \cdot \text{s}^{-1}$] (Table S1). $R_i^{\min}$ represent the source-sink terms from the mineral
 196 reactions [$\text{mol} \cdot \text{dm}_{\text{bulk}}^{-3} \cdot \text{s}^{-1}$]. In all simulations, infiltrating and pore solutions
 197 were initially in equilibrium with atmospheric oxygen (20% partial pressure)
 198 and carbon dioxide (0.04 %), corrected for the prevailing atmospheric pres-
 199 sure at Antamina; $\sim 4,400$ m above sea level. Gas partial pressures are main-
 200 tained constant at the top of the domain, while a free exit is modeled at the
 201 bottom boundary.

202 The different models described a 2cm grid cells, except for the experi-
 203 mental pile which was modeled using a coarser mesh (10 cm). Convergence
 204 is reached when the maximum concentration relative evolution between two
 205 successive iterations (over every species and every node) is below 10^{-6} . Con-
 206 vergence is assumed to not be reached above a certain number of Newton-
 207 Raphson iteration, after which MIN3P reduces the timestep. Also, when the
 208 solver requires more than 12 iterations, timestep is reduced. The maximum
 209 allowed timestep was set to 12h.

210 *2.2.2. Geochemical reactions*

211 Major minerals present in the waste rocks (Table S3) include the sulfide
 212 minerals, pyrite, chalcopyrite, sphalerite, molybdenite and galena. Other
 213 (non-sulfide) primary phases included calcite and silicate minerals, biotite,
 214 albite, quartz, anorthite, muscovite and wollastonite. Based on previous ob-
 215 servations, the following secondary minerals were considered: gypsum, ferri-
 216 hydrite, powellite (Conlan et al., 2012), amorphous silica and aluminum,
 217 wulfenite, jarosite, willemite (Skierszkan et al., 2016), as well as several
 218 Cu/Zn-(oxyhydr)oxides, sulfates and carbonates (Vriens et al., 2019a). The
 219 considered minerals are summarized up in Table S5 and their rate expres-
 220 sions are given in Table S6. We distinguished between quasi-equilibrium
 221 and kinetic rate expressions for fast and reversible versus slower and irre-
 222 versible dissolution reactions, respectively. Reversible and fast reactions can
 223 effectively be described by generalized transition state theory rate expres-
 224 sions (Mayer et al., 2002; Lasaga and Kirkpatrick, 2018), with Q_m and K_m
 225 representing respectively the ion activity product and the thermodynamic
 226 equilibrium constant and k_{eff} the rate constant (in $\text{mol} \cdot \text{dm}_{\text{bulk}}^{-3} \cdot \text{s}^{-1}$) :

$$R_m = k_{\text{eff}} \left(1 - \frac{Q_m}{K_m} \right) \quad (4)$$

227 For large rate coefficients, this equation yields quasi-equilibrium condi-
 228 tions, if the mineral phase in question is present. Aqueous and gaseous equi-
 229 librium constants, as well as aqueous speciation chemistry constants were
 230 adopted from the MINTEQ.v4 database.

231 Irreversible, slower mineral dissolution reactions were described by kinetic
 232 rate expressions adopted from the literature. Rate laws for sulfide and silicate
 233 minerals have been widely studied (e.g., Rimstidt et al. (1994)). All rate laws
 234 depend upon the experimental conditions and literature rate expressions are
 235 usually contain surface-area normalized rate constants in $\text{mol} \cdot \text{m}^{-2} \cdot \text{s}^{-1}$, and
 236 were corrected by what will be referred to as the reactive surface area A_{eff}
 237 (in $\text{m}^2 \cdot \text{dm}_{\text{bulk}}^{-3}$). To capture sulfide oxidation by dissolved oxygen and ferric
 238 ion (Singer and Stumm, 1970) in a single rate expression, the pyrite and
 239 sphalerite rate laws were adapted from Williamson and Rimstidt (1994) and
 240 Pan et al. (2012), respectively, in the forms:

$$R_{\text{pyrite}} = A_{\text{eff}}^{\text{Py}} \left(10^{-8.19} \frac{[\text{O}_2(\text{aq})]^{0.5}}{[\text{H}^+]^{0.11}} + 10^{-6.07} \frac{[\text{Fe}^{3+}]^{0.93}}{[\text{Fe}^{2+}]^{0.4}} \right) \quad (5)$$

$$R_{\text{sphalerite}} = A_{\text{eff}}^{\text{sph}} \left(10^{1.163} [H^+]^{0.11} [\text{Fe}^{3+}]^{0.154} \right) \quad (6)$$

For chalcopyrite, rate laws reported by Salazar et al. (2009), Rimstidt et al. (1994) and Kimball et al. (2010) were mostly developed under acidic conditions ($1 \leq \text{pH} \leq 3$) not representative of the wide range of drainage conditions encountered in our experiments ($2 \leq \text{pH} \leq 9$). Furthermore, chalcopyrite rate laws for $\text{pH} \leq 3$ exhibited a high-order dependence on pH ($[H^+]^{1.68}$). Considering the progressive acidification of over 5 pH units observed in some Antamina experiments, use of such a law would yield oxidation rates increasing by over 8 orders of magnitude. Therefore, the oxidation of chalcopyrite, but also that of molybdenite and galena, was described by a simple first-order dependence on dissolved oxygen:

$$R_{\text{chalcopyrite}} = A_{\text{eff}}^{\text{Chalco}} [\text{O}_2(\text{aq})], \quad (7)$$

Literature-adopted kinetic rate expressions for all considered sulfide and silicate phases are summarized in Table 1.

Table 1: Kinetic formulations for the mineral rates. Thermodynamic constants were taken from the MINTEQ database

Mineral	Rate expression R_m	
Pyrite	$A_{\text{eff}}^{\text{Py}} (10^{-8.19} \frac{[\text{O}_2(\text{aq})]^{0.5}}{[H^+]^{0.11}} + 10^{-6.07} \frac{[\text{Fe}^{3+}]^{0.93}}{[\text{Fe}^{2+}]^{0.4}})$	Williamson and Rimstidt (1994)
Sphalerite	$A_{\text{eff}}^{\text{sph}} \left(10^{1.163} [H^+]^{0.11} [\text{Fe}^{3+}]^{0.154} \right)$	Pan et al. (2012)
Chalcopyrite	$A_{\text{eff}}^{\text{m}} [\text{O}_2(\text{aq})]$	
Molybdenite		
Galena		
Quartz	$A_{\text{eff}}^{\text{Qu}} (10^{-12} + 10^{-13.8} [H^+]^{-0.25})$	Dove (1995)
Albite	$A_{\text{eff}}^{\text{Alb}} (10^{-9.69} [H^+]^{0.49} + 10^{-14.15} [H^+]^{-0.3})$	Chou and Wollast (1985)
Biotite	$A_{\text{eff}}^{\text{Bio}} [H^+]^{0.25}$	Acker and Bricker (1992); Bray et al. (2015)
Anorthite	$A_{\text{eff}}^{\text{An}} (10^{-5.87} [H^+]^{1.12})$	Brady and Walther (1989)
Muscovite	$A_{\text{eff}}^{\text{Mu}} (10^{-12.6} [H^+]^{0.08} + 10^{-13.5} [H^+]^{-0.1})$	Nickel (1973)
Others	$k_{\text{eff}}^{\text{m}} \left(\frac{Q_m}{K_m} - 1 \right)$	

2.3. Model parametrization and calibration

The reactive transport formulation was applied consistently to the 15 investigated experiments. For all experiments, system geometry (Table S1), waste-rock bulk density and mineral abundance was measured and directly

257 adopted. Only identified minerals (Table S3) were considered to calibrate
 258 the initial mineralogy. For all experiments other than the humidity cells,
 259 hydraulic parameters (porosity, saturated hydraulic conductivity and van
 260 Genuchten parameters) were adopted from previous tracer test analyses (sum-
 261 marized in Table S1). In all simulations, the same values of dispersivity δ ,
 262 specific-storage coefficient S_s and diffusivities D_0^g and D_0^l were used (Table
 263 S1). The only differences among the simulations of the various experiments
 264 were therefore i) initial and boundary conditions for flow (initial water con-
 265 tent and recharge at the top boundary); and ii) effective mineral rate con-
 266 stants (k_{eff} ; Equation 4) and surface area (A_{eff} ; in Equations 5, 6 and 7)
 267 values as in Table S6.

