

S1 Additional Information

S1.1 Introduction

The Supplementary Material includes a discussion of how we modeled organic carbon. We discuss the impact of factors affecting clay formation and silicate dissolution, such as rock age, erosion rate, and oxalate concentrations. We compare simple batch and equivalent 1-D models. We discuss the role of dolomite in generating alkalinity in shale weathering models. The Supplementary Material includes five tables: a list of mineral and aqueous reactions, the initial aqueous chemistry, the aqueous complexation reactions, the surface complexation reactions, and a comparison of alkalinity generation in batch and 1-D models. Ten figures are included as well, which illustrate the respective roles of rock age, erosion rate, and oxalate concentrations on silicate dissolution and the amount of alkalinity generated, as well as how carbonate dissolution impacts alkalinity in shale models, what clays form during rock weathering, and the amount of alkalinity generated by silicate dissolution versus lost by clay formation.

S1.2 Modeling oxalic acid

The influence of soluble organic matter on silicate dissolution and clay formation was tested by altering the amount of soluble organic matter. Plant matter decays in the near surface releasing soluble organic matter into the weathering profile (Jones et al., 1998; Lawrence et al., 2014). In rock simulations, this shallow release of soluble organic matter was modeled as sodium oxalate within the inflowing water. Using solely oxalate has some precedent. For one, previous research suggests that the total concentration of low molecular weight organics has a greater effect on weathering dynamics than the type of organic molecule (Lawrence et al., 2014), which deemphasizes the need to include multiple organic molecules of varying molecular weight. Moreover, the thermodynamics of oxalic acid speciation and complexation have been rigorously evaluated (Stillings et al., 1996; Stillings et al., 1998; Furrer and Stumm, 1986; Jones, 1998; Yoon et al., 2004; Ganor et al., 2009), making it an ideal species to include in reactive transport models. Lastly, as one of the more aggressive organic acids and ligands, oxalic acid and its inclusion in the model represents an endmember effect of organic acids on silicate weathering.

In most simulations, sodium oxalate was added at 0.1mM, which is the nominal upper end of oxalate concentrations in soil (Jones, 1998). Several simulations were run at 0.01mM or 0.5 mM oxalate to determine the impact of organic acids on silicate dissolution and clay formation. Once added to the profile, oxalate could be deprotonated, singly protonated, and fully protonated in solution, and it could also form surface complexes with plagioclase (Table S4). Oxalate complexed strongly with Al, which weathers from feldspars, and can alter clay formation. Oxalate also reacted with dissolved oxygen through aerobic respiration (Table S1), so organics can modify the amount of oxidative weathering occurring along the weathering profile.

S1.3 Other factors affecting plagioclase dissolution

In addition to the scenarios presented in the main text, we tested the impact of age of the rock, uplift/erosion rates, and soluble organic carbon concentrations. We present the influence of each of these parameters here.

S1.3.1 The evolution of rock weathering over time

With slow erosion of 0.01mm/yr, silicate dissolution and clay formation shifted gradually over time as shale, granite, and basalt developed weathering profiles (Figure S1). During shale weathering, alkalinity generation were strongly influenced by the dolomite and pyrite reaction fronts at early time periods and then primarily by silicate reactions once dolomite and pyrite were depleted. The alkalinity calculation included alkalinity generated from silicate and dolomite dissolution and alkalinity lost from pyrite dissolution. The dolomite and pyrite reaction fronts moved down-profile at roughly identical rates as carbonic and sulfuric acid reacted with carbonate and oxygen reacted with pyrite. The fronts were observed at ~2m at 5,000 years, ~4m at 10,000 years, and ~9m at 25,000 years. Dolomite dissolution generated most of the alkalinity over the first 20,000 years, but as dolomite was depleted, alkalinity generation decreased quickly over the first 25,000 years (Figure S2). Clay formation allowed for more plagioclase dissolution down-profile, resulting in slightly higher pH conditions than no clay models. The higher pH prevented some dolomite dissolution, counterintuitively generating slightly less alkalinity overall at 5,000 and 10,000 years (Figure S2). At 25,000 years, dolomite was almost completely reacted away in the no clay model, while the dolomite front still existed at the base of the profile in the clay model, so alkalinity was higher in the clay model (Figure S2). From 50,000 years onward, pyrite and dolomite were fully depleted and alkalinity was generated only through silicate reactions. Since clay formation allowed more plagioclase to weather over the first 50,000 years, less remained in the later portions of the model, so models without clays generated more alkalinity at these later time periods (Figure S2).

During granite weathering, plagioclase dissolution was consistent over the first 50,000 years, then slowed over the next 200,000 years (Figure S1B). The additional silicate dissolution promoted by clay formation generated more alkalinity than no clay models over the first 50,000 years (Figure S2). At 100,000 and 250,000 years, plagioclase dissolution slowed with slightly more alkalinity generated in no clay models since plagioclase was less depleted by chemical weathering.

During basalt weathering, plagioclase initially was not the primary silicate dissolving with volcanic glass and olivine dissolving faster. This fact as well as the presence of more plagioclase initially allowed plagioclase dissolution to proceed longer (significant dissolution still at 100,000 years) during basalt weathering than in granite or shale weathering (Figure S1C). As seen in shale and granite weathering, clay formation allowed for more silicate dissolution and alkalinity generation at early timescales, but less silicate was remaining to generate alkalinity at later timescales (Figure S2).

S1.3.2 Influence of erosion rate on rock weathering reactions

To more simply observe the evolution of reaction fronts over time, the erosion rate used in all base models (0.01mm/yr) was a relatively slow rate often seen in lowlands or moderate hills (0.0001-1mm/yr), but not observed in steep tectonically active terrain (0.1- >10mm/yr) (Montgomery, 2007). The erosion rate of 0.01mm/yr resulted in

the total removal of 0.1m (difference of only 0.08m) of rock over 10,000 years, so the reaction fronts could easily deepen since chemical weathering rates were much faster than erosion rates. With slow erosion, plagioclase content was variable with less plagioclase at depths of faster plagioclase dissolution (i.e., shallow depths and depths with low Al and/or optimal pH conditions) (Figure S3). If the erosion rate was increased to 0.2mm/yr, 2m of rock eroded, which allowed less weathered rock to emerge near the base of the profile (Figure S3). In addition, since erosion shifted the rock up-profile, plagioclase was more abundant at shallow depths and plagioclase content tended to be more uniform. At higher erosion rates, erosion eventually balanced chemical weathering, approaching steady state conditions by the end of our modeling timeframe (250,000 years) (Figure S4).

S1.3.3 Impact of oxalate concentrations on plagioclase dissolution and clay formation

We tested the impact of oxalate on Al speciation and clay formation by changing oxalate concentration from 0.1mM to 0.01mM and 0.5mM in weathering shale, granite, and basalt profiles. Our base model contained 0.1mM soluble organic carbon as sodium oxalate, which was depleted at depth by aerobic respiration of O₂. This concentration of soluble organic carbon may be an underestimate along weathering profiles according to stream measurements (Fabre et al., 2020; Liu and Wang, 2022).

For all three lithologies, lower oxalate concentrations (0.01mM versus 0.1mM) resulted in greater plagioclase dissolution with depth (Figure S5), generating additional alkalinity (Figure S6). Less Al was complexed with oxalate, allowing clays to form at shallower depths. With lower aqueous Al concentrations, the thermodynamics of plagioclase dissolution improved. In addition, plagioclase dissolved faster due to the Al-dependence on plagioclase dissolution rates. At higher oxalate concentrations, aerobic respiration did not fully remove oxalate, leaving dissolved organic carbon throughout the profile. The presence of Al-oxalate complexes throughout the profile led to minimal clay formation during shale and granite weathering, slowing plagioclase dissolution significantly (Figure S5). During basalt weathering, the dissolution of other silicates continued to produce alkalinity that eventually led to some clay formation and faster plagioclase dissolution at depth. Overall, higher oxalate concentrations prevented clay formation, slowed plagioclase dissolution, and decreased alkalinity generation (Figure S6).

S1.4 Batch models versus 1-D models

With batch models as context, the simple 1-D models of only plagioclase (and kaolinite) demonstrated more clearly how silicate dissolution and clay formation evolve in reactive transport with flowing fluids (Table 1). We first aimed to confirm if silicate weathering along the 1-D profile matched the evolution of silicate weathering over time in a batch profile. In theory, if a 1-D profile is chemically homogeneous, the system should evolve down-profile analogously to water aging in a batch system. The water residence time of our 1-D models was 2.5 years at the base. The alkalinity at the base of most 1-D models was within 2% of the alkalinity in the equivalent batch models at 2.5 years (Table S5). One 1-D model generated significantly less alkalinity than the equivalent batch model likely due to the dependence of plagioclase dissolution rates on Al and pH. While the batch reaction had anomalously high alkalinity due to low Al concentrations at that moment (Figure 3D), the 1-D model smoothed some of this behavior

(Figure 3G). Overall, the simple 1-D models were roughly equivalent to the batch models at the same residence time.

