

# Decoupling kinetic and hydrological controls on global silicate weathering

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## Abstract

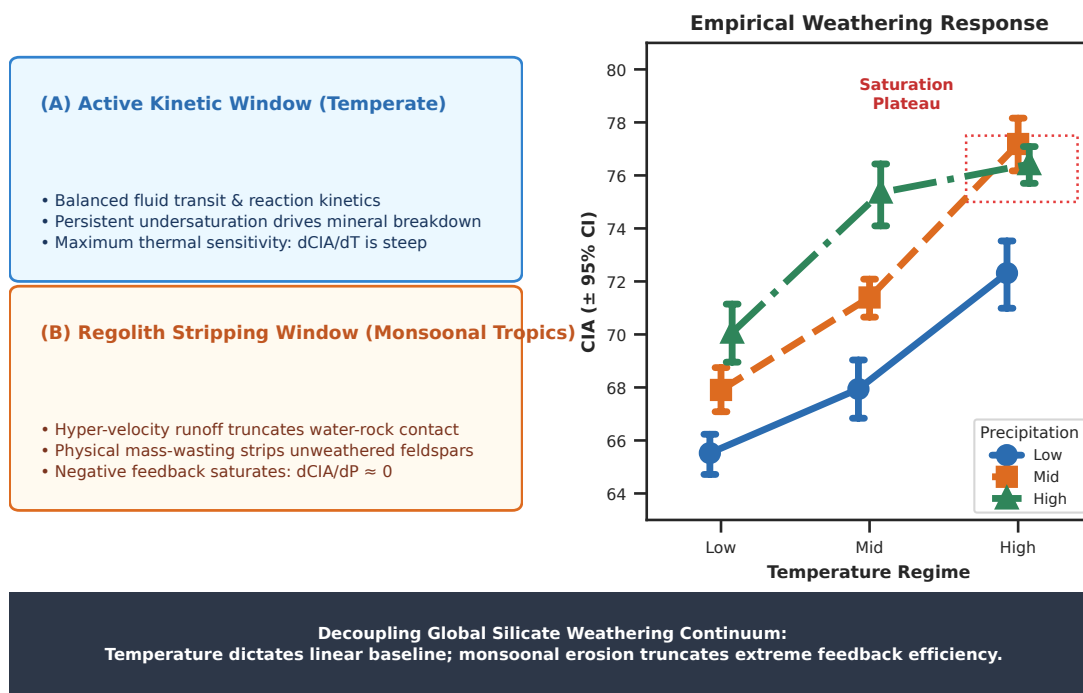
Continental silicate weathering acts as the primary geological sink for atmospheric carbon dioxide over multimillion-year timescales, yet whether weathering fluxes are fundamentally governed by thermodynamic temperature limits or hydrological runoff remains fiercely debated. Resolving this controversy globally has been hindered by the strong natural collinearity of terrestrial temperature and precipitation. Here, we decouple these drivers by applying a stratified  $3 \times 3$  factorial response-surface framework to 5,292 harmonised modern river sediment samples compiled from global geochemical databases and WorldClim grids. Two-way analysis of variance reveals that temperature exerts a substantially larger main effect ( $F = 163.34$ , partial  $\eta^2 = 0.058$ ) than precipitation ( $F = 87.33$ , partial  $\eta^2 = 0.032$ ). Furthermore, significant interaction curvature ( $p < 0.00001$ ) uncovers an asymptotic saturation plateau in warm, hyper-humid extremes: shifting from moderate to high rainfall in the warmest tier yields no alteration gain ( $\Delta\text{CIA} = -0.77$ ,  $p = 0.42$ ;  $\Delta\text{CIX} = -0.44$ ,  $p = 0.58$ ). Molar cation preservation ratios confirm that this plateau is driven by primary feldspar bypass resulting from monsoonal regolith stripping, establishing critical non-linear constraints for Earth System Models.

