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978-1-108-81900-8 — Reconstructing Precambrian pCO2 and pO2 Using Paleosols
Nathan D. Sheldon , Ria L. Mitchell , Rebecca M. Dzombak
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1 Introduction

The study of fossil soils (paleosols) began in 1726 with the first description of a buried Quaternary soil along the Danube River in Hungary, and many of the early foundational figures in geology such as James Hutton and Charles Lyell recognized that major unconformities represented erosional events (Retallack, 2013). However, paleosols were largely considered a curiosity within the realm of soil science or Earth science for almost 240 years after the initial description, before systematic efforts to recognize and document paleosols took off in the 1970s and 1980s. Paleosol-specific classification schemes and advances in stable isotope (e.g. Cerling, 1984) and whole-rock geochemistry (e.g. reviewed in Retallack, 1991) opened up new quantitative paleoclimatic reconstruction approaches, which in turn led to the compilation of extensive records of Phanerozoic paleosols (Sheldon and Tabor, 2009). Identifying Precambrian paleosols is more challenging (Retallack, 1992) because common Phanerozoic paleosol features such as root traces could not exist prior to the evolution of land plants in the Silurian (e.g. Kenrick and Crane, 1997), and many Precambrian weathering surfaces or paleosols had been deeply buried and subjected to metasomatism and/or metamorphism (Retallack, 1991).

Interest in paleosols as archives of the Earth's atmospheric composition in the Precambrian began in the 1980s. Because soils form at the Earth's surface, in direct contact with its atmosphere, they are potentially a simpler archive to interpret than marine deposits or chemical sediments such as banded iron formations (BIFs). Although some earlier workers drew qualitative conclusions about atmospheric oxygen from paleosols (Dimroth and Kennedy, 1976; Gay and Grandstaff, 1980), Heinrich (Dick) Holland was the first to propose explicitly that the chemical composition of paleosols could offer quantitative insights into the composition of the atmosphere under which they formed (Holland, 1984). The broader context for Holland's pioneering work was a community-wide debate on the amount of oxygen in the Precambrian atmosphere and the question of whether there had been a state-change (typically referred to as the Great Oxidation Event; GOE) between a nearly anoxic world and weakly oxygenated one. The Dimroth–Kimberley–Ohmoto model (DKO; Ohmoto, 1997) postulated that the Earth was oxygenated to modern levels early on its history, possibly in the Hadean, and the Cloud–Walker–Kasting–Holland model (CWKH; Holland, 1999) proposed a multistep oxygenation increase, with modern levels reached only in the Phanerozoic. At the centre of both sides of the argument was the oxidation state of Fe in Precambrian paleosols (Figure 1). Today, the broad debate has essentially been decided in favour of the CWKH model, although evidence for episodic 'whiffs' of oxygen prior to the GOE