S1.5 Role of dolomite on alkalinity generation in shale weathering models

Since carbonate dissolution releases Ca, Mg, and carbonate that are quantitatively removed by carbonate precipitation in the oceans, we subtracted carbonate dissolution from total alkalinity to better account for long-term geologic implications of shale weathering. Dolomite dissolution generated most of the alkalinity in early timesteps of shale weathering models, so this correction often changes the sign (positive or negative) and magnitude of alkalinity generation (Figure S7A). For this correction, we first calculated the amount of Mg^{2+} released by dolomite dissolution and then converted Mg release into alkalinity release, which was subtracted from the total alkalinity. For both clay and no clay models, the non-corrected alkalinity fluctuated considerably based on the rate of dolomite dissolution (highest at moderate CO_2 concentrations where both carbonic acid and carbonate was plentiful) (Figure S7B). However, the carbonate-corrected alkalinity was negative across CO_2 concentrations since sulfide dissolved at near identical rates to generate negative alkalinity (Figure S7B). Without clay formation, plagioclase dissolution was also limited by Al concentrations. With clay formation, Al was removed from solution, and plagioclase could dissolve more rapidly, but carbonate-corrected alkalinities were still primarily negative due to pyrite dissolution (Figure S7B). At low CO_2 concentrations, high pH conditions drove faster plagioclase dissolution, which generated slightly more alkalinity than pyrite dissolution removed.

Carbonate dissolution also shifted the pattern of alkalinity generation as flow rate was altered. For both clay and no clay models, the non-corrected alkalinity (including carbonate dissolution) increased with fluid residence time (slower flow rate) (Figure S7C). At slower flow rates, the carbonate reaction front was shallower, generating high alkalinity throughout most of the profile. At high fluid residence times, greater plagioclase dissolution for clay models generated greater alkalinity than no clay models when corrected for dolomite dissolution and less non-corrected alkalinity since the higher pH slowed dolomite dissolution. Corrected alkalinity actually decreased versus residence time for no clay models because plagioclase dissolution was minimal regardless of flow rate, while the pyrite reaction front was shallower at higher residence times.

S1.6 Carbon dioxide removal by basalt over time

Application of crushed basalt is commonly proposed as a carbon dioxide removal (CDR) strategy by enhancing rock weathering (ERW) (Hartmann et al., 2013; Derry et al., 2026). A recent study studied natural basaltic systems as analogs for ERW, which suggested that hydrologic controls and secondary precipitation likely limit CDR during ERW (Derry et al., 2026). Similarly, our systems focus on deep profiles of unaltered basalt with lower surface area than the crushed basalt applied to the surface of soils during ERW, but our system can still provide insight into CDR evolution over time, albeit at longer timescales. Assuming that alkalinity is fully derived from dissolution by carbonic acid and resulting alkalinity is transported to the oceans, alkalinity released by rock weathering can be converted into carbon dioxide removal (CDR) potential by multiplying alkalinity release by a factor of roughly 1.7

to approximate buffering of the ocean carbonate system to the addition of alkalinity and dissolved inorganic carbon (Renforth, 2019; Derry et al., 2026).

$$\text{CDR} = m \cdot n \cdot \sum_{j,z} (v_{j,i} - v_{j,t}) \cdot z \cdot \alpha_j / V_{m,j} \quad (\text{S1})$$

Where CDR is carbon dioxide removal in terms of kg per m² (converted to metric tons per hectare), m is the molar mass of CO₂ (0.044kg/mole), n is molar ratio (1.7) of CO₂ to alkalinity sequestered, v_{j,i} is the initial volume proportion of a mineral j versus the total volume, v_{j,t} is the volume proportion of a mineral j at time t, z is the discretization depth (m), α_j is the alkalinity coefficient of each mineral, and V_m is the molar volume of each mineral (m³/mole)

We calculated CDR for both clay and no clay models of our base basalt weathering model (Figure S8A). Initially, CDR rates (averaged between 0 and 5,000 years, 5,000 and 10,000 years, 10,000 and 25,000 years, 25,000 and 50,000 years, 50,000 and 100,000 years, and 100,000 and 250,000 years) were higher in the clay-containing model since clays drove greater silicate dissolution with depth (Figure S8B). CDR rates in our basalt models were similar to those observed in natural basalt systems (Derry et al., 2026). Due to faster silicate dissolution in the clay models, CDR rates decreased faster and became lower than no clay models (Figure S8B). No clay models eventually overtook clay models in total CDR at late timesteps as silicate dissolution slowed (Figure S8A). Since clay formation, particularly chlorite, removed alkalinity, the total amount of alkalinity generated in clay models was lower than no clay models once the thermodynamic advantage of clay formation no longer applied.

During ERW, the influence of clay formation is likely similar. If silicate dissolution is rapid and silicates near equilibrium with depth, clay formation can help drive additional silicate dissolution and alkalinity generation. However, if clays sequester significant amounts of cations, then clay formation may act as a net sink of alkalinity. During ERW, thin layers of finely ground basalt may also dissolve quickly. As this rock is depleted, clays cannot drive additional silicate dissolution, and clays act merely as alkalinity sinks.

S1.7 References

Bethke, C. M., Farrell, B., and Sharifi, M.: The Geochemist's Workbench® Release 15, 2021.

Derry, L. A., Maher, K., and Chadwick, O. A.: Critical zone processes limit alkalinity export from natural basaltic systems. *Nature*. <https://doi.org/10.1038/s41586-026-10936-3>, 2026.

Fabre, C., Sauvage, S., Probst, J.-L., and Sanchez-Perez, J. M.: Global-scale daily riverine DOC fluxes from lands to the oceans with a generic model. *Global and Planetary Change*, 194, 103294. <https://doi.org/10.1016/j.gloplacha.2020.103294>, 2020

184 Ferrier, K. L., and West, N.: Responses of chemical erosion rates to transient perturbations in physical erosion rates,
185 and implications for relationships between chemical and physical erosion rates in regolith-mantled hillslopes. *Earth*
186 *and Planetary Science Letters*, 474, 447-456. <https://doi.org/10.1016/j.epsl.2017.07.002>, 2017.

187

188 Furrer, G., and Stumm W.: The coordination chemistry of weathering: I. Dissolution kinetics of d-Al₂O₃ and BeO.
189 *Geochimica et Cosmochimica Acta*, 50, 1847–1860. [https://doi.org/10.1016/0016-7037\(86\)90243-7](https://doi.org/10.1016/0016-7037(86)90243-7), 1986.

190

191 Ganor, J., Reznik, I. J., and Rosenberg, Y. O.: Organics in Water-Rock Interactions. In *Thermodynamics and*
192 *Kinetics of Water-Rock Interaction* (eds. E. H. Oelkers and J. Schott). Springer–Verlag., 259–369.
193 <https://doi.org/10.2138/rmg.2009.70.7>, 2009.

194

195 Hartmann, J., West, A. J., Renforth, P., Kohler, P., De La Rocha, C. L., Wolf-Gladrow, D. A., Durr, H. H., and
196 Scheffran, J.: Enhanced chemical weathering as a geoengineering strategy to reduce atmospheric carbon dioxide,
197 supply nutrients, and mitigate ocean acidification. *Review of Geophysics*, 51, 113-149.
198 <https://doi.org/10.1002/rog.20004>, 2013.

199

200 Jones D. L.: Organic acids in the rhizosphere— a critical review. *Plant and Soil*, 205, 25–44.
201 <https://doi.org/10.1023/A:1004356007312>, 1998.

202

203 Lawrence, C., Harden, J., and Maher, K.: Modeling the influence of organic acids on soil weathering. *Geochimica et*
204 *Cosmochimica Acta*, 139, 487-507. <https://doi.org/10.1016/j.gca.2014.05.003>, 2014.

205

206 Liu, F., and Wang, D.: Dissolved organic carbon concentration and biodegradability across the global rivers: A meta-
207 analysis. *Science of the Total Environment*, 818, 151828. <https://doi.org/10.1016/j.scitotenv.2021.151828>, 2022.

