



Reconciling the role of clay mineral formation on net alkalinity generation during rock weathering: Insights from reactive transport models of shale, granite, and basalt

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Abstract. Clay minerals, while ubiquitous in soil, have wide-ranging and countervailing impacts on global biogeochemical cycles. Their compositional diversity makes predicting their formation conditions and impacts on soil solution chemistry a grand challenge. In this proof of concept study, we unpack the influence of clay mineral formation on alkalinity generation during rock weathering: a key process regulating atmospheric CO₂ levels over geologic time. Because they remove aqueous Si and Al from solution during formation, clay minerals may enhance silicate mineral dissolution and thereby enhance alkalinity generation. However, clays can also offset the alkalinity produced during silicate dissolution by generating acidity when they form. To identify whether, or to what extent, clay minerals enhance alkalinity generation, we employ reactive transport models of idealized granite, basalt, and shale weathering over a range of environmental conditions. Clay mineral formation typically increases net alkalinity generation by enabling greater silicate dissolution. This enhancement is most pronounced at low fluid flow rates and low soil CO₂ concentrations when thermodynamic conditions require clays for continued silicate dissolution and sustained alkalinity generation. However, clay-enhanced alkalinity generation diminishes at low erosion rates when primary mineral supply decreases; in less common instances where chlorite forms, clay formation can lead to a net alkalinity consumption. Overall, clay minerals promote CO₂ drawdown and modify the silicate weathering feedback.

Short summary. Silicate dissolution by carbonic acid generates alkalinity, leading to marine carbonate formation and net CO₂ removal from the atmosphere. Clay minerals manipulate rock weathering by removing alkalinity during precipitation, but also promoting primary silicate dissolution by removing aqueous Si and Al. By improving silicate thermodynamics, clay formation generally increases net alkalinity generation, except when high pH conditions drive formation of certain clays that decrease net alkalinity.



1 Introduction

35 Rock weathering plays prominent roles in soil formation and global atmospheric CO₂ levels over geologic time. Canonically, the dissolution of silicate minerals by carbonic acid produces alkalinity that enables marine carbonate formation (Walker et al., 1981; Berner et al., 1983; Berner, 1994; Archer et al., 2000). As atmospheric CO₂ concentrations and thus global temperature increases, silicate dissolution rates increase and thereby remove more CO₂ from the ocean-atmosphere system (Walker et al., 1981; Berner et al., 1983; Deng et al., 2022). Many argue that Earth's long-term (> 1 Myr) climate stability
40 relies on this negative feedback loop (Walker et al., 1981; Berner et al., 1983; Velbel, 1993a; Berner and Caldeira, 1997; Kump et al., 2000; Winnick and Maher, 2018). To combat increases in atmospheric CO₂ concentrations, the application of crushed rock or minerals to enhance silicate weathering has been proposed and applied at small scale (Beerling et al., 2020, Beerling et al., 2024; Harrington et al., 2023; Geerts et al., 2025; Cong et al., 2025). Silicate weathering rates and thus CO₂ removal rates in the terrestrial subsurface are influenced by fluid infiltration rates (Maher, 2010; Maher, 2011; Maher and Chamberlain,
45 2014), temperature (White and Blum, 1995; West et al., 2005), lithology (Bluth and Kump, 1994; Dessert et al., 2003; Ibarra et al., 2016), vegetation (Drever, 1994; Kelly et al., 1998; Ibarra et al., 2019), rates of rock uplift and erosion (Gaillardet et al., 1999; Maher and Chamberlain, 2014; Torres et al., 2016; Rugenstein et al., 2019; Bufe et al., 2024), and the thickness of bedrock fracturing and chemical weathering (West, 2012; St. Clair et al., 2015). Another factor that may play a prominent role in silicate dissolution rates and alkalinity generation is the formation of clays (e.g., Zhu, 2005; Winnick and Maher, 2018;
50 Shaughnessy and Brantley, 2023; Ramos et al., 2024), which are ubiquitous in weathering systems.

Clay minerals transform the chemical conditions and physical structure of weathering environments. During bedrock weathering and soil formation, water percolates through pore networks, concentrating solutes until Fe and Al minerals, such as clays, precipitate from solution (Navarre-Sitchler et al., 2013; Brantley et al., 2017). At the profile scale, clay formation can
55 reduce the permeability of a porous medium, which slows fluid flow and can alter flow paths (Neuzil, 2019; Carcione et al., 2019). Thin, aluminosilicate-rich layers are commonly observed on the surface of feldspars undergoing dissolution (e.g., Chou and Wollast, 1984; Nugent et al., 1998), which could decrease reactive surface area and inhibit primary mineral dissolution when these clay layers have low porosity (Velbel, 1993b). Clay formation during the weathering process is sensitive to Al availability and speciation, which, in addition to primary silicate dissolution rates, is influenced by pH and organic acid concentrations (Fig. 1) (Lawrence et al., 2014). From a thermodynamic perspective, the pace of primary silicate dissolution
60 can be altered by precipitation of secondary silicate minerals through their influence on primary mineral saturation states (Nagy et al., 1991; Alekseyev et al., 1997; Zhu, 2005; Zhu and Lu, 2009; Zhu et al., 2010; Maher et al., 2006; Maher et al., 2009; Winnick et al., 2022). Dissolution of primary silicate minerals produces higher concentrations of solutes, such as silicon (Si), aluminum (Al), and sodium (Na), as water is transported down-profile (Shaughnessy and Brantley, 2023) (Fig. 1). As clay
65 minerals form, they remove Al and Si from solution, maintaining undersaturation of primary minerals and allowing primary minerals to continue to dissolve down-profile (Maher et al., 2006; Maher et al., 2009; Zhu et al., 2010; Winnick et al., 2022).



While clay formation may enable greater primary mineral dissolution, its impact on net alkalinity fluxes and CO₂ drawdown may be distinct. By removing cations from solution and incorporating them into their structure or onto exchange sites, clays typically consume alkalinity (Garrels, 1965; Mackenzie and Garrels, 1966a; Mackenzie and Garrels, 1966b; Isson and Planavsky, 2018; Isson et al., 2020). Therefore, clays can alter the amount of alkalinity delivered to the ocean by removing cations (decreasing alkalinity) or by improving silicate dissolution (increasing alkalinity) (Fig. 1). The formation of clay species that incorporate conservative cations (Na⁺, K⁺, Ca²⁺ and Mg²⁺) into their structures (e.g., illite) or have high ion exchange capacities (e.g., smectite) consume significant amounts of alkalinity whereas the formation of phases that lack both alkaline/alkaline Earth cations and high exchange capacity (e.g., kaolinite) do not impact the alkalinity budget (Isson et al., 2020). Due to the numerous types and chemical variation of clay minerals (e.g., Hazen et al., 2013), clay formation can remove a wide range of solutes and thus the effect of clay formation on net alkalinity generation during silicate weathering requires further study.

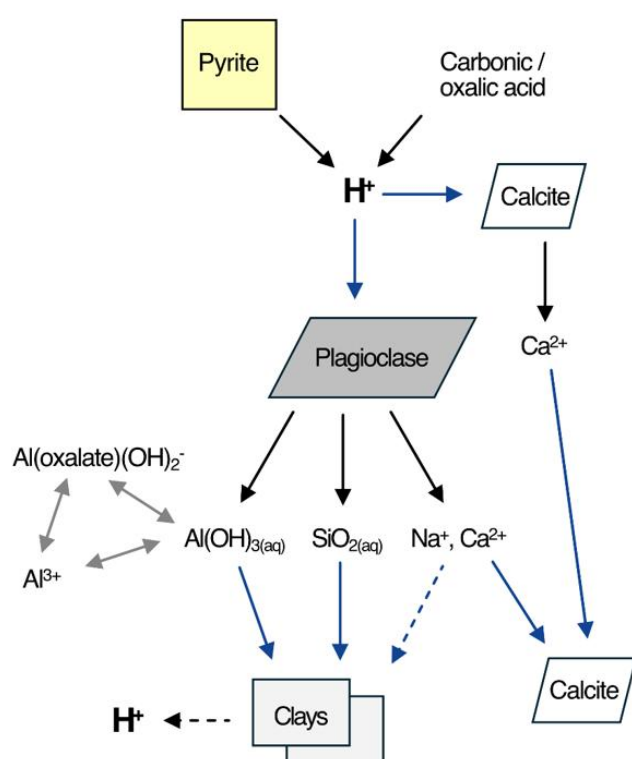


Figure 1: Relationship between sulfide, carbonate, and silicate dissolution as well as clay and carbonate precipitation along weathering fronts. Addition of ions illustrated with black arrows, loss of ions with blue arrows, and complexation with gray arrows. Pyrite dissolution removes alkalinity, while carbonate dissolution generates alkalinity. Plagioclase dissolution generates Al, Si, and alkalinity that may be incorporated into clays, such as kaolinite, illite, and smectite. The relationship between weathering rates and alkalinity generation may be tied to clay formation rates, Al speciation, and reaction fronts dependent on rock type. When silicate dissolution acts in concert with carbonate precipitation, CO₂ can effectively be removed from the atmosphere.



Since alkalinity generation is dependent on mineralogy (Bluth and Kump, 1994; Dessert et al., 2003; Ibarra et al., 2016), the influence of clay formation on silicate dissolution and net alkalinity generation should vary among constitutive rock types at the Earth's surface. Granites, basalts, and shale are three of the main subaerial rock types on Earth's surface (Ronov, 1972; Hartmann and Moosdorf, 2012) and thus serve as representative rock types that play a role in the global silicate weathering feedback. Fine-grained sedimentary rocks, hereafter referred to as shales, contain high levels of detrital clays, which provide ample surface area for additional clay formation as primary silicate minerals dissolve. Pristine granite and basalt do not contain clays, but as they weather, these rock types typically form detectable clay-rich zones with high surface area (Gilkes et al., 1973; He et al., 2008; Rasmussen et al., 2010; Hampl et al., 2023). As primary silicate minerals like plagioclase dissolve, clays, such as kaolinite, illite, and smectite, often form, which can concentrate near surface and move progressively deeper with increased weathering extent (Smith, 1957; He et al., 2008; Rasmussen et al., 2010). Basalt, which is often applied to soils for enhanced rock weathering, typically has greater plagioclase content than granite or shale, and contains more easily weathered minerals, such as pyroxene and olivine, that may generate additional alkalinity and clay minerals as a result (Harrington et al., 2023; Cong et al., 2025).