268 For each simulation, calibration proceeded in two steps. First, initial
 269 head conditions for flow were set to be representative of the average ob-
 270 served water content. Volumetric water content and the recharge boundary
 271 conditions were calibrated to reproduce the observed outflow, except for the
 272 piles where recharge was calibrated to the observed weather record (Vriens
 273 et al., 2019a). Once hydraulics were calibrated and subsequently fixed, reac-
 274 tive surface area and effective rate coefficients (A_{eff} and k_{eff}) were adjusted
 275 to reproduce leachate concentrations in an informal trial-and-error fashion.
 276 Emphasis was placed on reproduction of long-term drainage concentrations,
 277 rather than initial spikes in the drainage concentrations arising from flushing
 278 of pre-experimentally precipitated salts. As such, A_{eff} and k_{eff} values rep-
 279 resent the sole geochemical calibration factors and aggregate all influences
 280 of other unaccounted processes on the outflow chemistry, e.g., influence of
 281 temperature.

282 A number of hydrogeochemical feedbacks previously identified in mine
 283 waste-rock systems - including Antamina - were not explicitly incorporated
 284 in the model. These include, e.g., porosity and permeability changes through
 285 mineral precipitation (St.Arnault et al., 2019), gas advection (Amos et al.,
 286 2009; Vriens et al., 2018), preferential flow (Stockwell et al., 2006; Trinchero
 287 et al., 2011; Lahmira et al., 2017; Appels et al., 2018; Blackmore et al.,
 288 2018a), surface passivation and reactive surface area decreases (e.g., 'shrink-
 289 ing core model' Wunderly et al. (1996); Langman et al. (2014); St.Arnault
 290 et al. (2019)), microbial catalysis (Blackmore et al., 2018b) or chemical ad-
 291 sorption (Vriens et al., 2019b). In some cases, the exclusion of these pro-
 292 cesses is justified by experimental data, e.g., limited O_2 depletion and heat
 293 production to support convection). Porosity changes fall in the same cate-
 294 gory: simulated changes in the volumes of mineral phases were small (less

than 10% for the most reactive waste rock). The exclusion of other processes (e.g., preferential flow and evolution of reactivity) could not be justified from experimental evidence, but limited or no data was available to support their parametrization across the investigated experiments. Hence, these processes were not considered in line with our approach to develop a model "as simple as possible, as complicated as necessary" and the effects of these unresolved processes are integrated by the fitted geochemical rate constants. A quantitative analysis of these unresolved contributions is the primary focus of Vriens et al. (2020), while this study examines the ability of the model formulation and individual considered processes to capture long-term drainage dynamics across experimental scales.

2.4. Sensitivity analyses

Individual processes and feedbacks were investigated through a sequence of sensitivity analyses run on calibrated simulation models. Specifically, we considered the role of secondary mineral reaction rates (sensitivity on k_{eff}), evolution of reactive surface area (temporal evolution of A_{eff}) and the influence of hydraulic parameters and volumetric water content on drainage dynamics. Details and results of these sensitivity analyses can be found in the SI.

3. Results and Discussion

3.1. Humidity cells

The humidity-cell tests contained relatively homogeneous sieved waste rock with narrow particle size distributions and displayed no drainage acidification during the short term (up to 40 weeks) they were run. The simulated compositions in all investigated humidity-cell experiments are in good agreement with measured compositions (Figure 1).

In all humidity-cell experiments, neutral-drainage pH was observed. Simulations suggest that this is because of a stoichiometrically balanced sulfide oxidation and calcite dissolution, whose rates were approximately $10^{-5} \text{ mol dm}_{\text{bulk}}^{-3} \text{ day}^{-1}$ across waste rock types (Figure 2). These reasonable weathering rates suggest that no significant oxygen limitation occurs within the one-week wetting cycles. Calibrated pyrite reactive surface area and calcite effective rate coefficients varied less than a factor 4 between all the investigated experiments (Table S6).

Humidity-cell experiments are designed to examine whether the AP/NP balance affects the ultimate acidity and composition of drainage when all potential weathering products are mobilized. As such, humidity cells are assumed to not reach mineral saturation (Sapsford et al., 2009; Maest and Nordstrom, 2017). Yet, simulations reveal that some secondary mineral phases were close to saturation ($SI > -1$; Figure 2). Precipitation of secondary Fe-(oxyhydr)oxides, generalized as ferrihydrite in the model, and a copper hydroxide ($Cu(OH)_2$, tenorite in the MINTEQ database) induced below detection limits concentrations of Fe and Cu in the drainage respectively. Simulations suggest that ~ 50 - 150 mg/kg of ferrihydrite (1 - 3 mmol over the 2 kg waste rock) precipitated by the end of each humidity-cell experiment. Low drainage concentrations of Zn are primarily due to low Zn abundance (except for HC5) and the circumneutral pH which does not promote sphalerite oxidation (Equation 6). Other (near)saturated secondary mineral phases included wulfenite, whose precipitation attenuates Mo, as shown for humidity cell HC1 in Figure 1 and 2. The simulated low cumulative precipitation of these secondary phases through time (Figure 2) indicates that these minerals would not be readily detectable with conventional mineralogical techniques.

Humidity-cell experiments with skarn and intrusive waste rock released significant Ca and sulfate during the first ~ 20 days, possibly related to the dissolution of secondary gypsum that had precipitated on the waste rock prior to the start of the kinetic tests. Indeed, inclusion of a small amount of gypsum (0.02 % volume fraction) to the mineral assemblage led to a better representation of the observed "first flush" (dashed red-line in Figure 1) but was not further adopted in other simulations to ensure consistency across experiments.

3.2. Field barrels

Compared to the humidity cells, field-barrel experiments contained greater than two orders-of-magnitude more waste rock and were run more than 10 times longer, for 9 years, and under field conditions. A wide range of drainage signatures was observed in the suite of field barrels, ranging from metastable, seasonally oscillating, circumneutral drainage to gradually acidifying drainage with orders-of-magnitude increases in metal loads (Figure 3). Simulated drainage chemistries reproduce observed values for all investigated waste-rock types (Figure 3 and additional field barrels in Figure S3), including an accurate representation of temporal oscillation in drainage quality and quantity.