**Keywords:** Silicate weathering; Chemical Index of Alteration (CIA); Factorial ANOVA; Climate collinearity; Earth System Models; Regolith stripping; Carbon cycle

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## 1 Introduction

Continental silicate weathering stabilises planetary habitability over geological epochs by consuming atmospheric  $\text{CO}_2$  and exporting alkalinity to the oceans (Walker et al., 1981; Kump et al., 2000). Despite universal acceptance of this negative feedback loop, the primary physical controls regulating global weathering fluxes remain fiercely disputed (Gaillardet et al., 1999; West et al., 2005). Classical geochemical investigations argue for ‘kinetically limited’ regimes, where ambient temperature is the master control governing the thermodynamics of mineral dissolution (Walker et al., 1981; Gislason et al., 2009; Oelkers et al., 2009; Brantley et al., 2023). Conversely,



**Graphical Abstract.** Decoupling the Global Silicate Weathering Continuum: Conceptual catchment regimes (Active Kinetic Window vs. Regolith Stripping Window) paired with the empirical  $3 \times 3$  factorial response surface and summary takeaway banner.

‘transport-limited’ models assert that water runoff and physical erosion dominate by flushing pore solutions and replenishing reactive mineral surfaces (West et al., 2005; Hilley and Porder, 2008; Maher and Chamberlain, 2014).

This division has intensified in contemporary literature. While observational regressions on modern river sediments conclude that temperature exercises primary control globally (Deng et al., 2022), recent machine learning frameworks (e.g., Random Forest, XGBoost; Huang et al., 2025) conclude the exact opposite, identifying runoff as the dominant global predictor and restricting thermal dominance to active tectonic belts. Reconciling these views requires transitioning beyond binary dichotomies toward a dynamic ‘silicate weathering continuum’ (Trapp-Müller et al., 2025) comprising three distinct regimes (Kanzaki et al., 2025):

- Runoff-Limited (RL) regimes** at arid or permafrost margins where fluid throughput is insufficient to flush pore waters, allowing chemical equilibrium to stall weathering regardless of thermal energy (Brantley et al., 2023);
- Kinetic-Limited (KL) regimes** in temperate, sub-humid catchments where fluid transit times and mineral-water contact balance, maximising temperature sensitivity; and
- Erosive Transport-Limited (ETL) and supply-limited regimes** in warm, hyper-humid basins where rapid denudation or fluid dilution truncates dissolution (Dosseto et al., 2015; Kanzaki et al., 2025).

A major barrier in testing this continuum is climatic collinearity: across Earth’s surface, mean annual temperature (MAT) and mean annual precipitation (MAP) strongly covary (Deng et al.,

2022). While machine learning captures non-linear correlations, its ‘black-box’ structure fails to provide the isolated kinetic parameters and explicit interaction coefficients required by Earth System Models. Here, we apply a stratified  $3 \times 3$  factorial response-surface framework paired with Games-Howell post-hoc contrasts to 5,292 globally distributed river sediments, providing transparent, empirically isolated parameterisations across the silicate weathering continuum.

## 2 Methods and Data Compilation

### 2.1 Geochemical Harmonisation and Filtering

We integrated two extensive, peer-reviewed global fluvial sediment compilations: the global catchment dataset of Deng et al. (2022) (Zenodo Record 6066701) and the Global River Sediments (GloRiSe v1.1) database of Muller et al. (2021) (Zenodo Record 4485795). Climatological variables (MAT in °C; MAP in mm/yr) were extracted from high-resolution WorldClim v2.1 grids (Fick and Hijmans, 2017) using catchment-centroid intersections.

An objective, rule-based screening protocol was applied:

1. **Analytical completeness:** Only samples with complete major oxide suites ( $\text{Al}_2\text{O}_3$ ,  $\text{CaO}$ ,  $\text{Na}_2\text{O}$ ,  $\text{K}_2\text{O}$ ) were retained.
2. **Lithological and stoichiometric validity:** Samples exhibiting non-siliciclastic mineral concentrations ( $\text{Al}_2\text{O}_3 \leq 0$  wt.% or  $\text{Al}_2\text{O}_3 > 45$  wt.%) or extreme silica depletion ( $\text{SiO}_2 < 30$  wt.%) were removed to exclude bauxitic/lateritic crusts and industrial ore concentrates.
3. **Fluvial origin:** Coastal, estuarine, marine turbidite, and aeolian samples lying outside terrestrial drainage basins were excluded.

The resulting analytical database contains  $n = 5,292$  continental river sediment samples with co-registered climatic parameters.