208

209 Maher, K., Steefel, C. I., White, A. F., and Stonestrom, D. A.: The role of reaction affinity and secondary minerals in
210 regulating chemical weathering rates at the Santa Cruz Chronosequence, California. *Geochimica et Cosmochimica*
211 *Acta*, 73, 2804–2831. <https://doi.org/10.1016/j.gca.2009.01.030>, 2009.

212

213 Montgomery, D. R.: Soil erosion and agricultural sustainability. *Proceedings of the National Academy of Sciences*,
214 104, 13268-13272. <https://doi.org/10.1073/pnas.061150810>, 2007.

215

216 Nagy, K. L., Blum, A. E., and Lasaga, A.C.: Dissolution and precipitation kinetics of kaolinite at 80 °C and pH 3—
217 the dependence on solution saturation state. *American Journal of Science*, 291, 649-686.
218 <https://doi.org/10.2475/ajs.291.7.649>, 1991.

219

Nagy, K. L., and Lasaga, A. C.: Dissolution and precipitation kinetics of gibbsite at 80°C and pH 3: The dependence on solution saturation state. *Geochimica et Cosmochimica Acta*, 56, 3093-3111. [https://doi.org/10.1016/0016-7037\(92\)90291-P](https://doi.org/10.1016/0016-7037(92)90291-P), 1992.

Oelkers, E. H., and Gislason, S. R.: The mechanism, rates and consequences of basaltic glass dissolution: I. An experimental study of the dissolution rates of basaltic glass as a function of aqueous Al, Si and oxalic acid concentration at 25°C and pH = 3 and 11. *Geochimica et Cosmochimica Acta*, 65, 3671-3681. [https://doi.org/10.1016/S0016-7037\(01\)00664-0](https://doi.org/10.1016/S0016-7037(01)00664-0), 2001.

Oelkers, E. H., Schott, J., and Devidal, J.-L.: The effect of aluminum, pH, and chemical affinity on the rates of aluminosilicate dissolution reactions. *Geochimica et Cosmochimica Acta*, 58, 2011-2024. [https://doi.org/10.1016/0016-7037\(94\)90281-X](https://doi.org/10.1016/0016-7037(94)90281-X), 1994.

Palandri, J. L., and Kharaka, Y.K.: A Compilation of Rate Parameters of Water-Mineral Interaction Kinetics for Application to Geochemical Modeling. USGS Open File Report 2004-1068. <https://doi.org/10.3133/ofr20041068>, 2004.

Pokrovsky, O. S., Golubev, S. V., and Schott, J.: Dissolution kinetics of calcite, dolomite and magnesite at 25 °C and 0 to 50 atm pCO₂. *Chemical Geology*, 217, 239-255. <https://doi.org/10.1016/j.chemgeo.2004.12.012>, 2005.

Renforth, P.: The negative emission potential of alkaline materials. *Nature Communications*, 10, 1401. <https://doi.org/10.1038/s41467-019-09475-5>, 2019.

Stillings, L. L., Drever, J. I., Brantley, S. L., Sun, Y., and Oxburgh, R.: Rates of feldspar dissolution at pH 3–7 with 0–8 mM oxalic acid. *Chemical Geology*, 132, 79–89. [https://doi.org/10.1016/S0009-2541\(96\)00043-5](https://doi.org/10.1016/S0009-2541(96)00043-5), 1996.

Stillings, L. L., Drever, J., and Poulson S.: Oxalate adsorption at a plagioclase (An(47)) surface and models for ligand promoted dissolution. *Environmental Science and Technology*, 32, 2856–2864. <https://doi.org/10.1021/es980258d>, 1998.

Stolze, L., Arora, B., Dwivedi, D., Steefel, C. I., Li, Z., Carrero, S., Gilbert, B., Nico, P., and Bill, M.: Aerobic respiration controls on shale weathering. *Geochimica et Cosmochimica Acta*, 340, 172–188. <https://doi.org/10.1016/j.gca.2022.11.002>, 2023.

Wolery, T. J., Jackson, K. J., Bourcier, W. L., Bruton, C. J., Viani, B. E., Knauss, K. G., and Delany, J. M.: Current status of the EQ3/6 software package for geochemical modeling, in Melchior, D. C., and Bassett, R. L., editors,

Chemical Modeling of Aqueous Systems II: ACS Symposium Series 416, 104–116. <https://doi.org/10.1021/bk-1990-0416.ch008>, 1990.

Yoon, T. H., Johnson, S. B., Musgrave, C., and Brown, Jr, G. E.: Adsorption of organic matter at mineral/water interfaces: I. ATR-FTIR spectroscopic and quantum chemical study of oxalate adsorbed at boehmite/water and corundum/water interfaces. *Geochimica et Cosmochimica Acta*, 68, 4505–4518. <https://doi.org/10.1016/j.gca.2004.04.025>, 2004.

S2 Tables

Table S1: Mineral and aqueous chemical reactions

Mineral reactions	$\log(K_{eq})^a$	$\log(rate)^*$	ssa*	a ^x
Batch and 1-D models of plagioclase and kaolinite:				
plagioclase + 4.8H ⁺ -> 1.2Al ³⁺ + 0.8Na ⁺ + 0.2Ca ²⁺ + 2.8 SiO _{2(aq)} + 2.4H ₂ O	2.88	-16.9 ^{b,c}	1.14 ^b	total Al- -0.333 ^d
plagioclase + 4.8H ⁺ -> 1.2Al ³⁺ + 0.8Na ⁺ + 0.2Ca ²⁺ + 2.8 SiO _{2(aq)} + 2.4H ₂ O	2.88	-19.94 ^{b,c}	1.14 ^b	H ⁺ - -0.471 ^e , total Al- -0.333 ^d
plagioclase + 4.8H ⁺ -> 1.2Al ³⁺ + 0.8Na ⁺ + 0.2Ca ²⁺ + 2.8 SiO _{2(aq)} + 2.4H ₂ O	2.88	-14.5 ^{b,c}	1.14 ^b	H ⁺ - 0.317 ^e , total Al- -0.333 ^d
kaolinite + 6H ⁺ -> 2Al ³⁺ + 2SiO _{2(aq)} + 5H ₂ O	6.81	-20.5 ^{b,c}	10 ^b	total Al- -0.333 ^d
kaolinite + 6H ⁺ -> 2Al ³⁺ + 2SiO _{2(aq)} + 5H ₂ O	6.81	-24.37 ^{b,c}	10 ^b	H ⁺ - -0.472 ^e , total Al- -0.333 ^d
kaolinite + 6H ⁺ -> 2Al ³⁺ + 2SiO _{2(aq)} + 5H ₂ O	6.81	-18.63 ^{b,c}	10 ^b	H ⁺ - 0.777 ^e , total Al- -0.333 ^d
All rock types:				
illite + 8H ⁺ -> 0.25Mg ²⁺ + 0.6K ⁺ + 2.3Al ³⁺ + 3.5SiO _{2(aq)} + 5H ₂ O	9.03	-18 ^{c,f}	10 ^b	
smectite + 7.32H ⁺ -> 0.165Ca ²⁺ + 2.33Al ³⁺ + 3.67SiO _{2(aq)} + 4.66H ₂ O	5.59	-18.5 ^c	10 ^b	
chlorite + 16H ⁺ -> 5Mg ²⁺ + 2Al ³⁺ + 3SiO _{2(aq)} + 12H ₂ O	67.24	-18 ^c	10 ^b	
gibbsite + 3H ⁺ -> Al ³⁺ + 3H ₂ O	7.76	-16 ⁱ	10 ^b	
kaolinite + 6H ⁺ -> 2Al ³⁺ + 2SiO _{2(aq)} + 5H ₂ O	6.81	-20.5 ^{b,c}	10 ^b	total Al- -0.333 ^d
kaolinite + 6H ⁺ -> 2Al ³⁺ + 2SiO _{2(aq)} + 5H ₂ O	6.81	-24.37 ^{b,c}	10 ^b	H ⁺ - -0.472 ^e , total Al- -0.333 ^d
kaolinite + 6H ⁺ -> 2Al ³⁺ + 2SiO _{2(aq)} + 5H ₂ O	6.81	-18.63 ^{b,c}	10 ^b	H ⁺ - 0.777 ^e , total Al- -0.333 ^d