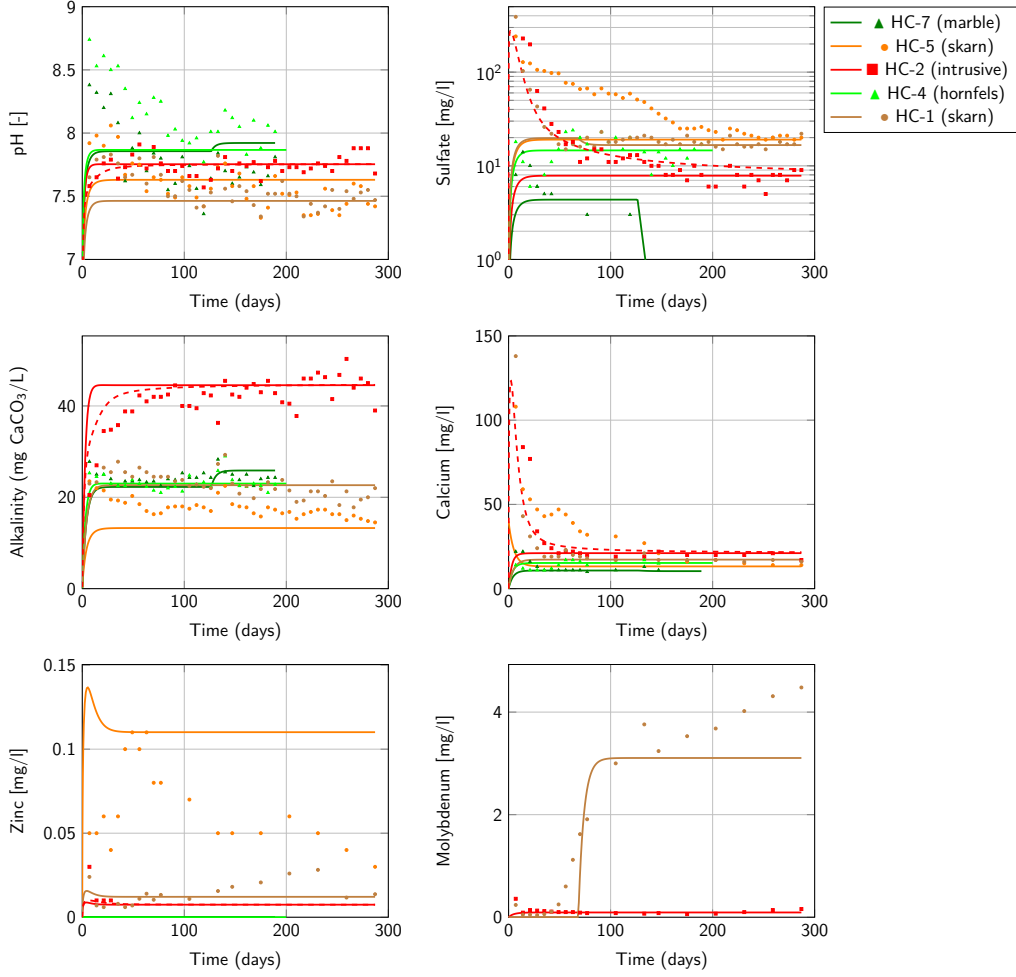


Figure 1: Recorded and simulated drainage chemistry for humidity test cells. Drainage pH, alkalinity, Ca and sulfate concentrations (logarithmic y-axis for the latter) are plotted for experiments and simulations that are color-coded based on their lithology. Solid lines indicate model results while markers indicate measured values. Mo concentrations are only displayed when they were above detection limits (HC-1 and HC-2 only). The red dashed line corresponds to the HC-2 simulation with an initial small amount of gypsum, whose rate decreases exponentially, using equation S2.

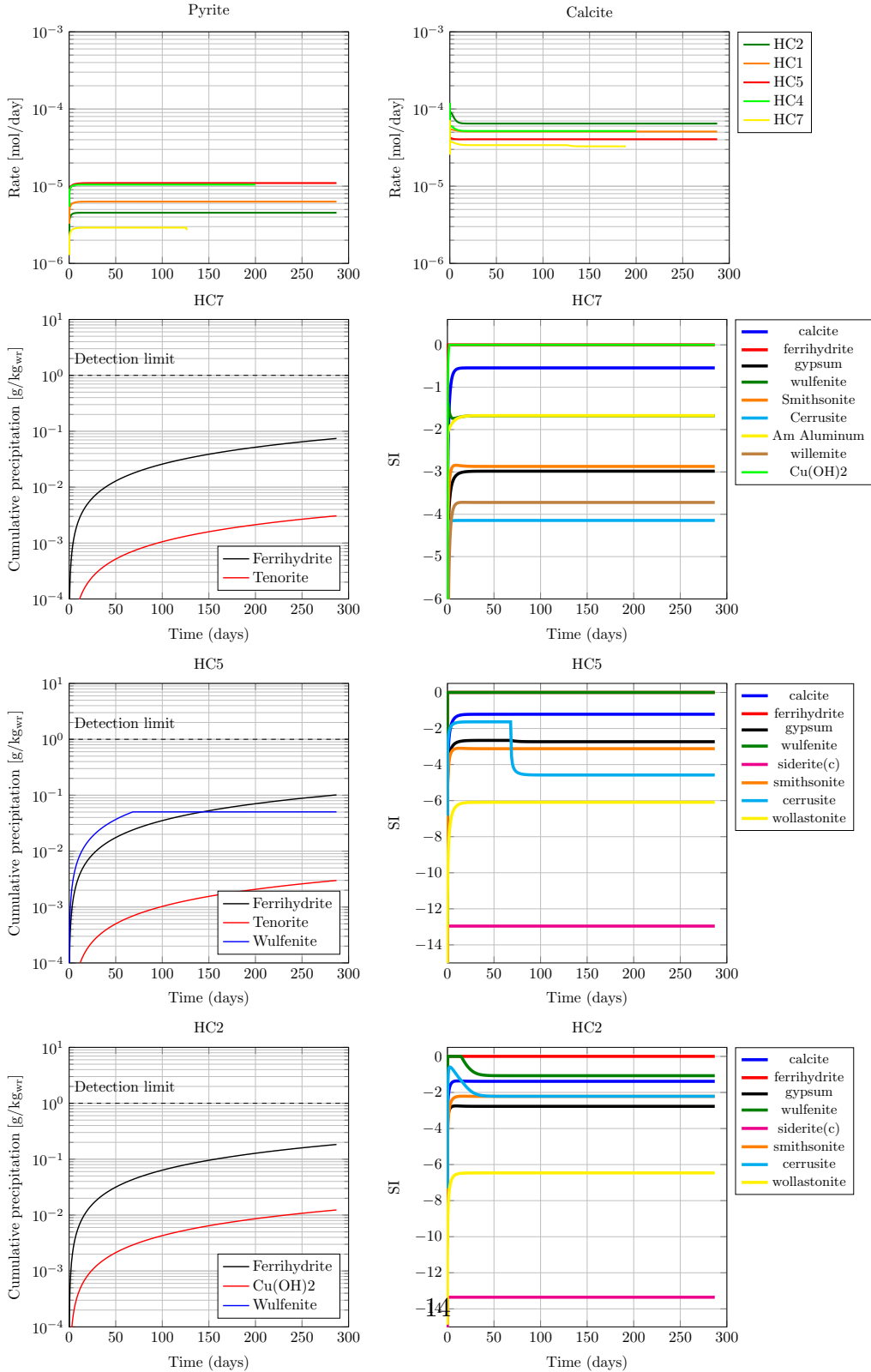


Figure 2: Top: Simulated rates of pyrite oxidation and calcite dissolution. Middle: evolution of secondary mineral precipitation for the three most reactive humidity cells, compared to typical XRD detection limit of 0.1 wt-%. Bottom: saturation indices (SI) of a series of

366 Simulated volumetric water content and oxygen profiles can be found in
 367 Figure S2. The seasonal variation in flow rates simulated for the field barrel
 368 experiments (Figure S1) affect the temporal evolution in simulated drainage
 369 chemistry (Figure 3): elevated infiltration during the wet season increases
 370 the waste-rock water content and dilutes solutes. Simulated mineral disso-
 371 lution rates (e.g., R_{pyrite} from Equation 5) also oscillate in time (Figure 4),
 372 potentially due to the evolution of the air-filled porosity that impacts oxygen
 373 supply to the waste rock in the field-barrels. Simulations indicate that oxy-
 374 gen levels generally remain very close to atmospheric levels (Figure S2), with
 375 a minimum oxygen content of 70% compared to ambient conditions, even for
 376 the most reactive field-barrel. Even though oxygen depletion was therefore
 377 probably limited, simulations suggest that small variations in oxygen and
 378 water content still impact sulfide oxidation rates through the evolution of
 379 ferrous and ferric iron concentrations (Equation 5). Coarser-grained materi-
 380 als like FB-M1 (Table S2) are drier (Figure S2), less reactive and therefore
 381 have a rather constant oxygen profile (Figure S2) and stable oxidation rates
 382 (Figure 4), compared to finer-grained and more reactive materials (FB-S4
 383 or FB-I9). Also, calcite weathering rates seem to be strongly correlated to
 384 the volumetric water content, even for low-reactivity field barrel with steady
 385 oxidation rates (FB-M1 on Figure 4). This is further confirmed by sensitivity
 386 analysis (Figure S7).

387 Field barrels FB-I2 (intrusive), FB-S1 and FB-S4 (skarn), FB-H1 (horn-
 388 fels) and FB-M1 (marble) remained circumneutral for the ≥ 10 -year study
 389 period. However, drainage from field barrel FB-I9 (intrusive) transitioned
 390 from ~ 6.5 to $\text{pH} \leq 3$ within 3 years, associated with orders-of-magnitude
 391 increasing concentrations of sulfate, Cu and Zn (Figure 3). Simulations show
 392 that this acidification was caused by depletion of calcite initially present in
 393 the field barrel (≤ 0.1 wt-%, see Table S3) within the first two years (Fig-
 394 ure 4). The absence of buffering by calcite initiated a feedback where pyrite
 395 and sphalerite oxidations was accelerated through the decreasing pH and in-
 396 creasing ferric iron concentration (Equations 5 and 6; Figure 4). The model
 397 was able to capture such rate increases without adjustments to the fitted rate
 398 parameters, because the rate expressions explicitly accounted for pH and dis-
 399 solved iron concentrations (Equations 5 and 6). Simulations show that acid
 400 was buffered in FB-I9 principally by dissolution of amorphous Fe-oxides (Fer-
 401 rrihydrite in Figure 4 dissolves after 4 years), and subsequently by dissolution
 402 of silicate phases such as wollastonite, present at ≥ 2 wt-% in FB-I9 (Table
 403 S3), albite and biotite (Figure 4). This sequence of mineral dissolution under

404 increasingly acidic conditions reflects a typical acid-rock drainage neutraliza-
405 tion series (Sherlock et al., 1995; Amos et al., 2015; Vriens et al., 2019a).