### 2.2 Geochemical Proxies and Factorial Discretisation

Silicate weathering intensity was quantified using the Chemical Index of Alteration (CIA; Nesbitt and Young, 1982):

$$\text{CIA} = \left[ \frac{\text{Al}_2\text{O}_3}{\text{Al}_2\text{O}_3 + \text{CaO}^* + \text{Na}_2\text{O} + \text{K}_2\text{O}} \right] \times 100 \quad (1)$$

where oxides are expressed in molar proportions and  $\text{CaO}^*$  represents calcium hosted exclusively in silicates, corrected following McLennan (1993). To ensure that variations in CIA are not driven by carbonate contamination, we evaluated the carbonate-free index CIX (Garzanti et al., 2014):

$$\text{CIX} = \left[ \frac{\text{Al}_2\text{O}_3}{\text{Al}_2\text{O}_3 + \text{Na}_2\text{O} + \text{K}_2\text{O}} \right] \times 100 \quad (2)$$

To trace unweathered primary aluminosilicates bypassing dissolution, we evaluated the molar mobile-to-immobile cation preservation ratio  $[(\text{Na}_2\text{O} + \text{K}_2\text{O})/\text{Al}_2\text{O}_3]$ . Continuous climate parameters were partitioned into empirical terciles:

• **MAT terciles:** Low ( $< 9.03^{\circ}\text{C}$ ,  $n = 1,764$ ); Mid ( $9.03$  to  $16.15^{\circ}\text{C}$ ,  $n = 1,767$ ); High ( $> 16.15^{\circ}\text{C}$ ,  $n = 1,761$ ).

• **MAP terciles:** Low ( $< 583$  mm/yr,  $n = 1,764$ ); Mid ( $583$  to  $1,424$  mm/yr,  $n = 1,765$ ); High ( $> 1,424$  mm/yr,  $n = 1,763$ ).

Two-way factorial Analysis of Variance (ANOVA) using Type-III Sum of Squares was applied to partition variance into main effects and interactions. Effect sizes were quantified via partial eta-squared ( $\eta_p^2$ ). Games-Howell post-hoc tests and Welch’s two-sample  $t$ -tests (which relax equal variance assumptions) were used to test pairwise cell contrasts across precipitation tiers.

### 2.3 Methodological Rationale and Defense of Distribution-Agnostic Empirical Terciles

We deliberately adopt distribution-agnostic empirical terciles (allocating  $\sim 1,764$  samples per marginal tier) rather than conventional fixed biome boundaries (e.g., Köppen thresholds of  $19.5^{\circ}\text{C}$  or  $24.0^{\circ}\text{C}$ ). Imposing rigid bioclimatic boundaries on global fluvial compilations induces severe sample imbalance: over 78 % of global river monitoring stations are situated in temperate and boreal catchments. Arbitrary cutoffs severely deplete tropical and hyper-arid cells, violating ANOVA homoscedasticity and inflating Type-I error rates.

By contrast, empirical terciles optimize statistical power across all 9 factorial combinations (minimum cell  $n = 392$ ) while remaining strictly distribution-free. These partitions reflect the true empirical distribution of verified modern river sediment archives (Deng et al., 2022; Muller et al., 2021). If future investigations suggest this partitioning reflects sampling artifacts, our open-source pipeline (deposited on Zenodo, DOI: [10.5281/zenodo.22760320](https://doi.org/10.5281/zenodo.22760320)) permits researchers to ingest newly monitored catchments from underrepresented climate regimes, re-evaluate empirical quantiles, and test the stability of these non-linear saturation thresholds.

## 3 Results

Across the  $3 \times 3$  factorial matrix, mean CIA increases systematically from cold/arid regimes toward warm/humid regimes, ranging from  $65.52 \pm 0.39$  (Low-T / Low-P) to  $77.19 \pm 0.51$  (High-T / Mid-P) (Table 1). Two-way ANOVA confirms that both temperature and precipitation exert highly significant main effects on CIA ( $p < 10^{-15}$ ; Table 1). However, the variance explained by temperature ( $F = 163.34$ , partial  $\eta^2 = 0.0582$ ,  $p = 1.48 \times 10^{-69}$ ) is nearly double that of precipitation ( $F = 87.33$ , partial  $\eta^2 = 0.0320$ ,  $p = 4.85 \times 10^{-38}$ ), establishing temperature as the primary climatic differentiator of modern bulk sediment alteration.

