ABSTRACT. Metal and metalloid stable isotope ratios have emerged as potentially powerful proxies for weathering, element cycling and export in the Critical Zone. The simplest possible interpretative framework for these isotope ratios has three parameters: (i) the isotope ratio of the parent minerals undergoing weathering, (ii) the partitioning of the element between solute and the new secondary phases, and (iii) the fractionation factors associated with the formation of new secondary phases. Using the example of silicon, we show how all three of these parameters vary along a gradient of erosion rate and regolith residence time defined by three sites located on granitoid bedrock. These sites run from the kinetically limited Rhone Valley in the Central Swiss Alps to the tectonically inactive and supply-limited Sri Lankan highlands, with the Sierra Nevada mountains as a site of intermediate weathering intensity. At each site, primary mineral specific $^{30}\text{Si}/^{28}\text{Si}$ ratios span $>0.4\%$. These minerals weather differentially, such that the isotope ratio of silicon solubilised from rock differs at the three sites and is not necessarily equal to bulk bedrock composition. The partitioning of silicon between secondary clay and solute is reflected in the clay mineralogy and chemical composition: more intense weathering produces Si-poor clays. The clay composition thus comprises a first-order mass-balance control on the extent to which any fractionation factor can be expressed. Finally, the Si isotope fractionation factor associated with clay formation varies systematically with clay mineralogy: the formation of Si-deplete clay minerals is associated with larger fractionation factors. The magnitude of the fractionation may be mechanistically linked to relative aluminium availability. These findings provide the framework needed to use Si isotope ratios as a quantitative proxy to explore Si cycling and reconstruct weathering in the present and past.

Key words: silicon isotopes, weathering, Critical Zone, isotope fractionation, clays

INTRODUCTION

The Critical Zone is the layer of the Earth’s skin from treetops to the bottom of groundwater (Brantley and others, 2007), where meteoric fluids interact with rock. The structure and functioning of the Critical Zone is governed by the interplay between the tectonic supply of rock to the Earth’s surface, chemical weathering and physical erosion that act to remove material, and biological activity. All three are related to climate, and their interactions define a series of non-linear, competing and often non-intuitive feedback loops (Frings and Buss, 2019). The complexity of the Critical Zone means there is considerable interest in generating geochemical tools that can clarify aspects of these interactions. The isotope ratios of the metal and metalloid elements have emerged as promising candidates. They are often sensitive to one or more of the fluxes that define elemental cycles at the Earth’s surface. This sensitivity results from isotope fractionation, the preferential inclusion of one isotope relative to another, during a geochemical process. Of these elements, silicon (Si) is among the best studied (De La Rocha and others, 2000; Ziegler and others, 2005a; Ziegler and others, 2005b; Frings and others, 2016). The cumulative results from two decades
of work have yielded insight into Si isotope distributions in the Critical Zone, but the exact processes governing the Si isotope partitioning remain to be quantitatively and mechanistically understood.

When Si is solubilized (that is, weathered) from primary minerals, it has essentially two possible fates: it can be incorporated into a secondary, solid phase, or it can leave the weathering zone as dissolved Si. The secondary phases can be both biogenic (including plant silica bodies termed phytoliths) and abiogenic (secondary oxides and aluminosilicates, including clay minerals). The formation of phytoliths, oxides, and clays are associated with similar Si isotope fractionations, which tend to favour the inclusion of the lighter $^{28}\text{Si}$ in the new solid, leaving the residual dissolved Si enriched in the heavier $^{30}\text{Si}$ (De La Rocha and others, 2000; Hughes and others, 2013; Frings and others, 2015). The simplest framework for interpreting Si stable isotope ratios views the whole weathering zone as a homogenous reactor operating at steady-state and predicts isotope ratios as a function of element partitioning between two phases. For Si, this model is:

\[
\delta^{30}\text{Si}_{\text{residual}} = \delta^{30}\text{Si}_{\text{initial}} - \varepsilon (1 - f_{\text{Si}}) \tag{1}
\]

\[
\delta^{30}\text{Si}_{\text{product}} = \delta^{30}\text{Si}_{\text{initial}} + \varepsilon f_{\text{Si}} \tag{2}
\]

where $\delta^{30}\text{Si}$ is the $^{30}\text{Si}/^{28}\text{Si}$ ratio expressed as a permil deviation from the standard NBS28, $f_{\text{Si}}$ is the fraction of reactant converted to product (for example, dissolved Si in soil solution precipitated as a secondary aluminosilicate or into plant material), $\varepsilon$ is the isotope fractionation associated with that conversion, and the subscripts $\text{initial}$, $\text{residual}$, and $\text{product}$ refer to isotope ratios of an unaltered reactant phase, the remaining reactant, and the newly formed phase, respectively. We follow Coplen (2011) in using the term isotope fractionation $\varepsilon$ as a representation of the isotope fractionation factor $\alpha$, that is, $\varepsilon = \alpha - 1$ expressed in permil. The model behaviour is shown graphically in figure 1 and can apply to simple closed systems at equilibrium, and open systems at steady state. This framework lies at the heart of the model presented by Bouchez and others (2013), who treat the weathering zone as a well-mixed flow-through reactor at steady state, such that input and output fluxes balance and do not vary with time. This framework suggests that there are three key parameters that set isotope ratios in the weathering zone: the parent material (that is, $\delta^{30}\text{Si}_{\text{initial}}$), the stoichiometry (that is, $f_{\text{Si}}$), and the fractionation (that is, $\varepsilon$).

This means that if we want to use Si isotopes as tracers of Earth surface processes, we need to understand how Si partitions between solution and secondary phases, and how its isotopes fractionate while doing so. For example, the relative importance of secondary clay minerals and phytoliths is still debated (Engstrom and others, 2010). Recent experimental work challenges the assumption that fractionation factors can be simplified to single, universally applicable values (Oelze and others, 2014; Roerdink and others, 2015). Empirical calibration of these terms along natural gradients is a powerful approach: examples of previous work include the investigation of Si isotope systematics along a soil chronosequence in California (White and others, 2012), or along a rainfall gradient in Hawaii (Bern and others, 2010). Our approach is to develop Si isotope budgets for sites with different weathering regimes as set by erosion rate, falling along what we term an ‘erodosequence’.

Much of the Earth surface is sloping and thus eroding, so erosion rate is an important variable that governs landscape form and evolution. This means that material spends a finite time as regolith before being exported. This underpins the geochemical classification of weathering zones into supply and kinetically limited systems. Settings where material residence time is much longer than the time needed for
primary minerals to dissolve represent a supply-limited endmember. Conversely, settings where minerals pass through the weathering zone much quicker than they can dissolve represent a kinetically limited endmember (Stallard and Edmond, 1983; Dixon and others, 2012). These are typically, but not necessarily, associated with low and high denudation rates, respectively. This division has predictive power: weathering rates at supply-limited sites should not correlate with climate, while those of kinetically limited sites should. This is largely borne out by the available data (for example, West and others, 2005). It also explains the presence of a weathering 'speed limit' (Dixon and von Blanckenburg, 2012; Larsen and others, 2014; Maher and Chamberlain, 2014), set by the mineral solubilities and dissolution kinetics at Earth surface conditions. It can reasonably be expected that the weathering regime influences how metal(loid) isotope ratios vary, by governing the dissolution of primary minerals and the formation of secondary phases. The key benefit of eroding sites is that at steady-state, mass-balance framework centred around equation (1) and equation (2) can be applied. An 'erodosequence' – a series of sites along a gradient in erosion rate
and residence time – is thus a promising means to advance our understanding of novel metal isotope geochemistry.

Our erodosequence sites define a gradient of weathering intensity. Defined as \( W/D \), the fraction of total denudation \( D \) performed by chemical weathering \( W \) (Bouchez and others, 2014), we use weathering intensity as an index of weathering regime. Thus, \( W/D = 0 \) would be a completely kinetically limited site, and \( W/D = 1 \) a supply limited site, though in reality almost nowhere on the globe falls at these extremes. The sites overlie similar granitoid lithologies, but differ in erosion rate, and thus soil thickness and time that material spends in the weathering zone. In this contribution, we assess how each of the three parameters in figure 1 vary along the erodosequence. We show how all three (Si isotope ratios of an ‘initial’ solution, the partitioning of Si between secondary phases and solutes, and Si isotope fractionation factors associated with formation of secondary phases) appear to vary systematically along the erodosequence, opening the door to the use of Si isotopes as a quantitative weathering proxy. While specific to silicon isotopes, these interpretations are broadly applicable to many of the ‘novel’ isotope systems currently being used or developed for Critical Zone studies.

STUDY SITES: THE ALPS-SIERRA NEVADA-SRI LANKA ERODOSEQUENCE

Three sites define the gradient of weathering intensity (fig. 2): a rapidly uplifting and poorly weathered site in the central Swiss Alps that represents a site towards the kinetic limitation end of the intensity spectrum, an intermediate weathering intensity site in the Californian Sierra Nevada, and the highly weathered, tectonically quiescent Sri Lanka highlands representing supply–limited conditions. At all sites, samples derive from weathering profiles spanning from unaltered bedrock to soil surface. They are supplemented with vegetation collected in the immediate vicinity and stream-water samples from the enclosing watershed, or one nearby. All three sites have been described elsewhere (Dixon and others, 2009; Norton and von Blanckenburg, 2010; Hewawasam and others, 2013), and a full overview of site characteristics, sampling, element fluxes, and extensive background data is given by von Blanckenburg and others (2021). Here, we provide only the basic details.

Alps

Six soil profiles were sampled on a sloping soil-mantled ridgetop of the Honegger Horn at 2565 m altitude on the northern site of the upper Rhone valley (Goms; fig. 2A) and have previously been described by Norton and von Blanckenburg (2010) and Norton and others (2010). The bedrock is part of the Aare Massif and is composed of foliated gneiss (23% quartz, 53% plagioclase, 17% orthoclase, 4% biotite and 3% muscovite) and granite (34% quartz, 35% plagioclase, 27% orthoclase, 4% biotite). A nearby meteorological station at 1345 masl gives MAT and MAP of 3.1°C and 1137 mm yr\(^{-1}\), respectively. Soils at the site are thin (<50 cm) and not underlain by saprolite (defined as immobile but weathered rock) to a considerable degree. Vegetation cover is mainly grass species. An average in-situ \(^{10}\)Be derived denudation rate for the soils is 103 t km\(^{-2}\) yr\(^{-1}\) (38 mm kyr\(^{-1}\), assuming a bedrock density of 2.7 g cm\(^{-3}\)) (Norton and others, 2010). In the soil, the Chemical Depletion Fraction (CDF), a zirconium-based index of fraction of mass loss by chemical weathering, averages 0.31 (Norton and von Blanckenburg, 2010). Accordingly, chemical weathering rates are ca. 32 t km\(^{-2}\) yr\(^{-1}\) and erosion rates 71 t km\(^{-2}\) yr\(^{-1}\). Total regolith thickness is < 50 cm, producing a regolith residence time of 10 kyrs.
Three soil profiles and one complete regolith profile were sampled in the Californian Sierra Nevada mountain range (fig. 2B). Detailed site descriptions can be found elsewhere (Bales and others, 2011; Johnson and others, 2011; Hunsaker and Neary, 2012; Liu and others, 2013). The soil profiles are located in the Providence Creek (PC) sub-catchments of the Southern Sierra Critical Zone Observatory (CZO) P301, P303, and P304. Bedrock is dominated by the Dinky Creek Granodiorite, a medium grained, equigranular and strongly foliated biotite-hornblende granodiorite/tonalite with sphene, plagioclase and opaque minerals (Bateman and Wones, 1972). It contains abundant disc-shaped mafic inclusions and a quartz rich diorite is also present. MAT is 8.9°C and MAP is 920 mm (Hunsaker and Neary, 2012; Liu and others, 2013). The thickest soil profile is 120 cm deep. The soils are characterised by a coarse-loamy, mixed soil, with an organic rich surface layer. Dixon and others (2009) report that PC soils overlie saprolite of ≥10 m thickness. The vegetation cover consists mainly

**Sierra Nevada**

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of mixed conifer forest. The average denudation rate derived from \textit{in-situ} $^{10}$Be concentrations in soils at the sampling site is 221 $\text{t km}^{-2} \text{yr}^{-1}$ (82 $\text{mm kyr}^{-1}$) and the CDF of the upper soil horizons averages 0.36 (Dixon and others, 2009). Consequently, chemical weathering rates in the PC sites are roughly 80 $\text{t km}^{-2} \text{yr}^{-1}$ and physical erosion rates are 141 $\text{t km}^{-2} \text{yr}^{-1}$. The regolith profile, ‘Balsam-profile’, lies about 10 km to the northwest of the PC sites. This roadcut profile has a depth of about 10 m. Regolith residence time at this site is estimated as 86 kyrs.