$\text{Fe}(\text{OH})_3 + 3\text{H}^+ \rightarrow \text{Fe}^{3+} + 3\text{H}_2\text{O}$	5.66	-9.5 ^f	0.5 ^f	
Shale:				
plagioclase + 4.8H ⁺ → 1.2Al ³⁺ + 0.8Na ⁺ + 0.2Ca ²⁺ + 2.8 SiO _{2(aq)} + 2.4H ₂ O	2.88	-16.9 ^{b,c}	1.14 ^b	total Al- -0.333 ^d
plagioclase + 4.8H ⁺ → 1.2Al ³⁺ + 0.8Na ⁺ + 0.2Ca ²⁺ + 2.8 SiO _{2(aq)} + 2.4H ₂ O	2.88	-19.94 ^{b,c}	1.14 ^b	H ⁺ - -0.471 ^e , total Al- -0.333 ^d
plagioclase + 4.8H ⁺ → 1.2Al ³⁺ + 0.8Na ⁺ + 0.2Ca ²⁺ + 2.8 SiO _{2(aq)} + 2.4H ₂ O	2.88	-14.5 ^{b,c}	1.14 ^b	H ⁺ - 0.317 ^e , total Al- -0.333 ^d
pyrite + 3.5O _{2(aq)} + H ₂ O → Fe ²⁺ + 2 SO ₄ ²⁻ + 2H ⁺	217.42	-8.1 ^f	0.05 ^f	
dolomite + 4H ⁺ → Ca ²⁺ + Mg ²⁺ + 2CO _{2(aq)} + 2H ₂ O	9.16	-8.6 ^{f,g}	0.069 ^g	
solid organic matter → oxalate ²⁻ + 2 H ⁺	-14.87	-18.5 ^f	10 ^b	
quartz → SiO _{2(aq)}	-4	-50 ^b	0.23 ^b	
Granite:				
plagioclase + 4.8H ⁺ → 1.2Al ³⁺ + 0.8Na ⁺ + 0.2Ca ²⁺ + 2.8 SiO _{2(aq)} + 2.4H ₂ O	2.88	-16.9 ^{b,c}	1.14 ^b	total Al- -0.333 ^d
plagioclase + 4.8H ⁺ → 1.2Al ³⁺ + 0.8Na ⁺ + 0.2Ca ²⁺ + 2.8 SiO _{2(aq)} + 2.4H ₂ O	2.88	-19.94 ^{b,c}	1.14 ^b	H ⁺ - -0.471 ^e , total Al- -0.333 ^d
plagioclase + 4.8H ⁺ → 1.2Al ³⁺ + 0.8Na ⁺ + 0.2Ca ²⁺ + 2.8 SiO _{2(aq)} + 2.4H ₂ O	2.88	-14.5 ^{b,c}	1.14 ^b	H ⁺ - 0.317 ^e , total Al- -0.333 ^d
K-feldspar + 4H ⁺ → Al ³⁺ + K ⁺ + 2H ₂ O + 3SiO _{2(aq)}	-0.28	-17.9 ^h	1.0 ^h	total Al- -0.333 ^d
biotite + 13H ⁺ + 0.75O _{2(aq)} → Al ³⁺ + K ⁺ + 3Fe ³⁺ + 3SiO _{2(aq)} + 7.5H ₂ O	38.47	-17.3 ^h	5.0 ^h	total Al- -0.333 ^d
amphibole + 22H ⁺ → 3Al ³⁺ + Na ⁺ + 2Ca ²⁺ + 4Mg ²⁺ + 6SiO _{2(aq)} + 12H ₂ O	101.99	-16.6 ^h	1.0 ^h	total Al- -0.333 ^d
quartz → SiO _{2(aq)}	-4	-50 ^b	0.23 ^b	
Basalt:				
plagioclase + 8H ⁺ → 2Al ³⁺ + Ca ²⁺ + 2SiO _{2(aq)} + 4H ₂ O	26.58	-16.9 ^{b,c}	1.14 ^b	total Al- -0.333 ^d
plagioclase + 8H ⁺ → 2Al ³⁺ + Ca ²⁺ + 2SiO _{2(aq)} + 4H ₂ O	26.58	-11.38 ^{b,c}	1.14 ^b	H ⁺ - 1.411 ^e , total Al- -0.333 ^d
pyroxene + 4.43H ⁺ + 0.1075O _{2(aq)} → 2SiO _{2(aq)} + Ca ²⁺ + 0.57Mg ²⁺ + 0.43Fe ³⁺ + 2.215H ₂ O	23.72	-16.3 ^h	1.0 ^h	total Al- -0.333 ^d
olivine + 4H ⁺ → SiO _{2(aq)} + 2Mg ²⁺ + 2H ₂ O	27.86	-14.7 ^h	0.2 ^h	total Al- -0.333 ^d
volcanic glass + 1.08H ⁺ → SiO _{2(aq)} + 0.36Al ³⁺ + 1.08H ₂ O	0.03 ^j	-15.7 ^h	2.0 ^h	total Al- -0.333 ^d
Aqueous reactions (all rock types)				Monod terms
Fe ²⁺ + 0.25O _{2(aq)} + H ⁺ → Fe ³⁺ + 0.5H ₂ O	8.47	-5.82 ^f		

total O₂- 6.25e-6,
 $0.5\text{O}_{2(\text{aq})} + \text{oxalate}^{2-} + 2\text{H}^+ \rightarrow 2\text{CO}_{2(\text{aq})} + \text{H}_2\text{O}$ 20.52 -3.00^f total oxalate- 1e-4

*Rate for mineral reactions is in mol/m²/s, rate for aqueous reactions is in mol/L/s, and specific surface area is in m²/g. Rate constants correspond to rates @ temperatures of 25°C. a- equilibrium constants from Wolery et al. (1990). Rates and specific surface area for plagioclase and kaolinite estimated from b- Lawrence et al. (2014) and c- Maher et al. (2009) and adjusted for Al- and pH-dependence based on d- Palandri and Kharaka (2004) and e- Oelkers et al. (1994). Dolomite, pyrite, and Fe hydroxide parameters from f- Stolze et al. (2023) and g- Pokrovsky et al. (2005). K-feldspar, biotite, amphibole, and pyroxene parameters from h- Ferrier and West (2017). Gibbsite rate estimated by difference in kaolinite and gibbsite precipitation rates from i- Nagy et al. (1991) and Nagy and Lasaga (1992). Volcanic glass stoichiometry and equilibrium constant from h- Oelkers and Gislason (2001).

Table S2: Initial aqueous chemistry of water flowing through weathering profiles in base models

solute	concentration (mM)
CO _{2(aq)}	in equilibrium with 15,000ppm CO _{2(g)}
O _{2(aq)}	in equilibrium with 20% O _{2(g)}
Na ⁺	0.1
Mg ²⁺	0.019
K ⁺	0.01
Ca ²⁺	0.032
HAIO _{2(aq)}	0
SiO _{2(aq)}	0
Cl ⁻	0.12
NO ₃ ⁻	0.03
Fe ²⁺	0
Fe ³⁺	0
SO ₄ ²⁻	0.03
oxalic acid	0.1
pH	5.5

Table S3: Aqueous complexation reactions

Aqueous reaction	log K
Al(OH) ₂ ⁺ + 2H ⁺ → Al ³⁺ + 2H ₂ O	10.59
Al(OH) _{3(aq)} + 3H ⁺ → Al ³⁺ + 3H ₂ O	16.17
Al(OH) ₄ ⁻ + 4H ⁺ → Al ³⁺ + 4H ₂ O	22.16
AlOH ²⁺ + H ⁺ → Al ³⁺ + H ₂ O	4.95
CaCl ⁺ → Ca ²⁺ + Cl ⁻	0.7
CaCl _{2(aq)} → Ca ²⁺ + 2Cl ⁻	0.64
CaOH ⁺ + H ⁺ → Ca ²⁺ + H ₂ O	12.85
HCO ₃ ⁻ + H ⁺ → CO _{2(aq)} + H ₂ O	6.34