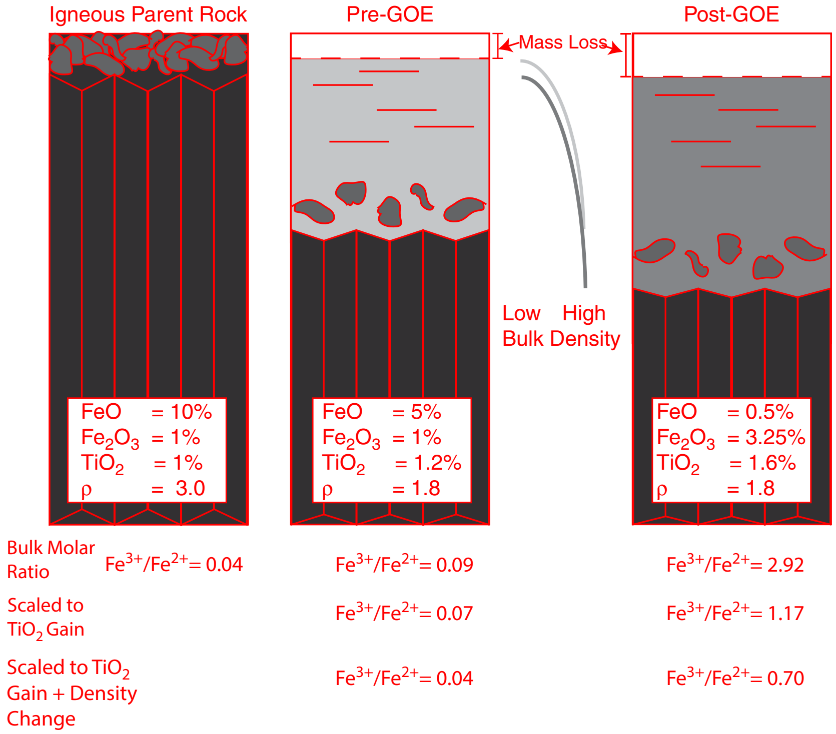

Figure 1 Schematic cartoons of pre- and post-GOE weathering. For both scenarios, exemplar data are given and in the table, changes in the Fe^{3+}/Fe^{2+} ratio are given for the bulk measured value, the ratio scaled to account for the immobile element Ti, and the ratio scaled for both Ti and that the bulk density of soil is less than that of bedrock. For the pre-GOE case, the Fe^{3+}/Fe^{2+} ratio appears to double relative to the parent material, but when mass balance and density change are accounted for, the value matches the parent rock. While the post-GOE Fe^{3+}/Fe^{2+} ratio has increased relative to the parent material, Fe^{2+} has not all been quantitatively retained in the soil given. If all of the parental Fe^{2+} had been oxidized to Fe^{3+}, then the 'fully oxidized' soil should have 6% Fe^{3+}. Thus, even though the Fe^{3+}/Fe^{2+} ratio indicates oxidation relative to the parent material, it fails to represent that Fe was still lost from the soil.

(Anbar et al., 2007) suggest that some of the arguments from the DKO model for evidence of occasional surface oxidation in the Archean were correct, even if their proposed levels of oxygen were never reached until the Phanerozoic.

While Holland was primarily interested in reconstructing pO_2, his interpretive framework for paleosols has led to a variety of approaches to reconstructing pCO_2 (e.g. Sheldon, 2006, 2013; Driese et al., 2011; Alfimova et al., 2014;

Kanzaki and Murakami, 2015) as well as more complex approaches to understanding pO_2 (Murakami et al., 2011; Yokota et al., 2013). Holland (1984; Holland and Zbinden, 1988; Pinto and Holland, 1988) proposed the following steady-state model for using paleosols to understand the balance between oxidation and carbon consumption (R) at the Earth's surface:

$$R = \frac{D_{O_2}}{D_{CO_2}} \sim \frac{0.25m_{FeO} + 0.5m_{MnO}}{2[m_{CaO} + m_{MgO} + m_{Na_2O} + m_{K_2O} + m_{CaMg(CO_3)_2}]} \tag{1}$$

where m_i values represent molar concentrations. D_{O_2} represents the O_2 required to oxidize all of the Fe^{2+} and Mn^{2+}, based upon the idea that they are the two most abundant reduced metals in most rocks. D_{CO_2} represents the carbonic acid required to remove all Ca, Mg, Na, and K, based upon the idea that they are the four most common rock-forming cations that are mobile during weathering (Sheldon and Tabor, 2009). Other rock-forming elements such as Al and Ti are essentially immobile during weathering, except under somewhat exceptional pH conditions (i.e. $pH < 4$ or $pH > 9$). Other elements like Si have complex weathering behaviours where they are immobile in some minerals (e.g. quartz) and highly mobile in others (e.g. feldspars). There are two key caveats to this approach: 1. post-burial alteration and diagenesis need to be considered, particularly with K, which is subject to metasomatic redistribution (Maynard, 1992; Driese et al., 2007); and 2. that Eq. (1) represents a case of 'one equation–two unknowns', meaning that either D_{O2} or D_{CO2} must be known or estimated to obtain the other value.

An example of this type of calculation, and of how it may be refined using more recent pCO_2 models can be found in Figure 2. Holland et al. (1989) estimated R for the ~1.9 Ga Flin Flon paleosol and, based upon various sensitivity tests, argued for a pO_2 ranging between 1.2×10^{-3} to 3×10^{-2} PAL (pre-Industrial atmospheric levels), with a best-guess value of 2×10^{-3} PAL, but noted that the pCO_2 could have varied over three orders of magnitude. Sheldon (2006) used a mass-balance model to estimate pCO_2 using the same dataset (Table 1), so by using that value and the calculated R value from Holland, it is possible to refine pO_2 estimates further (Figure 2). The revised estimates are both more precise relative to the earlier work that assumed pCO_2 without any quantitative constraints, and affirm results based upon marine proxies that suggest low pO_2 throughout the Proterozoic (Lyons et al., 2014; Planavsky et al., 2018).