406 A number of secondary mineral phases identified in the field-barrel exper-
407 iments by St.Arnault et al. (2019) and Vriens et al. (2019b) were near satu-
408 ration in the simulation, including gypsum, various Fe-, Cu-(oxyhydr)oxides
409 and Cu-(hydroxy)sulfates, as well as willemite, wulfenite and powellite (as
410 shown through their precipitation depicted in Figure 4). This supports the
411 notion that significant metal attenuation takes place under neutral drainage
412 conditions. For instance, simulations suggest that ~ 1 mole of secondary Cu-
413 hydroxy-sulfates (~ 450 grams of brochantite and ~ 350 grams of antlerite
414 over the 350 kg waste rock) precipitated in field barrel FB-I9 during the first 4
415 years (Figure 4), with a conversion from brochantite to antlerite. Once acidic
416 conditions developed within FB-I9, both these phases rapidly re-dissolved:
417 the net effect of this re-dissolution coupled to the ongoing chalcopyrite oxi-
418 dation explains the Cu mobilization spike observed after 2 years (Figure 3).
419 Moreover, precipitation of jarosite (~ 1.4 g/kg of waste rock) acts to attenu-
420 ate Fe as ferrihydrite starts to dissolve under acidic pH (Figure 4). Typically,
421 simulated drainage composition was highly sensitive to the secondary min-
422 eral assemblage, as illustrated by the effect of the ferrihydrite reaction rate
423 illustrated by a sensitivity analysis (Figure S5 in SI): the limit case where
424 ferrihydrite is inert (or not included in the model), induces more acidic condi-
425 tions in the drainage, with a positive feedback on oxidation rates of primary
426 minerals and therefore the overall sulfate loading. These examples demon-
427 strate the value of modeling to help identify secondary-mineral controls that,
428 because of their low abundances or amorphicity, would be challenging to
429 determine experimentally in heterogeneous weathered waste rock.

430 There are other explanations for the limited buffering capacity of field
431 barrel FB-I9: a progressive passivation through secondary mineral precipita-
432 tion (e.g., St.Arnault et al. (2019)), or a reactivity decrease caused by pref-
433 erential weathering of finer-calcite grains (Beckingham et al., 2016; Seigneur
434 et al., 2019). As shown in the sensitivity analysis in the SI (Figure S6), a
435 better agreement between simulated and measured Ca concentrations can be
436 obtained by progressively reducing calcite reactivity (k_{eff}) during dissolu-
437 tion. The shrinking core model (Ritchie, 1994; Levenspiel, 1998), or other
438 approaches (e.g., Jeon et al. (2007)) to model the impact of precipitation on
439 the decrease in reactivity could be considered to address decreasing mineral
440 reactivity over the course of weathering. However, these approaches may also
441 lack in experimental evidence to be properly parametrized (e.g., the thickness

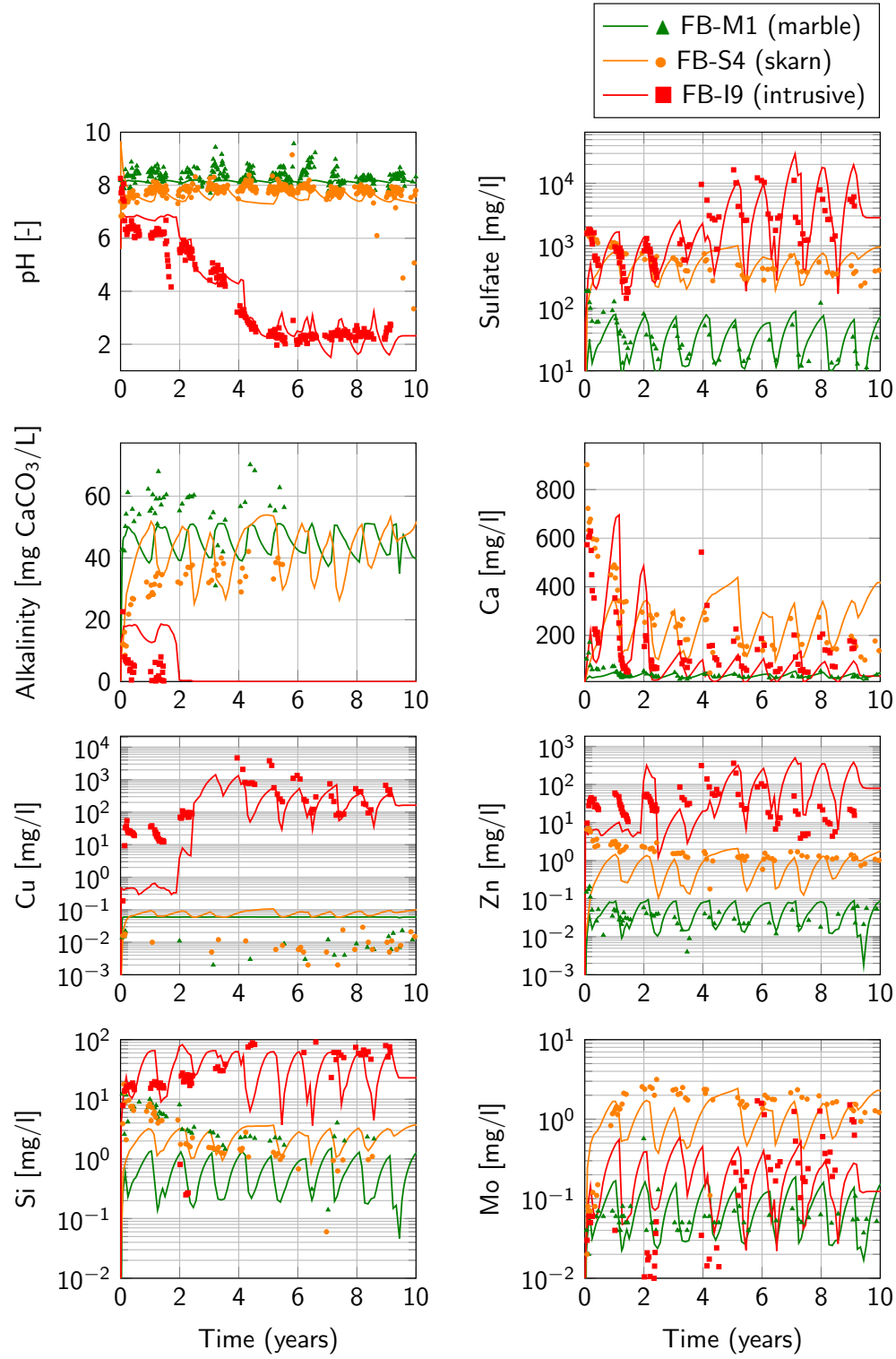


Figure 3: Observed and simulated drainage chemistry for the field barrels. Experiments and simulations are color-coded by their lithology and show drainage pH, alkalinity and aqueous concentrations of Ca, Si, Mo (linear y-axis) as well as sulfate, Cu and Zn (all logarithmic y-axes). Legend applies to all frames. Solid lines indicate model results while markers indicate measured values. Results for additional experiments FB-I2 (intrusive), FB-H1 (hornfels) and FB-S1 (skarn) are given in Figure S3