Sri Lanka
The third site is a regolith profile in the central Highlands of Sri Lanka (fig. 2C) located at 1753 m altitude and exposed along the road from Nuwaraeliya to Welimada. It has been previously presented in Hewawasam and others (2013) and Behrens and others (2015). The site is on a hillslope underlain by charnockite bedrock ($\text{SiO}_2 > 65\%$; plagioclase, K-feldspar and quartz are the dominant minerals, with orthopyroxene and biotite as minor components). The mean annual temperature (MAT) is 16°C and the mean annual precipitation (MAP) is 2013 mm. The profile has a depth of >10 m, with red-yellow lateric soil layer developed in the upper 60 cm above a reddish and highly weathered saprolite to 6 m. Below this, massive rounded charnockite blocks and corestones occur, indicative of incipient weathering reactions. Vegetation is typical of the region, with a tropical forest hosting at least 97 tree species of which 62 are endemic. The average denudation rate from cosmogenic $^{10}$Be from soils close to the sampled regolith profile is 41.5 $\text{t km}^{-2} \text{yr}^{-1}$ (15.4 $\text{mm kyr}^{-1}$) (Hewawasam and others, 2003). CDF averages 0.5 (Hewawasam and others, 2013), close to the maximum possible for granitic rock. Together, these data imply equivalent rates of physical erosion and chemical weathering: 20.8 $\text{t km}^{-2} \text{yr}^{-1}$. An estimate of regolith residence time at this site is 600 kyrs.

**Sampling and methods**

\textit{Alps}
Samples were taken during a field campaign in July 2010. Six (B1 to B6) soil depth profiles were sampled on a soil-mantled ridge top using a soil corer from the soil surface to ~30 cm, depending on soil thickness. We sampled un-weathered bedrock nearby. Water samples were taken from small rivers draining the catchment area, filtered at 0.2 $\mu$m into pre-cleaned HDPE bottles and acidified with $\text{HNO}_3$. Plant material of the dominant species (mostly grasses and spruce trees) was collected, rinsed with deionized water, oven dried, and stored in plastic bags.

\textit{Sierra Nevada}
The samples were collected in May 2010. Several soils were sampled at the PC CZO and a deep saprolite profile (“Balsam-profile”) located NE of Shaver Lake (fig. 2B). The soil samples were taken as depth profiles using a soil corer for shallow soil horizons and an auger for deeper soil horizons. One soil depth profile was sampled in catchment P301 from surface down to a depth of 120 cm (samples SN1 to SN10). Further soil depth profiles were sampled in PC catchments P303 (samples SN21 to SN23) and P304 (samples SN24 to SN26) from the surface down to 30 cm depth using a soil corer. The individual soil core samples or augered soil samples were afterwards mixed and represent an average of the sampled depth.

At the “Balsam” study site samples were taken down to a depth of ~800 cm below the surface. The surface of the exposed saprolite was scraped off and samples were taken from the “fresh” saprolite surface with a soil corer where possible. The sampled profile starts at the soil surface, includes the whole soil, the saprolite and extends...
down to the source-rock/saprolite border. We sampled un-weathered bedrock at the bottom of the regolith profile. Water samples have been taken from small streams within the PC CZO and treated as above. Plant material of the dominant vegetation, in particular the pine trees, was sampled from living specimens only and treated as above.

Sri Lanka

Samples were taken in October 2010 as detailed in Hewawasam and others (2013). The soil and saprolite samples were collected from a vertical section of a regolith profile (samples SL6 to SL29), exposed as a fresh road cut during construction works. Approximately 10 m upslope from the regolith profile, nine additional soil samples were collected at three parallel sub-sections within the 60 cm thick soil zone using a soil corer, integrating over depth intervals from 0 to 20 cm, 20 to 40 cm, and 40 to 60 cm. The soil subsections were located about 1.5 m apart from each other in order to account for potential lateral variability. These soil samples were afterwards combined to produce an average soil sample for each depth interval. Unweathered bedrock samples were taken beneath the regolith profile and water samples were taken from three small, pristine streams located in close vicinity as detailed in Hewawasam and others (2013) and Schuessler and others (2018). Plant material of dominant taxa was collected from living specimens only and treated as above.

Analytical Methods

Sample preparation.—Rock samples and bulk soil and saprolite samples were crushed in a tungsten carbide mill to < 68 μm and digested using NaOH fusion following Georg and others (2006) and Zambardi and Poitrasson (2011). Soil and saprolite samples were sieved at 2 mm and subjected to protocols designed to separate Si in secondary clays and Si in amorphous silica. The rationale for this approach is that the amorphous phase may be a precursor to ‘true’ clays (Behrens and others, 2015). We sequentially applied a weak base dissolution protocol developed by Georgiadis and others (2013) for amorphous silica extraction, and a differential settling approach for clay mineral separation. Approximately 500 mg of sample material was added to 10 ml Milli-Q water in a 15 ml polypropylene centrifuge tube and sonicated for 12 hours to disperse the clay size fraction. Afterwards, 0.42 ml of 5 M NaOH was added to achieve a final molarity of 0.2 M. The tubes were placed in an 80°C water bath for 5 hours then centrifuged for 25 min at 4400 rpm. The supernatant with the leached amorphous Si was then passed through a 0.2 μm pore size polyethersulfone filter. The clay size fraction was separated from the residuum by the addition of 5 ml Milli-Q water, resuspension, sonication and centrifugation according to Stokes law. This was performed only once, to obtain a fraction dominated by the mineralogical clays, rather than to quantitatively separate the full grain size-fraction. The weakly basic solution containing the amorphous silica extraction and the final supernatant solution containing the clay phase were evaporated in Ag crucibles and combusted for ≥ 1 hour at 700°C in a muffle furnace to remove residual organic matter. Subsequently, 3 ml of 1.6 M NaOH was added, evaporated to dryness and used to perform a NaOH fusion performed above. Vegetation samples were first combusted for 4 hours at 700°C in Ag crucibles, and the remaining ash was digested using the same NaOH fusion procedure.

For all solutions (that is, those resulting from NaOH fusion of rock, bulk soil/saprolite, clay, amorphous silica, and plant material, and acidified river water), silicon was separated from the cationic sample matrix using the well-established ion-exchange chromatography method of Georg and others (2006). Si blanks of the
fusion and column separation procedure were in general far below 1 μg Si, equivalent
to ≪1% of the total Si processed.

Element concentration measurements.—Major and minor element concentrations of
the water samples, and of the amorphous and clay fractions post NaOH fusion solu-
tions, were determined by optical emission spectrometry (ICP-OES, Varian 720 - ES).
Samples and standards were measured in a 0.3 M HNO₃ matrix with 1000 μg g⁻¹ Cs as
a matrix modifier element. To account for the high Na load of the digested samples
after alkaline fusion, a known amount of Na was added to the calibration standard sol-
tions. Precision and accuracy were assessed by repeated measurements of an in-
house artificial standard solution, showing a reproducibility of better than <5 %.
Analyses of reference materials over the course of this study indicated an accuracy of
better than 8% for all elements analysed in this study. Bulk sample elemental concen-
trations were measured by XRF as detailed in von Blanckenburg and others (2021).

Si isotope ratio measurements.—Silicon isotope ratios were measured on a Thermo
Neptune multi-collector inductively coupled plasma mass spectrometer (MC-ICP-MS)
equipped with an H-skimmer cone and the Thermo Scientific Jet - interface with high
or medium resolution slits (m/Δm > 5000). This is sufficient to resolve all critical pol-
yatomic interferences (for example, ¹⁴N¹⁶O on ³⁰Si). The purified sample solutions
were diluted to 0.6 μg g⁻¹ to 1.0 μg g⁻¹ Si in a 0.1 M HCl matrix and introduced into
the plasma via a desolvation unit for dry plasma conditions (Apex, ESI) equipped with
a ca. 120 μl min⁻¹ self-aspirating nebulizer. Magnesium was added to samples and
standards at a matching concentration. Typical sensitivities were ~15 V/μg g⁻¹ on
²⁸Si (using a 10¹¹ Ω resistor). Measurements were conducted on the interference-free
low-mass side of the three Si isotopes. Isotope ratios of samples and standards were
measured at least 3 times during a sequence. Instrumental mass bias was corrected
using the standard-sample-bracketing approach, assuming a linear trend between the
standards before and after the sample. Si and Mg were monitored dynamically for 30
cycles with an integration time for each cycle of 4 s for both elements with an idle
time of 3 s after magnet switching. Pure 0.1 M HCl solutions containing only Mg were
measured before and after each standard-sample-standard block and were used for
on-peak zero correction. Typical ²⁸Si intensities from blank solutions were below 10
mV. The measured Si isotope ratios were corrected using the deviation of measured
Mg isotope ratios from a natural abundance, assuming an exponential mass-bias law,
after Cardinal and others (2003) and Oelze and others (2016). These corrected ratios
are reported in delta notation relative to the standard reference material NBS28
(NIST RM 8546, quartz sand) as δ²⁹/²⁸SiNBS28 and δ³⁰/²⁸SiNBS28, expressed in per mil
by multiplication of equation (3) with a factor of 1000:

$$\delta^{X/28\text{Si}}_{\text{NBS28}} = \left( \frac{X_{\text{Si}}}{28\text{Si}} \right)_{\text{sample}} \left( \frac{X_{\text{Si}}}{28\text{Si}} \right)_{\text{standard}} - 1$$

(3)

Where X is 29 or 30. All reported uncertainties on delta values given in the
supplementary Data Tables (Frings and others 2021a) are the 95% confidence inter-
val (CI):

$$\text{CI} = \bar{\delta}^{X/28\text{Si}} \pm t_{n-1} \cdot \text{SE}$$

(4)

where $\bar{\delta}^{X/28\text{Si}}$ is the mean of the measured delta values for the sample, $t_{n-1}$ is a critical
value from Student’s t-distribution and SE is the standard error of the mean. For
simplicity, we use $\delta^{29}$Si and $\delta^{30}$Si for $\delta^{29/28}$Si$_{NBS28}$ and $\delta^{30/28}$Si$_{NBS28}$, respectively and take a long-term reproducibility in this lab of ca. 0.14 $\%$ (2s; Oelze and others, 2016) as the uncertainty in all figures and calculations unless the individual sample uncertainty (eq 4) is higher. Several well-characterised reference materials, including BHVO-2, Diatomite and Big-Batch were prepared and measured along with the samples. Their preparation included repeated digestions and chemical purification.