$\text{H}_2\text{SiO}_4^{--} + 2\text{H}^+ \rightarrow \text{SiO}_2(\text{aq}) + 2\text{H}_2\text{O}$	22.96
$\text{Al}^{+++} + 2\text{H}_2\text{O} \rightarrow \text{HAlO}_2(\text{aq}) + 3\text{H}^+$	-16.42
$\text{HCl}(\text{aq}) \rightarrow \text{H}^+ + \text{Cl}^-$	-0.67
$\text{HSiO}_3^- + \text{H}^+ \rightarrow \text{SiO}_2(\text{aq}) + \text{H}_2\text{O}$	9.95
$\text{KCl}(\text{aq}) \rightarrow \text{K}^+ + \text{Cl}^-$	1.49
$\text{MgCl}^+ \rightarrow \text{Mg}^{++} + \text{Cl}^-$	0.13
$\text{NaAlO}_2(\text{aq}) + 4\text{H}^+ \rightarrow \text{Al}^{+++} + \text{Na}^+ + 2\text{H}_2\text{O}$	23.63
$\text{NaCl}(\text{aq}) \rightarrow \text{Na}^+ + \text{Cl}^-$	0.78
$\text{NaHSiO}_3(\text{aq}) + \text{H}^+ \rightarrow \text{Na}^+ + \text{SiO}_2(\text{aq}) + \text{H}_2\text{O}$	8.3
$\text{NaOH}(\text{aq}) + \text{H}^+ \rightarrow \text{Na}^+ + \text{H}_2\text{O}$	14.79
$\text{OH}^- + \text{H}^+ \rightarrow \text{H}_2\text{O}$	14
$\text{CO}_3^{--} + \text{H}^+ \rightarrow \text{HCO}_3^-$	10.33
$\text{CaCO}_3(\text{aq}) + \text{H}^+ \rightarrow \text{Ca}^{++} + \text{HCO}_3^-$	7
$\text{CaHCO}_3^+ \rightarrow \text{Ca}^{++} + \text{HCO}_3^-$	-1.04
$\text{MgCO}_3(\text{aq}) + \text{H}^+ \rightarrow \text{Mg}^{++} + \text{HCO}_3^-$	7.35
$\text{MgHCO}_3^+ \rightarrow \text{Mg}^{++} + \text{HCO}_3^-$	-1.04
$\text{NaCO}_3^- + \text{H}^+ \rightarrow \text{Na}^+ + \text{HCO}_3^-$	9.81
$\text{NaHCO}_3(\text{aq}) \rightarrow \text{Na}^+ + \text{HCO}_3^-$	-0.15
$\text{SrCO}_3(\text{aq}) + \text{H}^+ \rightarrow \text{Sr}^{++} + \text{HCO}_3^-$	7.46
$\text{H-Oxalate}^- \rightarrow \text{oxalate}^{--} + \text{H}^+$	-4.27
$\text{Oxalate}^{--} + 2\text{H}^+ \rightarrow \text{oxalic acid}(\text{aq})$	5.52
$\text{Al-oxalate}^+ \rightarrow \text{Al}^{+++} + \text{oxalate}^{--}$	-7.1
$\text{Al-oxalate}_2^- \rightarrow \text{Al}^{+++} + 2\text{oxalate}^{--}$	-13
$\text{Al-oxalate}_3^{---} \rightarrow \text{Al}^{+++} + 3\text{oxalate}^{--}$	-16.3
$\text{AlOH-oxalate}_2^{--} + \text{H}^+ \rightarrow \text{Al}^{+++} + 2\text{oxalate}^{--} + \text{H}_2\text{O}$	-6.84
$\text{AlOH-oxalate}(\text{aq}) + \text{H}^+ \rightarrow \text{Al}^{+++} + \text{oxalate}^{--} + \text{H}_2\text{O}$	-2.57
$\text{AlOH}_2\text{-oxalate}^- + 2\text{H}^+ \rightarrow \text{Al}^{+++} + \text{oxalate}^{--} + 2\text{H}_2\text{O}$	3.12
$\text{Ca-oxalate}(\text{aq}) \rightarrow \text{Ca}^{++} + \text{oxalate}^{--}$	-3
$\text{Ca-oxalate}_2^{--} \rightarrow \text{Ca}^{++} + 2\text{oxalate}^{--}$	-8.1

279

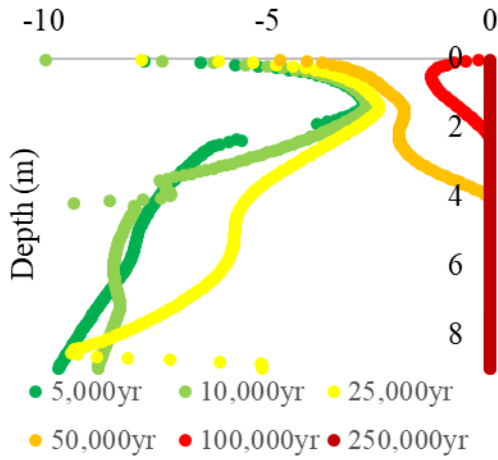
280 **Table S4: Surface complexation reactions- >AlOH on plagioclase at 6.0×10^{-6} mole/m²**

Surface complexation	log K
$>\text{AlO}^- + \text{H}^+ \rightarrow >\text{AlOH}$	8.5
$>\text{AlOH}_2^+ \rightarrow >\text{AlOH} + \text{H}^+$	-1.9
$>\text{AlOxH} + \text{H}_2\text{O} \rightarrow \text{oxalic acid}(\text{aq}) + >\text{AlOH}$	-7.3
$>\text{AlOx}^- + \text{H}_2\text{O} + \text{H}^+ \rightarrow \text{oxalic acid}(\text{aq}) + >\text{AlOH}$	-2.4

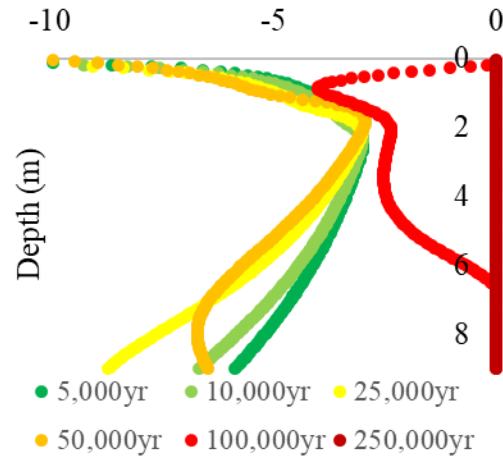
Table S5: Alkalinity generation by plagioclase dissolution and kaolinite formation in a batch reactor after 2.5 years of reaction versus alkalinity at the base of a 1-D profile (2.5 year residence time) at various plagioclase content and CO₂ concentrations

Batch Reactor	500 ppm CO₂	5,000 ppm CO₂	50,000 ppm CO₂
8% plagioclase	0.297 mM	0.271 mM	0.304 mM
15% plagioclase	0.337 mM	0.317 mM	0.370 mM
50% plagioclase	0.359 mM	0.839 mM	0.674 mM
1-D Flow System	500 ppm CO₂	5,000 ppm CO₂	50,000 ppm CO₂
8% plagioclase	0.278 mM	0.270 mM	0.302 mM
15% plagioclase	0.341 mM	0.314 mM	0.366 mM
50% plagioclase	0.364 mM	0.574 mM	0.671 mM
(1D – Batch)/Batch	500 ppm CO₂	5,000 ppm CO₂	50,000 ppm CO₂
8% plagioclase	-7%	-1%	-1%
15% plagioclase	1%	-1%	-1%
50% plagioclase	1%	-32%	0%

A) Plagioclase dissolution rates
mole/m³/sec X 10¹⁰



B) Plagioclase dissolution rates
mole/m³/sec X 10¹⁰



C) Plagioclase dissolution rates
mole/m³/sec X 10¹⁰

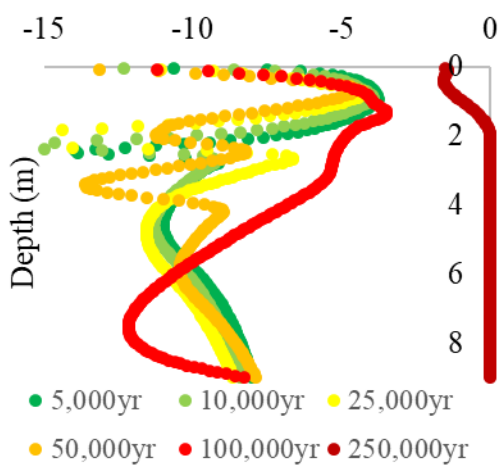


Figure S1: Depth profiles of plagioclase dissolution for A) shale, B) granite (B), and C) basalt over 250,000 years of weathering