The dynamics of clay mineral formation along weathering profiles may shift dramatically amongst shale, granite, and basalt. The types of clay and their formation rates closely relate to Si and Al concentrations as well as pH, which are influenced by reaction fronts involving silicate and non-silicate phases. Shales often contain carbonate minerals, such as dolomite or calcite (Yaaton, 1962) and the sulfide mineral pyrite due to the reducing conditions in which they form (Khan et al., 2022; Zhou et al., 2024). As these shales weather, they form reaction fronts where downward flowing meteoric water reacts with carbonate and sulfide minerals that result in sharp increases in reaction rates over narrow depths (Jin et al., 2010; Brantley et al., 2013; Brantley et al., 2017; Wan et al., 2019; Gu et al., 2020; Stolze et al., 2023), accounting for the greatest proportion of weathering fluxes along an entire profile (Lichtner et al., 1986). Dissolution of silicate minerals, such as plagioclase, K-feldspar, amphibole, and olivine release Si, Al, and alkalinity, driving clay formation. Clay formation may drive additional silicate dissolution by removing solutes until saturation is reached at depth, releasing greater alkalinity that is difficult to directly attribute to secondary mineral precipitation.

In this proof of concept study, we use batch and one-dimensional (1-D) reactive transport models to test the thermodynamic influence of clay formation on primary silicate dissolution and together their control on net alkalinity generation. We provide simplified analyses of alkalinity generation at variable CO₂ concentrations in models that include and exclude clay formation.

The exclusion of clay does not represent a natural system but instead allows us to more directly illustrate the impact of clays on the thermodynamics of silicate dissolution and alkalinity generation through the net weathering reaction (e.g., Bouchez and Gaillardet, 2014; Ibarra et al., 2016; Winnick and Maher, 2018). The sensitivity of net alkalinity generation to mineralogy is analyzed by comparing silicate dissolution and clay formation in shale, granite, and basalt, with a particular focus on their dependencies with reaction fronts. Previous reactive transport studies have studied the co-evolution of reaction fronts and clay



120 mineral formation (Lichtner and Waber, 1992; Lawrence et al., 2014; Heidari et al., 2017; Winnick et al., 2022; Stolze et al.,
 2023; Stolze et al., 2024). However, inconsistent results among these studies make it challenging to discern the source of the
 disparities, which could be due to differences in ascribed mineralogies or modeling strategies. By generating reaction fronts
 across different mineral assemblages using consistent modeling techniques, we aim to more explicitly apportion the influence
 of clay formation on alkalinity generation and its dependence on both environmental and extrinsic weathering drivers.

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2 Methods

2.1 Modeling software

Rock weathering is simulated using the reactive transport software CrunchTope, which uses a finite difference approach to
 solve the advection-dispersion-reaction equation for conserved solutes and gases in space and over time (Druhan et al., 2013;
 130 Steefel et al., 2015). The equation, in its generic, one-dimensional form, can be expressed as

$$\frac{\partial C_i}{\partial t} = -v \frac{\partial C_i}{\partial x} + \alpha v \frac{\partial^2 C_i}{\partial x^2} + \frac{\rho}{\phi} \sum_j R_j(C_j) \tag{1}$$

where C_i is the concentration (mol/L) of a given solute i , v is the flow velocity (m/yr), α is the dispersivity (m) for solute i , ρ
 is the soil density (kg soil/dm³ soil), ϕ is the porosity (dm³ water/dm³ soil) and $\sum_j R_j(C_j)$ represents the sum of all chemical
 reactions R_j (mol/kg soil/yr) affecting the concentration of solute i . These reactions include mineral dissolution and formation,
 135 surface and aqueous complexation, aqueous speciation, and microbially facilitated oxidation and reduction. The uplift and
 weathering of solid phase X_k (mol/kg soil) is shown as

$$\frac{\partial X_k}{\partial t} = u \frac{\partial X_k}{\partial x} - \sum_j R_j(C_j). \tag{2}$$

where uplift u (m/yr) advects minerals up through the domain (opposite fluid flow) but are subject to the same reactions as
 shown in Eq. (1). Here the sign of the reaction term is opposite Eq (1) since loss of mineral mass corresponds to an accrual of
 140 solutes in the aqueous phase, and vice versa.

Table 1: Workflow of silicate weathering models

Type of model	Mineral reactions present	Aqueous reactions present	Parameters tested
Batch reactions	Plagioclase (and kaolinite)	None	Presence of kaolinite, plagioclase content, CO ₂ concentration
Simple 1-D reactions	Plagioclase (and kaolinite)	None	Presence of kaolinite, plagioclase content, CO ₂ concentration



1-D rock reactions

See Table S1

Fe(II) oxidation, Presence of clays, rock type, CO₂
aerobic respiration concentration, flow rate, erosion rate,
oxalate concentration

2.2 Batch models of plagioclase dissolution and kaolinite formation

145 To illustrate how clay minerals can induce additional plagioclase dissolution without the influence of advective and diffusive transport, 0-D batch simulations are conducted with and without clay formation enabled (Table 1). The clay-free models do not represent a realistic scenario but instead provide first-order constraints on how clays remove Si and Al to alleviate thermodynamic limits for plagioclase dissolution. These batch simulations contain highly simplified mineralogy to remove confounding factors (e.g., clay stoichiometry) on alkalinity. Plagioclase (Alb80:An20) is used as the sole primary silicate since
150 plagioclase represents the key silicate mineral dissolving across shale, granite, and basalt (Maher et al., 2009; Ferrier and West, 2017; Winnick et al., 2022) (Table S1). For these simple simulations of plagioclase dissolution and clay formation, kaolinite is chosen as the single representative clay since it is the major clay formed during subsequent simulations of shale, granite, and basalt weathering, which also include illite, smectite, chlorite, and gibbsite (Table S1). Kaolinite removes no alkalinity, so these simplified batch models represent best case scenarios of how clays drive additional alkalinity generation. Since kaolinite
155 has no direct effect on alkalinity, these models also clearly illustrate the thermodynamic influence of clay formation on plagioclase dissolution and alkalinity generation.

Silicate dissolution has been modeled using non-linear or parallel rate laws that recreate empirical reactions rates versus saturation state (Alekseyev et al., 1997; Hellmann and Tisserand, 2006). More mechanistic surface-based models account for
160 the effects of H⁺ and Al³⁺ on the rates plagioclase dissolution rates (Helgeson et al., 1984; Oelkers et al., 1994). Here, plagioclase dissolution and kaolinite precipitation reactions are modeled using a pH- and Al-dependent Transition State Theory (TST)-style rate law (Lasaga, 1984; Steefel et al., 2015). For example, the dissolution of plagioclase into solution was calculated by

$$R = k_1 \prod_j a_j^{x_j} A \left(1 - \frac{Q}{K_{eq}(T)} \right) \quad (3)$$

165 where k_1 ($10^{-15.4}$ mol/m²/s) is the rate constant, $\prod_j a_j^{x_j}$ is the product of solute activities that inhibits or catalyzes the dissolution rate, x_j is the degree of dependence, A is the total mineral surface area (m² surfaces/kg soil), Q is the ion activity product, and $K_{eq}(T)$ is the temperature-dependent equilibrium constant of the reaction.

Plagioclase is modeled as a dissolution-only reaction, which uses a TST-style rate law to determine dissolution rates, but
170 prevents unwarranted precipitation of plagioclase. Kaolinite is modeled as a reversible TST reaction where kaolinite could both dissolve and precipitate. Kaolinite precipitation could influence the plagioclase dissolution rate by removing Si and Al



from solution, allowing plagioclase to remain undersaturated. Secondary precipitation rates have previously been observed to control dissolution rates of primary silicates (Alekseyev et al., 1997; Zhu and Lu, 2009; Zhu et al., 2010).

175 Batch experiments contain either 8, 15, or 50 volume percent plagioclase to test how higher primary silicate content influence clay formation and alkalinity generation over time. An addition of 10% kaolinite to each clay model promotes robust clay formation, while non clay simulations contain 0% kaolinite. For consistency, porosity is set at 25% across simulations by adjusting the amount of quartz (with a negligible reaction rate). For example, if a simulation has 15% plagioclase and 10% kaolinite, 50% quartz is included. Batch reactions are run up to 1,000,000 years with equilibrium achieved by 100,000 years
180 in all simulations. As plagioclase and kaolinite react, special attention is paid to alkalinity generated at 2.5 years, which is equivalent to the transit time of water in the 1-D models (section 2.3).

2.3 Reactive transport of plagioclase dissolution and kaolinite formation

In conjunction with the batch models, simple 1-D models of plagioclase dissolution and kaolinite formation are also conducted,
185 to visualize silicate dissolution and clay formation with depth in a weathering profile. The chemical evolution of silicate dissolution and clay formation is roughly equivalent spatially along a weathering profile versus temporally in a batch reaction. However, in the 1-D models, since mineralogy slowly evolves and a gradational weathering front appears, reaction rates and aqueous chemistry are slightly affected. Simple 1-D models are conducted with 8%, 15%, or 50% plagioclase along with 0% or 10% kaolinite and variable quartz content for a porosity equal to 25%. A 10 m depth is selected to allow plagioclase to
190 approach equilibrium without the inclusion of clay formation. With a total depth of 10 m and a Darcy flux of 1 m/yr, the water residence time is 2.5 years at the base of the column. Weathering profiles are simulated over 250,000 years as water flowed through a one-dimensional profile composed of 200 uniform grid cells with 5 cm widths (total of 10 m). In all 1-D models, we focus on results at 10,000 years when plagioclase is still plentiful, but reaction fronts have started to develop to best illustrate the influence of clay formation on silicate dissolution and alkalinity generation.

