Appendix A. Detailed Methods

Appendix A.1. Solid phase geochemical analyses

Samples of river bank sediments and rocks were collected from across the entire study site in order to constrain the elemental and isotopic composition of different lithologic end-members. Sub-samples of the river bank sediments were separated using a riffle splitter and powdered in a ball mill. Rock samples were disaggregated using an agate mortar and pestle before being ground in a ball mill.

Appendix A.1.1. Bulk XRF measurements

To determine the content of non-volatile elements in the river bank sediment samples, the samples were mixed in a 1:2 ratio with lithium metaborate and then doubly fused in graphite crucibles at 1000°C. The twice fused glass beads were then polished and analyzed by X-ray fluorescence spectroscopy (XRF) at Pomona College. A suite of 35 elements were analyzed. Only measurements of Na, Ca, Mg, and Sr concentrations are discussed in this paper. The stream sediment reference material STSD-2 (Environment Canada) was processed and analyzed using the same procedure in order to check for accuracy. For all reported elements, the measured values of STSD-2 agree with certified values within 10%.

Appendix A.1.2. Solid phase sulfur isotope measurements

Sulfide minerals within rock samples from the Kosñipata valley are present as both macroscopic crystals and veins as well as microscopic disseminated crystals. When macroscopic, sulfide minerals were sampled for sulfur isotopic analyses using a diamond-coated steel drill bit and analyzed without any further preparation. When microscopic, the reduced sulfur compounds were converted to H_2S and precipitated as Ag_2S using the chromium reduction method of Gröger et al. (2009). Briefly, the sample powders were mixed with ethanol and concentrated HCl and then reacted with an acidic $Cr^{2+}Cl_2$ solution in a N_2-flushed digestion vessel. During the reaction, the digestion vessels were heated from below with a hotplate. The liberated H_2S gas was passed through a condenser and bubbled through a solution of

$AgNO_3$ and NH_4OH in order to trap S^{2-} as Ag_2S. For each sample, approximately 1 gram of powder was reacted for one hour.

After the reaction was completed, the Ag_2S was separated from the $AgNO_3$ and NH_4OH solution by centrifugation, rinsed three times with de-ionized water (DIW; 18.2 MΩ resistivity), and dried overnight in an oven at 60°C. Sub-samples of both the pyrite and homogenized Ag_2S powders were sent to the University of Arizona Environmental Isotope Lab where the sulfur isotopic composition was measured using an elemental analyzer coupled to a gas-source IRMS (ThermoQuest Finnigan Delta PlusXL). To check the accuracy and reproducibility of the chromium reduction procedure, an in-house pyrite standard was processed during each session and the procedure was replicated for select samples. Overall, calculated yields for the standards were similar (80-90 %; based on mass of recovered Ag_2S) and the isotopic composition of the Ag_2S produced from the pyrite standard was identical, within the analytical uncertainty (0.15 ‰), to the un-processed pyrite. Similarly, variability between replicate sample extractions was similar in magnitude to the analytical uncertainty (± 0.2 ‰).

Appendix A.1.3. Sequential river bank sediment leaches

In order to selectively dissolve carbonate minerals in the river bank sediment samples, a sequential leaching procedure based on the method of Leleyter and Probst (1999) was used. Both ground and un-ground sediment samples were tested, but only the leaches of the un-ground sediment samples were found to selectively dissolve carbonates to a degree that allowed for the determination of their chemistry. For the un-ground samples, 4-6 grams of sediment were separated from the total sample using a riffle splitter and then split into two roughly equal aliquots that were leached separately in 50 mL polypropylene (PP) centrifuge tubes.

During each leaching step, the sediment samples were kept at room temperature and stirred by laying the tubes on a shaking table set to 200 rpm. After each leaching step, the leachate was first separated from the sediments by centrifugation. The supernatant was then decanted and filtered with a 0.2 μm nylon filter. Before the next leaching step, the sediment

samples were rinsed three times with DIW.

To remove soluble salts, the sediments were first leached with 10 mL of DIW for 30 minutes. Next, exchangeable elements were removed by leaching the sediments with 10 mL of 1M NH_4Cl for 2 hours. Finally, carbonate minerals were selectively dissolved by leaching the sediments for 5 hours with 10 mL of a 1M acetic acid solution that was set to a pH of $\sim$4.5 by titration with NH_4OH.

After filtration, the acetic acid leachates were evaporated to dryness in PP vials in a clean laboratory and then re-dissolved in 5% HNO_3. The concentrations of Al, Si, Na, Ca, Mg, Sr, and Li in the leachate solutions were determined with an Agilent 4100 microwave plasma atomic emission spectrometer (MP-AES) calibrated using synthetic standards. The results are reported as nanomoles of element leached per gram of sample.