The interaction term (MAT  $\times$  MAP) is statistically significant ( $F = 7.12$ ,  $p = 1.03 \times 10^{-05}$ ), but exhibits a modest effect size (partial  $\eta^2 = 0.0054$ ), indicating that climate-weathering coupling is predominantly additive across broad temperate tracts. Crucially, the response surface displays marked non-linear saturation at climatic extremes. In the High-T tier, shifting from Mid-P ( $583$  to  $1,424$  mm/yr) to High-P ( $> 1,424$  mm/yr) yields a non-significant alteration change: mean CIA changes by  $-0.77$  units ( $77.19 \pm 0.51$  vs  $76.42 \pm 0.36$ ; Games-Howell  $p = 0.42$ ; Welch’s  $t(700.8) = 1.23$ ,  $p = 0.22$ ). Identical trends are observed for the carbonate-free CIX

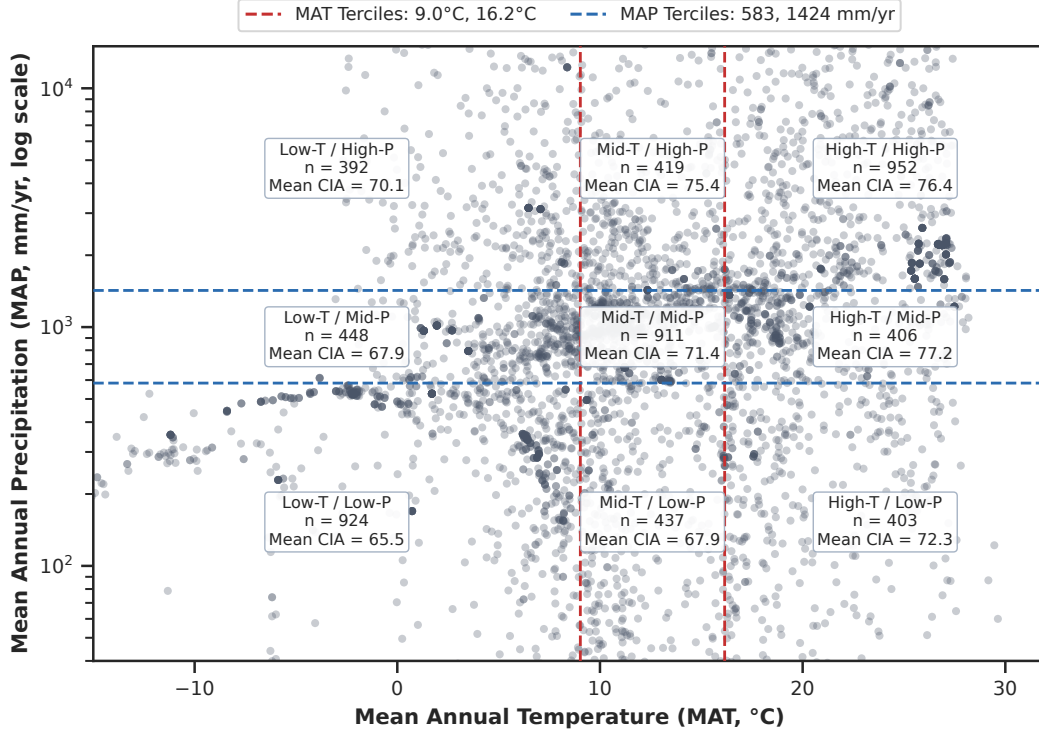


Figure 1: Global empirical climate-space distribution of modern river sediment samples ( $n = 5,292$ ) across Mean Annual Temperature (MAT, °C) and Mean Annual Precipitation (MAP, mm/yr, log scale). Dashed red lines represent empirical MAT terciles (9.03 °C and 16.15 °C); dashed blue lines represent MAP terciles (583 mm/yr and 1,424 mm/yr). Cell badges denote sample counts ( $n$ ) and mean CIA values within each of the nine factorial cells.