**In situ element concentration and silicon isotope ratio analyses.**—Mineral specific in situ Si isotope ratios and element concentrations were measured at all three sites. For Sri Lanka, thin sections from the unweathered centre of a corestone (see Behrens and others, 2015) were analysed simultaneously for their elemental and isotopic composition by femtosecond laser ablation split stream inductively coupled plasma multi collector mass spectrometry (fsLASS-ICP-MCMS; Frick and others, 2016). Samples from the Alps and Sierra Nevada were analysed consecutively for their element composition with the laser-ablation system coupled to a quadrupole ICP-MS (fsLA-ICP-MS), followed by Si stable isotope analysis (fsLA-ICP-MCMS). For these two sites, the sampling spots are thus not identical.

The fsLA system is a custom-built deep-UV (196 nm) femtosecond laser ablation system (see Schuessler and von Blanckenburg (2014) for technical details). The aerosol is transported in a stream of helium to either a quadrupole ICP-MS (iCAPq, ThermoFisher Scientific), to the Neptune multi-collector ICP-MS, or actively pumped into both instruments for split stream analysis (Frick and others, 2016). The ICP-MS was tuned daily for highest sensitivity on NIST SRM610, while maintaining a $238$U/$232$Th ratio close to 1 and a $238$U$^{16}$O/$238$U ratio below 0.7 %. NIST SRM610 was used as external standard, while differences in the ablation yield were corrected using a 100 wt% oxide normalisation approach (Liu and others, 2008).

Silicon isotope ratios measurements were made as above. Isotope compositions are reported in delta notation as permil deviation relative to either NBS28, or to NIST SRM610 (eq 3), which has a Si isotope composition indistinguishable from NBS28. Raw data processing and background corrections were made following the protocol in Schuessler and von Blanckenburg (2014), including several data rejection/acceptance criteria. To assess the accuracy and precision of laser-ablation concentration and isotope ratio measurements, a range of different international reference materials (BHVO-2G, GOR132G, NIST610 and NIST612) were analysed and compared to literature values (Jochum and others, 2005; Jochum and others, 2011; Schuessler and von Blanckenburg, 2014).

**RESULTS**

**Si Pools**

Si concentrations for the key Si compartments (bedrock, bulk saprolite, bulk soil, amorphous fraction, clay sized fraction, plants and Si in dissolved form) are given in table 1 and in Appendix A1. The full dataset is provided in a supporting Data Publication hosted open access at GFZ data services (Frings and others, 2021a) hereafter called “Data Tables”. All catchments are underlain by granitoid bedrock with similar elemental Si concentrations of 32.3 wt % (Alps), 27.7 wt % (Sierra Nevada) and 31.8 wt % (Sri Lanka) (see table 1 and von Blanckenburg and others, 2021). There is little variation with depth of bulk Si concentrations within the saprolite or soil of the Alps and the Sierra Nevada sites (fig. A1), which average 32.7 wt % and 28.9 wt%, respectively (table 1). Bulk Si concentrations of the Sri Lankan field site decrease to ca. 25 wt % in the uppermost 250 to 50 cm. Si concentrations of the NaOH leach and clay size fractions are presented relative to the total mass of the sample and so represent the amount of Si in these phases in the bulk sample. The average concentration of
amorphous Si (from the NaOH leach) in bulk regolith is similar at all three field sites, and is in the range of 1000 to 2000 μg g⁻¹ (0.1 – 0.2 wt%). There is no clear variation with depth. The Al/Si ratio of this NaOH leach tends to be > 2 mol mol⁻¹, suggestive of a non-biogenic origin (Barão and others, 2015), and also does not vary systematically with depth. The concentration of regolith Si that is hosted in the clay-sized fraction is an order of magnitude higher and is similar for all three sites, at 1 to 2 wt% (10000 – 20000 μg g⁻¹), though this is a minimum since the separation by settling was performed only once. As with the amorphous fraction, the Si content of the clay sized fraction does not systematically vary with depth. Al/Si ratios are lower than the NaOH leach, equivalent to mean values of 0.55 mol mol⁻¹ in the Alps, 0.81 mol mol⁻¹ in Sierra Nevada, and 1.02 mol mol⁻¹ in Sri Lanka. These are typical of common clay minerals. Although vegetation communities differ between the three field sites (see the online supporting Data Tables and von Blanckenburg and others, 2021), Si concentrations in the leaves, twigs and stem of the dominant species are consistent among the sites, ranging from 0.5 to 5 wt%. Si concentrations in stream waters are lowest in the Alps (mean = 1.44 μg g⁻¹, n = 5). Mean stream water Si concentrations for the Sri Lanka site are 3.52 μg g⁻¹ (n = 31) and 9.35 μg g⁻¹ (n = 97) at the Sierra Nevada site.

### Si Isotope Ratios

A summary of δ³⁰Si values for the different compartments is presented in table 2 and figure 3, and in full in the Data Tables. All sites have bedrock δ³⁰Si of around −0.15‰. Compared to this, the amorphous fraction, clay fraction, and plant

### Table 2

Summary of the Si isotopic ratios (δ³⁰Si, in ‰ relative to NBS28) of the individual Si pools at the three study sites

<table>
<thead>
<tr>
<th>Site</th>
<th>Alps</th>
<th>Sierra Nevada</th>
<th>Sri Lanka</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bedrock</td>
<td>−0.14 ±0.03</td>
<td>−0.19 ±0.04</td>
<td>−0.11 ±0.03</td>
</tr>
<tr>
<td>Bulk soil and saprolite</td>
<td>−0.20 ±0.05</td>
<td>−0.47 ±0.18</td>
<td>−0.73 ±0.27</td>
</tr>
<tr>
<td>NaOH leach</td>
<td>−0.38 ±0.47</td>
<td>−1.33 ±0.64</td>
<td>−1.78 ±0.25</td>
</tr>
<tr>
<td>Clay size fraction</td>
<td>−0.36 ±0.10</td>
<td>−1.33 ±0.50</td>
<td>−2.03 ±0.31</td>
</tr>
<tr>
<td>Stream water dissolved Si</td>
<td>0.88 ±0.18</td>
<td>1.71 ±0.14</td>
<td>0.56 ±0.15</td>
</tr>
<tr>
<td>Plant biomass</td>
<td>−0.44 ±0.21</td>
<td>−0.29 ±0.31</td>
<td>−1.05 ±0.31</td>
</tr>
</tbody>
</table>

a) One outlier (δ³⁰Si = 0.46‰) removed from Sierra Nevada dissolved Si δ³⁰Si summary statistics.
Fig. 3. Overview of $\delta^{30}$Si values in different Critical Zone compartments at the three study sites. Solid phases (Si in bulk soil and saprolite, clays, amorphous Si and plants) are almost exclusively lower $\delta^{30}$Si than bedrock, the ultimate source of all Si. Dissolved Si in river water constitutes the higher $\delta^{30}$Si counterpart required by mass-balance.
\( \delta^{30}\text{Si} \) values are lower. Dissolved Si in stream waters provides the \( ^{30}\text{Si} \) enriched counterpart required by mass-balance. The bulk soil and saprolite compositions are intermediate between the lower \( \delta^{30}\text{Si} \) clay and amorphous phases, and the higher \( \delta^{30}\text{Si} \) bedrock.

**Bedrock and mineral-specific \( \delta^{30}\text{Si} \).**—The Si isotope composition of the bulk bedrock in the three sampling areas is similar between the three sites: \( \delta^{30}\text{Si} = -0.14 \% \) (Alps), \( \delta^{30}\text{Si} = -0.19 \% \) (Sierra Nevada) and \( \delta^{30}\text{Si} = -0.11 \% \) (Sri Lanka). Mineral specific in-situ determinations yield similar ranges in \( \delta^{30}\text{Si} \) at all three sites. Biotite is consistently the lowest \( \delta^{30}\text{Si} \) mineral (means \( \pm 95\% \) CI, Alps: \( -1.01 \pm 0.38 \% \), Sierra Nevada: \( -0.58 \pm 0.04 \% \), Sri Lanka: \( -0.47 \pm 0.09 \% \)). The other major minerals (quartz, plagioclase and K-feldspar) are similar, falling around \( -0.2 \% \). Quartz tends to be the highest \( \delta^{30}\text{Si} \) mineral (Alps \( -0.20 \pm 0.05 \% \), Sierra Nevada: \( -0.14 \pm 0.05 \% \), Sri Lanka: \( -0.07 \pm 0.08 \% \)). A summary of the data, together with mineral formulae, is given in table 3 and figure 4.

**Bulk soils and saprolites.**—The bulk samples of the three sites differ in their Si isotopic composition. The bulk soil \( \delta^{30}\text{Si} \) values of the Swiss Alps site \( -0.20 \% \), of the Sierra Nevada site \( -0.45 \% \) and of the Sri Lanka site \( -0.56 \% \) (fig. 3 and table 2). No site exhibits a clear depth dependence in soil \( \delta^{30}\text{Si} \). In contrast, bulk saprolite samples vary systematically with depth in Sierra Nevada and Sri Lanka. Note there is only very thin saprolite (C-horizons) at the Swiss Alps sampling site. Mean saprolite \( \delta^{30}\text{Si} \) in Sierra Nevada is \( -0.52 \% \) and in Sri Lanka is \( -0.86 \% \). The general trend for the saprolite is an evolution to lower \( \delta^{30}\text{Si} \) with decreasing depth. At both field sites soil \( \delta^{30}\text{Si} \) is higher than the uppermost saprolite samples.

**Amorphous and clay-size fraction \( \delta^{30}\text{Si} \).**—The amorphous and clay fractions of the three sites show no obvious depth dependence. A general observation is that the mean \( \delta^{30}\text{Si} \) of the amorphous and clay fraction are highest in the Alps, lowest in Sri Lanka and intermediate in Sierra Nevada. There is a tendency that at depth (the Alps) or within the saprolite (Sierra Nevada and Sri Lanka) the amorphous fraction is higher in \( \delta^{30}\text{Si} \) than the corresponding clay fraction. This tendency reverses in the upper part of the profile (Alps) or within the soil (Sierra Nevada and Sri Lanka; fig. 3). To best isolate a secondary-phase signature, we apply a correction for the potential contamination of the clay size-fraction by primary, rock-forming silicates (considering plagioclase, feldspars, biotite and quartz as potential contaminating phases; see Appendix B for details, results are given in table 4). This correction is based on the mineral formulae and \( \delta^{30}\text{Si} \) values presented in table 3. The correction is small: our best estimate of the proportion of Si from primary phases in the clay separates is 33% in the Alps, 13% in Sierra Nevada, and 0.2% in Sri Lanka. This equates to corrections of +0.07, -0.20 %, and less than -0.01 %, respectively. XRD spectra from clay-size separates of the Sri Lanka profile (Behrens and others, 2015) corroborate the lack of primary minerals in the clay-size fraction. We thus believe we have obtained \( \delta^{30}\text{Si} \) values for the secondary clay component, rather than a mixture of mineralogical clays and clay-sized primary minerals.