These types of refinements to both estimates of pCO_2 and pO_2 based upon paleosols have implications for constraining temperature history and habitability of the early Earth, as well as providing guidance for what we might expect to find on other Solar System bodies or on exoplanets as we refine our ability to analyze

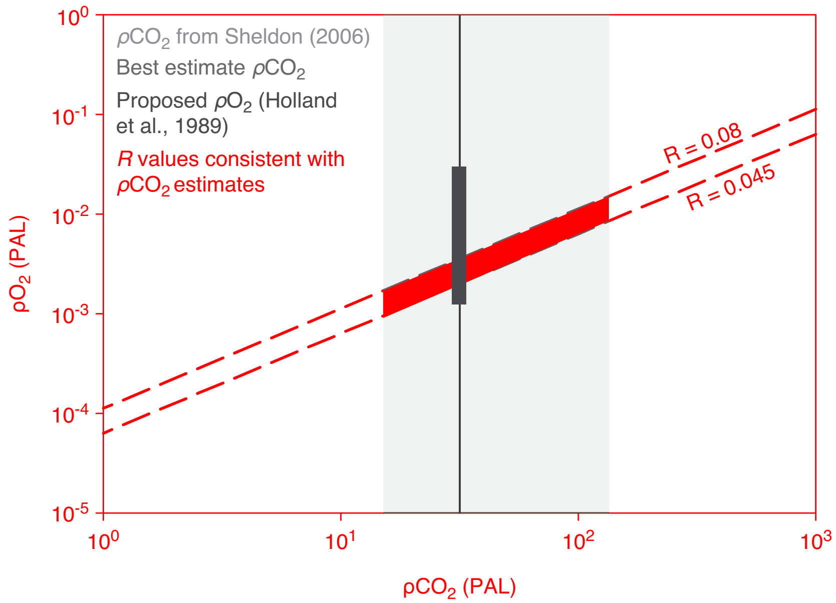

Figure 2 pCO_2 versus pO_2 for the 1.9 Ga Flin Flon paleosols. Holland et al. (1989) calculated R values (Eq. 1) for the Flin Flon paleosol or 0.045 (basalt parent) and 0.08 (greenstone parent) and used those values to calculate pO_2 ranging from 1.2×10^{-3} to 3×10^{-2}. Using pCO_2 estimates from Sheldon (2006) based upon the same dataset, we can refine estimated pO_2 further to 1.7×10^{-3} to 1.5×10^{-2}, which narrows the range and which affirms low Proterozoic pO_2 as proposed by various authors.

them remotely. Furthermore, quantitative estimates of pCO_2 and pO_2 have relevance for the geologic history of other greenhouse gases such as CH_4 or N_2O (e.g. Fiorella and Sheldon, 2017; Zhou et al., 2017). Changes in pO_2 are also linked to the history of seawater sulfate and to limits to biogeochemical cycling (e.g. Olson et al., 2016) in marine and terrestrial aquatic environments. For the rest of this Element, we will describe both previously proposed and currently used methods for reconstructing pCO_2 and pO_2 from paleosols, placing results from those methods into the broader Precambrian geologic context, examining some critical outstanding problems, and proposing several directions for future work.

2 Materials/Methods

Following the advent of land plants in the Silurian (Kenrick and Crane, 1997), one of the primary means for identifying paleosols is to look for root traces, which may range from kerogenized remains of the original roots to rhizoliths

Table 1 Strengths and weaknesses of different proxy approaches for $p\mathrm{CO}_2$ and $p\mathrm{O}_2$