Appendix A.2. Dissolved phase geochemical analyses

Water samples were collected using slightly different methods depending upon the sampling year. For samples collected before 2012, water was collected from the river surface using a clean PP bottle, filtered on site with a 0.2 μm porosity nylon filter, and split into two 60 mL high-density polyethylene bottles (HDPE). One of the 60 mL HDPE bottles was preserved with 2 drops of high purity HCl dispensed from an acid-washed Teflon dropper bottle for cation analyses. The other HDPE bottle was left unpreserved. In the laboratory, samples with any remaining particulates (e.g., from flocculated aggregates forming after field filtration) were re-filtered before analysis with a 0.2 μm nylon porosity filter.

After 2012, water samples were collected from the river surface with a clean PP bucket and transferred to 10 L plastic bags before filtration. Within 24 hours of collection, the samples were filtered with 0.2 μm porosity polyethersulfone (PES) filters housed in a teflon filtration unit with a peristaltic pump and tygon tubing. The filtrate was collected directly into two clean 60 mL HDPE bottles. One of the 60 mL HDPE bottle was preserved with 60 μL of concentrated distilled HNO_3 dispensed from a teflon vial with an acid-washed pipette tip. The other HDPE bottle was left unpreserved.

Appendix A.2.1. Cation and Si concentrations

To determine the concentrations of Na, K, Ca, Mg, Si, Li, and Sr, the acidified water samples were analyzed using an MP-AES calibrated with synthetic standards. Precision and accuracy was assessed by analyzing a reference material every 15 samples. For Ca, Mg, Na, K, and Si, the reference material ION-915 was used (Environment Canada). For Li, the reference material TMDA-51.4 (Environment Canada) was used. For Sr, an in-house prepared $SrCO_3$ solution was used. Replicate analyses of each solution reveals an analytical precision within 5% (1σ) for each analyte.

Appendix A.2.2. Anion concentrations

To determine the concentrations of Cl^- and SO_4^{2-}, the un-acidified samples were analyzed with a Metrohm ion chromatograph equipped with a Metrosep A4/150 column and a conductivity suppressor. The elements were eluted from the column with 3.2 mM Na_2CO_3 and 1.0 mM $NaHCO_3$ at a flow rate of 0.7 mL min^{-1}. The instrument was calibrated using synthetic standards. Precision and accuracy was assessed by analyzing a certified reference material (ION-915, Environment Canada) after every 15 samples. Replicate analyses of ION-915 reveals an analytical precision within 5% (1σ) for each analyte.

Appendix A.2.3. Sulfate-sulfur isotope measurements

To measure the $\delta^{34}S_{V-CDT}$ of dissolved SO_4^{2-}, SO_4^{2-} was purified from $\sim$ 1-10 mL of sample using either a cation or anion exchange resin following established protocols (Paris et al., 2013). Before separation, all samples were evaporated to dryness within a clean laboratory. For samples purified using a cation exchange resin, the sample residue was re-dissolved in 0.25 % HCl and introduced into a column containing Bio-Rad AG50X8 resin following Paris et al. (2013). For sample purified using an anion exchange resin, the sample residue was re-dissolved in 0.5 % HCl and introduced into a column of AG1X8 resin following Paris et al. (2014). After elution from the columns, the samples were evaporated to dryness and then re-dissolved in 5% HNO_3. Before analysis, all samples were diluted and mixed with a sodium

solution to match the sodium and sulfate concentrations of the bracketing standard. The samples were then analyzed using a Thermo Neptune Plus multi-collector inductively coupled plasma mass spectrometer (MC-ICP-MS) at Caltech using sample-standard bracketing to correct for instrumental drift and mass bias following Paris et al. (2013).

Replicate purification of sulfate and measurement of its sulfur isotopic composition from select samples reveals variability of up to 0.2 ‰. This uncertainty value is reported in all figures and tables but is not included after each value in the main text for brevity.

Appendix A.2.4. Strontium isotope measurements

To measure the radiogenic ($^{87}Sr/^{86}Sr$) isotopic composition of dissolved Sr, the acidified samples were purified using an automated HPLC separation with Sr Spec resin at the Institute de Physique du Globe Paris (IPGP; Meynadier et al. 2006). The purified samples were evaporated to dryness, re-dissolved in 0.5 M HNO_3 and analyzed on a Thermo Neptune plus MC-ICP-MS at IPGP. A solution made from the NIST carbonate reference material SRM987 was used to check accuracy regularly. To correct for Kr interference, the ^{83}Kr/^{84}Kr and ^{83}Kr/^{86}Kr ratios were determined using the blank solution at the beginning of the run and the ^{83}Kr signal was monitored for each sample and standard. To correct for Rb interference, the ^{87}Rb signal of a 5 ppb Rb solution was measured at the beginning of the run and the ^{85}Rb signal was monitored for each sample and standard.