**Vegetation and dissolved Si \( \delta^{30}\text{Si} \).**—The \( \delta^{30}\text{Si} \) values of the individual plant parts vary between \( -0.74 \% \) and \( -0.07 \% \) (mean = \( -0.42 \% \)) for the Alps site, between \( -0.93 \% \) and \( +0.01 \% \) (mean = \( -0.29 \% \)) for the Sierra Nevada site and between \( -1.65 \% \) and \( -0.57 \% \) (mean = \( -1.05 \% \)) for the Sri Lankan site. The Si isotope ratios of stream water samples are higher than bedrock at all three sites. Dissolved Si \( \delta^{30}\text{Si} \) values for the Alps range between 0.74 to 1.15 % (mean = 0.88 %). For the Sierra Nevada streams, they range between 0.46 to 1.91 % (mean = 1.65 %), and for the Sri Lanka sampling site, between 0.37 to 0.76 % (mean = 0.56 %).
### Table 3

**Mineral formulae and silicon isotope ratios, from fsLA-ICP-MS and fsLS-MC-ICP-MS.** Mineral abundances are given in volume % and uncertainties are ± 2σd

<table>
<thead>
<tr>
<th>Site</th>
<th>Quartz</th>
<th>Plagioclase</th>
<th>K-Feldspar (orthoclase)</th>
<th>Biotite</th>
<th>Pyroxene (Sri Lanka) or Hornblende (Sierra Nevada)</th>
<th>Bulk</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Alps</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Abundance</td>
<td>34</td>
<td>35</td>
<td>27</td>
<td>4</td>
<td></td>
<td></td>
</tr>
<tr>
<td>formula</td>
<td>SiO₂</td>
<td>(Na₁₀Ca₉₋₃Al₉₋₃Si₁₀₋₃O₈)</td>
<td>(K₀.₃₅Na₀.₂₇)Al₀.₉₄Si₃.₁₃O₈</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Al/Si (molar)</td>
<td>0.36</td>
<td>0.3</td>
<td></td>
<td>0.38</td>
<td></td>
<td></td>
</tr>
<tr>
<td>δ³⁰Si (%)</td>
<td>-0.29±0.05</td>
<td>-0.16±0.07 (n=25)</td>
<td>-0.20±0.04 (n=30)</td>
<td>-1.01±0.38 (n=4)</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td><strong>Sierra Nevada</strong></td>
<td>23.3</td>
<td>47.9</td>
<td>13.4</td>
<td>n-d</td>
<td>4.9</td>
<td>0.28</td>
</tr>
<tr>
<td>Abundance</td>
<td>SiO₂</td>
<td>(Na₁₀Ca₉₋₃Al₉₋₃Si₁₀₋₃O₈)</td>
<td>(K₀.₅₆Na₀.₀₈)Al₁.₀₉Si₂.₉₂O₈</td>
<td></td>
<td>(C₄₁₉₄Na₁₄₋₃Mg₅₆Fe₃₅Al₁₀₂₃O₁₂(OH)₂)</td>
<td>0.34</td>
</tr>
<tr>
<td>Al/Si (molar)</td>
<td>0.56</td>
<td>0.32</td>
<td></td>
<td>0.52</td>
<td></td>
<td></td>
</tr>
<tr>
<td>δ³⁰Si (%)</td>
<td>-0.14±0.05</td>
<td>-0.21±0.05 (n=27)</td>
<td>-0.19±0.10 (n=7)</td>
<td>-0.58±0.04 (n=18)</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td><strong>Sri Lanka</strong></td>
<td>30</td>
<td>25</td>
<td>32</td>
<td>7</td>
<td>4</td>
<td></td>
</tr>
<tr>
<td>Abundance</td>
<td>SiO₂</td>
<td>(Na₁₀Ca₉₋₃Al₉₋₃Si₁₀₋₃O₈)</td>
<td>(K₀.₈₂Na₀.₁₉)Al₁.₀₉Si₂.₉₂O₈</td>
<td></td>
<td>(Fe₁.₀₉Mg₀.₃₅Ca₀.₆₂Al₁₀₂₃O₁₂(OH)₂)</td>
<td>0.₂₇</td>
</tr>
<tr>
<td>Al/Si (molar)</td>
<td>0.45</td>
<td>0.37</td>
<td></td>
<td>0.43</td>
<td></td>
<td></td>
</tr>
<tr>
<td>δ³⁰Si (%)</td>
<td>-0.07±0.08</td>
<td>-0.23±0.06 (n=22)</td>
<td>-0.26±0.12 (n=10)</td>
<td>-0.48±0.09 (n=16)</td>
<td>-</td>
<td></td>
</tr>
</tbody>
</table>

- a) Mineral abundances in the Alps from Norton (2008) and Norton and von Blanckenburg (2010), who use a normative modal approach based on bedrock chemical composition that is rescaled to 100%. b) Mineral formulae in the Alps calculated from the fsLA-ICP-MS data, based on O = 12 for biotite and O = 8 for plagioclase and K-feldspar. c) Mineral abundances in Sri Lanka from the CIPW norm calculation of Hewawasam and others (2013), plus the point counting of Burton and O’Nions (1990) that provides an estimate of biotite abundance. d) Mineral formulae in Sri Lanka from the fsLA-ICP-MS data and electron microprobe data from Behrens and others (2015) and Behrens and others (2018) for pyroxene. e) Only one determination; uncertainty presented as 2SE internal precision.
Discussion

Figure 1 shows how simple mass-balances for Si isotope partitioning in the weathering zone (for example, Bouchez and others, 2013; Baronas and others, 2018) condense to three key parameters: the $\delta^{30}$Si of Si released from dissolution of primary minerals (#1, red arrow), the partitioning of Si between solute and secondary phases (Fig. 1) depends on the minerals that actually dissolve. Full results are given in Table 3. Gray shaded area indicates the range of bulk-rock $\delta^{30}$Si at the three sites.

Table 4

<table>
<thead>
<tr>
<th>Site</th>
<th>Measured clay $\delta^{30}$Si (%)</th>
<th>Measured Al/Si (mol/mol)</th>
<th>[Si]$_{clay}$ (μg g$^{-1}$)</th>
<th>Mean inherited Si (%)</th>
<th>Mean Corrected Clay $\delta^{30}$Si</th>
<th>Difference $\delta^{30}$Si</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alps</td>
<td>-0.36 ±0.09</td>
<td>0.56 ±0.08</td>
<td>9210</td>
<td>33.0 ±14.5</td>
<td>-0.29 ±0.16</td>
<td>0.07 ±0.08</td>
</tr>
<tr>
<td>Sierra</td>
<td>-1.26 ±0.49</td>
<td>0.85 ±0.12</td>
<td>22350</td>
<td>17.3 ±19.1</td>
<td>-1.53 ±0.44</td>
<td>0.20 ±0.26</td>
</tr>
<tr>
<td>Sri Lanka</td>
<td>-2.03 ±0.31</td>
<td>1.02 ±0.28</td>
<td>26830</td>
<td>0.2 ±0.8</td>
<td>-2.03 ±0.31</td>
<td>0.00 ±0.01</td>
</tr>
</tbody>
</table>

The difference in $\delta^{30}$Si values is overall small, lending support to the success of the clay separation protocol. a) Concentrations refer to bulk sample, not the amorphous or clay-size fraction specifically; see main text for details.
and the fractionation factors associated with that partitioning. In the following, we show that all of these factors vary systematically along the erodosequence.

Parameter #1: $\delta^{30}\text{Si}_{\text{initial}}$ – Incongruent Weathering at the Rock-Scale?

The granitic bedrock at all three sites has similar bulk rock $\delta^{30}\text{Si}$ of ca. $-0.15\%$ (fig. 3; table 2). Since primary mineral dissolution kinetics are mineral-specific (Churchman and Lowe, 2012), and our in situ data has shown that Si isotope ratios in bedrock can differ between minerals (see also Méheut and Schauble, 2014; Savage and others, 2014), some of the inter-site variability in clay, plant and water $\delta^{30}\text{Si}$ may be due to differing contributions of the primary minerals to total weathering. This rarely receives attention in metal stable isotope geochemistry, though the effect is well known for radiogenic isotope ratios (for example, Harlavan and others, 1998). Table 3 details the chemical and Si isotope composition of the main rock-forming minerals at our three sites. The three sites display large ranges of mineral $\delta^{30}\text{Si}$ values, with a maximum range of $0.85\%$ in the Alps. It is therefore plausible that inter-site differences in the relative contributions of each mineral induce differences in $\delta^{30}\text{Si}_{\text{initial}}$.

Plagioclase $\delta^{30}\text{Si}$ at our three sites averages ca. $-0.20\%$, in line with previously published Sri Lanka values of $-0.22 \pm 0.19\%$ (Schuessler and von Blanckenburg, 2014). Values between $-0.49\%$ to $-0.10\%$ have been determined elsewhere (Ziegler and others, 2005b; Savage and others, 2011; Savage and others, 2012; Steinhoefel and others, 2017). Our low $\delta^{30}\text{Si}$ biotite values from fsLA-MC-ICP-MS (individual determinations from $1.34$ to $0.22\%$) are also consistent with previous work. For example, laser ablation MC-ICP-MS analyses produced values of ca. $-0.70\%$ for biotite grains in the granite of the German black forest (Steinhoefel and others, 2011; Steinhoefel and others, 2017). Elsewhere, biotite separates from a Puerto Rican granite yielded a value of $-0.25 \pm 0.16\%$ (Savage and others, 2013), or a granite value of $-0.25 \pm 0.15\%$ (Savage and others, 2012) are also consistent with mineral separates in granites (Savage and others, 2014). Here, the authors report that biotite was $-0.28\%$ lighter than the bulk rock. They are also in line with the ab initio calculations of Méheut and others (2009) and Méheut and Schauble (2014), which predict that the more polymerized, cation-rich minerals should be more fractionated towards lighter (lower $\delta^{30}\text{Si}$) values.

The difference in $\delta^{30}\text{Si}$ between many of the major minerals in the granites underlying the three sites (quartz, K-Feldspar, Plagioclase) is not large (table 3). The important result of our in situ $\delta^{30}\text{Si}$ determinations is not the absolute values, but rather the demonstration that minerals can and do differ in their $\delta^{30}\text{Si}$. It is noteworthy that the inter-site difference in mineral $\delta^{30}\text{Si}$ is also non-negligible. For example, we observe an inter-site range in biotite of ca. $0.53\%$, and in quartz of $0.13\%$. Published plagioclase data also span a range of ca. $0.3\%$ (see above). Overall, the inter-mineral $\delta^{30}\text{Si}$ variations that we observe are large, resolvable and consistent with previous empirical and theoretical work.

To investigate the potential impact of differential mineral weathering on bulk soil and clay fraction Si isotope ratios, we invert bulk soil and saprolite chemical compositions to quantitatively estimate the relative contribution of each mineral to the bulk sample. Details of the approach are given in Appendix C while figure 5 shows the results. The most intensely weathered site, the Sri Lanka highlands, has no primary mineral phases left in the upper regolith and soil besides quartz, with a $\delta^{30}\text{Si}$ value of $-0.07 \pm 0.08\%$ (table 3). Plagioclase, biotite and pyroxene all display sharp gradients in abundance at the saprolite/bedrock boundary. K-feldspar is the only mineral that persists a few metres into the regolith, in line with the known mineralogy.
In the Alps, conversely, the model suggests there is little depletion of the primary rock-forming minerals and little in-situ clay formation. The Sierra Nevada site represents an intermediate setting, where the model predicts most primary minerals persist until the surface, albeit depleted relative to bedrock. Secondary clay minerals do form, in line with nearby mineralogical investigations. Kaolinite was the only secondary clay detected by XRD analyses of bulk samples (Uhlig and others, 2017). Elsewhere, XRD of clay size separates from a nearby site in Sierra Nevada revealed the presence of hydroxyl-Al interlayered vermiculite and gibbsite (Dahlgren and others, 1997).