Approach	**Strengths**	**Weaknesses**	**References**
$p\mathrm{CO}_2$			
Steady state[1,4]	Relatively few free parameters; should work for incomplete profiles	Diagenesis; requires assuming $p\mathrm{O}_2$ to calculate $p\mathrm{CO}_2$	Holland (1984); Holland and Zbinden (1988); Pinto and Holland (1988); Zbinden et al. (1988); Rye and Holland (1998)
Mineral equilibrium[1,5]	*Equilibrium K values well constrained for most minerals*	*Diagenetic alteration of mineral assemblage; assumes stoichiometric minerals; reliability of thermodynamic data; oversimplifies weathering*	Rye et al. (1995); Hessler et al. (2004)
Mass balance[3-4]	Firmly grounded in soil science	Diagenesis; requires assumptions for some parameters (e.g. MAP, soil formation time); non-quantitative	Sheldon (2006; 2013); Mitchell and Sheldon (2010); Driese et al. (2011); Alfimova et al. (2014)[2]; Rybacki et al. (2016)
Dissolution kinetics[3,5]	*Grounded in process-based understanding of weathering and mineral dissolution*	*Diagenesis; complex to apply; different kinetic assumptions give very different results; final answer is still basically a mineral equilibrium calculation and is subject to all of the issues associated with that method*	Alfimova et al. (2014)[2]; Kanzaki and Murakami (2015; 2018a, 2018b)[3]

Table 1 (cont.)

Approach	Strengths	Weaknesses	References
pO2			
Steady state[1,4]	Relatively few free parameters; should work for incomplete profiles	Diagenesis; requires assuming $p\text{CO}_2$ to calculate $p\text{O}_2$	Holland (1984); Holland and Zbinden (1988); Pinto and Holland (1988); Zbinden et al. (1988); Rye and Holland (1998)
Fe(III)/Fe(II) [1]	*Fe minimally impacted by diagenesis*	*Non-unique interpretations; ignores basic soil science*	Ohmoto et al. (1996); Holland (1999); Utsunomiya et al. (2003)
Mass balance[1,4]	Firmly grounded in soil science	Diagenesis; requires assumptions for some parameters (e.g. MAP, soil formation time)	Driese (2004); Driese et al. (2007); Murakami et al. (2016)
Oxidation kinetics[3,5]	*Grounded in process-based understanding of weathering and mineral dissolution*	*Complex to apply; simplistic set of minerals considered*	Murakami et al. (2011); Yokota et al. (2013)
Cr isotopes[1,4]	Potential to measure both source and sink; clearly reflects surface conditions; cycle is linked other redox-sensitive metal Mn	Cr reactions with ligands; relies on understanding of Mn oxidation; potential for mobilization during high-temperature alteration	Crowe et al. (2013); Babechuk et al. (2017, 2019); Colwyn et al. (2019)

[1] Denotes model that can be considered qualitative or semi-quantitative
[2] Denotes forward modelling approach
[3] Denotes inverse modelling approach
[4] Denotes a model that relies on assuming a key unknown variable
[5] Denotes a model that relies on stoichiometric minerals and equilibrium

that represent mineral replacement of roots to drab-haloed root traces that reflect redoximorphic conditions during the oxidation of the original organic matter following burial. Other common features include colour changes, horizonation, burrows, pedogenic carbonates, and diagnostic micro-structures (e.g. gilgai micro-relief in Vertisols) that can be used to reconstruct pedogenic processes (e.g. Retallack, 1991; Sheldon and Tabor, 2009). The elemental and isotopic composition of subsurface B horizons can be used to reconstruct a variety of features including mean annual precipitation (MAP), mean annual temperature (MAT), soil productivity, and atmospheric pCO_2 (Sheldon and Tabor, 2009). Unfortunately, some of those features (e.g. root traces, burrows) reflect complex life that evolved during the Phanerozoic and others (e.g. colour) can change during diagenesis or subsequent exposure. Furthermore, because the climofunctions that are used to reconstruct MAP or MAT are based upon modern vegetated ecosystems, they are inappropriate for use with Precambrian paleosols. This has not prevented some authors (intentionally not cited here) from misusing the Phanerozoic climofunctions, but, at present, readers should be skeptical of any paper that purports to reconstruct MAP or MAT quantitatively from a Precambrian paleosol. Finally, a curious feature of Precambrian paleosols is the dearth of pedogenic carbonate, which is common from the Silurian–present (Sheldon and Tabor, 2009). This, unfortunately, removes one of the primary ways that paleosols can be used to reconstruct pCO_2 (Cerling, 1984). There are at least four possible explanations for this difference between pre- and post-Silurian paleosols, presented in increasing order of likelihood: 1. pre-Silurian ecosystems were too wet or were aseasonal, so carbonate could not be formed; 2. post-Silurian carbonate growth is metabolically mediated by plant and/or microbial processes in the rhizosphere, so carbonate was rare prior to land plants; 3. soil productivity at depth was insufficient to produce enough CO_2 to promote subsurface carbonate growth; or 4. atmospheric pCO_2 was high enough that weathering environments were generally too acidic ($pH < 6$) for subsurface carbonate growth. Finally, even if Precambrian pedogenic carbonate is identified, because diagenetic alteration of pedogenic carbonate is likely, it will be relatively rare that a reliable reconstruction can be made.