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2.4 Reactive transport models of rock weathering with shale, granite, and basalt mineral assemblages

Adding more realistic mineralogy (including non-silicate minerals and additional clay minerals), rock weathering is simulated for shale, granite and basalt to provide insight into the influence of mineralogy and reaction fronts on silicate weathering and net alkalinity generation. Equilibrium constants are primarily from the EQ3/EQ6 thermodynamic database (Wolery et al.,
200 1990) with rate constants and surface areas taken from various studies (Pokrovsky et al., 2005; Maher et al., 2009; Lawrence et al., 2014; Stolze et al., 2023).

The simulated shale contains primarily quartz, plagioclase, various clay minerals, Ca carbonate, and Fe sulfide, representing an average shale mineralogy (Table 2) (Yaaton, 1962; Golla et al., 2021; Stolze et al., 2023). The shale contains 8% plagioclase
205 of mostly felsic composition (Alb80:An20) as modeled in the simple batch and 1-D models. As observed in typical shales (Gu



et al, 2020; Golla et al., 2021), the modeled shale contains both 1:1 and 2:1 clays: kaolinite ($\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$) (1:1), illite ($\text{K}_{0.6}\text{Mg}_{0.25}\text{Al}_{2.3}\text{Si}_{3.5}\text{O}_{10}(\text{OH})_2$) (2:1), smectite ($\text{Ca}_{0.165}\text{Al}_{2.33}\text{Si}_{3.67}\text{O}_{10}(\text{OH})_2$) (2:1), and chlorite ($\text{Mg}_5\text{Al}_2\text{Si}_3\text{O}_{10}(\text{OH})_8$) (2:1:1) as well as the Al hydroxide gibbsite ($\text{Al}(\text{OH})_3$). Illite is the primary clay included in the shale simulations with 33% by volume, consistent with most shales (Blatt and Tracy, 1996). A smaller proportion of smectite (10%), chlorite (3%), kaolinite (3%), and gibbsite (1%) are also included in all shale simulations. Dolomite is chosen to represent carbonate minerals in shale simulations since it is often the primary carbonate observed in shales (Wan et al., 2019; Stolze et al., 2023). Additionally, pyrite is also included since pyrite is often found in shales that have not been oxidatively weathered. Dolomite and pyrite form reaction fronts, which control oxidative and acid-base weathering dynamics. Dissolved oxygen reacts both with pyrite and aqueous Fe(II), forming Fe(III), which quickly precipitated as Fe(III) hydroxide (Table S1).

Table 2: Mineral compositions of modeled rock types

Mineral	Volume percent	Mineral	Volume percent	Mineral	Volume percent
Shale		Granite		Basalt	
Quartz	19%	Quartz	43%	Plagioclase	40%
Plagioclase	8%	K-feldspar	30%	Pyroxene	25%
Dolomite	6%	Plagioclase	15%	Volcanic glass	15%
Pyrite	0.5%	Biotite	5%	Olivine	5%
Fe(OH) ₃	2%	Amphibole	2.0%	Fe(OH) ₃	1%
solid organic matter	1%	Fe(OH) ₃	0.1%	Kaolinite	0.1%
Illite	33%	Kaolinite	0.1%	Illite	0.1%
Kaolinite	3%	Illite	0.1%	Smectite	0.1%
Smectite	10%	Smectite	0.1%	Chlorite	0.1%
Chlorite	3%	Chlorite	0.1%	Gibbsite	0.1%
Gibbsite	1%	Gibbsite	0.1%	Porosity	13.5%
Porosity	13.5%	Porosity	4.4%		

The granite contains nearly double the amount of plagioclase (15%) than shale (8%), but with the same chemical composition (Alb80:An20). The granite includes 43% quartz and 30% K-feldspar. The granite also contains quartz (43%), K-feldspar (30%), biotite (5%), which slowly react with oxygen over time, generating Fe(III), which precipitates as Fe(III) hydroxide as well as amphibole (2%) that generates significant amounts of alkalinity. In CrunchTope, a mineral must initially be present to form during the simulation, so minimal amounts of illite, kaolinite, smectite, chlorite, and gibbsite are included in granite and basalt models to allow clays to form during the weathering process (Table 2). The granite includes 0.1% of all clays or gibbsite, which allows these secondary minerals to form as plagioclase weathered away.



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The basalt is composed largely of plagioclase (40%) with a mafic endmember (An100). The secondary minerals included are kaolinite, illite, smectite, chlorite, and gibbsite (all at 0.1%), which are identical to the granite. The basalt also includes 25% pyroxene ($\text{CaMg}_{0.57}\text{Fe}_{0.43}\text{Si}_2\text{O}_6$), which oxidizes slowly over time, generating Fe(III) as well as volcanic glass (15%) and olivine (5%), which react relatively rapidly.

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2.5 Boundary conditions for reactive transport models

For most 1-D simulations, water infiltrates at a rate of 1 m/year with a dispersivity of 10 cm (Eq. 1), which generates a dispersion coefficient of $0.1 \text{ m}^2/\text{year}$. To test the impact of flow rate on clay formation, simulations of granite, basalt, and shale weathering, which includes carbonate reactions, are also run at 0.25 m/year and 2 m/year. CrunchTope allows for the modeling of erosion by adding new material (with a composition identical to the initial bedrock) to the bottom of the domain at the same rate that weathered material is removed from the top of the domain. To demonstrate chemical weathering of new rock in flat regions (e.g., application of basalt for enhanced rock weathering), modeled rocks erode at a relatively low rate of 0.01 mm/year for most 1-D simulations. These models generate weathering fronts that move down-profile over model time since chemical weathering rates are faster than physical erosion rates. Several models are also run at higher erosion rates of 0.2 mm/year to allow erosion of weathered material to balance chemical weathering and promote steady state conditions within our modeling timeframe. Models under these higher erosion rates are compared to analogous models at low erosion rates to illustrate how weathering intensity shifts the role of clays in generating alkalinity.

Our top-down rock weathering models uses steady boundary conditions. For 1-D simulations, a Dirichlet (constant value) boundary condition is applied at the top of the profile with an idealized rainwater composition flowing into the profile. The rainwater contains low concentrations of primary solutes with a temperature of 15 degrees C, representative of an average rainwater composition and temperature (Table S2) (Carroll, 1962). Primary solutes form a variety of secondary solutes through aqueous complexation and speciation (Table S3). Aqueous aluminum complexes with hydroxide, oxide, and oxalate, while Ca, Mg, and Na form carbonate and chloride complexes. The chemistry of the inflowing water and atmosphere are assumed to be constant over the entire simulation, which allows for more direct comparisons of the effect of mineralogy, organic compounds, feldspar dissolution type, flow rate, and erosion rate. The weathering profiles are fully water saturated with gases diffusing down-profile at $0.01 \text{ cm}^2/\text{s}$. An initial CO_2 concentration of 15,000 ppm, representative of common elevated pCO_2 levels in soil (Brook et al., 1983; Romero-Mujalli et al., 2019), is used at the top of the profile for base models of shale, granite, and basalt weathering to recreate solute release in natural systems. Atmospheric O_2 is set at 20%, which equilibrates with inflowing water. O_2 reacts with pyrite, biotite, or pyroxene during shale, granite, or basalt weathering, respectively. Aerobic respiration of O_2 is coupled to oxidation of oxalate through a Monod-type kinetic formulation (Lawrence et al., 2014) (Table S1).



CO₂ concentrations are also varied to test their impact on silicate weathering, clay formation, and alkalinity generation. CrunchTope calculates the pH using charge balance to account for acidification by CO₂ as H₂CO₃ dissociates to HCO₃⁻. Winnick and Maher (2018) calculates and models the influence of CO₂ concentrations on silicate weathering and clay formation approaching and at equilibrium with primary and secondary minerals. This study develops scaling relationships between CO₂ concentrations and weathering rates, but it does not directly test how the absence of clay formation or the type of lithology affects silicate dissolution rates. Here, we aim to demonstrate how clay formation impacts weathering rates and alkalinity generation at different CO₂ concentrations.

2.6 Alkalinity determinations

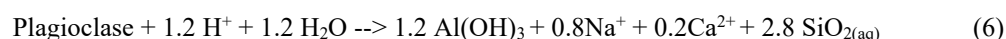
The balance of silicate dissolution and clay formation is illustrated by alkalinity calculations. Total alkalinity is calculated using the explicitly conservative definition of Wolf-Gladrow et al. (2007), which is equal to the sum of conservative cations and anions and the total concentration of N and S species:

$$TA = Na^+ + K^+ + Li^+ + 2 \cdot Mg^{2+} + 2 \cdot Ca^{2+} + 2 \cdot Sr^{2+} - Cl^- - 2 \cdot SO_4^{2-} - NO_3^- \quad (4)$$

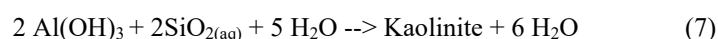
Total alkalinity is calculated using the generated CrunchTope concentration files as the sum of charge from Na⁺, K⁺, Ca²⁺, Mg²⁺, Li⁺, and Sr²⁺ minus Cl⁻, SO₄²⁻, and NO₃⁻. This expression is equivalent to the total alkalinity calculated by using the excess of all proton acceptors versus donors (includes all Al, DOC, and DIC species) relative to their reference level species at a pH of 4.5 (Dickson, 1981; Middelburg et al., 2020). The amount of alkalinity added (ΔA) by chemical reactions occurring across the weathering profile is calculated by subtracting the initial alkalinity of the idealized rainwater (TA₀) from the average alkalinity (TA_{ave}) observed along the profile:

$$\Delta A = TA_{ave} - TA_0 \quad (5)$$

As silicates dissolve, they generate alkalinity by contributing Na⁺, K⁺, Ca²⁺, and Mg²⁺ into solution. During plagioclase dissolution, 1.2 units of total alkalinity are generated:



Kaolinite has no effect on total alkalinity:



3 Results

We first present the results of batch models to demonstrate how kaolinite formation drives silicate dissolution and alkalinity generation by extending when plagioclase reaches equilibrium. We compare simple batch models with 1-D models of plagioclase dissolution and clay formation to demonstrate how reactive transport impacts the approach to equilibrium. The simple 1-D models are then compared with 1-D models of shale, granite, and basalt that contain more realistic silicate and clay mineralogies. With the inclusion of these minerals and their associated reaction fronts, the reactive transport models delineate how mineral weathering reactions proceed with depth for each of the three rock types. We also demonstrate the importance of



CO₂ concentrations and flow rate on silicate dissolution and clay formation. We then explore the thermodynamics of clay formation and how the types of clays formed influences alkalinity generation.