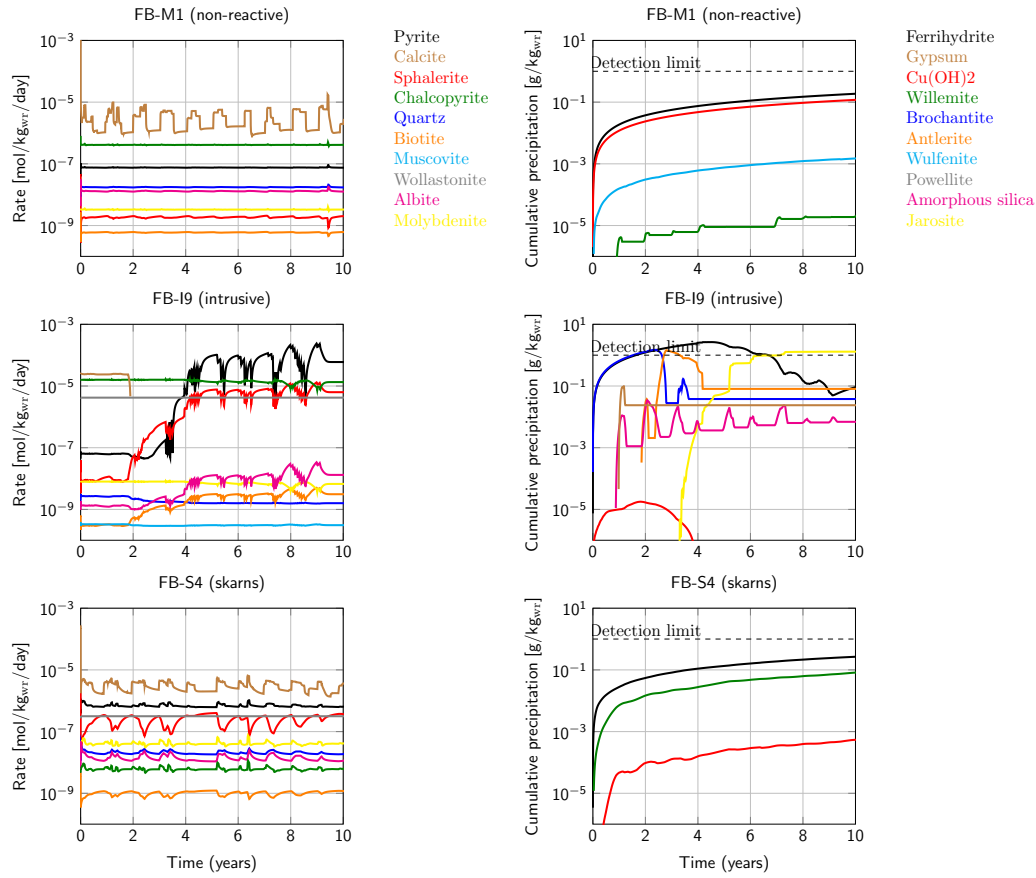


Figure 4: Simulated rates of primary mineral dissolution (left column) and cumulative precipitation of secondary minerals (right) in the three field barrel experiments presented in Figure 3. Simulated precipitation of secondary minerals are compared to a typical XRD detection limit of 0.1 wt-%

442 and diffusivity of reactive rim).

443 That we are able to capture the essential solute mobilization dynamics
444 from materials subject to field conditions displaying variable geochemical
445 drainage conditions ($2 \leq \text{pH} \leq 9$), with different hydraulic behavior and
446 geochemical properties which can be a-priori estimated based on bulk-average
447 characterization of the waste-rock systems, demonstrates the robustness of
448 our modelling approach.

449 The fitted pyrite reactive surface areas used in the field-barrel simulations
450 varied from each other with less than one order-of-magnitude, and were gen-
451 erally two orders-of-magnitude lower than those used in the humidity cells
452 simulations (Table S6). This difference is associated to the coarser-grained
453 rock and the effects of lower ambient temperature in the field barrels (Vriens
454 et al., 2020). The fitted pyrite reactive surface area for waste rock in FB-I9
455 was lower than for FB-I2, a similar reactive, intrusive waste rock, but with
456 relatively larger grain size (Table S2). A strong correlation exists between
457 the physical surface areas deduced from particle size distributions and fitted
458 reactive surface areas (Vriens et al., 2020). Despite a lower surface area,
459 acid generation in FB-I9 results from the low carbonate (Table S1) and high
460 chalcopyrite (Tables S3 and S4) contents.

461 3.3. Composite laboratory column

462 Although similar in size to the field barrels and of shorter duration, the
463 laboratory column experiment added complexity because it was composed
464 of three different waste rock types that were vertically stacked: the bottom
465 drainage carried the aggregate signal of all waste-rock types. Yet, observed
466 drainage rates and internal moisture-content profiles (Figure S1 and top right
467 of Figure 6, respectively) could be well captured by our model using unad-
468 justed hydraulic properties that were fixed for each waste-rock layer.

469 Simulated drainage chemistries generally agree with observations as well
470 (Figure 5). The initial important flush of oxidation product (observed for
471 many elements; Figure 5) is because of the progressive build-up occurring
472 during the wetting-up of the column (the first 120 days where no outflow
473 occurred) and can be observed from the element concentration profiles (Fig-
474 ure 6).

475 The laboratory column experiment produced basal drainage that was
476 mildly acidic ($4.5 \leq \text{pH} \leq 5$); drainage was not sampled from within the col-
477 umn from the individual waste-rock layers. The simulated outflow chemistry
478 matched that of the outflow when acidity was simulated as mostly produced

479 in the uppermost layers that contained reactive waste rock with high sulfide
 480 content (up to 6 wt-%, Table S3), and low NP/AP ratios, at rates of up to
 481 $10^{-5} \text{ mol dm}_{\text{bulk}}^{-3} \text{ day}^{-1}$ (see Figure S4). Local porewater pH in the uppermost
 482 column layers dropped to $\text{pH} \leq 2.5$, while sulfide oxidation and acidity pro-
 483 duction were negligible in the bottom marble rock. These sulfide oxidation
 484 rates are comparable to those simulated for field barrels with similarly reac-
 485 tive waste rock (e.g., up to $10^{-5} \text{ mol dm}_{\text{bulk}}^{-3} \text{ day}^{-1}$ FB-I9, Figure 4). Simulated
 486 pyrite reactive surface areas for the column top layer were higher than those used
 487 in the field barrels but lower than the humidity cells.

488 The simulations suggest that wollastonite, which was identified in the
 489 central part of the column (Table S3), is the primary buffering phase in
 490 the more reactive waste rock segments ($\sim 10^{-5} \text{ mol dm}_{\text{bulk}}^{-3} \text{ day}^{-1}$, see Figure
 491 S4). Several mineral phases were saturated in the top waste-rock layers
 492 (Figure 6), e.g., amorphous Silica and Fe-oxides, as well as jarosite and Cu-
 493 (hydroxy)sulfate phases. These are the same mineral phases important to
 494 obtain a quantitative agreement between measured and simulated (acidic)
 495 drainage of field-barrel FB-I9 (which had waste rock similar to that in the top
 496 layers in the laboratory column) our reactive transport framework therefore
 497 suggests that incorporation of these phases is important for simulating acid
 498 rock drainage.

499 The fact that the composite column drainage had a $\text{pH} \leq 5$ implies that
 500 neutralization of acidic drainage percolating from the uppermost layers in the
 501 lower marble layer was not very effective. This is surprising considering that
 502 the bottom marble layer consisted virtually exclusively of carbonates and sil-
 503 icates (up to 75 wt-% calcite, Table S3). The ineffective neutralization can be
 504 explained by smaller relative surface areas (coarse grains within this layer, see
 505 Table S2) and a shorter contact time with percolating drainage through flow
 506 channeling. Despite the observed limited neutralization, the drainage con-
 507 tains significant Ca ($\geq 500 \text{ mg/L}$), which cannot have been solely produced
 508 from wollastonite dissolution, as indicated by the low aqueous Si concentra-
 509 tions. As the drainage composition is in equilibrium with gypsum throughout
 510 the duration of the laboratory experiment (Figure 6), the slightly acidic pH
 511 and high Ca and sulfate concentrations likely are due to the dissolution of
 512 pre-existing gypsum, which formed during waste rock storage prior to the
 513 experimental period (Blackmore et al., 2018b). Pre-experimental gypsum
 514 could act as a passivation agent, reducing calcite dissolution during the ex-
 515 periment (St. Arnault et al., 2019). As only one single seasonal infiltration
 516 cycle was applied, these simulations depend strongly on the uncertain initial

517 (first flush) conditions. Further research over several pore volumes of infil-
518 tration is required to disentangle the roles of surface area passivation and
519 flow channeling on the observed drainage dynamics.