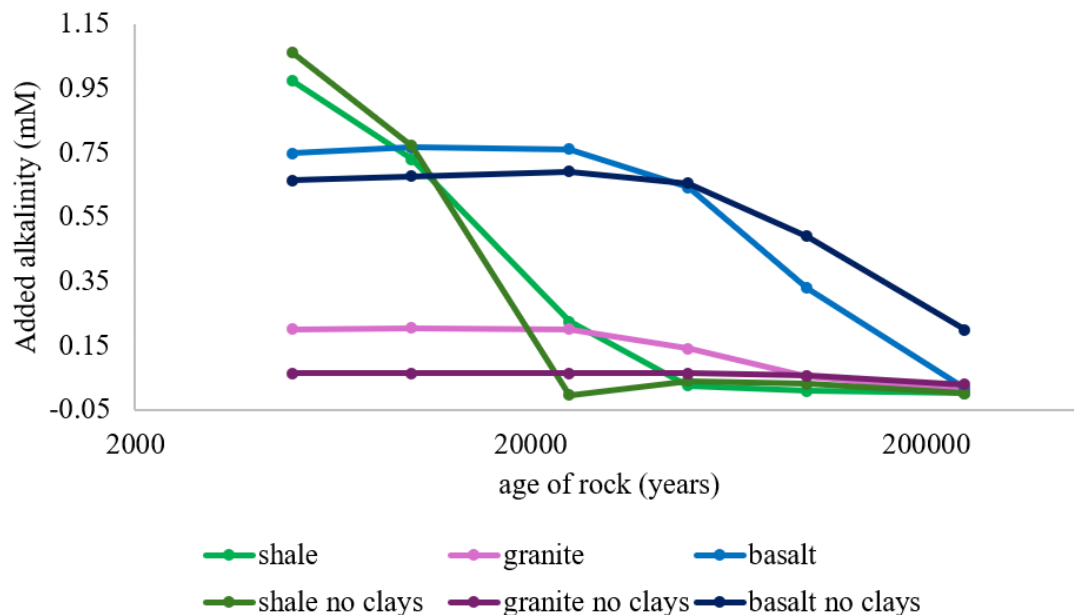


Figure S2: Alkalinity generated by shale, granite, and basalt with and without clay formation as chemical weathering progresses.

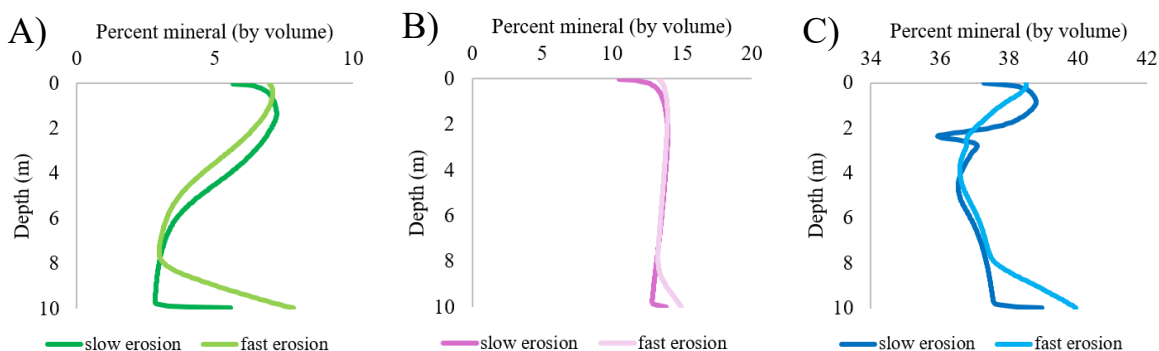


Figure S3: Depth profiles of plagioclase dissolution (A- shale, B- granite, C- basalt) after 10,000 years of weathering at slow (0.01mm/yr) and fast (0.2mm/yr) erosion rates.

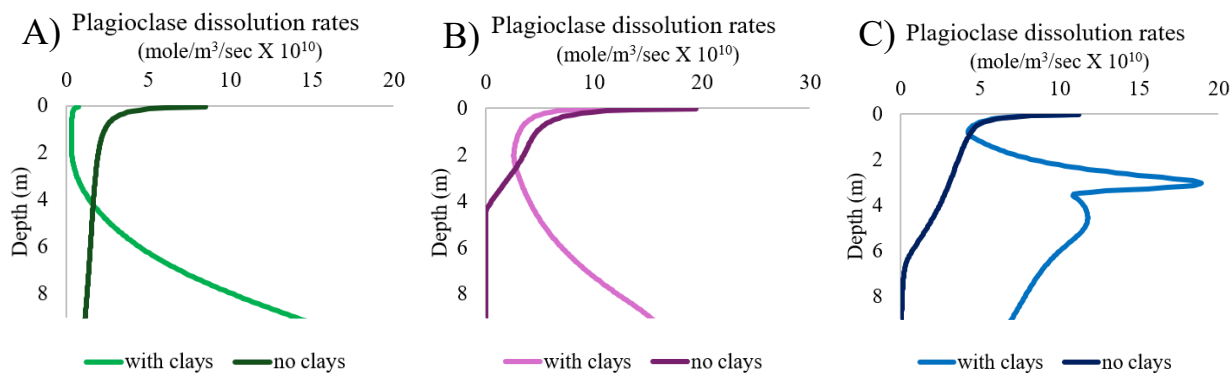


Figure S4: Depth profiles of plagioclase dissolution (A- shale, B- granite, C- basalt) near steady state at high erosion rates (0.2 mm/year).

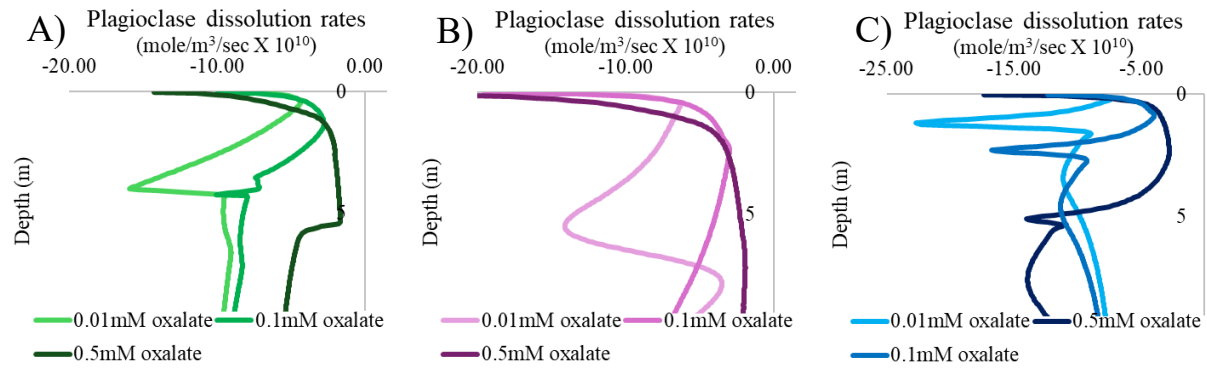


Figure S5: The effect of oxalate concentrations on plagioclase dissolution during A) shale, B) granite, and C) basalt weathering

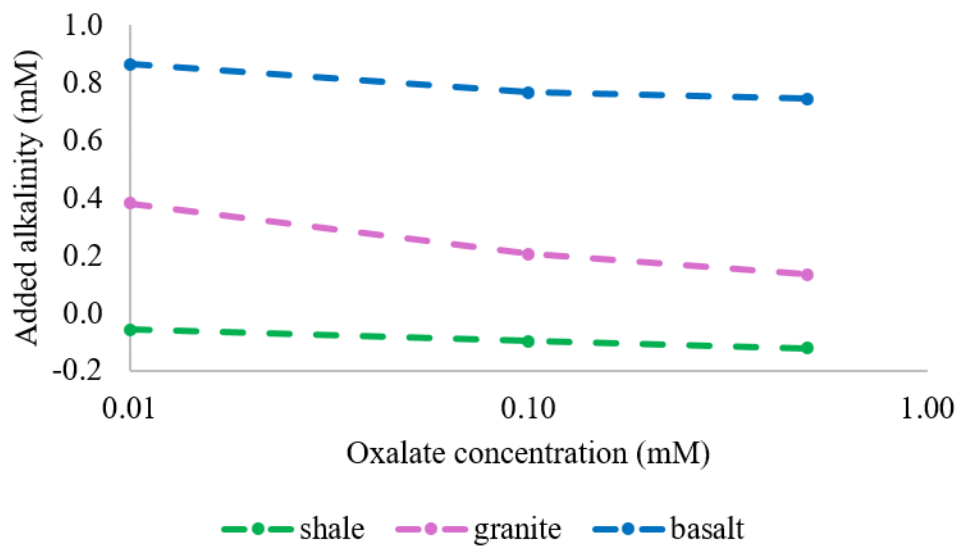


Figure S6: Alkalinity generation versus initial oxalate concentration during shale, granite, and basalt weathering