Because of these challenges, other methods have been devised to reconstruct pCO_2 and pO_2 from Precambrian paleosols and to account for diagenetic alteration. Retallack (1992) outlined field criteria for identifying Precambrian paleosols, Maynard (1992) identified key geochemical observations from modern soils and postulated how they differed for Precambrian paleosols, and Rye and Holland (1998) proposed a set of six conditions that need to be met for the chemistry of a paleosol to be considered reflective of the original pedogenic processes: 1. composition different to the underlying parent material; 2. vertical

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changes in texture through the paleosol profile; 3. vertical changes in mineralogy through the paleosol profile; 4. vertical changes in chemistry through the paleosol profile; 5. evidence for soft-sediment deformation or processes; and 6. sub-greenschist facies metamorphic grade. If all of those conditions are met, then a number of different approaches exist for reconstructing pCO_2 (Figure 3, 5) and pO_2 (Figures 4–5) from Precambrian paleosols as outlined in the following. Strengths and weaknesses of each approach are summarized in Table 1.

One key point is that the approaches to understanding both pCO_2 and pO_2 from Precambrian paleosols encompass a range of model types that include purely observational models that are semi- or non-quantitative in terms of specific gas pressures (e.g. Fe^{3+}/Fe^{2+} ratio), forward modelling (e.g. Alfimova et al., 2014), and inverse modelling (e.g. Sheldon, 2006; Kanzaki and Murakami, 2015).

2.1 Methods for Reconstructing CO_2 Levels

Four different methods (Table 1) have been proposed for reconstructing atmospheric pCO_2 using paleosols: 1. steady-state oxidant demand versus acid demand (Eq. 1), 2. mineral equilibrium of co-existing phases, 3. mass-balance modelling of pedogenesis, and 4. mineral dissolution kinetics of pedogenesis. Generally speaking, regardless of which approach is taken, reconstructed pCO_2 during the Precambrian is consistently many times greater than pre-Industrial atmospheric levels (PAL). Among the three methods that have not yet been discussed, the third and fourth can be considered to provide reasonable constraints while the second is problematic for a number of reasons, but all will be discussed briefly. Equation 1 has shown an example of the first method and other papers using this approach are listed in Table 1.

2.1.1 Mineral Equilibrium

The principle behind reconstructing pCO_2 (or pO_2 for that matter) based upon mineral equilibrium is that if coexisting mineral phases were originally formed in equilibrium with one another, then that coexistence reflects the environmental conditions at the time of their formation. All of the previous attempts based upon paleosols (Rye and Holland, 1995), weathering rinds on river gravel clasts (Hessler et al., 2004), and BIFs (Ohmoto et al., 2004) have been based upon the presence or absence of carbonate minerals, typically siderite ($FeCO_3$), or Fe(II)-layered silicate minerals. For example, Hessler et al. (2004) considered the equilibrium between siderite and greenalite ($Fe_3Si_2O_5(OH)_4$) according to the following reaction:

$$3FeCO_3 + 2SiO_{2(aq)} + 2H_2O \Leftrightarrow \; Fe_3Si_2O_5(OH)_4 \tag{2}$$

and inferred, based upon the absence of greenalite, that pCO_2 at 3.2 Ga had to be above ~8x PAL for a reaction temperature of 25 °C. In theory, this approach is sound, but there are many issues (Table 1; summarized in greater detail in Sheldon (2006)) with this approach: 1. It assumes that the present-day mineral assemblage is the same as it was at the time of formation, even though many of the rocks have been deeply buried or obviously subjected to diagenesis; 2. It assumes perfectly stoichiometric minerals (e.g. pure siderite versus a mix of siderite and other carbonates); 3. It assumes the temperature is well known or can be estimated relatively precisely, but uncertainties of even 10 °C can dramatically change the results; 4. Most of the existing attempts rely on minerals such as greenalite that represent the metamorphic assemblage and which do not form at Earth's surface conditions; and 5. It assumes that the entire complex process of weathering can be reasonably captured by a single mineral-pair equation. Given all of those limitations, this method can be considered semi-quantitative at best.