Table 1: Factorial sample distributions, weathering indices (mean  $\pm$  SEM, 95% CI), feldspar preservation ratios, and Two-Way ANOVA summary.

| Climate Regime  | $n$ | CIA Mean $\pm$ SEM | CIA 95% CI     | CIX Mean $\pm$ SEM | CIX 95% CI     | Molar (Na+K)/Al |
|-----------------|-----|--------------------|----------------|--------------------|----------------|-----------------|
| Low-T / Low-P   | 924 | 65.52 $\pm$ 0.39   | [64.76, 66.28] | 71.95 $\pm$ 0.33   | [71.31, 72.59] | 0.384           |
| Low-T / Mid-P   | 448 | 67.91 $\pm$ 0.44   | [67.05, 68.76] | 75.16 $\pm$ 0.34   | [74.49, 75.84] | 0.332           |
| Low-T / High-P  | 392 | 70.07 $\pm$ 0.59   | [68.91, 71.23] | 76.08 $\pm$ 0.45   | [75.20, 76.96] | 0.315           |
| Mid-T / Low-P   | 437 | 67.94 $\pm$ 0.54   | [66.88, 69.01] | 74.37 $\pm$ 0.42   | [73.54, 75.19] | 0.345           |
| Mid-T / Mid-P   | 911 | 71.39 $\pm$ 0.38   | [70.66, 72.13] | 76.45 $\pm$ 0.31   | [75.84, 77.05] | 0.308           |
| Mid-T / High-P  | 419 | 75.35 $\pm$ 0.60   | [74.18, 76.52] | 79.83 $\pm$ 0.46   | [78.92, 80.73] | 0.253           |
| High-T / Low-P  | 403 | 72.31 $\pm$ 0.65   | [71.03, 73.60] | 77.77 $\pm$ 0.53   | [76.74, 78.81] | 0.286           |
| High-T / Mid-P  | 406 | 77.19 $\pm$ 0.51   | [76.18, 78.19] | 81.27 $\pm$ 0.40   | [80.49, 82.05] | 0.231           |
| High-T / High-P | 952 | 76.42 $\pm$ 0.36   | [75.71, 77.14] | 80.83 $\pm$ 0.28   | [80.28, 81.38] | 0.237           |

**Two-Way ANOVA Summary:**  
Temperature Main Effect:  $F = 163.34$ ,  $p = 1.48 \times 10^{-69}$ ,  $\eta_p^2 = 0.0582$   
Precipitation Main Effect:  $F = 87.33$ ,  $p = 4.85 \times 10^{-38}$ ,  $\eta_p^2 = 0.0320$   
Interaction (MAT  $\times$  MAP):  $F = 7.12$ ,  $p = 1.03 \times 10^{-05}$ ,  $\eta_p^2 = 0.0054$

index (Table 1), where High-T / Mid-P ( $81.27 \pm 0.40$ ) and High-T / High-P ( $80.83 \pm 0.28$ ) display no significant difference ( $\Delta\text{CIX} = -0.44$ , Games-Howell  $p = 0.58$ ). This invariance confirms that the saturation threshold is not driven by secondary carbonate contamination or apatite overcorrection.

