

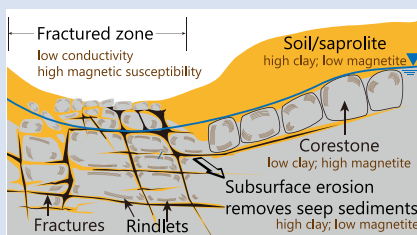
Subsurface particle transport shapes the deep critical zone in a granitoid watershed

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Abstract



Understanding the inter-relationships between chemical weathering and physical erosion remains a first order puzzle in Earth surface dynamics. In the Río Icacos watershed in the Luquillo Critical Zone Observatory, Puerto Rico, where some of the world's fastest weathering of granitoid watersheds has been measured, we show that chemical weathering not only releases dissolved solutes, but also weakens the rock around the fractures until particles detach and are mobilised by subsurface flow through fractures. These sand-sized particles are more weathered than corestones, but much less weathered than soils/saprolites. Subsurface removal of these clay-enriched, magnetite-depleted particles from the fractures could explain zones with enhanced magnetic susceptibility and decreased terrain conductivity that are observed in geophysical surveys. Subsurface particle transport may thus contribute to geophysical signatures and help sustain high weathering fluxes at Río Icacos and other steep and highly fractured landscapes.

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Introduction

In watershed studies, identification of the input and output components of a mass balance model is the first and the most critical step to quantify fluxes and their importance in the evolution of the critical zone—the layer from the canopy of the trees to the groundwater (Chadwick *et al.*, 1990; Riebe *et al.*, 2017). However, many models are based on incorrect *a priori* assumptions, and end up neglecting important fluxes. For example, most denudation studies are based on the assumption that subsurface losses occur only through the chemical mobilisation of solutes with physical erosion only important for the mobile soil layer (see Riebe *et al.*, 2017 and references therein). However, soil and sediment particles also move below the land surface and even below the soil layer. Subsurface particle transport has been discussed by geomorphologists (e.g., Dunne, 1990), but weathering implications have only been highlighted in a few locations (e.g., Bern *et al.*, 2015; Kim *et al.*, 2018).

To explore the significance of subsurface particle transport in the Luquillo Mountains, Puerto Rico at a site where such transport has been noted (Harrison *et al.*, 2020), we examined “seep sediments” collected from a seep along a steep slope and stream sediments from stream beds in the Río Icacos watershed. As one of the fastest weathering and eroding granitoid systems in the world (White and Blum, 1995), this site has been well studied (White *et al.*, 1998; Buss *et al.*, 2008; Shanley *et al.*, 2011; Comas *et al.*, 2019), allowing us to elucidate how sub-

surface particle transport contributes to shaping the deep critical zone.

Weathering in the Río Icacos Watershed

The Río Icacos is a bowl-shaped 3.26 km² watershed located in the headwaters of the Río Blanco in the Luquillo Mountains of northeastern Puerto Rico (Fig. 1a). This humid, montane tropical forested watershed is almost exclusively developed on the Río Blanco Quartz Diorite, a pluton that contains predominantly plagioclase and quartz (White *et al.*, 1998). In Río Icacos, it has been well documented that spheroidal weathering, initiated by biotite oxidation and volume expansion, fractures to form cm-sized, onion-like rindlets that wrap around increasingly spheroidal corestones (Buss *et al.*, 2008). Each rindlet is characterised by fine micro-cracks and is separated from other rindlets by larger macro-cracks. The zone of rindlets (~0.5–1 m in thickness) transforms to the thick layer of overlying saprolite and soil. In the following, we first discuss the potential importance of seep sediments and then present evidence for the mechanism of their formation.

Characteristics of Seep and Stream Sediments

Seep sediments were sampled from a perennial seep emanating from between corestones in a roadcut wall along Route 191

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(Fig. 1b), situated on a steep slope from mountain top to river bottom. The weekly yield of seep sediments produced at the seep during the sampling periods (August–November, 2016) varied by more than one order of magnitude and showed positive correlations with peak discharge and peak rainfall (Fig. 2). The particle size distribution of seep sediments, which varies with discharge (Fig. S-1), is dominated by particles in the upper sand size range (median size: 0.4–1.6 mm). Dissolved Si concentrations in water sampled at the seep during the study measured $375 \pm 35 \mu\text{M}$, consistent with groundwater that has circulated to tens of metres depth (cf. Shanley *et al.*, 2011; Hynek *et al.*, 2017).