3.1 Kaolinite boosts plagioclase dissolution

295 Our simple batch models provide direct evidence for clay mineral formation engendering additional plagioclase dissolution. Initially, total alkalinity is identical between clay-containing and no clay models since kaolinite does not affect total alkalinity (Eq. 7) (Fig. 2A). Simulations that exclude kaolinite formation approach equilibrium within the first 10 years of model time as plagioclase dissolution saturates the fluid in Si and Al (Fig. 2A). Simulations including kaolinite take much longer (approximately 10,000 years) to nearly reach equilibrium due to the slower precipitation rate constant of kaolinite versus
300 plagioclase dissolution. As these simulations near equilibrium, kaolinite precipitation and plagioclase dissolution slow as observed by the slower increase in alkalinity with time (Fig. 2A).

In batch reactions at 15,000 ppm CO₂ with 15% plagioclase and no kaolinite formation, pH only increases from 4.97 to 6.15 with Al³⁺ still representing a significant proportion of the total Al concentration (125 μM) at 0.41 μM. At this circumneutral
305 pH and nontrivial Al³⁺ concentration, plagioclase reaches equilibrium with only 0.38 mM Na, 0.05 mM Ca, and 0.29 mM Si dissolved. Since kaolinite removes Si and particularly Al from solution, while not removing alkalinity, clay containing models predictably promotes greater plagioclase dissolution and generates more alkalinity than no clay models, but the degree of alkalinity improvement over time is substantial. Since kaolinite has a higher Al/Si ratio (1:1) than plagioclase (3:7), Al is removed to near completion, while Si concentrations actually increase due to greater plagioclase dissolution. The total Al
310 concentration is only 0.12 μM with a trivial amount as Al³⁺, promoting greater plagioclase dissolution as observed by Na, Ca, and Si concentrations increasing to 1.09 mM, 0.23 mM, and 1.58 mM, respectively. As more plagioclase dissolves in the clay-containing simulation, alkalinity eventually is 8.5 times larger with the inclusion of clays (Fig. 2A).

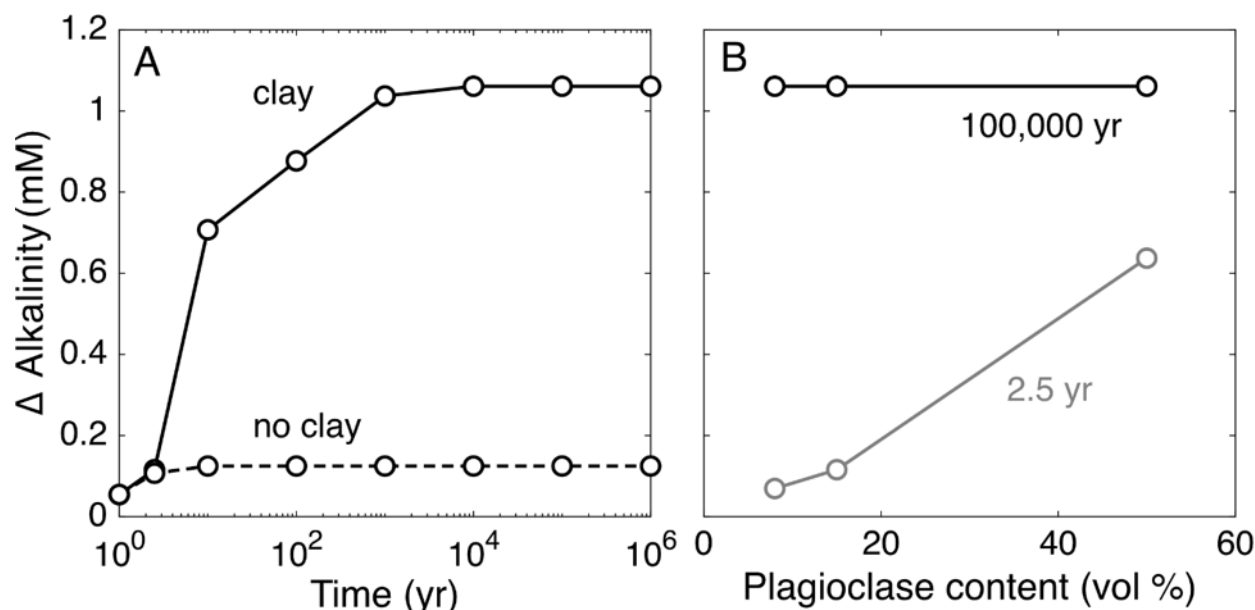


Figure 2: A) Reaction time versus added alkalinity of batch models starting with 15% plagioclase at 15,000 ppm CO₂ including and excluding kaolinite formation. Without slow kaolinite formation, plagioclase dissolution reaches equilibrium quickly at low alkalinity, while alkalinity increases slowly over time with kaolinite precipitation. Alkalinity has reached equilibrium by 100,000 years, and does not change by 1,000,000 years. B) Plagioclase content versus alkalinity for batch models at 15,000 ppm CO₂ including kaolinite precipitation after 2.5 years and 100,000 years of reaction time (lines simply interpolate between the three tested plagioclase contents).

The amount of plagioclase included in batch simulations, which spans the modal proportions seen in a range of silicate rocks, influences alkalinity generation at early timescales. At 2.5 years of reaction, alkalinity generation increases versus plagioclase content (Fig. 2B). Initially, plagioclase content controls the amount of silicate dissolution and the level of kaolinite oversaturation. At higher plagioclase content, a greater abundance of plagioclase surface area is available, so dissolution rates are higher. With faster plagioclase dissolution, aqueous Si and Al concentrations increase more, further oversaturating kaolinite and leading to faster clay precipitation. While the plagioclase content affects the time necessary for the system to attain equilibrium through surface area controls on kinetic rates, the alkalinity generated at equilibrium is not dependent on plagioclase content. At equilibrium, only a small percentage of plagioclase has dissolved, whether 8 volume percent or 50 volume percent is initially present (Fig. 2B). Therefore, the amount of initial plagioclase available has very little bearing on the amount of alkalinity generated at equilibrium timescales.

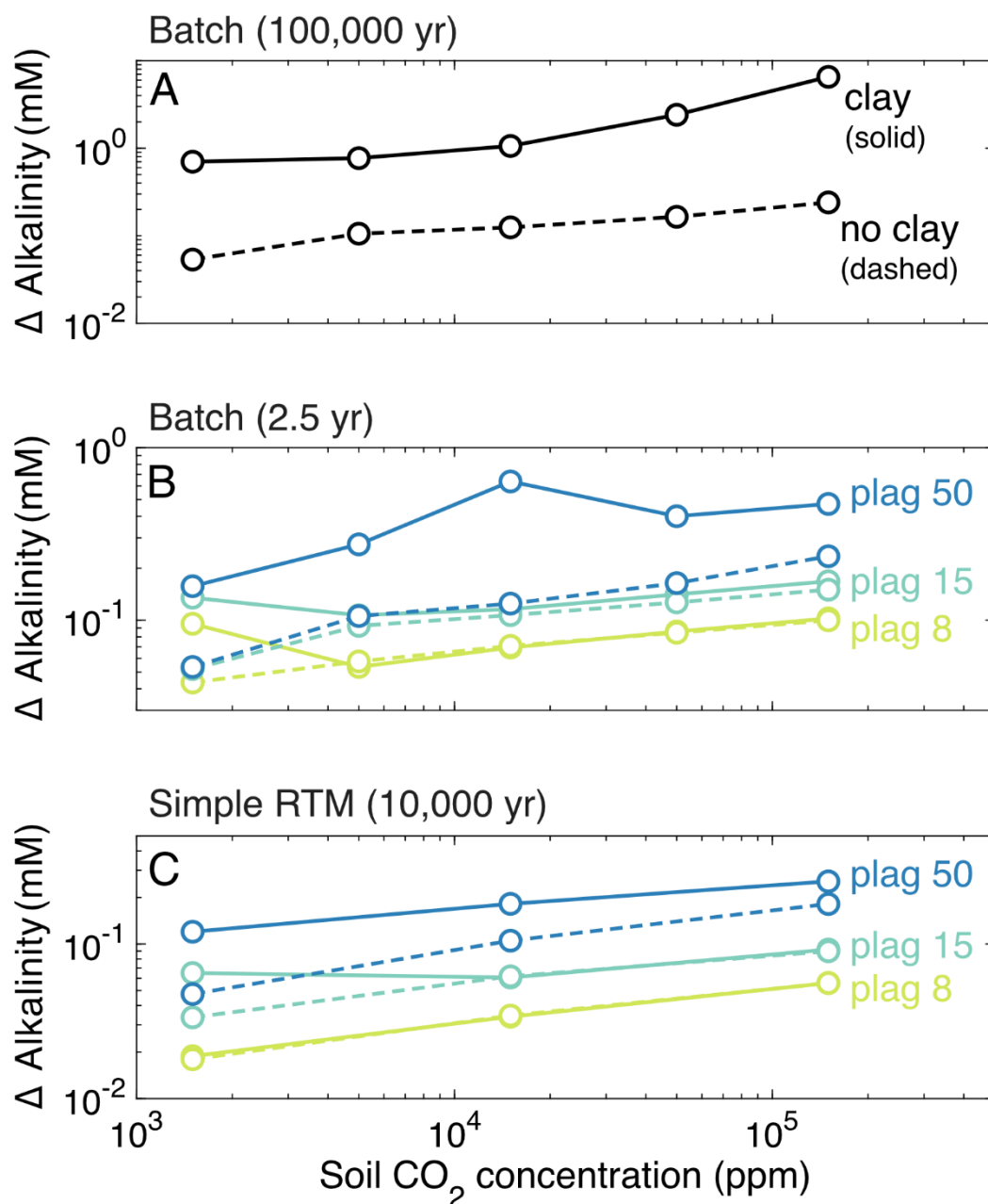


Figure 3: A) Initial soil CO_2 concentrations versus alkalinity for batch models at equilibrium (100,000 years of reaction time) with and without kaolinite precipitation. B) Initial soil CO_2 concentrations versus alkalinity of batch models (with and without kaolinite formation) with 8%, 15%, and 50% plagioclase after 2.5 years of reaction. C) Inflowing CO_2 concentrations versus average alkalinity for 1-D profiles subjected to 10,000 years of weathering for models with 8%, 15%, and 50% plagioclase.