2.1.2 Mass Balance

A third approach to reconstructing pCO_2 from paleosols is using mass-balance calculations that characterize acid consumption during pedogenesis. A full description of this modelling approach and a sensitivity analysis of the individual parameters that need to be assumed can be found in Sheldon (2006, 2013), but the basic principle is that the total amount of elemental loss relative to the parent material must be a function of the amount of acid (in the form of CO$_2$) consumed during pedogenesis, scaled for the length of time over which the paleosol formed. There are three potential sources of acid creation/consumption: 1. acid delivered by rain (X_{rain}), 2. acid delivered by direct diffusion from the atmosphere ($X_{diffusion}$), and 3. acid delivered from biospheric production ($X_{biology}$). Schematically, this is given as:

$$\frac{M}{T} = X_{rain} + X_{diffusion} + X_{biology} \approx pCO_2 \left[\frac{K_{CO_2} r}{10^3} + \kappa \frac{D_{CO_2} \alpha}{L} + f(biology) \right] \tag{3}$$

where M/T is the weathering flux (mol cm^{-2}yr^{-1}), K_{CO_2} is the Henry's Law constant for CO$_2$, r is the rainfall rate (cm yr^{-1}), D_{CO_2} is the diffusion constant for CO$_2$ in air, a is the ratio of diffusion in soil divided by diffusion in air for CO$_2$, κ is a constant that relates the ratio of seconds in a year to the number of cm^3 per mole of gas at standard temperature and pressure, and L is the depth to the water table,

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which for bedrock-parented paleosols, is equivalent to the decompacted thickness of the paleosol. In general, the parameter *f(biology)*, which represents some unknown function for the role of biology, is considered to be essentially zero. While it is unlikely that biological productivity was non-existent in the Precambrian, without a fossil record in most paleosols, this number is very difficult to constrain. Even in cases where microbial or fungal life was present, it was likely concentrated in the upper part of paleosols and sparse or non-existent with depth, which suggests that $f(biology) \ll X_{rain}$ or $X_{diffusion}$. The primary strengths of this approach are that it is relatively straightforward to quantify uncertainties, it gives estimates that are internally consistent for 2.7 Ga (Driese et al., 2011), 2.2 Ga (Sheldon, 2006), and 1.1 Ga (Mitchell and Sheldon, 2010; Sheldon, 2013) when there are multiple coexisting paleosols, and it gives results that are consistent with independent estimates from organic fossils and stromatolites (Figure 3). A final line of support for this model is that the degree of chemical weathering observed in both marine deltaic sediments (i.e. weathered surface sediments; Mitchell and Sheldon, 2016) and other paleosols not used to reconstruct $p\text{CO}_2$ tracks the $p\text{CO}_2$ history that can be reconstructed through the late Paleoproterozoic to early Phanerozoic (Figure 3). The primary weaknesses of this model are that it works best for bedrock-parented paleosols where L can be measured rather than assumed, and that r and T have to be assumed and impart significant uncertainty to the estimates of a factor of 3 (Table 1).

For example, Rybacki et al. (2016) applied the method to a 2.06 Ga weathering profile where L and T were essentially unknowns and did an extensive sensitivity analysis of those parameters. While their best-constrained $p\text{CO}_2$ estimates were in line with penecontemporaneous estimates, they noted that the range of possible error became much larger than when L or T is well constrained. Accordingly, they suggest cases where this method will not be applicable.

2.1.3 Dissolution Kinetics

The final approach to reconstructing $p\text{CO}_2$ from paleosols is through the use of mass dissolution kinetics. A full description of this modelling approach and a sensitivity analysis of the various parameters can be found in Kanzaki and Murakami (2015). In particular, anyone interested in this approach is directed to their extensive supplementary documentation, which outlines the rationale behind their parameterization in great detail. Briefly though, their method follows these steps: 1. calculate porewater anion and cation concentrations at the time of weathering, 2. compare charge balance of calculated anion and cations with carbonate species and dissolved CO_2, and 3. calculate $p\text{CO}_2$ by assuming equilibrium at a given temperature using a pH value derived from