Twelve stream sediment samples were collected from beds of the Río Icacos and Quebrada Guaba (an Icacos tributary draining Guaba Ridge, Fig. 1a). The geochemical, mineralogical, and textural signatures indicate the stream sediments are likely mixtures of seep sediments + soils/saprolites. As shown by Buss *et al.* (2008), the composition of the quartz diorite changes as it is transformed first into rindlets, then saprolite, and ultimately soil. Specifically, the extent of depletion in Ca and Na (increasing depletion of plagioclase) increases

roughly from corestone to rindlet to seep sediment to stream sediment to soil/saprolite (Fig. 1c). The X-ray diffraction (XRD) patterns and the grain size distributions show the same trends, consistent with weathering extent in these materials (Supplementary Information). Similarly, the concentrations of cosmogenic ^{10}Be in stream sediments at Río Icacos are lower as compared to the soils (Brown *et al.*, 1995; Brocard *et al.*, 2015). These results are consistent with stream sediments in the Río Icacos deriving not only from soils, but also from less weathered materials. These materials were previously assumed to have been delivered by landslides scouring material from depth (Brown *et al.*, 1995; Dosseto *et al.*, 2014). Here, we propose an alternative or additional pathway that these materials are transported as particles through the subsurface.

The characteristics of the seep sediments allow us to constrain the sources of stream sediments at Río Icacos. Assuming that 1) stream sediments are composed of soil/saprolite plus a less weathered component, 2) Al is not solubilised during chemical weathering, and 3) the less weathered component is chemically similar to seep sediments, we estimated $46 \pm 22 \%$ and $88 \pm 10 \%$ of Na and Ca in the stream sediments at the gages