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In contrast, aqueous CO_2 concentration controls the amount of alkalinity generated in batch models at equilibrium. The amount of alkalinity generated in batch models including and excluding kaolinite precipitation increases with CO_2 concentration (Fig.



340 3A). As observed in Winnick and Maher (2018), alkalinity in clay-containing models increases with higher CO₂ concentrations, which is governed by mineral solubility and reaction stoichiometry. The amount of alkalinity generated by clay models increases more dramatically with increasing CO₂ concentrations than simulations not including clays (Fig. 3A). CO₂ concentrations does not significantly affect the time for the system to fully approach equilibrium, which are controlled more by kaolinite precipitation rates. However, CO₂ concentrations influence plagioclase dissolution rates at early timescales (2.5
345 years of reaction) where alkalinity generation for both clay-containing and no clay models generally increase slightly with CO₂ concentrations (Fig. 3B). With increasing CO₂ concentrations, the amount of carbonic acid increases, but the pH-dependence of plagioclase dissolution and kaolinite precipitation rates temper the increase in alkalinity. For 8% and 15% plagioclase models, alkalinity decreases slightly at moderate CO₂ concentrations where pH conditions are circumneutral (slowest plagioclase dissolution and kaolinite precipitation) before increasing at higher CO₂ levels (Fig. 3B). The inclusion of kaolinite
350 improves alkalinity generation most at low CO₂ concentrations where kaolinite precipitates quickly and plagioclase would have neared equilibrium without clay formation. Kaolinite has little to no effect at higher CO₂ concentrations where the system has not approached equilibrium. For 50% plagioclase, alkalinity generally increases with a bump at moderate CO₂ concentrations in clay models due to transient Al behavior affecting Al-dependent plagioclase dissolution rates (Fig. 3B). For higher plagioclase contents, clay formation better enhances alkalinity generation since kaolinite removes the higher
355 concentrations of aqueous Al and Si that drive the system towards equilibrium.

In simple 1-D models of plagioclase and kaolinite, chemistry evolves spatially as the water residence time increases with depth. At the top of the profile, water only begins to react with plagioclase and kaolinite, while water has reacted with the solid phase for 2.5 years by the time it reaches the bottom of the profile. Average alkalinity with depth is lower than alkalinity at the base
360 of the profile since shallow waters has less time to react with plagioclase and generate alkalinity. With an increase in CO₂, alkalinity generally increases, but the magnitude is dependent on plagioclase content as observed in batch reactions (Fig. 3). Also as seen in batch models, kaolinite formation improves alkalinity generation primarily at low CO₂ levels and high plagioclase contents where plagioclase approaches equilibrium without clays.

3.2 Alkalinity generation during rock weathering of shale, granite, and basalt

365 While simple 1-D models includes only plagioclase and kaolinite (that does not remove alkalinity), rock models explore how clays impact net alkalinity generation using distinct lithologies and several clay minerals with variable direct effects on alkalinity. Rock models add the complexities of distinct lithologies instead of only differing plagioclase content (Table 1). Shale contains 8% plagioclase (Alb80:An20) and 3% kaolinite, but also contains additional clays: 33% illite, 10% smectite, and 3% chlorite. Granite has 15% plagioclase (Alb80:An20) as well as 43% quartz, 30% K-feldspar, 5% biotite, and 2%
370 amphibole, while basalt contains 40% plagioclase (anorthite), 25% pyroxene, 15% volcanic glass, and 5% olivine. These additional silicate minerals also dissolve and add alkalinity. We evaluate the relationship between CO₂ concentrations and silicate weathering by varying the partial pressure of CO₂ entering the soil profile. CO₂ is varied from 1,500 ppm (representing



low soil CO₂) to 150,000 ppm (very high soil CO₂). As CO₂ concentrations vary, solution pH at the upper boundary is calculated by charge balance with CO₂ forming carbonic acid, bicarbonate, and carbonate.

375 The amount of alkalinity generated is generally higher in clay containing models and tends to increase with soil pCO₂ (Fig. 4). During granite and basalt weathering, alkalinity generation in both clay and no clay models increase as more carbonic acid dissolves additional silicate minerals. In granite models, alkalinity is higher in all clay containing models, which removes Al from solution, and allows silicates to continue to dissolve (Fig. 4A). In basalt models, alkalinity is lower in clay containing models at low soil pCO₂ where silicates near equilibrium either with or without clay formation. The precipitation of chlorite
380 clays in these models removes Mg from solution, lowering alkalinity. At higher CO₂ concentrations, clay formation shifts more towards kaolinite and illite, which remove less alkalinity (Fig. 4A). Clay formation significantly improves silicate dissolution with depth, allowing for much higher alkalinity generation at high soil pCO₂. Total alkalinity for shale models both with and without clays is generally controlled by dolomite dissolution with highest alkalinity at moderate soil pCO₂. After 10,000 years of weathering, high soil pCO₂ depletes most dolomite from the shale profile, so the highest alkalinities occur at
385 moderate soil pCO₂ (Fig. 4A).

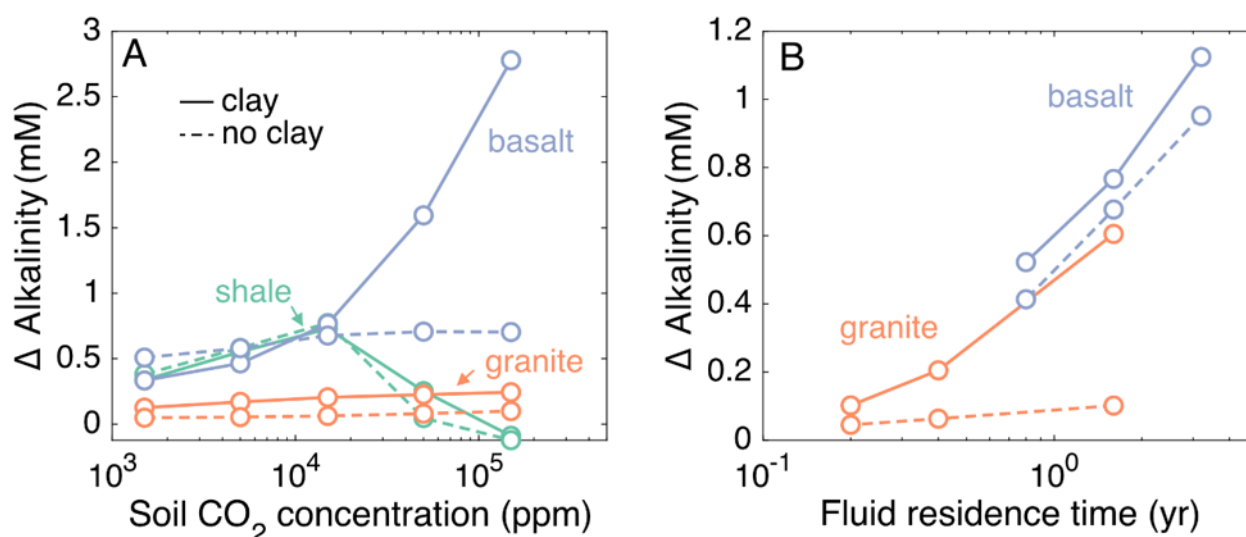


Figure 4: A) Alkalinity generated versus CO₂ concentrations for granite, basalt, and shale weathering (rock profile subjected to 10,000 years of weathering). B) Alkalinity generated by granite and basalt with and without clay formation at different flow rates (slower flow=high fluid residence time, faster flow=short fluid residence time). Alkalinity generation during shale weathering is primarily influenced by dolomite dissolution, which is further discussed in the Supporting Information.

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Flow rate also influences alkalinity generation across rock types and the presence of clays. Across lithologies and the presence or absence of clay formation, alkalinity concentrations increase with fluid residence time (decrease with flow rate) (Fig. 4B). While alkalinity concentration decrease with flow rate, alkalinity flux, which is the product of concentration and discharge, increases with flow rate. The total amount of alkalinity discharged to the oceans increases as more water flows through weathering profiles. Clay formation generates greater alkalinity than no clay models, which becomes increasingly clear at

395



higher fluid residence times (Fig. 4B). During rock weathering at fast flow rates, silicate dissolution occurs similarly with or without clay formation. However, at slow flow rates (high fluid residence times), silicate dissolution slows significantly without clay formation as aqueous Si and Al concentrations increase with depth. Clay formation removes these solutes and promotes additional silicate dissolution and alkalinity generation.