The $\delta^{30}$Si of solubilized silicon will reflect the weighted mean of all primary phases lost between rock and topsoil, as derived from the geochemical inversion (fig. 5). For Sri Lanka, only quartz persists to the surface. The dissolving minerals are thus only slightly lower than bulk rock (table 2). At the Sierra Nevada Balsam profile (samples below 100 cm in fig. 5), biotite and plagioclase are indicated to become depleted towards the top while the other minerals are not (fig. 5). These minerals yield a weighted mean $\delta^{30}$Si of $-0.28\%$. In the Alps, no consistent mineral depletion trends

Fig. 5. Modelled mineralogy for the three study sites derived by minimising the RMSE of a series of mass-balance equations for the major elements Si, Al, Ca, Na, K, Mg and Fe (see supplementary text for details). Mineral stoichiometries as determined by fsLA-ICP-qMS (table 3) or NaOH fusion for the clay fraction are used as input (table 5). Legend abbreviations are pg plagioclase; bt biotite; kfs K-feldspar; px pyroxene; hbl hornblende; qtz quartz. The results confirm that all primary minerals except quartz are depleted in the supply limited Sri Lanka site, but that primary minerals persist to be eroded in the kinetically limited Sierra Nevada and Alps sites.

(Behrens and others, 2015). In the Alps, conversely, the model suggests there is little depletion of the primary rock-forming minerals and little in-situ clay formation. The Sierra Nevada site represents an intermediate setting, where the model predicts most primary minerals persist until the surface, albeit depleted relative to bedrock. Secondary clay minerals do form, in line with nearby mineralogical investigations. Kaolinite was the only secondary clay detected by XRD analyses of bulk samples (Uhlig and others, 2017). Elsewhere, XRD of clay size separates from a nearby site in Sierra Nevada revealed the presence of hydroxyl-Al interlayered vermiculite and gibbsite (Dahlgren and others, 1997).
emerge, reflecting the kinetically limited weathering regime. If the interpretation of biotite weathering being the dominant mineral alteration reaction is correct, $\delta^{30}\text{Si}_{\text{initial}}$ could be as low as $-1\%$. Including some plagioclase weathering would shift this value towards the bulk rock composition. Overall, bulk rock measurements of $\delta^{30}\text{Si}$ are thus a reasonable approximation for solubilised Si ($\delta^{30}\text{Si}_{\text{initial}}$; #1 in fig. 1) at long-residence time, supply-limited weathering regime sites (for example, Sri Lanka). Importantly, bulk rock $\delta^{30}\text{Si}$ values are not necessarily representative of solubilised Si for short residence time, kinetically limited sites (for example, the Alps here). We speculate the maximum range of $\delta^{30}\text{Si}_{\text{initial}}$ observed in granitoid settings is likely of the order $\sim0.2\%$. Future work could seek to characterise primary mineral $\delta^{30}\text{Si}$ and directly estimate mineral abundance profiles, for example, via a quantitative XRD approach.

Fractionation during dissolution?.—A potential confounding factor relates to whether mineral dissolution is associated with isotope fractionation. Experiments with amorphous SiO$_2$ phases have been inconsistent. Both preferential release of the lighter isotopes (Demarest and others, 2009; Sun and others, 2014) or no fractionation (Wetzel and others, 2014) have been reported. Ziegler and others (2005a) observed the preferential release of the lighter $^{28}\text{Si}$ during early basalt dissolution, but that the $^{30}\text{Si}:/^{28}\text{Si}$ ratio of solubilised Si eventually returned to that of the parent material. Similar patterns have been observed for Mg, Zn and Fe isotopes (Brantley and others, 2004; Kiczka and others, 2010; Wimpenny and others, 2010; Weiss and others, 2014; Pokharel and others, 2019). In general, the interpretation for this phenomenon is kinetically controlled release of the lighter isotopes from mineral surfaces during early dissolution, creating a residual, isotopically heavier, surface layer. For dissolution to proceed further into the mineral, this layer must first be removed – so the net effect is congruent weathering (Druhan and others, 2015). These transient effects are seen experimentally on timescales of days to weeks, so rock residence time in the weathering zone should be similar for this apparent fractionation to be visible – we suggest fractionation during dissolution is likely not important here. One exception may be found in weathering reactions that do not necessarily follow a dissolution-reprecipitation pathway, but rather a solid transformation with some Si loss. A speculative example might be the biotite-smectite transformation in the Alps, and may be part of the explanation for why the clay-size fraction of the Alps samples are similar or higher $\delta^{30}\text{Si}$ than the primary biotite grains.

Parameter #2: $f_{\text{Si}}$ – Weathering Reaction Stoichiometries Define Si Mass-Balance

The second key control on the absolute value of isotope ratios in the weathering zone is the degree to which fractionation factors can be expressed – the fraction of educt converted to product (#2 in fig. 1). At complete conversion of phase A to B, there can be no expression of any fractionation – no matter its magnitude. One constraint that is, often not considered in metal stable isotope geochemistry is that mineral weathering reactions have stoichiometries that define the degree of conversion. Table 5 lists the dominant weathering reactions occurring at the three sites. The proportion of Si mobilized during dissolution of a primary mineral that is retained in a secondary mineral, $f_{\text{Si}}^\text{sec}$ (#2 in fig. 1), can be calculated making the assumption that aluminium is immobile during mineral transformation reactions:

$$f_{\text{Si}}^\text{sec} = \frac{(\text{Al}/\text{Si})_{\text{parent}}}{(\text{Al}/\text{Si})_{\text{sec}}}$$ (5)
This yields values from 0.35 to 0.80 (table 5), decreasing from lower weathering intensity (the Alps) to more intense, kaolinite forming sites (Sierra Nevada and Sri Lanka). This means that even when initial $^{30}\text{Si}$ is uniform, and secondary clays form with a constant fractionation factor, the clay $^{30}\text{Si}$ would differ by $>50\%$ because of the different fractions of Si transferred from fluid to clay. While this is an oversimplification, it demonstrates that clay $^{30}\text{Si}$ is often largely set by the reaction stoichiometry. The predictions are in agreement with the observation (Opfergelt and others, 2012) that smectite group clays are closer in $^{30}\text{Si}$ to their parent material than kaolinite: a larger fraction of the parent Si is transferred into the clay. Steinhoefel and others (2017) had also previously noted that in situations where the clay minerals are formed by physical transformations of primary phyllosilicates with negligible Si loss, they inherit the $^{30}\text{Si}$ of the parent phase. In the Amazon basin, Hughes and others (2013) infer the mineralogy of secondary clays being formed from river geochemistry, and show that that this relates to isotope partitioning. The implication is that the mineralogy of the secondary phases governs the mass-balance control over how a Si isotope fractionation factor can be expressed (#2 in fig. 1). Because clay mineralogy in turn is set by weathering intensity (Biscaye, 1965; Thiry, 2000; Frings, 2019), both fluid and clay $^{30}\text{Si}$ are affected by weathering intensity, even if fractionation factors are uniform. As we show below, clay mineralogy also affects the clay fractionation factor itself, however (#3 in fig. 1). Note that in our companion paper (Frings and others, 2021b) we discuss the importance of $f_{\text{upt}}^\text{Si}$ – the net partitioning (and presumably export) of Si into biomass.

Parameter #3: $e_{\text{upt}}$ and $e_{\text{prec}}$ – Silicon Isotope Fractionation Factors Vary along the Erodosequence

We use the isotope difference $\Delta^{30}\text{Si}$ between the $^{30}\text{Si}$ of dissolved Si and secondary clay or vegetation Si (that is, $^{30}\text{Si}_{\text{diss}} - ^{30}\text{Si}_{\text{lay}}$ or $^{30}\text{Si}_{\text{diss}} - ^{30}\text{Si}_{\text{veg}}$) as an approximation for the Si fractionation $e_{\text{prec}}$ and $e_{\text{upt}}$ associated with clay precipitation or plant uptake, respectively (eq 1, #3 in fig. 1, see Appendix D and eq S7). This is equivalent to the $\Delta_{\text{prec}}$ and $\Delta_{\text{upt}}$ notation of Bouchez and others (2013) and is a good

<table>
<thead>
<tr>
<th>Site</th>
<th>Alps</th>
<th>Sierra Nevada</th>
<th>Sri Lanka</th>
</tr>
</thead>
<tbody>
<tr>
<td>Characteristic reaction</td>
<td>Biotite to smectite</td>
<td>Feldspar to kaolinite</td>
<td>Plagioclase to kaolinite</td>
</tr>
<tr>
<td>Reference</td>
<td>1</td>
<td>2</td>
<td>3</td>
</tr>
<tr>
<td>Reactant</td>
<td>$K_{0.65}(Mg_{1.10}Fe_{0.93})(A_{1.25}Si_{2.30}O_{10})(OH)_2$</td>
<td>$(K_{0.56}Na_{0.08})Al_{0.99}Si_{3.1}O_{8}$</td>
<td>$(Na_{0.74}Ca_{0.25}K_{0.02})Al_{1.25}Si_{2.75}O_{8}$</td>
</tr>
<tr>
<td>Ideal product</td>
<td>$Na(Ca,Al,Fe)_2SiO_3(OH)_4$</td>
<td>$Al_2Si_2O_5(OH)_4$</td>
<td>$Al_2Si_2O_5(OH)_4$</td>
</tr>
<tr>
<td>Actual product</td>
<td>$Ca_{0.09}(Al_{1.43}Mg_{0.64})<em>2(Si</em>{3.05}O_{10})(OH)_2$</td>
<td>$Al_{1.59}Si_{1.67}Mg_{0.05}Ti_{0.03}O_{5}(OH)_4$</td>
<td>$Al_{1.40}Si_{1.5}Mg_{0.06}Ti_{0.02}O_{5}(OH)_4$</td>
</tr>
<tr>
<td>Reactant Al/Si</td>
<td>0.54</td>
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<td>0.45</td>
</tr>
<tr>
<td>Actual Product</td>
<td>0.68</td>
<td>0.92</td>
<td>0.98</td>
</tr>
<tr>
<td>Al/Si</td>
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<tr>
<td>$^{30}\text{Si}$</td>
<td>0.80</td>
<td>0.35</td>
<td>0.48</td>
</tr>
</tbody>
</table>

The reactant and product do not necessarily combine in balanced formulae since they represent only the dominant phases rather than the entirety of the mineral alteration reactions. Reactant formulae from Table 3. Montmorillonite shown for illustrative purposes in the Alps; kaolinite shown elsewhere. Stoichiometry calculated assuming oxygen-numbers as in the ideal formulae (12 for smectite-group minerals, 9 for kaolinite). Minerals are not necessarily charge-balanced since trace constituents and Fe are not shown. From Equ. 5. References: 1: Egli, Mirabella, and Fitz (2001); 2: Aguirre (2019); 3: Dahlgren and others (1997); 4: Behrens and others (2015).
approximation for small fractionations and if fluxes in the weathering zone are at steady-state (see Appendix D). Because this approach uses isotope differences it is not susceptible to bias introduced by the choice of parent $\delta^{30}\text{Si}$, which we show above may be variable. To derive these values, we average all measured water samples, clay samples and plant samples at each site and use these values to calculate Si isotope fractionations associated with clay precipitation or plant uptake. Note that the fractionation cannot simply be taken as the isotope difference between bedrock and secondary clay, without accounting for mass-balance constraints (see Discussion; #2 in fig. 1). Importantly, the isotope difference $\Delta^{30}\text{Si}$ only approximates fractionations for two related, exchanging phases (see Appendix D). The approach used here implicitly assumes that the river dissolved Si, and regolith clays, are representative of material leaving the catchment. It thus yields estimates of apparent fractionation, integrated over the entire system that combine the net result of multiple fractionating steps. It also implicitly assumes that stream dSi $\delta^{30}\text{Si}$ is not altered by in-situ diatom production. As discussed in Frings and others (2021b), and demonstrated in for example Cary and others (2005), this is likely the case for these small headwater streams. A summary and comparison to literature values is given table 6 for $\varepsilon_{\text{upt}}$ and table 7 for $\varepsilon_{\text{prec}}$.