The individual analytical uncertainty on each of the dissolved ^{87}Sr/^{86}Sr ratio measurements is less then 0.1 permil. Nonetheless, given the large range of variability between samples, the measured ^{87}Sr/^{86}Sr ratios are only be reported to three decimal places in the main text.

Appendix A.3. Inversion Model

The inversion model is based on the mixing equation:

$$X/\Sigma^{+}_{measured} = \sum_{f=1}^{n} F_f \times X/\Sigma^{+}_{f} \tag{A.1}$$

where $X/\Sigma^+_{measured}$ is a measured elemental ratio of element X, F_f is the fractional contribution of end-member f, X/Σ^+_f is the elemental ratio of end-member f, and n is the number of end-members. For isotopic ratios, we use the modified mixing equation:

$$\delta X_{measured} \times X/\Sigma^+_{measured} = \sum_{f=1}^{n} F_f \times X/\Sigma^+_f \times \delta X_f \tag{A.2}$$

where $\delta X_{measured}$ is the measured isotopic ratio of element X and δX_f is the isotopic ratio of end-member f.

To perform the inversion, a single value for each end-member ratio (X/Σ^+_f and δX_f) is randomly drawn from a predefined uniform distribution (see Table 1). Then, using these random end-member values and the measured ratios ($X/\Sigma^+_{measured}$ and $\delta X_{measured}$), the fractional contribution from each end-member (F_f) is calculated using the mldivide command in MATLAB 2015b. For each sample, we repeat this approach 6×10^4 times in order to ensure that a sufficient number of random end-member combinations are used so that the reported confidence intervals do not change appreciably between replicate calculations. If any of the calculated mixing fractions are negative, the results of that simulation are discarded. While this general approach applies to all of the mixing models, details specific to the different versions described in the main text are included below. The precise end-member definitions are included in Table 1.

Appendix A.3.1. Na-Ca-Mg-Cl-SO_4-$\delta^{34}S$ inversion

To apportion the solute budget between limestone, dolomite, granite, shale, rainfall, and evaporites, we use Cl/Σ^+, Na/Σ^+, Ca/Σ^+, Mg/Σ^+, SO_4/Σ^+, and $\delta^{34}S$. With the added constraint that the fractional contributions from each end-member must all sum to one, this model includes 7 equations, which is one greater than the number required for 6 end-members. Consequently, we calculate a least squares solution for each simulation. Since some of the simulations calculated this way will have large errors, we calculate the sum of the squared residuals (SSE) for each simulation. For each sample, we calculate a reference SSE by

determining the 5^{th} percentile value of SSE for all of the simulations for that sample. We then select only the subset of simulations where the SSE is less than this reference value. Together, all of the constraints result in an average of 224 valid simulations for each sample. For this model, the *a posteriori* values of SO_4/Σ^+ for the carbonate and silicate end-members are used to determine the proportions of sulfuric acid weathering for each sample. For reference, the exact mixing model is included as a MATLAB script (`Torres_etal_A_inversion.m`).

Appendix A.3.2. Na-Ca-Mg-Cl inversion

To apportion the solute budget between limestone, dolomite, granite, shale, and rainfall, we use Cl/Σ^+, Na/Σ^+, Ca/Σ^+, and Mg/Σ^+. With the added constraint that the fractional contributions from each end-member must all sum to one, this model includes 5 equations. Since the system is not over-constrained, we calculate an exact solution for each combination of random end-members. Together, all of the constraints result in an average of 4649 valid simulations for each sample. For reference, the exact mixing model is included as a MATLAB script (`Torres_etal_B_inversion.m`).

Appendix A.4. Sr isotope model

For each simulation that produces a set of realistic mixing proportions, the predicted Sr/Σ^+ and $^{87}Sr/^{86}Sr$ are calculated using equations A.1 and A.2. This calculation is repeated 1000 times using different end-member values for Sr/Σ^+ and $^{87}Sr/^{86}Sr$. Combinations of end-members and mixing fractions that produce values of Sr/Σ^+ that are more than 5% from the measured values are discarded. For reference, the exact mixing model is included as a MATLAB script (`Torres_etal_C_inversion.m`).