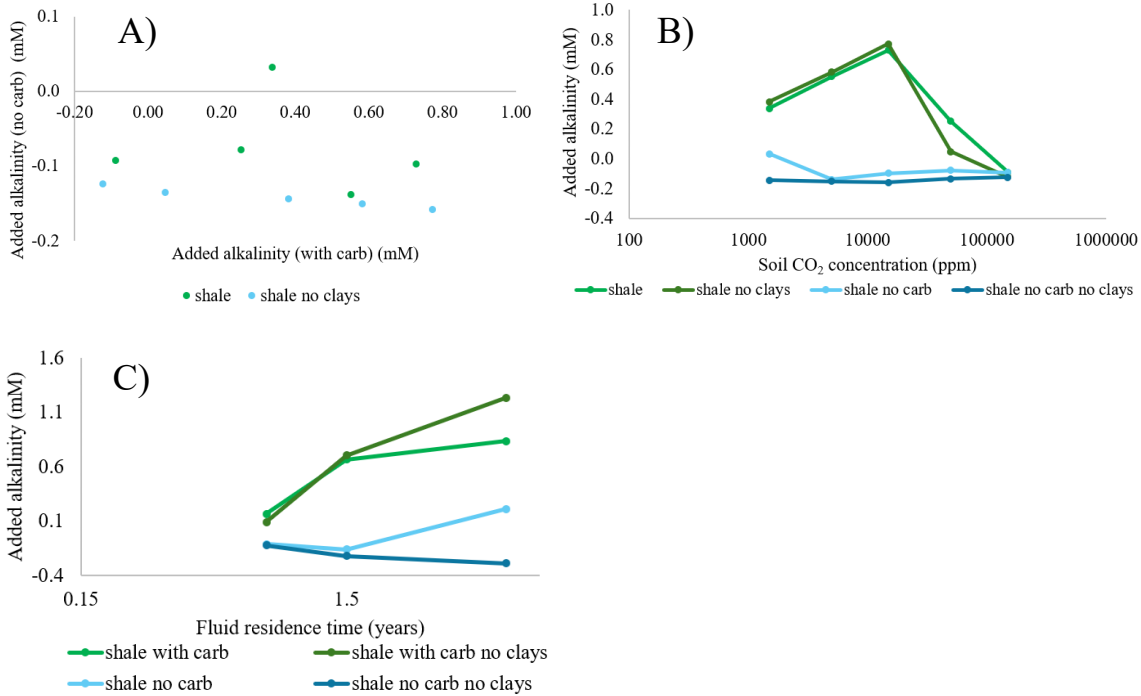


Figure S7: A) The amount of added alkalinity not corrected for carbonate dissolution versus added alkalinity corrected for carbonate dissolution in shale models with and without clay formation. B) The amount of added alkalinity versus CO₂ concentrations for shale models with and without clay formation both including and excluding carbonate dissolution. C) The amount of added alkalinity versus fluid residence time for shale models with and without clay formation both including and excluding carbonate dissolution.

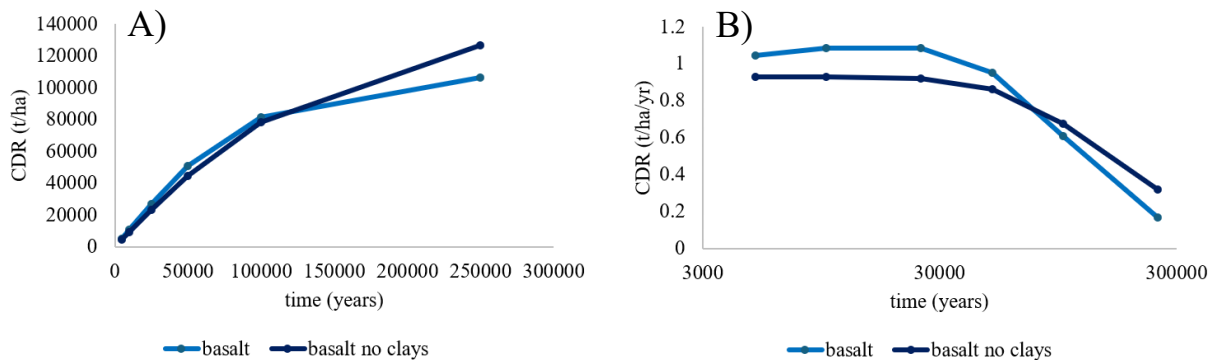
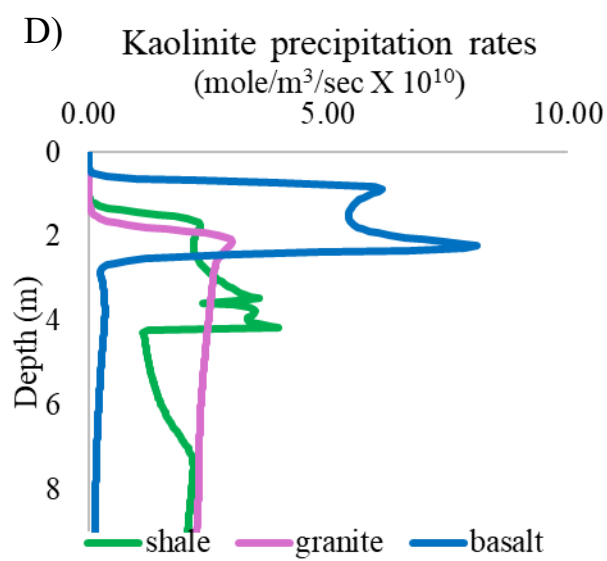
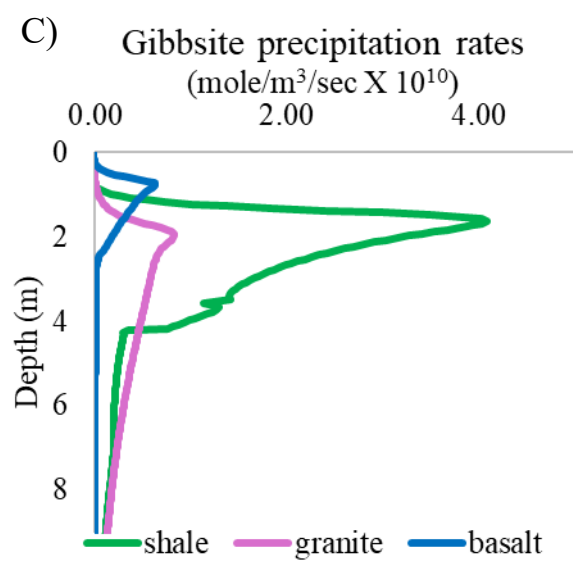
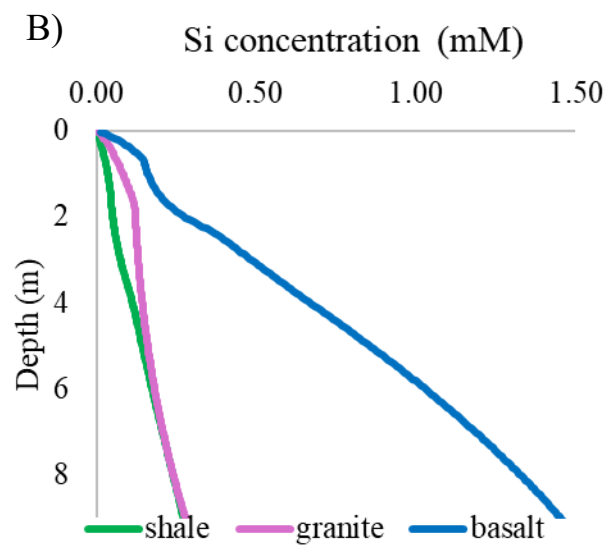
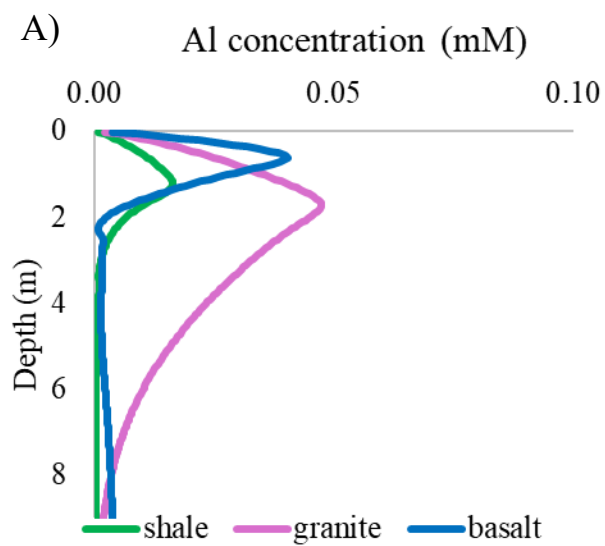


Figure S8: A) CDR (tons/hectare) versus modeled time for basalt models with and without clay formation as chemical weathering progresses. B) CDR rate (tons/hectare/year) versus modeled time.