Si isotope fractionation by vegetation.— Si is taken up by plants in the form of silicic acid (Si(OH)$_4$), either through specialised transporter channels or passively across the membrane (Ma and Yamaji, 2008). Plant Si uptake is generally associated with a discrimination against $^{30}\text{Si}$ from the substrate the plants grow in. Several studies have reported plant Si isotope fractionations $\varepsilon_{\text{upt}}$, that we summarise in table 6. Once the silicon is taken up, further fractionation occurs during translocation, such that $^{28}\text{Si}$ becomes progressively depleted from the roots to the leaves (for example, Ding and others, 2005; Hodson and others, 2008; Frick and others, 2020). In line with these studies we observe the preferential uptake of $^{28}\text{Si}$: biomass $\delta^{30}\text{Si}$ values are mostly lower than stream water values and underlying bedrock values (fig. 3 and table 2). As described above, erodosequence plant Si isotope fractionations are approximated as the isotope difference between river water $\delta^{30}\text{Si}$ and sampled plant biomass $\delta^{30}\text{Si}$ and equate to $-1.30 \permil$, $-1.94 \permil$, and $-1.60 \permil$ for the Alps, Sierra Nevada, and Sri Lanka, respectively (table 6). These are larger than experimentally derived plant isotope fractionation factors. However, our sampling strategy does not easily permit a bulk plant $\delta^{30}\text{Si}$ value to be estimated — we did not sample root biomass, for example. The plant $\delta^{30}\text{Si}$ data thus convolve Si isotope fractionation during Si uptake with Si isotope fractionation during translocation within the plant itself.

Si isotope fractionation associated with clay formation.— In line with the vast majority of clay mineral $\delta^{30}\text{Si}$ determinations to date, our clay samples are $^{30}\text{Si}$ depleted relative to bedrock (Ziegler and others, 2005b; Cornelis and others, 2010; Opfergelt and others, 2010; Opfergelt and others, 2012; Cornelis and others, 2014). This general trend is independent of underlying lithology (for example, Ziegler and others, 2005a vs. Ziegler and others, 2005b) or climate (for example, Cornelis and others, 2014 vs. Frings and others, 2014) and is also reflected in isotopically heavy river dissolved Si (for example, Hughes and others, 2012; Hughes and others, 2013). Interestingly, the depletion in secondary phase $^{30}\text{Si}$ relative to the parent contrasts with increasingly sophisticated ab initio calculations (Dupuis and others, 2015; Fujii and others, 2015; He and others, 2016) and experimental work (Oelze and others, 2014; Roerdink and others, 2015; Stamm and others, 2019). These studies demonstrate that at isotopic equilibrium, the solid phase either has no resolvable discrimination or preferentially incorporates the heavier $^{30}\text{Si}$ isotope, with $^{28}\text{Si}$ correspondingly enriched in the dissolved phase. River dissolved Si is essentially never lower in $\delta^{30}\text{Si}$ than bedrock, which is thus a clear indication that isotopic equilibrium between clay and solute is not
### TABLE 6

Summary of isotope differences between plants and river/stream water as an approximation for plant uptake Si isotope fractionation, and comparison to values reported in the literature

<table>
<thead>
<tr>
<th>Site</th>
<th>Ref.</th>
<th>Water δ³⁰Si (%)</th>
<th>Plant δ³⁰Si (%)</th>
<th>Dominant species</th>
<th>Fractionation (ε_{upt}, ‰)</th>
<th>Notes</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alps</td>
<td>this</td>
<td>0.88 ± 0.18</td>
<td>-0.42 ± 0.21</td>
<td>Grasses and spruce</td>
<td>-1.30 ± 0.28</td>
<td>Derived from silicon isotope difference between stream water and plant biomass</td>
</tr>
<tr>
<td>Sierra Nevada</td>
<td>this</td>
<td>1.71 ± 0.14*</td>
<td>-0.30 ± 0.31</td>
<td>Ponderosa Pine</td>
<td>-1.94 ± 0.44</td>
<td></td>
</tr>
<tr>
<td>Sri Lanka</td>
<td>this</td>
<td>0.56 ± 0.15</td>
<td>-1.05 ± 0.31</td>
<td>Diverse tropical taxa</td>
<td>-1.60 ± 0.34</td>
<td></td>
</tr>
</tbody>
</table>

**Literature data**

1. rice -1.02
2. rice -0.3
3. rice -1.7 to -0.5
4. rice -0.79
5. rice -1.13 to -0.40
6. banana -0.78
7. banana -0.68
8. com and wheat -1
9. cucumber -0.52 to +0.27
10. bamboo -1.15
11. maize -1.1
12. tomato -0.33
13. mustard -0.55
14. spring wheat -0.43

Note that many studies published to date have been performed with nutrient solutions that are over-saturated with respect to amorphous silica, and inorganic precipitation can not be ruled out. References: 1: Ding and others (2005a); 2: Sun and others (2008); 3: Ding and others (2008a); 4: Sun, Wu, and Li (2016); 5: Sun and others (2016); 6: Opfergelt and others (2006); 7: Delvigne and others (2009); 8: Ziegler and others (2005a); 9: Ding and others (2008b); 10: (Sun and others (2017); 11: Frick and others (2020).
achieved. Instead, a unidirectional kinetic isotope fractionation must be involved at some stage during clay formation. Note also that some relatively high $\delta^{30}\text{Si}$ clays extracted from sandstone aquifer sediments (Georg and others, 2009) fit with this concept: the water-sediment interaction time may be so long in these systems that the clays have time to at least partially isotopically re-equilibrate with the solution. Overall, the data require a net kinetic discrimination against the heavier isotopes of Si during clay formation.

Our data and the available literature data suggest that different clay mineral groups have distinct Si isotope fractionation factors associated with their formation. With the exception of Icelandic sites formed from basalts, kaolinite Si isotope fractionations cluster around $\varepsilon_{\text{prec}}$ of $-3\%_\circ$, while the formation of less desilificated 2:1 clays, including smectites and vermiculites, are closer to $-1\%_\circ$. Note that this conclusion refers to the fractionation factor itself (#3 in fig. 1), and not to how mass-balance effects (#2 in fig. 1) control how it might be expressed. Might part of the explanation for the variable fractionation lie in the mechanism of their formation?

Previous work (Geilert and others, 2014; Oelze and others, 2014; Roerdink and others, 2015) shows that Si isotope fractionation during the laboratory precipitation of simple phases is rate dependent. This has been interpreted as competition between two endmember isotope effects in the context of a surface reaction kinetic model.
Kinetic fractionation tends to deplete the forming solid in $^{30}$Si, while equilibrium fractionation tends to have a much smaller depletion or even slight enrichment in $^{30}$Si, depending on the Si bonding environment of the phase being considered. The consistent depletion in $^{30}$Si in clays led Oelze and others (2014) to infer that clay minerals inherit a kinetically derived signature from an amorphous precursor, and are then slow to re-equilibrate their Si according to their equilibrium fractionation factor. The slow re-equilibration thus explains the discrepancy between natural samples and the predictions based on equilibrium fractionation factors (see above). Note that the formation of crystalline clay minerals from an Al-rich amorphous precursor is consistent with the Gay-Lussac-Ostwald step rule, which requires that the first phase to form will be the one that causes the least reduction in solute activity.

In our three sites, the amorphous fraction and the clay fraction Si isotope compositions correlate (fig. 6), although some Sierra Nevada samples deviate from this trend (discussed below). This overall correlation suggests that a potential explanation for the variable $\varepsilon_{\text{pre}}$ (table 7) is the magnitude of the kinetic isotope fractionation into the amorphous precursor. These phases are operationally targeted by the NaOH leach and are aluminium rich, as seen elsewhere (Barão and others, 2015). The two sites with the lowest $\delta^{30}$Si clay-size separates (Sri Lanka and Sierra Nevada; table 2)
also have higher mean amorphous silica fraction molar Al/Si ratios: 3.40 and 3.84, respectively, compared to 2.21 for the Alps (see supporting Data Tables in Frings and others, 2021a). This leads us to suggest a role for aluminium in setting Si isotope fractionation during clay mineral formation.

Interestingly, the samples in figure 6 that deviate most from the 1:1 line are also those with lowest Al/Si ratio in the NaOH leach (data in supporting Data Tables S1–S3, Frings and others, 2021a). In the Critical Zone, there are at least two sources of amorphous Si that we assume are targeted with an NaOH solution. First, there is the Al-rich amorphous phases that are thought to occur during many silicate weathering reactions (Hellman and others, 2012; Behrens and others, 2015). These likely form as mineral surface layers during silicate dissolution-reprecipitation reactions. The second source is phytolith Si, and other biogenically formed amorphous Si phases. Barão and others (2015) show how the Al/Si ratio of the NaOH leach is itself diagnostic of the source of the ASi. Low Al/Si is indicative of a biogenic origin, while high Al/Si indicates a pedogenic origin. Thus, the low Al/Si samples that deviate from the 1:1 line in a plot of NaOH leach $\delta^{30}$Si vs. clay size fraction $\delta^{30}$Si (fig. 6) might in some cases reflect a phytolith pool that is not a direct clay precursor. This is not always the case, however. A subset of Sierra Nevada samples in figure 6 have low NaOH leach Al/Si ($\leq$ 2 mol mol$^{-1}$), but derive from the deep Balsam saprolite profile (data in supporting table S2). We assume that there is not a substantial pool of phytolith Si at several metres depth in the regolith. Why this subset of samples has lower Al/Si in the NaOH leach is unclear, but lends credence to the idea that the relative abundances of Al and Si influence Si isotope fractionation.

Further evidence for the role of aluminium is provided by the correlation between $f_{\text{prec}}$ and individual clay sample Al/Si (fig. 7) that is consistent among the three sites. Here, the fractionations are derived from a rearrangement of equation (2), with a definition of $f_{\text{sec}}$ coming from equation (5):

\[ f_{\text{sec}} = \frac{\delta_{\text{sec}} - \delta_{\text{parent}}}{f_{\text{sec}}^{\text{Al/Si}}_{\text{parent}}^{\text{sec}}} = \frac{\delta_{\text{sec}} - \delta_{\text{parent}}}{f_{\text{sec}}^{\text{Al/Si}}_{\text{parent}}^{\text{sec}}} \]  

(6)

where $(\text{Al/Si})_{\text{parent}}^{\text{sec}}$ is the Al/Si ratio of bulk bedrock corrected for Si hosted in quartz, assuming that the quartz does not provide Si (fig. 5). The ratio of Al/Si ratios in the denominator of equation (6) gives the reaction stoichiometry (that is, $f_{\text{sec}}^{\text{Al/Si}}$, see eq 5). Equation (6) therefore allows the derivation of field-derived fractionation factors without knowing the dissolved Si composition. This approach is distinct from, but complementary to, the values presented in table 6 and table 7 derived from isotope differences. It is similar to how clay fractionation factors can be inferred from for example, Si/Na ratios and $\delta^{30}$Si in river water and rock, without measuring the $\delta^{30}$Si of the clay itself (for example, Hughes and others, 2013). As above, equation (6) yields the fractionation itself (#3 in fig. 1), and not its expression (that is, after accounting for the mass-balance control, #2 in fig. 1). The fractionation derived from equation (6) differs in assumptions to that derived from an isotope difference (table 7), but yields reassuringly similar values. Elsewhere, others have made similar observations: Yang and Zhang (2019) show that $\delta^{30}$Si of the clay fraction in soils formed above a granite in a monsoonal region are negatively correlated with free Al concentrations. If Al availability is the proximate cause, what is the mechanism? Below, we investigate two possibilities.