Appendix A.4.1. Li/Σ^+ model

For each calculation that produces a set of realistic mixing proportions, the Li/Σ^+ of the sample is calculated using equation A.1. Only shale and granite are considered as Li sources. To get Li/Σ^+ values for these end-members, we multiply the Li/Na ratios from Dellinger

et al. (2015) by the end-member Na/Σ^+ used in the simulation. For reference, the exact mixing model is included as a MATLAB script (`Torres_etal_D_inversion.m`).

Appendix A.5. Effect of weathering on pCO_2

The fluxes of alkalinity and DIC delivered to the ocean by chemical weathering depend upon the relative magnitude of different weathering reactions. Here, we consider how the proportion of cations sourced from carbonate weathering and the proportion of total weathering driven by sulfuric acid set the relative amounts of alkalinity and DIC production. By defining reference ratios of alkalinity to DIC that are associated with no change in pCO_2, we determine which combinations of weathering reactions increase or decrease atmospheric pCO_2 over different timescales.

Appendix A.5.1. Relevant Chemical Reactions

To quantify the effects of different weathering reactions on the budgets of alkalinity and DIC, we start by writing the acid consuming (carbonate and silicate dissolution) and acid producing (carbonic acid disassociation and pyrite oxidation) half-reactions. We then combine these half reactions in order to write full reactions for the weathering of carbonate and silicate minerals by carbonic and sulfuric acids. Finally, by comparing the relative amounts of DIC and alkalinity production resulting from each reaction, we determine how the proportion of cations sourced from carbonate weathering and the proportion of total weathering driven by sulfuric acid set the effect of weathering on atmospheric pCO_2 over different timescales.

The half-reactions for the proton-promoted dissolution of carbonate and silicate minerals can be written as:

$$2H^+ + CaCO_3 \leftrightarrow Ca^{2+} + H_2CO_3 \tag{A.3}$$

and

$$4H^+ + Ca_2SiO_4 \leftrightarrow H_4SiO_4 + 2Ca^{2+} \tag{A.4}$$

The corresponding half-reactions for acid generation by the disassociation of carbonic acid and the oxidation of pyrite can be written as:

$$H_2CO_3 \leftrightarrow 2H^+ + CO_3^{2-} \tag{A.5}$$

and

$$4FeS_2 + 15O_2 + 14H_2O \leftrightarrow 8SO_4^{2-} + 16H^+ + 4Fe(OH)_3 \tag{A.6}$$

The acid consuming half reactions (carbonate and silicate dissolution) can be combined with the acid generating half reactions (carbonic acid disassociation and pyrite oxidation) to generate full reactions describing the weathering of carbonate and silicate minerals by carbonic and sulfuric acid. To do this, we combine the above equations with the assumption that the number of moles of protons generated and consumed should be equal. We also follow the convention of writing all species as the dominant species at the carbonic acid equivalence point. In particular, this means that we will write all DIC species as H_2CO_3 and balance reactions by adding H^+ ions as needed. The utility of this approach is that, after canceling out species that appear on both sides of an equation, any H_2CO_3 species that appear on the right hand side of an equation reflect DIC generation and any H^+ species that appear on the left hand side of an equation reflect alkalinity production. This approach yields the full equations:

$$2H^+ + CaCO_3 \leftrightarrow Ca^{2+} + H_2CO_3 \tag{A.7}$$

$$0.5FeS_2 + \frac{15}{8}O_2 + \frac{7}{4}H_2O + CaCO_3 \leftrightarrow Ca^{2+} + H_2CO_3 + SO_4^{2-} + 0.5Fe(OH)_3 \tag{A.8}$$

$$4H^+ + Ca_2SiO_4 \leftrightarrow H_4SiO_4 + 2Ca^{2+} \tag{A.9}$$

and

$$FeS_2 + \frac{15}{4}O_2 + \frac{7}{2}H_2O + Ca_2SiO_4 \leftrightarrow H_4SiO_4 + 2Ca^{2+} + 2SO_4^{2-} + Fe(OH)_3 \qquad \text{(A.10)}$$

for carbonate-carbonic, carbonate-sulfuric, silicate-carbonic, and silicate-sulfuric weathering respectively.

To compare their effects on DIC and alkalinity, we normalize all of the full weathering reactions (equations A.7 - A.10) by the charge equivalents of cations released, which is the quantity shown in Table A.1. This normalization insures that the results are not sensitive to the chosen mineral formula. This is particularly important for silicate minerals, which typically contain cations other than Ca^{2+} in appreciable amounts. This normalization also aids in the assessment of field data since estimates of chemical weathering in rivers are based on measurements of cation release.