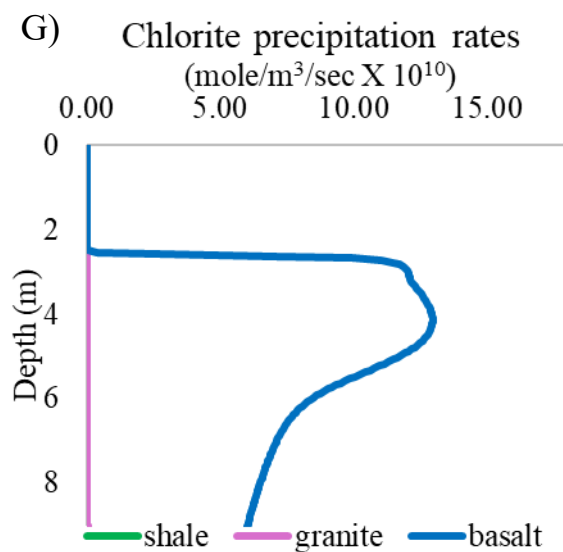
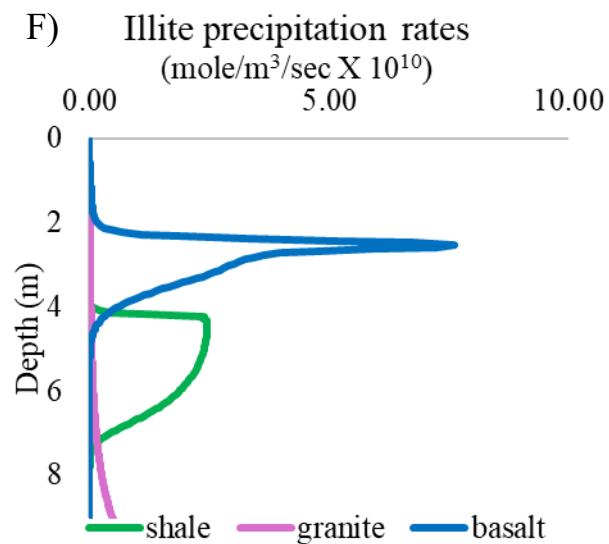
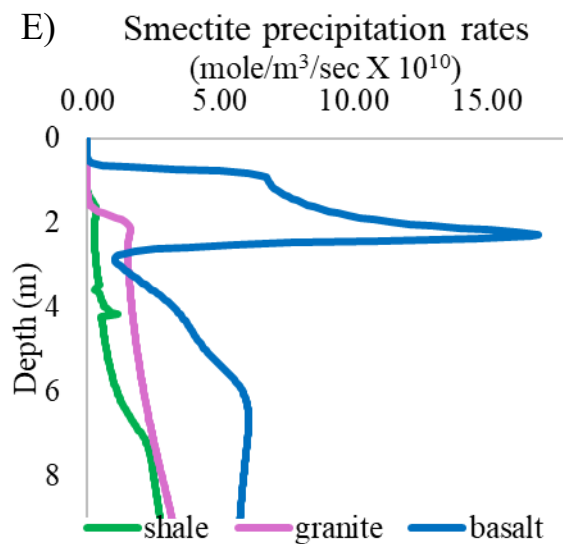


Figure S9: Depth profiles of aqueous A) Al and B) Si concentrations as well as formation of C) gibbsite, D) kaolinite, E) smectite, F) illite, and G) chlorite in clay containing models of shale, granite, and basalt weathering.

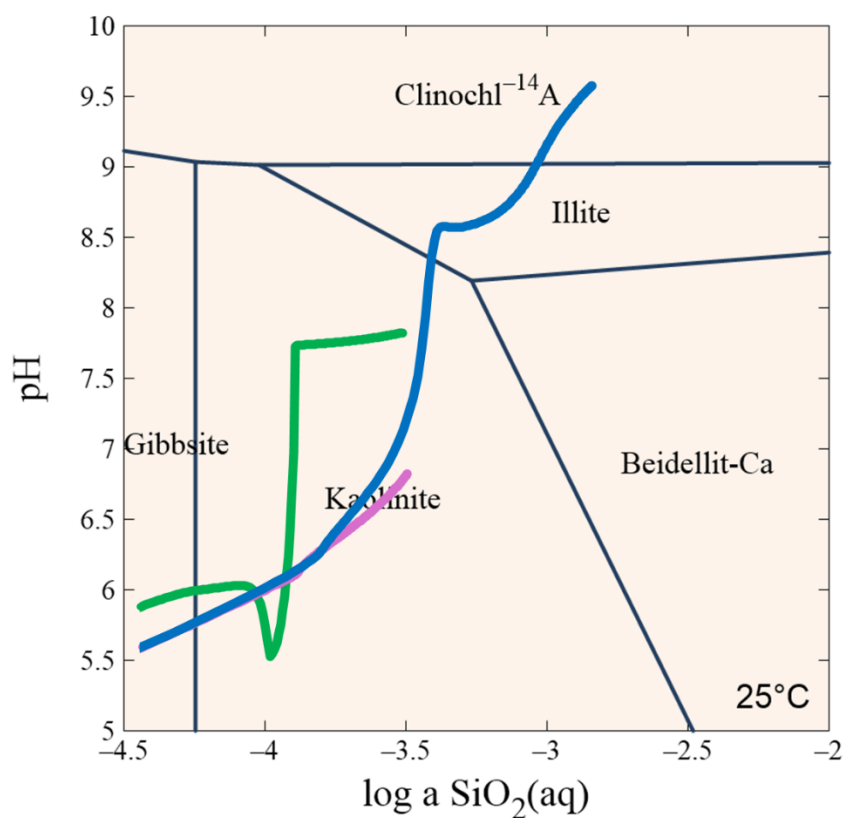


Figure S10: Stability diagram of clay formation versus aqueous Si concentration and pH at 0.1 mM Ca, 0.05 mM K, and 0.01 mM Mg. Reaction paths of shale, granite, and basalt are illustrated in green, pink, and blue, respectively (pH and Si increase with depth). Stability diagram created using Geochemist's Workbench (Bethke et al., 2021).

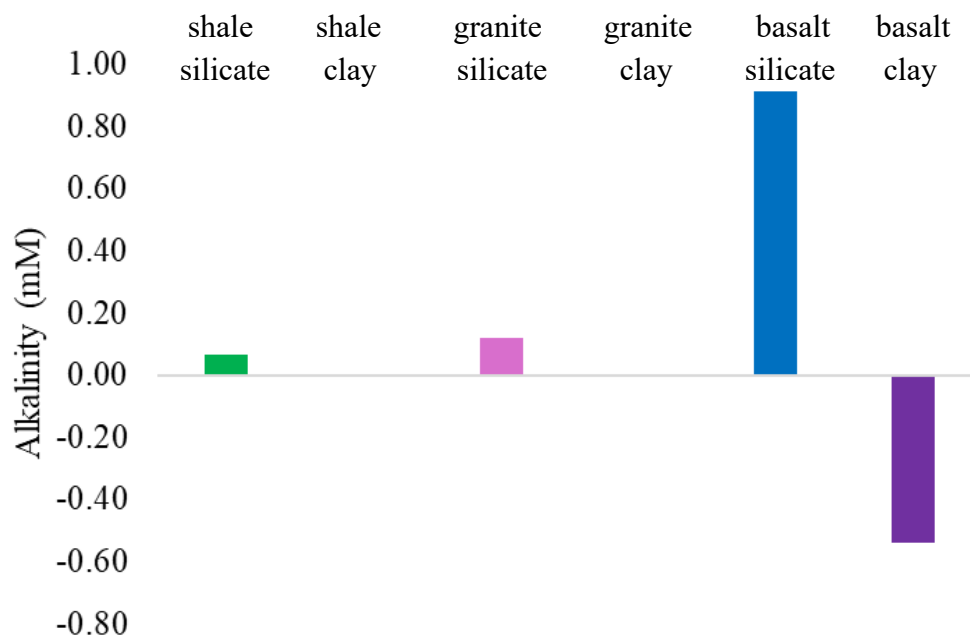


Figure S11: The amount of alkalinity generated by silicate dissolution reactions and alkalinity removed by clay precipitation reactions for rock weathering models at 15,000 ppm CO₂. No chlorite precipitates during shale and granite weathering, so the removal of alkalinity by clay formation is minimal.