520 3.4. *Experimental piles*

521 The experimental waste-rock piles are the largest experiments in the An-
522 tamina research program. While seasonal flow variability for the smaller-
523 scale systems examined thus far could be quantitatively reproduced by the
524 adopted uniform-flow description, seasonal variation in drainage rates from
525 the larger experimental piles was significantly muted, even though cumula-
526 tive long-term dynamics were well captured (Figure S1). This suggests that
527 a uniform description may be valid for smaller-scale experiments with limited
528 physical heterogeneity, but a single-domain flow description cannot reproduce
529 seasonal oscillations at larger scales, because of the increased heterogeneity
530 and contribution of preferential flow paths. This aligns with tracer test re-
531 sults from Antamina that have shown that matrix flow dominates transport
532 at smaller scales, but that multi-domain flow formulations better capture
533 solute dynamics from larger-scale experiments with strong contrasts in hy-
534 draulic properties (Blackmore et al., 2014; Pedretti et al., 2017), with fast
535 flow amounting up to 15% of the total flow. Additional research would be
536 required to study the representativity of our modelled mineral rates in a sin-
537 gle continuum compared to the inherent nature of these multiple-continua,
538 to investigate the potential of this approach to be integrated in even larger
539 spatial scales.

540 While drainage from sublysimeter piles 1C and 3C remained neutral over
541 the course of a decade, drainage in pile 2C acidified over several years (Fig-
542 ure 7), similar to what was observed for field barrel FB-I9: both systems
543 consisted of reactive, sulfide-rich waste rock (Vriens et al., 2019a)). Oxygen
544 distributions can be highly non-uniform throughout the piles (Vriens et al.,
545 2019c). Even though no significant thermal gradients have been observed in
546 the experimental piles, advective-driven supply of oxygen through the height
547 of the pile is likely, especially near the atmospheric boundaries (Vriens et al.,
548 2019c). Indeed, in large-scale waste-rock piles, the generally coarser parti-
549 cles and larger pores promote oxygen ingress by barometric (wind-driven)
550 advection through the pile batters (Amos et al., 2009; Vriens et al., 2018,
551 2019c). Our simulation of pile 2C suggests that a purely diffusive flux from
552 oxygen from the top boundary is not sufficient to maintain sulfide oxida-
553 tion rates high enough to produce the measured sulfate concentrations in the

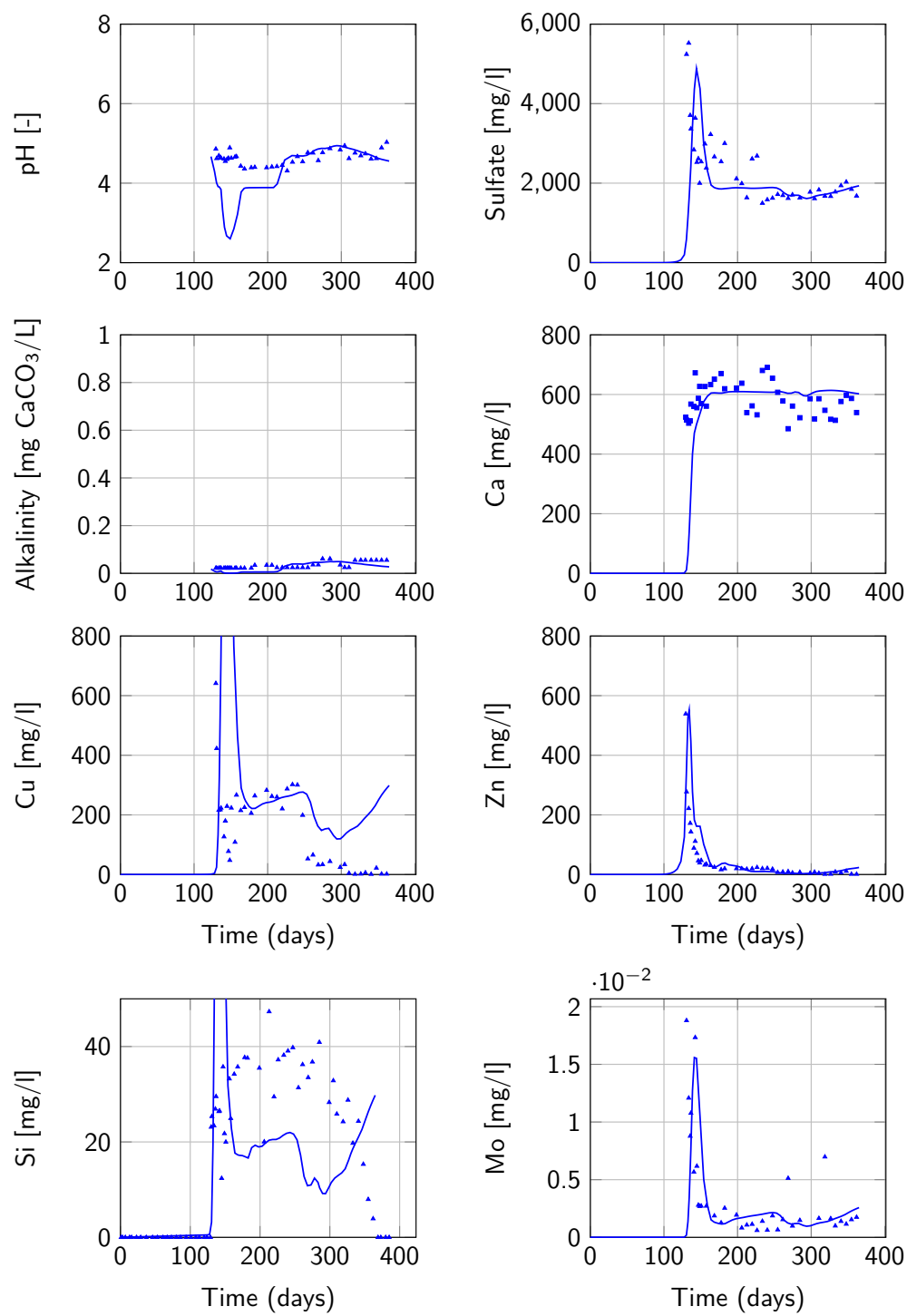


Figure 5: Observed and simulated basal drainage chemistry for the composite laboratory column for pH, alkalinity and aqueous concentrations of sulfate, Ca, Cu, Zn, Si and Mo.