Using the coefficients in Table A.1, we can write equations for the production of alkalinity and DIC by weathering where

$$Alkalinity = (z \times (0x + 0y)) + ((1 - z) \times (x + y) \qquad \text{(A.11)}$$

and

$$DIC = (z \times (0.5x + 0y)) + ((1 - z) \times (0.5x + 0y) \qquad \text{(A.12)}$$

with z being the proportion of weathering driven by sulfuric acid, x being the charge equivalents of cations contributed by carbonate weathering, and y being the charge equivalents of cations contributed by silicate weathering.

Appendix A.5.2. Short Timescales

In the modern ocean, the ratio of alkalinity to DIC is approximately one. Consequently, on timescales shorter than the timescale associated with marine carbonate burial, atmospheric pCO_2 will increase if the ratio of alkalinity to DIC delivered by rivers is less than

Table A.1: Alkalinity and DIC contributions per unit cation released (charge equivalents) for different weathering reactions

Mineral/Acid	**ΔAlk**	**ΔDIC**
Carbonate-Carbonic	1	0.5
Carbonate-Sulfuric	0	0.5
Silicate-Carbonic	1	0
Silicate-Sulfuric	0	0

1. We note that this is strictly valid for the modern oceanic alkalinity to DIC ratio. To graphically show the implied effects of different combinations of weathering reactions on atmospheric pCO_2, we set equations A.11 and A.12 both equal to one in order to solve for parameter combinations that yield no change in atmospheric pCO_2 on short timescales, which gives the relationship

$$z_{short} = 1 - (0.5 \times R) \tag{A.13}$$

where R is the proportion of cations sourced from carbonate weathering, i.e.:

$$R = \frac{x}{x + y} \tag{A.14}$$

In a plot of R versus z (Figure 7), data that plot above the line described by Equation A.13 are associated with CO_2 release on timescales shorter than carbonate precipitation assuming close to modern conditions.

Appendix A.5.3. Long Timescales

Carbonate burial exports alkalinity and DIC from the ocean in a 2 to 1 ratio (reverse of equation A.7). So, on timescales longer than carbonate burial but shorter than pyrite burial ($< 10^7$ years; Berner and Berner 2012), atmospheric pCO_2 will increase if rivers deliver alkalinity and DIC to the ocean in a ratio that is less than 2. We suggest that this reference alkalinity to DIC ratio should be valid regardless of the oceanic alkalinity to DIC ratio. To graphically show the implied effects of different combinations of weathering reactions on atmospheric pCO_2 over long timescales, Equations A.11 and A.12 can be solved for when

Alk/DIC is equal to two, which gives the equation:

$$z_{long} = 1 - R \tag{A.15}$$

In a plot of R versus z (Figure 7), data that plot above the line described by Equation A.15 are associated with pCO_2 increase on timescales longer than carbonate precipitation but shorter than pyrite burial.

References

Berner, E.K., and Berner, R.A., 2012, Global environment: water, air, and geochemical cycles: Princeton University Press.

Dellinger, M., Gaillardet, J., Bouchez, J., Calmels, D., Louvat, P., Dosseto, A., Gorge, C., Alanoca, L., and Maurice, L., 2015, Riverine Li isotope fractionation in the Amazon River basin controlled by the weathering regimes: Geochimica et Cosmochimica Acta, doi:10.1016/j.gca.2015.04.042.

Gröger, J., Franke, J., Hamer, K., and Schulz, H.D., 2009, Quantitative recovery of elemental sulfur and improved selectivity in a chromium-reducible sulfur distillation: Geostandards and Geoanalytical Research, v. 33, p. 17–27, doi:10.1111/j.1751-908X.2009.00922.x.

Leleyter, L., and Probst, J., 1999, A new sequential extraction procedure for the speciation of particulate trace elements in river sediments: International Journal of Environmental Analytical Chemistry, v. 73, no. 2, p. 109–128.

Meynadier, L., Gorge, C., Birck, J.L., and Allègre, C.J., 2006, Automated separation of Sr from natural water samples or carbonate rocks by high performance ion chromatography: Chemical Geology, v. 227, no. 1-2, p. 26–36, doi:10.1016/j.chemgeo.2005.05.012.

Paris, G., Adkins, J.F., Sessions, A.L., Webb, S.M., and Fischer, W.W., 2014, Neoarchean carbonate-associated sulfate records positive 33S anomalies: Science, v. 346, no. 6210, p. 739–742.

Paris, G., Sessions, A.L., Subhas, A.V., and Adkins, J.F., 2013, MC-ICP-MS measurement of δ^{34}S and Δ^{33}S in small amounts of dissolved sulfate: Chemical Geology, v. 345, p. 50–61, doi:10.1016/j.chemgeo.2013.02.022.