3.3 Reaction fronts, changing pH conditions, and thermodynamics of clay formation

Silicate dissolution, clay mineral formation, and aqueous Al concentrations are intricately linked. The total amount of clay formed across weathering rock profiles is generally controlled by the amount of available Al. Plagioclase has a lower Al to Si ratio ($\text{Al/Si} = 0.43$) than all the modeled clays (e.g., kaolinite: $\text{Al/Si} = 1$), so as clays form, they remove a greater proportion of Al than Si. Thus, the total amount of clays formed is controlled by the amount of Al available from silicate dissolution with aqueous Al concentrations below 0.01 mM at the base of shale, granite, and basalt profiles (Fig. S9A). The balance between Al release by silicate dissolution and Al removal by clays and gibbsite is illustrated by Al concentrations at depth. Al concentrations initially increase with depth as silicates dissolve then decrease and remain depleted as clay minerals become saturated and form down-profile. Since plagioclase has a higher proportion of Si to Al than clays, Si removal could not match Si additions, and Si concentrations increase across the entire profile during the weathering of shale, granite, and basalt (Fig. S9B). This phenomenon has also been measured in the field where collected pore waters of a weathering granite observe Si concentration increasing up to 0.5 mM with depth, while Al concentrations reach only a maximum of 2 μM (Maher et al., 2009).

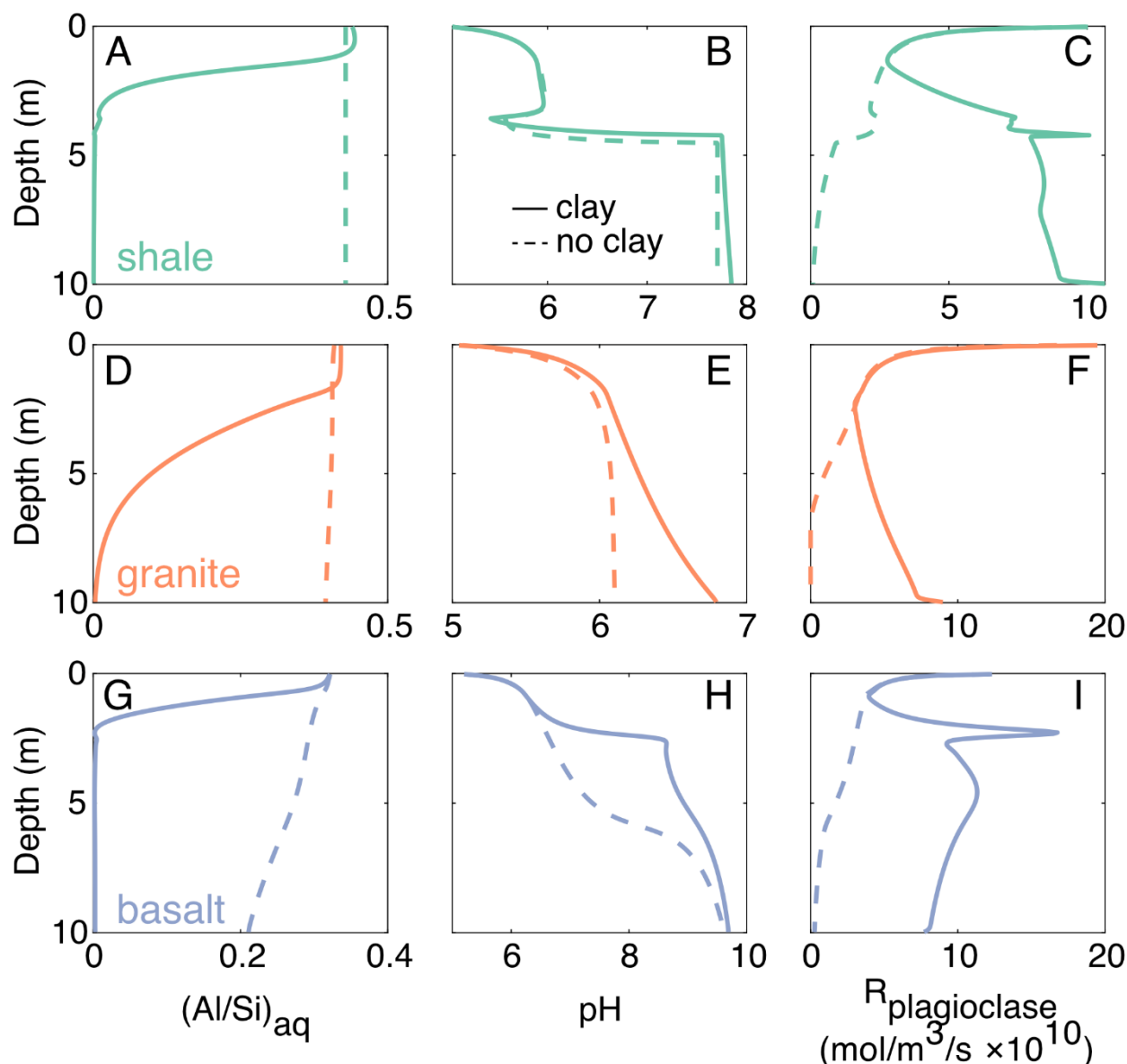
As shale, granite and basalt chemically weather, reactive minerals are removed, which alter the amount of alkalinity generated (Supporting Information). At our base erosion rates (0.01 mm/year), chemical weathering outpaces erosion, resulting in a decrease in silicate dissolution rates and alkalinity generation over time as plagioclase and other minerals weather away (Fig. S2). Since clays promote additional plagioclase dissolution, plagioclase weathers away faster with the inclusion of clays, resulting in less alkalinity generated versus no clay models at late timesteps when plagioclase is depleted in highly weathered rocks. At higher erosion rates (0.2 mm/year), weathering profiles near steady state with primary silicates still available. At shallow depths, silicates are more depleted in clay models, so plagioclase dissolution occurs at lower rates than no clay models (Fig. S4). However, the inclusion of clays improves silicate dissolution at depth, resulting in greater overall silicate dissolution and alkalinity generation (Fig. S4). Thus at lower weathering intensities (higher erosion rates) as newer rock is exposed to the surface, clays generally enhance silicate dissolution and alkalinity generation.

Silicate dissolution and acid-base reaction fronts cause increases in aqueous Si concentrations and sharp shifts in pH, respectively, which influence the type of clays formed along a weathering profile. As illustrated by the stability diagram of Si concentrations versus pH, gibbsite forms preferentially at low Si concentrations since it contains no Si (Fig. S10). At circum-neutral pH, kaolinite ($\text{Al/Si} = 1$) forms best as Si concentrations increase until smectite forms preferentially at high Si concentrations ($\text{Al/Si} = 0.63$). As pH increases, illite ($\text{OH/Al} = 3.48$) and eventually chlorite ($\text{OH/Al} = 8$) begins to form over



430 kaolinite ($\text{OH}/\text{Al}=3$) and smectite ($\text{OH}/\text{Al}=3.14$) (Fig. S10). Distinctive weathering profiles develop in shale, granite, and
basalt, resulting in diverging trends in clay mineral formation. During shale weathering, the location of the dolomite reaction
front (at approximately 4m) typically controls secondary mineral precipitation (Fig. 5). At this reaction front, pH and Mg^{2+}
concentrations increased, which leads to formation of illite over kaolinite (Fig. S9). The modeled illite contains K, which was
only supplied by rainwater, so illite precipitates until the limited amount of K is depleted. The weathering granite does not
435 contain a carbonate reaction front, so the pH increases less than shale, resulting in predominantly kaolinite formation down-
profile (Fig. 5). In the basalt, strong silicate dissolution of plagioclase and pyroxene causes a large increase in pH, even without
a carbonate reaction front. This strong increase in pH is consistent with pH measured in pore waters during basalt weathering,
which are often highly alkaline at ~ 9 (Arnorsson et al., 2002; Pohlmann et al., 2016). pH continues to increase down-profile,
leading to precipitation of illite and eventually chlorite (Fig. 5).

440
As clays form and remove Al from solution, more silicate dissolution occurs with depth. While plagioclase is not the only
silicate dissolving during weathering, it provides a clear illustration of how clay formation influenced silicate dissolution.
Plagioclase dissolution in the three rock types is compared with and without clay formation. Plagioclase dissolution at depth
is enhanced by clay formation for all lithologies (Fig. 5). By removing Si and particularly Al from solution (Fig. 5), plagioclase
445 remains undersaturated and continues to dissolve across the entire profile. Since plagioclase dissolution is pH- and Al-
dependent, shifts in dissolution rate are observed for shale, granite, and basalt. At the top of each profile, Al concentrations
and pH conditions are at their lowest, so plagioclase dissolution is most rapid (Fig. 5). As pH becomes more neutral and Al
accumulates, plagioclase dissolution slows. In no clay models, Al concentrations continue to increase until plagioclase nears
equilibrium. With clay formation, aqueous Al is removed, which allows plagioclase to continue to dissolve (Fig. 5). During
450 basalt weathering, clay formation drives Al concentrations to a local minimum at 2m depth, promoting faster plagioclase
dissolution. Across all rock types, the inclusion of clay formation allows additional plagioclase dissolution down-profile. With
clay precipitation, approximately 370%, 180%, and 360% more plagioclase dissolves for shale, granite, and basalt, respectively
than without any clay formation.