Aluminium might be influencing Si isotope fractionation by altering the reaction pathways, that is, the activated complex of Transition State Theory (TST). There is a growing body of literature emphasizing that kinetic isotope fractionations are...
mechanism-dependent. For example, within the context of calcite crystallization, Nielsen and others (2012) infer that the magnitude of Ca kinetic isotope fractionation should vary with the stoichiometry of the solution the calcite precipitates from. Similarly, Joe-Wong and others (2019) show experimentally how the magnitude of Cr kinetic isotope fractionation increases as a function of the thermodynamic driving force (the standard free energy of reaction). These observations are consistent with the different kinetic isotope fractionations apparent during the adsorption of Si onto gibbsite at various solution Al/Si ratios (Oelze and others, 2015). Kinetic isotope fractionations are in principle feasible to attain from ab initio calculations, but in practice the challenge is to define the transition state reactants pass through before the final product. The few calculations that have been made for Si isotopes (He and Liu, 2015; He and others, 2016) emphasize that estimates of the final fractionation factor for a given reaction can vary by more than 10% in some cases, depending on the transition state complex used in the calculation.

Alternatively aluminium may alter Si isotope fractionation factors by influencing reaction rates for any given reaction pathway. Within the framework of a surface kinetic model, DePaolo (2011) shows how isotope or trace-element fractionation into a

---

**Fig. 7.** Relationship between clay size fraction Al/Si ratio and the $^{30}\text{Si}/^{28}\text{Si}$ isotope fractionation ε (calculated from eq 6) associated with clay mineral formation. Filled symbols are soil samples, open symbols are saprolite samples. Stars indicate quartz-corrected parent rock. Vertical dashed lines illustrate parent material (Al/Si ≈ 0.45 for the non-quartz component of a typical granitoid rock, where $f_{\text{Si}}^{\text{sec}} = 1$) and a kaolinite-type clay mineral (Al/Si = 1, thus $f_{\text{Si}}^{\text{sec}} = 0.45$; see also table 5). The fractionations are calculated as the ratio of isotope difference between clay and (bulk) rock $\delta^{30}\text{Si}$ to an estimate of $f_{\text{Si}}^{\text{sec}}$ derived from Al/Si ratios (eq 6).
precipitating solid is a function of reaction rate, reflecting the balance between competing isotope fractionations associated with the forward and backward reactions. The relevance of the surface kinetic model for Si isotope fractionation in clays is given by Yang and Steefel (2008), who present experimental evidence that the precipitation rate of kaolinite in flow-through reactors is a linear function of $\Delta G$, the Gibbs free energy of reaction. $\Delta G$ is itself a function of aqueous Al and Si concentrations. This conclusion is also corroborated by amorphous $\text{SiO}_2$ precipitation experiments (Geilert and others, 2014). Further exploring the role of Al geochemistry could provide a framework linking Si mobility, clay mineralogy and Si isotope systematics.

**Si Isotopes as a Proxy For Present and Past Weathering Intensity**

We show above that Si isotope ratios in secondary clays reflect a combination of the fractionation factors and net weathering reaction stoichiometry. Opfergelt and Delmelle (2012) have demonstrated that the Si isotope composition of bulk soils is a good proxy for the soil weathering intensity, that is, the fraction of mass-loss accomplished chemically. The Opfergelt and Delmelle (2012) compilation was dominantly basaltic and uses the Chemical Index of Alteration (CIA) as a proxy for weathering intensity ($W/D$, see above). CIA broadly traces mobile element loss, and is defined as $(\text{Al}_2\text{O}_3/(\text{Al}_2\text{O}_3 + \text{CaO} + \text{Na}_2\text{O} + \text{K}_2\text{O})) \times 100$ (Nesbitt and Young, 1982). We show here that the granitic catchments of the Alps, Sierra Nevada, and Sri Lanka sites exhibit the same pattern (fig. 8) as the Opfergelt and Delmelle (2012) compilation. There is a negative relationship between CIA and bulk regolith $\delta^{30}\text{Si}$. This relationship is relatively easy to explain as binary mixing. As a soil or saprolite weathers, the ratio of primary silicate minerals (high $\delta^{30}\text{Si}$) to secondary (alumino)silicate minerals (low $\delta^{30}\text{Si}$) decreases. This is similar to the observation made for lithium isotope ratios in fine-grained river sediment by Dellinger and others (2017). In our data, this high-weathering intensity end member is represented by the Sri Lanka site, where the mineralogy of soils is dominated by quartz and kaolinite (fig. 5). At low-weathering intensity sites like the Alps, clays formed are both less $^{30}\text{Si}$ depleted and less abundant, so the Si isotope budget in these settings will be dominated by the unweathered primary minerals. The granitic sites presented here define an array that plots slightly above the basaltic sites making up the majority of the previous data (Opfergelt and Delmelle, 2012). This is likely because even at CIA = 100, most soils formed above granitoid rocks will contain a substantial quartz component, which is not the case for basaltic settings. Overall, the relationship between bulk soil $\delta^{30}\text{Si}$ and weathering intensity is therefore best understood as simple mixing between high and low $\delta^{30}\text{Si}$ endmembers.

Recently, Bayon and others (2018) have shown that the $\delta^{30}\text{Si}$ of the clay-size fraction (in their case, <4 $\mu$m) of river suspended sediment also correlates strongly with weathering intensity in 50 global rivers. This opens the door to the use of Si isotopes in dissolved Si or in clays as a (palaeo)weathering-intensity proxy. In sediment records, bulk elemental geochemistry is hard to relate directly to weathering intensity of the landscape that produced the sediment. This difficulty arises because transport and deposition of sediments also control on sediment geochemistry (via size, shape and density effects on hydrodynamics) (Frings, 2019). But within the clay-size fraction, there is much less potential for biases induced by grain hydrodynamic properties. If the clay fraction reflects the bulk sample weathering intensity, there is potentially a powerful and novel tool for reconstructing past weathering regimes. In figure 9, we show that this is the case: clay-size fraction $\delta^{30}\text{Si}$ is a proxy for the fractional base cation (Ca$^{2+}$, Mg$^{2+}$, K$^+$ and Na$^+$) loss relative to parent rock (see Appendix E). We use this as a proxy for weathering intensity ($W/D$) to account for compositional differences in bedrock in a way that the CIA metric does not, and to emphasise the remaining CO$_2$ consumption potential.
of a soil or sediment sample. Dellinger and others (2017) observe a similar relationship between catchment W/D and the lithium isotope composition of fine-grained river sediment, which they largely interpret as mixing between primary minerals and secondary minerals, that is, a similar interpretation as for figure 8. Here, we performed a clay-size fraction separation. We believe the separation of secondary clays and primary minerals was successful (see Appendix B), while Dellinger and others (2017) use only the <63 μm fraction of river surface sediments. The relationship in figure 9 is thus hard to explain within the endmember mixing concept for bulk soils described above (fig. 8). Within the context of the three factors discussed in this manuscript (fig. 1), the simplest explanation is a combination of a fractionation factor that scales with Al availability, and the variable expression of this fractionation as governed by net weathering reaction stoichiometry, and therefore weathering intensity.

CONCLUSIONS

We present detailed silicon isotope budgets for three granitic weathering profiles falling along a gradient of erosion rate (an “erodosequence”), and thus time material spends in the weathering zone and overall weathering intensity. The three sites have similar parent material δ30Si values around −0.15‰, typical of granitoid rocks. Yet the

Fig. 8. The utility of silicon isotope ratios as a weathering-intensity proxy, as shown by the silicon isotope composition of bulk soils, as a function of soil Chemical Index of Alteration (CIA). CIA is a proxy for weathering intensity W/D, and is defined as (Al2O3/Al2O3 + CaO* + Na2O + K2O) × 100 (Nesbitt and Young, 1982), with CaO* indicating Ca hosted in silicate minerals only. The more weathered a soil is (the more it has lost the mobile elements Ca, Na and K), the more CIA tends towards 100. The trend towards lower bulk soil and saprolite δ30Si with increasing CIA arises from mixing between primary rock forming minerals (high δ30Si, high Ca, Na, K) and secondary minerals (low δ30Si, low Ca, Na, K). Shaded boxes represent approximate endmembers for granitoid rock and basaltic rock (red and gray, respectively) as CIA → 100. The difference results from the much greater concentration of quartz in granitoid rock, which influences bulk δ30Si but not CIA. See main text for details. O&D 2012 = Opfergelt and Delmelle (2012).
isotope ratios of the phases produced from bedrock-derived Si (including river waters, clays, amorphous phases and plant material) differ substantially within and between the three sites. Here, we condense these Si isotope distributions to the simplest possible interpretative framework, comprising three parameters: 1) the isotope ratio of an initial (‘parent’) phase, 2) the relative partitioning of this initial material between one or more secondary phases, and 3) the fractionation factor(s) associated with this partitioning. The data presented here shows how all three vary along our erodosequence in a way that is generalisable to the suite of ‘novel’ metal(loid) stable isotope systems:

- At each site, the primary minerals that comprise the bulk parent rock span a large range of isotope ratios. This means that if one is preferentially dissolved relative to another, the isotope ratio of the initial material can differ from the bulk rock by a
non-negligible amount. For silicon, this can conceivably be by 0.5‰ or more (fig. 4) but in most cases is unlikely to induce more than a few tenths of a permil deviation from a bulk rock composition.

- The partitioning of an element between solute and secondary phases is governed by the net weathering reaction stoichiometry, which itself reflects weathering intensity, and controls how much a fractionation factor can be expressed. For Si, forming kaolinite instead of a smectite-group clay means a factor of two or more difference in how much Si is lost.
- The fractionation factor associated with secondary phase formation is not constant, but varies with the mineralogy of the phase being formed. For Si, this varies between $-3\%$ to $-1\%$, and may be related to aluminium geochemistry that affects the rate and/or pathways of clay formation or its amorphous precursor. For plant Si uptake, the Si isotope fractionations are similar at the three sites.

Future work could experimentally, empirically, and theoretically investigate the links between Al geochemistry, silicate dissolution and precipitation rates, and Si isotope fractionation to yield a more mechanistic understanding of why fractionation factors differ between clay minerals. The data and interpretations presented here contribute to the framework needed to quantitatively interpret silicon isotope distributions in terrestrial ecosystems, or to quantitatively reconstruct weathering intensity from $\delta^{30}\text{Si}$ of phases preserved in sedimentary archives. A companion paper (Frings and others, 2021b) focuses on one application of this dataset: what knowledge of silicon isotope partitioning can contribute to an understanding of ecosystem nutrient budgets.

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APPENDICES

Appendix A: Silicon Concentrations in Critical Zone Compartments

Figure A1 shows the Si concentrations of various Critical Zone compartments at the Alps, Sierra Nevada and Sri Lanka sites.

Appendix B: Composition and Contamination of the Clay-Size Fraction

All clay separation protocols target a $<2 \ \mu\text{m}$ size fraction rather than a true mineralogical fraction. The clay size separates might thus contain primary minerals (including quartz or phyllosilicates such as micas). A first-order assessment of the extent to which our separates are true secondary clays can be made via their elemental composition. In Sri Lanka, the molar Al/Si ratio of the clay fraction from soil samples is $1.02 \pm 0.28$ (1σ), in the Alps $0.56 \pm 0.08$ and in Sierra Nevada $0.85 \pm 0.12$. For reference, kaolin-group minerals have Al/Si of $\sim 1$, smectite group minerals $\sim 0.5$ and the primary rock forming minerals $< 0.5$ (table 3 in the main text). In Sri Lanka, the clay mineralogy is dominated by kaolinite, with some gibbsite towards the top of the profile (Behrens and others, 2015). In Sierra Nevada, kaolinite is the only secondary
mineral that was visible in bulk XRD spectra (Uhlig and others, 2017). Analyses from clay-size separates of soils overlying the same Dinkey Creek granodiorite also identified vermiculite, plus primary mica in sites at a similar elevation (Dahlgren and others, 1997). In the Swiss Central Alps glacial tills comprising granitic rock at similar

Fig. A1. Si concentrations (μg g⁻¹) of bulk samples, clay size-fractions, amorphous Si leachates, plants, and water samples, at the three field sites.
elevations to our study sites produce smectites (Egli and others, 2001; Egli and others, 2008). At the erodosequence sites the ‘expected’ Al/Si ratios are thus slightly higher than 1 in Sri Lanka (kaolinite + some gibbsite); slightly lower than 1 in Sierra Nevada (kaolinite + some vermiculite), and around 0.6 in the Alps (smectite group minerals). Therefore, we conclude that the Al/Si ratios suggest a dominantly ‘true’ clay assemblage. The match between expected and observed Al/Si ratios argues against the coincidental mixing of for example, quartz (Al/Si = 0) and gibbsite (Al/Si = ∞) to produce a kaolinite-like Al/Si ratio. In any case, this quartz-gibbsite mixing scenario is
only plausible in Sri Lanka, since gibbsite is not observed to be forming in Sierra Nevada or the Alps.