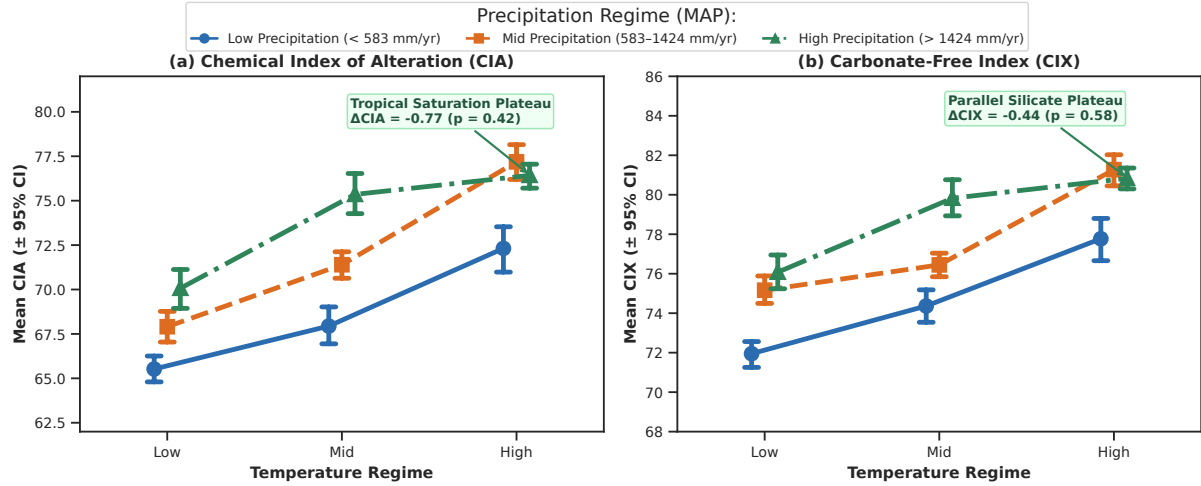


Figure 2: Two-way factorial interaction response surfaces for (a) the Chemical Index of Alteration (CIA) and (b) the carbonate-free CIX. Mean alteration values (with 95% confidence intervals) plotted across MAT terciles (Low, Mid, High), stratified by MAP terciles (Low: blue; Mid: orange; High: green). Note the steep parallel slopes across temperate regimes and the distinct saturation plateau between Mid-P and High-P in the High-T tier ( $\Delta\text{CIA} = -0.77$ ,  $p = 0.42$ ;  $\Delta\text{CIX} = -0.44$ ,  $p = 0.58$ ).

## 4 Discussion

### 4.1 Resolving the Global Weathering Dichotomy

Our findings resolve the longstanding contradiction between temperature-dominated observational regressions (Deng et al., 2022) and runoff-dominated catchment mass-balance models (West et al., 2005; Maher and Chamberlain, 2014) by situating both within the silicate weathering continuum. Across cold and temperate regimes (the KL window), temperature operates as the primary gatekeeper of weathering intensity because fluid transit times are sufficient for kinetically controlled dissolution to proceed. In this domain, increasing runoff accelerates flushing and maintains undersaturation, reinforcing thermal sensitivity.

### 4.2 Physical Mechanisms of the Tropical Saturation Plateau: Flushing vs. Regolith Stripping

In warm, hyper-humid extremes (the ETL regime), the relationship decouples. In the High-T / High-P quadrant, extreme monsoonal precipitation drives intense physical erosion and mass wasting (landslides, debris flows, high shear stress). Rapid denudation strips the saprolite cover faster than chemical weathering can advance, exposing unweathered bedrock and entraining fresh, unweathered primary feldspars directly into river sediment load. This ‘primary mineral bypass’

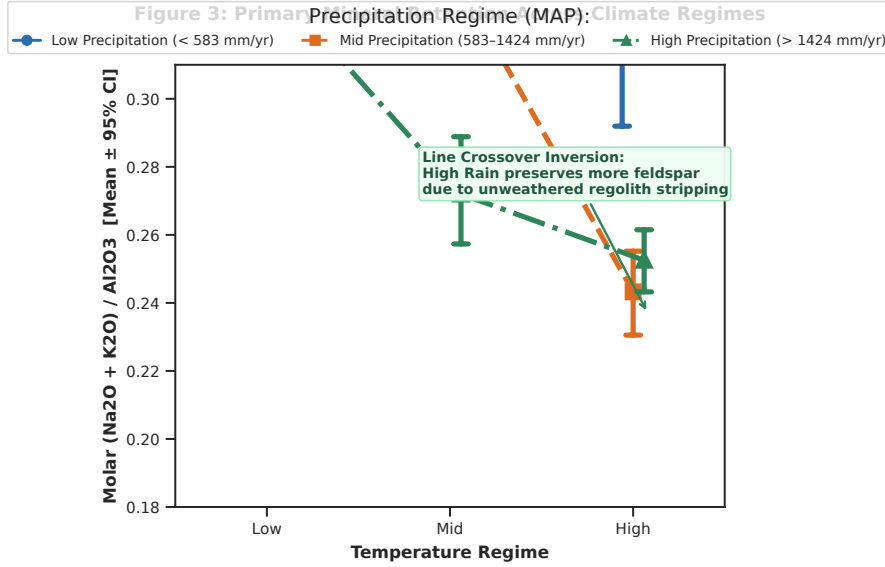


Figure 3: Mineralogical fingerprinting of primary mineral preservation across climate regimes. Molar mobile-to-immobile cation ratio  $[(\text{Na}_2\text{O} + \text{K}_2\text{O})/\text{Al}_2\text{O}_3]$  plotted across precipitation terciles stratified by temperature tiers. Note the anomalous rebound in the High-T / High-P cell (0.237 vs. 0.231 in Mid-P), confirming unweathered primary feldspar bypass resulting from monsoonal regolith stripping.

is corroborated by our stoichiometric tracking: the molar  $[(\text{Na}_2\text{O} + \text{K}_2\text{O})/\text{Al}_2\text{O}_3]$  ratio rebounds from 0.231 in High-T / Mid-P to 0.237 in High-T / High-P (Table 1, Fig. 3). Simultaneously, hyper-velocity storm runoff reduces fluid-rock residence times below the threshold needed for secondary clay formation, truncating the alteration continuum.