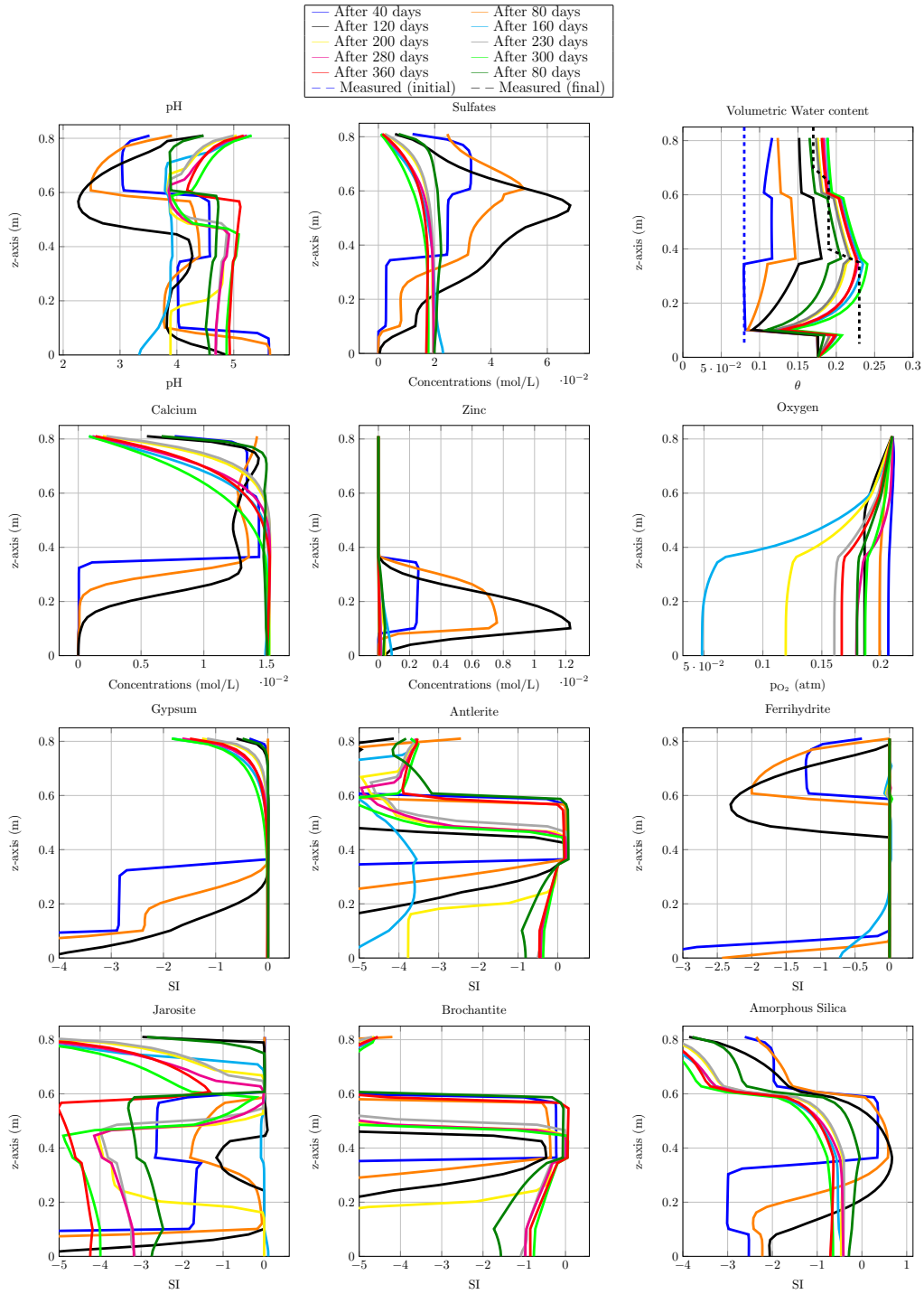


Figure 6: Depth-profiles of simulated solute concentrations and volumetric water content (upper two rows) and mineral saturation indices of selected mineral phases during the leaching of the composite laboratory column²³. No drainage exited the column until 120 days of weathering (Figure 5).

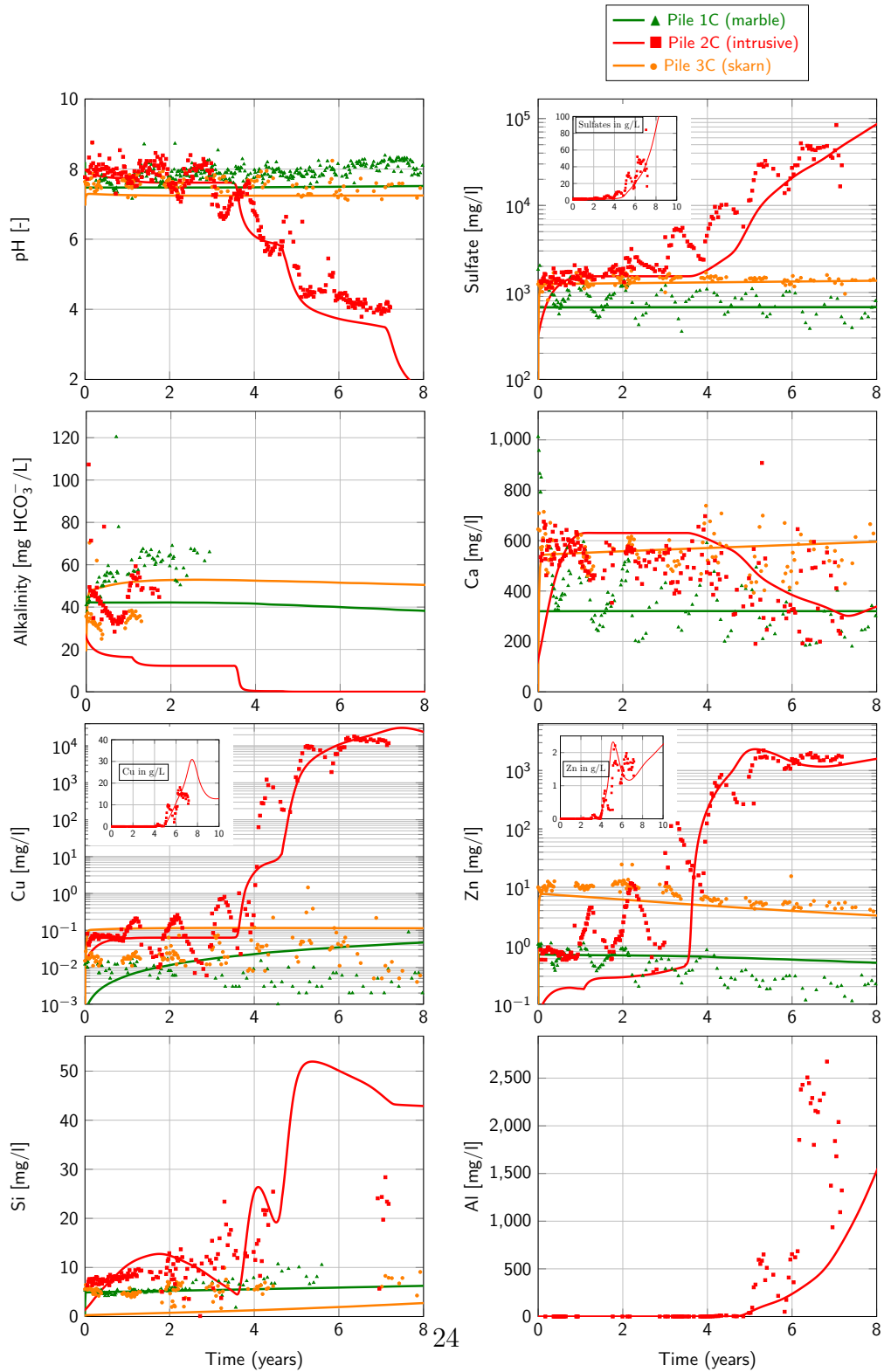


Figure 7: Measured and simulated drainage chemistry for lysimeter/tipping-phase C in experimental piles 1, 2 and 3 for pH, alkalinity and aqueous concentrations of Ca, sulfate, Cu and Zn (note logarithmic y-axes). The legend applies to all frames. Solid lines indicate model results while markers indicate measured values.