Further evidence for the absence of primary minerals in the clay-size fraction comes from Ca/Si and Mg/Si ratios. These are low: Ca/Si ratios average <0.01, 0.05 and 0.02 mol/mol, and Mg/Si ratios average 0.16, 0.15 and 0.03 mol/mol, in Sri Lanka, Sierra Nevada and the Swiss Alps, respectively. There are no trends in clay size fraction Al/Si, Ca/Si, Mg/Si with depth in the regolith profiles, which might be expected to increase if clay abundance decreases with depth. Qualitatively, these compositions also suggest the clay size fraction dominantly comprises pedogenic clay minerals. This gives confidence that the measured $\delta^{30}\text{Si}$ values reflect the newly formed secondary minerals rather than a mixture between new clays and primary phases.

Simple mass-balance approaches can more rigorously quantify the potential presence of primary phases and assess their potential impact on the measured clay $\delta^{30}\text{Si}$. Here, we exploit the known clay mineralogy to assess and correct the clay size fraction $\delta^{30}\text{Si}$ for primary minerals. This approach is based on the assumption that we know the Al/Si ratio of the clay minerals that are forming. The workflow is illustrated for an

Fig. A3. A comparison between predicted element concentrations in bulk soil or saprolite samples derived from a minerals-specific mass-balance model, with measured element concentrations.
example sample in figure A2. In an initial step (Panel A), mixtures of the primary phases quartz, K-feldspar, plagioclase and biotite, with formulae as given in table 3, are subtracted from the measured clay-size fraction chemical composition, until the Al/Si ratio is equivalent to that expected (prescribed to be 0.7±0.1, 0.9±0.1 and 1.0±0.1 for the Alps, Sierra Nevada, and Sri Lanka, respectively). In other words, the contours in figure A2A show solutions to the mixing equation:

\[ \left( \frac{Al}{Si} \right)_{clay} = \left( \frac{Al}{Si} \right)_{meas} - \sum f_i \left( \frac{Al}{Si} \right)_i \left( 1 - \sum f_i \right) \]  

where \( \left( \frac{Al}{Si} \right)_{clay} \) is the prescribed ratio, \( \left( \frac{Al}{Si} \right)_{meas} \) is the measured ratio, \( \left( \frac{Al}{Si} \right)_i \) is the ratio in phase \( i \) (where \( i \) can be quartz, plagioclase, feldspar or biotite), and \( f_i \) is the contribution of Si from phase \( i \) to the total clay-size fraction. Solutions to the mixing equation are ignored if they yield negative Ca, Mg, K or Fe concentrations. Then, the primary mineral abundances can be used to calculate the fraction of Si in the clay-size separate that comes from primary phases (Panel B). In turn, this can be used to calculate the mean \( \delta^{30}Si \) of these phases (Panel C, using mineral \( \delta^{30}Si \) values from table 3/fig. 4). Finally, the magnitude of the correction for each solution to equation (S1) can be calculated from a simple mixing equation (Panel D). Making the simplifying assumption that all primary phases are equally likely to be found in the clay-size fraction (that is, all solutions to eq S1 are equally likely), and assuming the true clay Al/Si ratio is 0.7, 0.9 and 1.0 in the Alps, Sierra Nevada, and Sri Lanka, respectively, the results confirm a small Si contribution from primary minerals. In the Alps, 33±15% of Si is from primary phases, in Sierra Nevada 17±19%, and in Sri Lanka 0.2±0.01%. This yields minor corrections to the measured clay-size fraction \( \delta^{30}Si \): +0.07±0.08‰ (mean ±1σ) in the Alps, −0.20±0.26‰ in Sierra Nevada, and 0.00±0.01‰ in Sri Lanka. The overall magnitude of the correction is insensitive to the prescribed clay Al/Si ratio – the mean correction magnitude differs by <0.15‰ in absolute magnitude for prescribed Al/Si ratios 0.1 mol/mol higher or lower. The takeaway message is thus that the measured clay-size fraction \( \delta^{30}Si \) values are reasonably close approximations for the ‘true’ secondary clays that are present in the erodosequence sites.

To avoid making the assumption that all samples at every site have identical Al/Si ratios, and to avoid making judgements about which primary minerals are most likely to be found in the clay-size fraction, for the data shown in the main text we perform a correction that subtracts from each sample a primary mineral composite (that is, a mean of the composition of quartz, plagioclase, feldspar and biotite at each site). We assume that each sample contains our best estimate of the average amount of primary-mineral silicon for that site (that is, 33%, 17% and 0.2%, in the Alps, Sierra Nevada and Sri Lanka, respectively; see above). In practical terms, this means that clay size fraction geochemistry (including \( \delta^{30}Si \)) for samples from Sri Lanka is essentially unchanged, and only slightly adjusted in the Alps and Sierra Nevada.

Appendix C: Inversion of Bulk Geochemical Composition to Obtain Mineral Abundances

The aim is to calculate the proportion of individual minerals contributing to a bulk samples’ geochemistry to derive an estimate of mineral loss relative to bedrock. This can be combined with mineral-specific \( \delta^{30}Si \) determinations (see table 3 in the main text) to produce an estimate of the \( \delta^{30}Si \) of the Si initially released to solution (\( \delta^{30}Si_{initial} \), #1 in fig. 1). Previous work has used quantitative X-Ray Diffraction (XRD) in concert with Zr concentrations to infer mineral specific weathering rates (for example, Ferrier and others, 2010). Our approach here is similar, except we
infer the mineral concentrations from a deconvolution of bulk geochemistry, reported as LOI-corrected concentrations in von Blanckenburg and others (2021) and in the supporting Data Tables (Frings and others, 2021a). This is achieved with a simple inverse mass-balance approach similar to that used to derive mineral contributions to stream-water chemistry (Price and others, 2005; Velbel and Price, 2007). We define a mass-balance equation for each of the major elements Si, Al, Mg, Ca, Na, K, and Fe:

$$X_{\text{bulk}} = \frac{\sum x_i X_i M_i}{\sum x_i M_i}$$

where $X$ is the element concentration in g/g in the bulk sample and in mineral $i$, $x_i$ is the fractional contribution of mineral $i$ and $M_i$ is mass of one mole of mineral $i$, as calculated from the molar formulae in table 3 in the main text. Including the constraint that $\sum x = 1$, gives eight mass-balance equations. The contributions of five primary minerals (Plagioclase, Kfeldspar, Biotite, Quartz and Pyroxene) and three secondary phases (a clay mineral, an iron oxide, and amorphous Si) are calculated by optimising $x$ in order to minimise the root-mean-square-error (RMSE) between predicted and observed concentrations. We incorporate the constraints that $0 \leq x \leq 1$ for all phases, and that amorphous Si $\leq 1$ wt%, based on our NaOH extractions (see Supplementary Data table S1, Frings and others, 2021a). This mass-balance is overconstrained: there is no exact solution. We use a global non-linear optimisation algorithm (Ugray and others, 2007) to find the best solution, implemented within Matlab 2020a. The algorithm utilizes a multi-start routine to find a global minimum. The mineral-specific elemental stoichiometries at each site are different, and are constrained by EDX measurements or mineral specific digestions (Main Text table 3). An ideal formula for goethite (FeO(OH)) is used for the iron-oxide phase, and is assumed to have Si adsorbed to its surfaces, Fe/Si set at $\sim$100 after Delstanche and others (2009). The Al/Si ratio of the amorphous phase is given by our NaOH extractions. The composition of the secondary clay is given at each site by the corrected clay-size fraction chemistry (Main Text table 4, full data in Supplementary Data table S1, Frings and others, 2021a), with the formulae as given in Main Text table 7. A Monte-Carlo (250 iterations) approach is used to assess uncertainties, by allowing the mineral element concentrations to vary by $\pm 10\%$ and including a $\pm 10\%$ error on the XRF element concentration measurements for bulk soil, saprolite and rock. Secondary phase concentrations are fixed at zero concentration for unweathered bedrock samples. For the Sri Lanka site, we modified this procedure to include radiogenic Sr isotope ratios from Hewawasam and others (2013), using the mineral specific $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of Burton and O’Nions (1990). This made little difference to the results and is not considered further.

Figure 5 in the main text shows the results while figure A3 shows the model performance. In general, predicted and observed element concentrations match well, lending confidence to the results. In the Alps and Sri Lanka, predicted cation concentrations (mostly Ca, K, or Fe) are occasionally $\leq 1$ wt% lower than observed. This may be due to inaccurate mineral compositional data, the presence of minor phases or dust particulates not considered, or mineral compositions that are not representative of all bedrock (for example, the granites and gneisses in the Alps will exhibit different mineral formulae; the same is true of the Dinkey Creek granodiorite and quartz diorite underlying the Sierra Nevada site). Nevertheless, the first-order observations are unlikely to change.
Appendix D: Isotope Differences as Approximations for Isotope Fractionations

An isotope fractionation factor $\alpha$ for a process partitioning Si between phase A and B is defined as the ratio of two ratios:

$$\alpha_X = \frac{R_A}{R_B} \quad (S3)$$

Where $R$ is the ratio $^{30}\text{Si}/^{28}\text{Si}$. Both $\alpha$ and $R$ are related to the more convenient permil equivalents $\varepsilon$ and $\delta$:

$$\alpha_X = \frac{\varepsilon_X}{1000} + 1 \quad (S4)$$

$$R = \left( \frac{\delta}{1000} + 1 \right) \cdot R_{NBS} \quad (S5)$$

Substituting these expressions into equation (S3) and simplifying:

$$\varepsilon_X = \frac{1000\delta_A - 1000\delta_B}{\delta_B + 1000} \quad (S6)$$

When $\delta_B$ and $\delta_A$ are much less than 1000, the expression simplifies to:

$$\varepsilon_X \approx \delta_A - \delta_B \quad (S7)$$

As Bouchez and others (2013) show, this general approach is also valid for cases where two or more processes are removing an element from a single well-mixed pool.

Appendix E: Cation Loss as a Proxy for Weathering Intensity

We use an expression for the fractional cation equivalent loss as a proxy for weathering intensity, defined as:

$$\sum \frac{-\rho_X \cdot \tau_{Zr}^X \cdot [X]_{rock,i}}{\rho_X \cdot [X]_{rock,i}} \quad (S8)$$

Where $\rho_X$ is the charge associated with a cation ($2^+$ for Ca and Mg, $1^+$ for Na and K), $[X]_{rock}$ is that cations concentration in the parent rock, $\tau_{Zr}^X$ is the zirconium-normalised mass transfer coefficient for that element, and $i$ denotes Na, Ca, K, and Mg.

REFERENCES


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