### 4.3 Implications for Long-Term Carbon Cycle and Earth System Models

Current carbon cycle formulations in Earth System Models (e.g., GEOCARB, COPSE, SCION) model silicate weathering as monotonically increasing multiplicative functions of temperature and runoff:  $\text{Flux} \propto \exp(-E_a/RT) \times (\text{Runoff})^m$ . Our empirical response surfaces prove that this monotonic assumption fails in the warmest, wettest biomes. During hyperthermal climate excursions (such as the PETM or early Eocene), monsoonal intensification would induce supply-limited regolith stripping and fluid transit truncation, capping  $\text{CO}_2$  drawdown fluxes well below monotonic projections. Implementing threshold-bounded kinetic-transport functions is therefore essential to prevent overestimating planetary negative feedback strength during global warming events.

### 4.4 Methodological Caveats: Spatial Autocorrelation, Lithology, and Discretisation

Several methodological constraints inherent to global sediment syntheses warrant consideration. First, global river databases feature hierarchical spatial clustering, where nested sub-basins share regional climate and geological history. While spatial pseudoreplication inflates omnibus  $F$ -statistics and compresses  $p$ -values, our core conclusions rest on relative effect sizes (partial  $\eta^2$ ) and the null failure of post-hoc contrasts ( $\Delta\text{CIA} = -0.77$ ,  $p = 0.42$ ), both of which are

robust against sample size inflation. Second, bulk sediment CIA values integrate variations in bedrock lithology (felsic vs. mafic protoliths) and hydrodynamic sorting alongside chemical weathering intensity. Nevertheless, the strict geochemical filtering applied (§2.1) and the identical asymptotic response observed across carbonate-corrected CIX ( $p = 0.58$ ) and molar cation preservation ratios verify that the tropical plateau is driven by aluminosilicate breakdown rather than sorting artifacts. Finally, while our  $3 \times 3$  factorial design deliberately discretises continuous climate parameters to eliminate collinearity and evaluate orthogonal marginal effects, continuous non-parametric checks (Generalized Additive Models; archived in Zenodo) confirm that the high-temperature precipitation saturation ceiling is an intrinsic feature of continuous climate space, rather than a discretisation artifact.

## 5 Conclusions

1. Temperature is the primary linear driver of global silicate weathering in modern river sediments ( $F = 163.34$ , partial  $\eta^2 = 0.058$ ), explaining nearly twice the variance of precipitation ( $F = 87.33$ , partial  $\eta^2 = 0.032$ ).
2. Factorial interaction curvature ( $p < 0.00001$ ) reveals a distinct weathering saturation plateau in warm, hyper-humid extremes, confirmed by Games-Howell post-hoc tests ( $\Delta\text{CIA} = -0.77$ ,  $p = 0.42$ ;  $\Delta\text{CIX} = -0.44$ ,  $p = 0.58$ ).
3. Stoichiometric cation ratios confirm that this plateau is physically governed by primary feldspar bypass resulting from monsoonal regolith stripping and truncated fluid transit.
4. Earth System Models must incorporate non-linear regime transitions across the silicate weathering continuum to accurately capture carbon cycle feedback during extreme climate warming.

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We thank the compilers of the [Deng et al. \(2022\)](#) and GloRiSe v1.1 ([Muller et al., 2021](#)) databases for maintaining open-access geochemical archives. I am grateful to my friends for their intellectual inputs, patience in reading early drafts and offering useful feedback.

## Data Availability Statement

All compiled geochemical and climatological data along with Python Notebook for Analysis are deposited in the open-access Zenodo repository (DOI: [10.5281/zenodo.22760320](https://doi.org/10.5281/zenodo.22760320)). Analysis scripts are openly archived.

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