455 **Figure 5: Depth profiles of Al/Si ratio (A- shale, D- granite, G- basalt), pH (B- shale, E- granite, H- basalt), and plagioclase dissolution (C- shale, F- granite, I- basalt) after 10,000 years of rock weathering at low erosion rates (0.01 mm/year) with and without clay formation.**

3.4 Influence of clay formation on alkalinity generation across all models

460 Some types of clay minerals remove alkalinity, but clay formation also promotes additional silicate dissolution. Here, we focus on plagioclase dissolution since plagioclase is contained in all rock models, but other silicates, such as biotite, pyroxene, and olivine also release Si, Al, and alkalinity during dissolution. Each mole of Alb80:An20 that dissolves releases 1.2 moles of Al and 1.2 moles of alkalinity (1 mole alkalinity added per mole Al added). As observed above, clay formation removes Al to



near completion by the bottom of each profile. Through removing Al from solution, clay formation promotes additional silicate dissolution and alkalinity generation (1 mole alkalinity per mole Al for Alb80:An20). Kaolinite and gibbsite precipitation remove no alkalinity, while smectite and illite remove relatively small amounts (0.14 and 0.48 moles per mole Al removed, respectively). Since these clays remove less alkalinity per mole Al than the amount of alkalinity added by plagioclase, they engender net alkalinity generation. On the other hand, chlorite precipitation removes more alkalinity at 5 moles per mole Al removed, so chlorite formation is a net alkalinity sink. In our models, chlorite formation requires high pH conditions, which are only observed during basalt weathering. In general, clay formation engenders more alkalinity generation through silicate dissolution than removal by clay precipitation itself (Fig. S11). However, these models do not account for surface passivation effects where clay forms on silicate surfaces and slows silicate dissolution rates or for porosity/permeability changes where clays clog pore spaces and slow flow through regolith.

By using an alkalinity ratio, we can directly compare the effect of clay formation on alkalinity generation, defined as:

$$\text{alk ratio} = \Delta A_{\text{sil and clays}} / \Delta A_{\text{no clays}} \quad (8)$$

Where $\Delta A_{\text{sil and clays}}$ is the amount of added alkalinity generated by models including both silicate dissolution and clay formation and $\Delta A_{\text{no clays}}$ is the amount of added alkalinity generated by models excluding clay formation.

Generally, more alkalinity and higher alkalinity ratios are generated with greater plagioclase content (Fig. 6A). Without clay formation, plagioclase approaches equilibrium rapidly as Si and Al dissolve, so additional plagioclase does not significantly increase alkalinity generation. Therefore, the amount of plagioclase dissolution versus plagioclase content does not change as much in the no clay models as in the clay-containing simulations where clays promote additional plagioclase dissolution down-profile. At low plagioclase content, silicates can dissolve with or without clay formation, but at higher plagioclase content, clay formation is more critical in removing aqueous Al and Si and promoting greater silicate dissolution (Fig. 6A). Since batch and simple 1-D models contain only kaolinite, which does not remove alkalinity, alkalinity ratios increase consistently with plagioclase content as kaolinite becomes more necessary to promote silicate dissolution. For rock models, chlorite forms during basalt (50% plagioclase) weathering, which promotes silicate dissolution but removes alkalinity, resulting in a net positive alkalinity ratio, albeit lower than that observed in granite (15% plagioclase).

With increasing $p\text{CO}_2$, more alkalinity is generated by models both including and excluding clay formation as more carbonic acid promotes greater silicate dissolution. In batch and simple 1-D models, the smallest alkalinity ratio is at the highest $p\text{CO}_2$ levels (Fig. 6B). With more carbonic acid, greater plagioclase dissolution occurs with or without clay formation, so alkalinity ratios tend to be lower. However, in rock models, the alkalinity ratio increases with CO_2 concentrations, which is primarily caused by basalt weathering (Fig. 6B). At low $p\text{CO}_2$ levels, basalt weathering causes pH to increase over 9.0, driving chlorite formation. At higher CO_2 concentrations, less chlorite forms during basalt weathering, and clays are a net source of alkalinity by enhancing silicate dissolution.

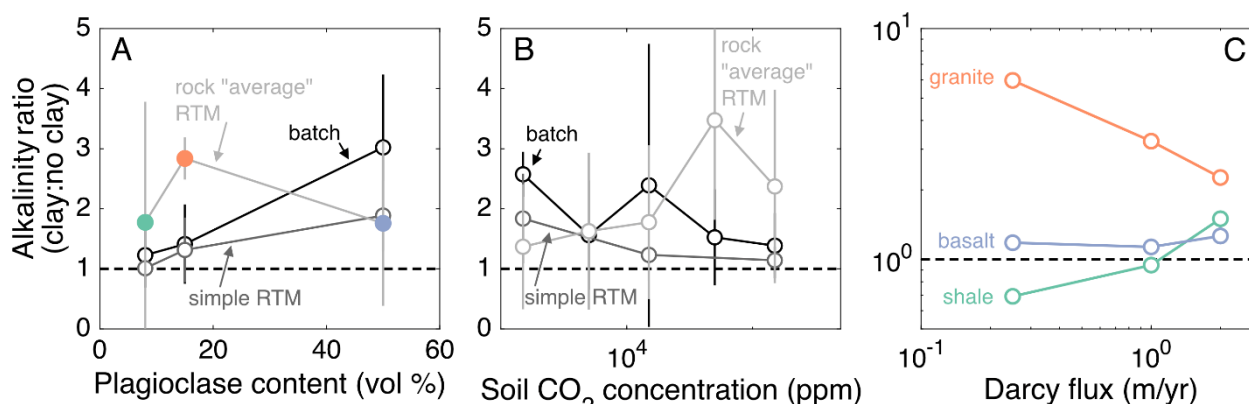


Figure 6: Alkalinity ratio (alkalinity generated by clay containing models divided by alkalinity generated in no clay models) versus A) plagioclase content and B) CO₂ concentrations across all model types (batch, simple 1-D, and 1-D rock). C) Alkalinity ratio versus flow rate for 1-D rock models. When varying CO₂ concentrations or flow rate, the average alkalinity ratio for each model type is calculated across different plagioclase contents/lithologies. When varying plagioclase content, the average alkalinity ratio is calculated across different CO₂ concentrations. An equivalence line (equal alkalinity generated by clay-containing and no clay models) is shown as a dashed line.

Alkalinity removal or generation by silicate dissolution and clay formation is timescale dependent. As observed in batch reactions, clay formation initially has little effect on alkalinity generation, but over time acts as a net source of alkalinity by promoting additional silicate dissolution (Fig. 2A). The time dependence of clay formation on alkalinity is also illustrated by how weathering intensity influences granite and basalt weathering (Fig. 6C). During granite weathering at slow flow rates (low weathering intensity), silicate minerals approach equilibrium and dissolution slows without clay formation. At high flow rates (high weathering intensity), primary silicates are farther from equilibrium with or without clays. Therefore, alkalinity ratios decrease at high weathering intensities for granite and basalt weathering (Fig. 6C).

4 Discussion

4.1 Comparison to natural systems

While our models are not meant to fully replicate realistic weathering processes, our simulations still compare favorably to natural weathering systems. These models focus on how clays impact the thermodynamics of silicate dissolution and influence net alkalinity generation, but they ignore much of the complexities of natural weathering, such as mixing, climate, vegetation, reaction extent, and mineralogic variability. To confirm that our models approximate natural rock weathering, we compare model outputs to Si and alkalinity measurements for watersheds with primarily shale, granite, or basalt lithology from GLORICH (the GLObal River Chemistry Database), which contains major solute chemistry data and lithology information for streams worldwide (Hartmann et al., 2019). We construct box-and-whisker plots of Si and alkalinity concentrations at discharge below the 10th percentile flow for watersheds with primarily shale, granite, or basalt lithology. Chemistry at low flow is selected to focus on waters more directly related to chemical rock weathering, which removes some effects of dilution as runoff increases (Bluth and Kump, 1994; White and Blum, 1995; Ibarra et al., 2016).



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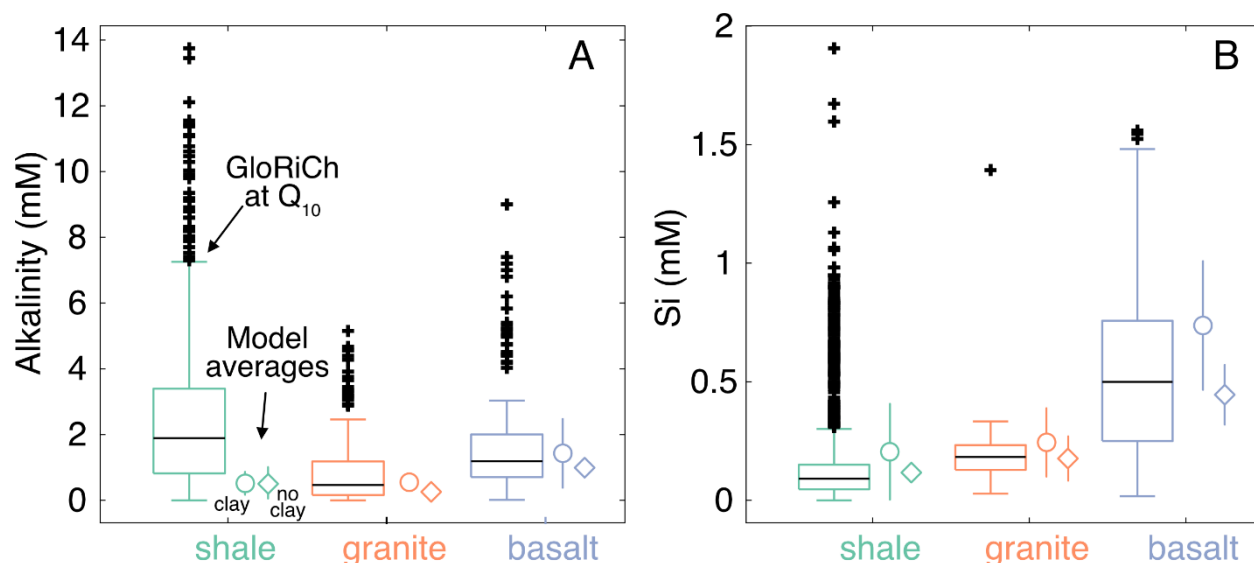


Figure 7: Comparison of alkalinity and Si measurements from primarily shale, granite, and basalt watersheds in the GLORICH database versus modeling outputs (average of clay and no clay models shown with range across CO₂ concentrations and flow rates).