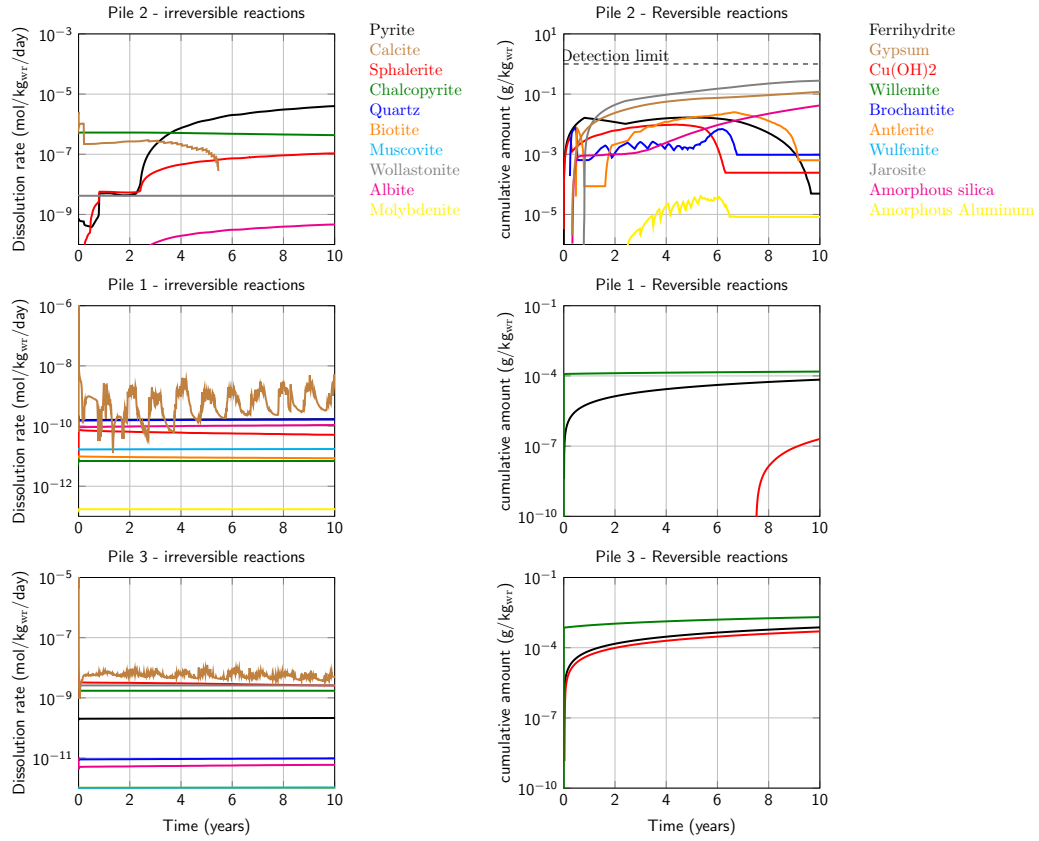


Figure 8: Simulated primary mineral dissolution rates (left column) and precipitated mass of selected secondary minerals (right column) during the weathering of the experimental piles. Simulated precipitation of secondary minerals are compared to a typical XRD detection limit of 0.1 wt-%

leachates ($\geq 50 \text{ g L}^{-1}$). This suggests that oxygen depletion is unlikely and that oxygen is supplied laterally through the pile batters by either diffusion and possibly advection. A lateral oxygen source is represented in the 1-D model as a constant oxygen pressure through the height of the pile 2C. Our adopted reactive transport framework and pile geometry do not explicitly include oxygen transport through sideward ingress into the piles. Therefore, the experimental waste-rock piles serve as a final test of the adopted one-dimensional uniform model formulation to reproduce waste-rock drainage dynamics at larger scales: the material in experimental pile 2C is similar to that in field barrel FB-I9 (Tables S3 and S4) and a quantitative comparison of reactive transport parameters between these two experiments can provide useful information regarding scale dependence of the adopted model (Vriens et al., 2020).

Simulated sulfide-oxidation rates in piles 1-3 varied between 10^{-9} and $10^{-6} \text{ mol dm}_{\text{bulk}}^{-3} \text{ day}^{-1}$ and align with bulk weathering rates that were experimentally determined from drainage loading rates, temperature profiles and *in-situ* poregas measurements, i.e. converted to molar units; 10^{-7} and $10^{-10} \text{ mol S dm}_{\text{bulk}}^{-3} \text{ day}^{-1}$ (Vriens et al., 2019a). Simulated pyrite reactive surface areas for the experimental piles were more than one order of magnitude lower compared to the field barrels. The reproduction of drainage acidification in pile 2C drainage was accompanied by acid-buffering dissolution of carbonate, Fe/Al-oxides, and silicate minerals (Figure 8) similar to the neutralization sequence described for FB-I9 above (Figure 4), with influence of Cu-sulfate (antlerite, brochantite) and jarosite. Additionally, simulated precipitation of secondary minerals aligned between simulations of FB-I9 and pile 2C (Figure 4 and Figure 8), with a general one order-of-magnitude lower cumulative precipitation.

Our reactive transport framework was able to simulate both FB-I9 and pile 2C, systems with same rock but on different scales, using similar geochemical factors (sulfide and silicate reactive surface areas and calcite effective rate constants; Table S6).

Finally, in all experimental piles, simulated drainage quality was strongly influenced by equilibria with calcite, ferrihydrite and gypsum (Figure 8). Simulated zinc concentrations were regulated by the precipitation/dissolution of willemite, a zinc silicate which has been previously identified at Antamina as a candidate for zinc attenuation (Skierszkan et al., 2016). The larger sizes of the waste-rock piles and higher average hydraulic residence time of ~ 1 year in the piles - much longer than those in the smaller-scale experiments

592 investigated - allowed secondary minerals precipitates to larger extents. This
593 yields a higher sensitivity to secondary mineral reaction rates compared to
594 smaller-scale field barrel FB-I9 (Figure S5).

595 4. Conclusions

596 Reactive transport modelling of coupled geochemical and physical trans-
597 port processes governing waste-rock weathering and drainage is prone to
598 uncertainties associated with process selection and parameterization. The
599 consistent reactive transport model we used to simulate the widely varying
600 waste-rock systems represents a trade-off between data availability, resolu-
601 tion, and quality versus model sophistication and parameter identifiability.
602 Well-constrained processes with high-quality data allowed some processes and
603 properties to be represented with higher confidence: we have a reasonably
604 good control on bulk-average mineral abundances and therefore waste-rock
605 reactivity, as well as on grain-size distributions and hydraulic (tracer tested)
606 parameters of the waste rock. Yet, some features such as the details of inter-
607 nal heterogeneity within the larger-scale piles remained unquantifiable (e.g.,
608 permeability) and require calibration. The deployed 1-D single-domain ap-
609 proach captured trends of smaller-scale experiments with good mass balance,
610 but it sacrificed spatiotemporal accuracy for identifiable model parameters
611 on longer-term larger-scale experiments fit for the purpose of assessing long-
612 term drainage patterns, but perhaps not shorter-time scale fluctuations or
613 the geochemistry at specific internal locations. The uncertainty associated to
614 the impact of misrepresenting internal saturation profiles on mineral rates,
615 despite being addressed in the sensitivity analyses, remains a crucial question
616 for the upscaling of our approach.

617 The presented model was applied to quantify individual processes and
618 feedbacks contributing to drainage dynamics. Simulations show that oxygen
619 availability reduced mineral reaction rates, predominantly in simulations of
620 larger-scale experiments (≥ 10 m) with reactive (several wt-% S) waste rock.
621 Reactive mineral surface areas estimated from physical grain size distribu-
622 tions provided consistent proportionality and could be used to reproduce
623 weathering dynamics of the same rock types on different experimental scales.
624 Finally, our reactive transport model revealed that secondary minerals play a
625 critical role in controlling drainage quality, with key phases in the simulated
626 experiments being based on experimental identification in prior studies (e.g.,
627 gypsum, Fe-oxyhydroxides as well as less-abundant phases such as antlerite

628 and brochantite). While antlerite and brochantite may serve as surrogates
629 for all Cu-sulfates (observational data suggests low abundance and poor crys-
630 tallinity), less-abundant secondary phases were crucial to reproduce certain
631 drainage dynamics, for instance Cu mobilization under acidifying conditions
632 in field barrel FB-I9 and experimental pile 2C. Our results highlight the use
633 of process-oriented and field-parameterized models to resolve dynamics that
634 are challenging to identify experimentally, especially from smaller-scale tests
635 of shorter duration.

636 Overall, we have shown that a well-chosen model formulation, applied
637 consistently and utilizing readily available parameters and thermodynamic
638 data, can explain drainage dynamics from waste-rock systems across sev-
639 eral orders-of magnitude different scales, while only fitting key reaction-rate
640 parameters. Many of the most consequential properties, particularly min-
641 eral abundances, and grain size distributions, can be constrained a priori,
642 reducing the uncertainty and number of fitting parameters that must be de-
643 termined. Hence, our model formulation is useful to explain the processes in
644 the experiments examined here and may be useful for similar and larger-scale
645 systems. However, some processes, such as heat transport and gas migration
646 (convection) or preferential flow (Blackmore et al., 2014), are negligible on
647 the scales examined here. Applicability of our approach is thus restricted
648 to relatively small-scale experiment displaying low degrees of heterogeneity.
649 Similarly, its performance for predictive purposes remains to be demonstrated
650 (Vriens et al., 2020), as processes affecting mineral reactivity and weathering
651 rates on longer timescales (e.g., reduced through passivation) were not con-
652 sidered. Despite these uncertainties, this work demonstrates that evidence-
653 based reactive transport models that explicitly account for key processes and
654 are parametrized experimentally may be used to examine and possibly pre-
655 dict waste-rock weathering dynamics across a laboratory-to-practice scale
656 range - contributing to improved risk management.

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669 **Supplementary Material**

670 Supporting Information (Supporting Methods, Tables S1-S8 and Figures
671 S1-S7) contains additional methodological details, parameters for the reactive
672 transport models and additional figures related to the presented simulations.

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