530 Model outputs of alkalinity match well with granite and basalt catchments with models possibly underestimating alkalinity generation in shale (Fig. 7). Alkalinity generation in shale is driven primarily by dolomite dissolution, so the underestimate could be due to the equilibrium constant we choose for dolomite or the fact that more carbonaceous shale are contained among shale lithology in the GLORICH database. Si concentrations are similar between models and stream measurements across lithologies (Fig. 7). Modeling results also are consistent with previous studies of chemical weathering of granites and basalts.

535 Basalt weathering generates average alkalinity and Si concentrations of 1.2 mM and 0.45 mM, respectively in stream waters (Ibarra et al., 2016). Several studies of granite weathering observe an average alkalinity of 0.7 mM and Si concentration of 0.3 mM (Oliva et al., 2003; Ibarra et al., 2016).

4.2 Implications of clay formation on the carbon cycle

540 Clays influence the rate and depth of silicate dissolution, which acts as a long-term sink for carbon dioxide by reacting with carbonic acid, producing alkalinity that enables marine carbonate formation (Walker et al., 1981; Berner et al., 1983; Berner, 1994; Archer et al., 2000). In terrestrial settings, which this work primarily focuses, weathering of feldspar and mafic minerals by dilute freshwater releases alkalinity as well as Si and Al that gets partly incorporated into clays. Under most conditions studied here, secondary mineral formation removes Al from solution, thermodynamically promoting additional silicate

545 dissolution and generating a net increase in alkalinity during terrestrial rock weathering. This study allows us to hypothesize how weathering intensity, mineralogy, and soil pCO₂ each play a key role in how clay formation impacts the carbon cycle.



Weathering intensity regulates the importance of clay formation on the carbon cycle by influencing the saturation of silicate minerals. At low weathering intensities, aqueous Al, Si, and cations accumulate down-profile, slowing silicate dissolution (Fig. 6C). Clay formation removes some of these solutes, allowing silicate dissolution with depth. With less rainfall, flow rates may slow, heightening the influence of clay formation for alkalinity generation in terrestrial settings. At high weathering intensities, primary silicates are depleted, particularly with secondary mineral formation, so clays can result in less alkalinity generation (Fig. S2).

The amount of primary silicate minerals present in rocks influences the importance of clay formation for maintaining undersaturation of those silicates. With less silicate dissolution, less Si and Al are released into solution, and silicates can dissolve down-profile without clay formation (Fig. 6A). With large amounts of primary silicates present, clay formation is necessary to remove Si and Al, which promotes greater silicate dissolution and alkalinity. Silicate minerals that contain little to no Al, such as olivine, are less affected thermodynamically by clay formation. Mineralogy also controls which type of clay minerals form. During granite weathering, pH remains circumneutral at depth with primarily kaolinite forming, which does not remove alkalinity. Basalt weathering generates significant alkalinity, which drives pH up and results in chlorite formation at depth, which removes alkalinity (Fig. S11). For enhanced rock weathering applications, silicate dissolution rates and the types of clays formed as weathering progresses may control the effectiveness of the treatment (see Supporting Information for more discussion). If basalt or olivine treatments generate large amounts of chlorite or high cation exchange capacity clays, these clays may limit alkalinity generation and CO₂ drawdown. However, if low cation exchange capacity clays dominate, they could improve alkalinity generation.

Our analysis underscores that soil pCO₂ concentrations will modify the influence of clay mineral formation on alkalinity generation, and thus the strength of the silicate weathering feedback. Canonically, the silicate weathering feedback is written as

$$F_{sil,w} = k(RCO_2)^n \quad (9)$$

where k represents a base-level CO₂ drawdown flux (mol C/yr), RCO_2 is the ratio of pCO₂ to pre-industrial pCO₂ (280 ppm), and n is an exponent that determines the sensitivity of the CO₂ drawdown flux to CO₂ levels in the weathering environment, referred to as the silicate weathering feedback strength (Berner, 1992; Penman et al., 2020). The value of n has some mineralogical basis (e.g., pCO₂ dependence of feldspar dissolution; Lagache, 1965; Walker et al., 1981), but given the parametric form of the equation, also integrates effects from uplift, fluid flow, and vegetation. When considering the influence on clay formation in this framework, the inclusion of clay minerals across rock types amounts to an increase in k but a decrease in n : in other words, an increase in weatherability but a decrease in the feedback strength.

Conventionally, clays are believed to weaken the silicate weathering feedback through removing cations and alkalinity (Isson and Planavsky, 2018; Isson et al., 2020; Krause et al., 2023). Here we have demonstrated that clay formation can play another



role in the strength of the weathering feedback through the under-appreciated mechanism of enhancing silicate dissolution and alkalinity release. For the simplified plagioclase and kaolinite system, as CO₂ concentrations increase, kaolinite formation tends to have a smaller effect on alkalinity generation. At low pCO₂ levels, pH becomes circum-neutral quickly and silicate minerals near equilibrium without Al removal by secondary minerals (Fig. 6B). At higher pCO₂ levels, pH remains lower with depth, promoting silicate dissolution even without secondary mineral formation. However, during basalt weathering, clay formation promotes the feedback between pCO₂ and alkalinity generation. At low pCO₂ levels, pH increases rapidly, resulting in chlorite formation that consumes alkalinity (Fig. 6B). At higher CO₂ concentrations, other clay minerals dominate and promote net alkalinity generation. Therefore, terrestrial clay formation is expected to strengthen the silicate weathering feedback during basalt weathering, but generally weakens the feedback in less basic lithologies.

4.3 Future modeling directions

Our reactive transport simulations are meant to provide a simplified representation of how clay formation influences the thermodynamics of silicate dissolution and net alkalinity generation, so our models are not meant to fully replicate realistic mineral kinetics or fluid flow. Previous studies have utilized mechanistic nucleation models or Si- and pH-dependent models (Hellevang et al., 2013; Yang and Steefel, 2008; Isson and Planavsky, 2018; Trapp-Muller et al., 2025). While nucleation models may provide a more mechanistic approach to clay precipitation, they require numerous unknown parameters (Trapp-Muller et al., 2025). Si- and pH- dependent models use an empirically derived precipitation rate law (Isson and Planavsky, 2018). Our models avoids these unknowns by using a simple TST formulation for secondary mineral formation. While TST rate laws can lead to overestimations of precipitation rates (Trapp-Muller et al., 2025), the fact that most clay minerals are highly oversaturated with high Si concentrations gives us confidence that clay formation rates were primarily driven by silicate dissolution and not by the type of rate law chosen.

Our modeling approach also has several limitations that likely lead to overestimating how clays enhance silicate weathering. By filling fast-flowing pores, clay formation can decrease the permeability and porosity of weathering rock, altering and slowing fluid flow (Neuzil, 2019; Carcione et al., 2019). CrunchTope does not adjust permeability as mineralogy evolves, so decreases in permeability and fluid flow are not accounted, likely promoting greater silicate weathering rates at depth than expected in nature. In CrunchTope, porosity updates after each time step with porosity calculated as the remaining volume not taken up by the mineral assemblage.

$$\phi = 1 - \sum_i \phi_i \quad (10)$$

where ϕ is porosity and ϕ_i is the mineral volume fraction of an individual mineral

Porosity does not influence the constant Darcy velocity (m³/m²/yr), but does impact the linear velocity (m/yr) of the inflowing fluid, which increases when porosity decreases.

$$v = q/\phi \quad (11)$$

where v is the linear velocity, ϕ is the porosity, and q is the Darcy velocity



If clay formation is rapid, it can fill pores, increasing linear velocity and limiting reaction time with silicate minerals (Eq. 1). However, clay formation could not keep pace with rapid carbonate or silicate dissolution in shale and basalt, so porosity increases at shallow depths within weathering shale and basalt, leading to slower linear velocities. We also do not include passivation of silicate surfaces through secondary coatings. As feldspars dissolve, thin, aluminosilicate-rich layers commonly form on their surfaces (e.g., Chou and Wollast, 1984; Nugent et al., 1998), which can decrease reactive surface area and inhibit primary mineral dissolution (Velbel, 1993b). CrunchTope does not have a method to directly model passivation, so we do not include passivation within our models. Decreasing mineral surface area or permeability would lead to a decay in silicate dissolution and clay precipitation rates, but clays should still improve silicate dissolution overall as long as silicates are approaching equilibrium at depth. Future models could explore how permeability changes and surface passivation temper the improvement of silicate dissolution thermodynamics through clay formation.

5 Conclusions

During modeled weathering, primary silicate dissolution is closely related to clay formation. Across simulations, the total amount of Al removed by clays is nearly identical to the amount of Al released by silicate dissolution. pH conditions and Si concentrations control the types of secondary minerals formed with gibbsite and kaolinite forming at low pH and Si concentrations, illite and smectite at higher Si concentrations, and chlorite at high pH. In batch models, clay formation promotes significantly more plagioclase dissolution by removing Si and Al from solution. Greater plagioclase dissolution with clays is also observed along 1-D profiles. Without clay formation, plagioclase approaches equilibrium by the base of simple 1-D or rock weathering models, but with clay formation, plagioclase continues to dissolve with depth across most weathering profiles. By boosting plagioclase dissolution during rock weathering, clay formation acts as a net alkalinity source for most models. The one exception arises when chlorite forms at high pH conditions, which acts as an alkalinity sink. The increase in silicate dissolution with clays is particularly pronounced at low $p\text{CO}_2$, slow flow rates, or high plagioclase content where plagioclase and silicates near equilibrium without clay formation. At low CO_2 levels, clays enhance silicate dissolution, but not to the same degree at high CO_2 concentrations, so clays may dampen the sensitivity of alkalinity generation to CO_2 concentrations.

Data Availability

Model input files and data analysis spreadsheets are available through Zenodo at <https://doi.org/10.5281/zenodo.17064490>

Author contribution

Jemison: conceptualization, data curation, formal analysis, investigation, methodology, visualization, writing-original draft, writing- review and editing

Winnick: conceptualization, formal analysis, funding acquisition, methodology, software, writing- review and editing

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Zhou: writing- review and editing

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655 **Competing Interests**

The authors declare that they have no conflict of interest.

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