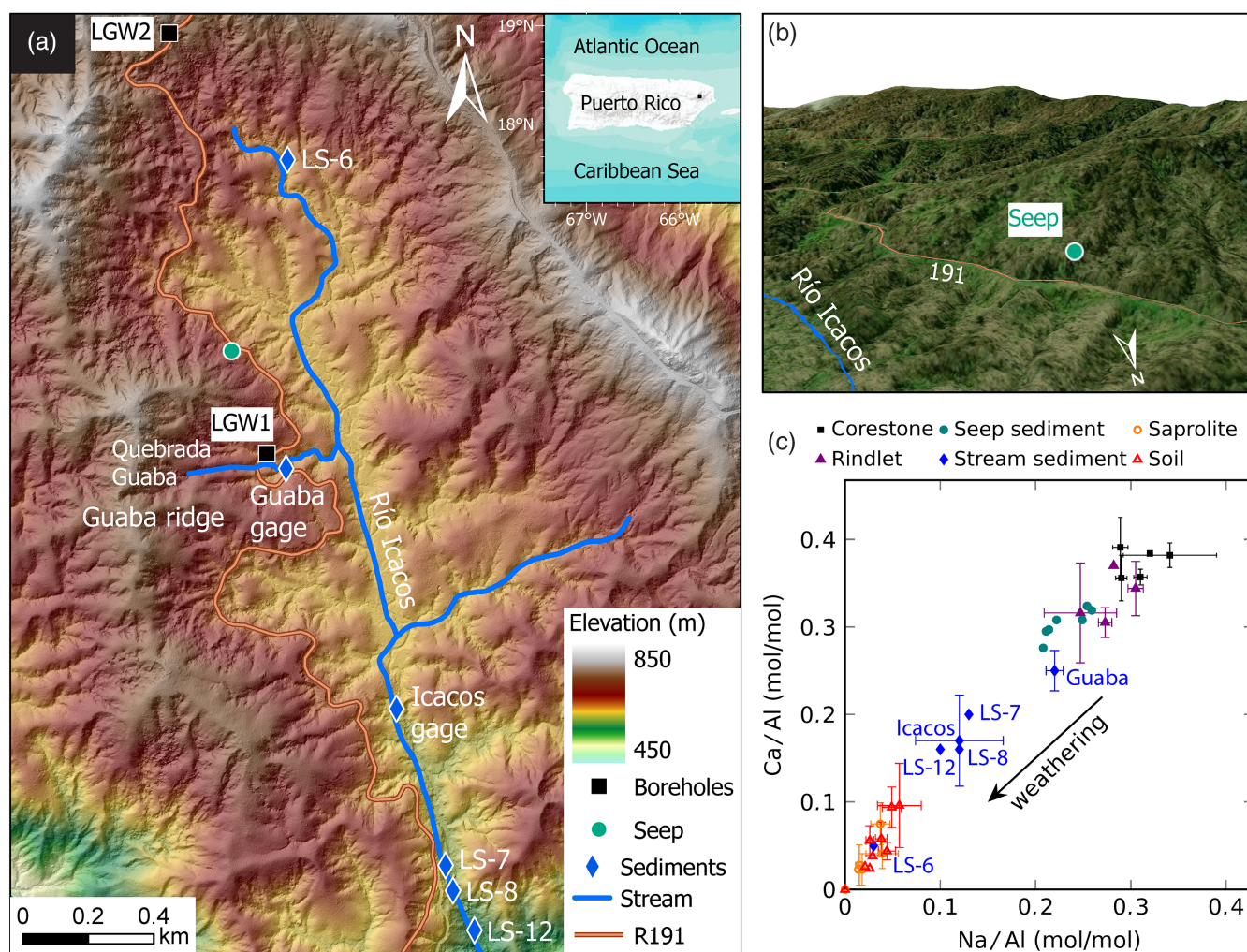


Figure 1 (a) Study locations at Río Icacos watershed in Puerto Rico. Colours indicate elevation, which are from USGS 3D Elevation Program through Open Topography. (b) Sampling location of seep sediments. Aerial imagery is from Esri (2017). (c) Na/Al and Ca/Al molar ratios of different solid end members (corestone, rindlet, seep sediment, stream sediment and saprolite/soil) determined through bulk analysis. Most Na and Ca are present in plagioclase in the bedrock, so as plagioclase weathers, the Na/Al and Ca/Al molar ratios decrease (Al is assumed to be not solubilised during plagioclase weathering).

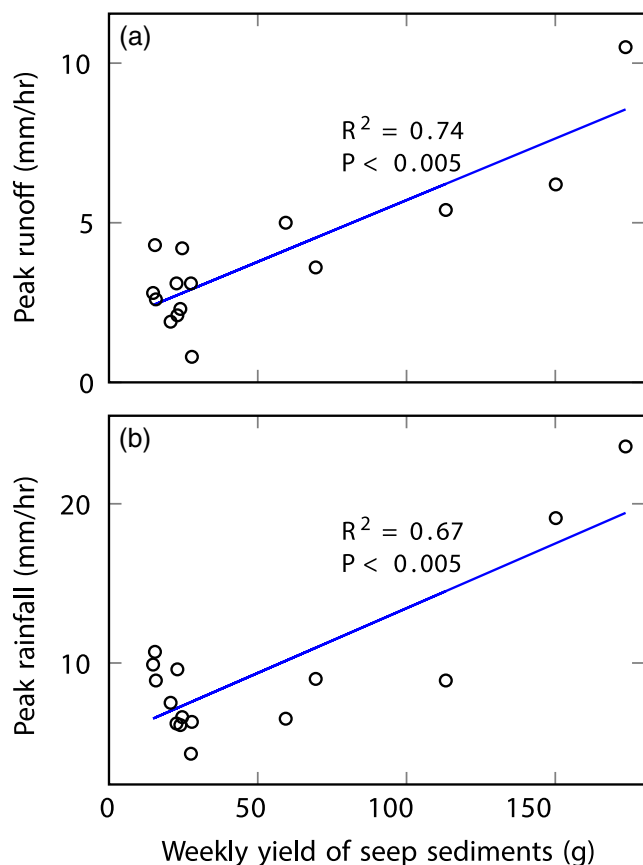


Figure 2 (a) Hourly peak runoff and (b) maximum rainfall intensity during the sampling week versus weekly accumulated mass of seep sediments. $P = p$ value.

of Río Icacos and Quebrada Guaba (Fig. 1a), respectively, are sourced from seep sediments or similar less weathered materials (Supplementary Information).

How Subsurface Particle Transport Occurs at Río Icacos

We now consider how such seep sediments might form. In rocks, chemical processes can reduce rock cohesion and enhance the hydraulic conductivity and allow subsurface erosion to occur (Dunne, 1990; Lamb *et al.*, 2006). In the following sections, we summarise observations that document these requirements for subsurface particle transport at Río Icacos: 1) fracture surfaces show enhanced chemical weathering, and 2) the fractured network can support sufficient flow velocities, driven by high hydraulic gradients, to entrain particles.

At Río Icacos, the oxidation of biotite is hypothesised to fracture rock at depth and create fracture-delineated rindlets around the outermost parts of each corestone (e.g., spheroidal weathering; Fletcher *et al.*, 2006; Buss *et al.*, 2008). The textures and compositions of the rindlet interiors are similar to that of the corestones because weathering roughly occurs from outside to inside (Fig. S-2). For example, the degree of alteration of the plagioclase and biotite increases dramatically toward the fracture surface (Fig. 3a–d). Alteration consists of fracturing of the plagioclase as calcic cores become increasingly dissolved or replaced by kaolinite (Fig. 3c). Biotite grains, which become partially to fully altered to vermiculite, increasingly exfoliate parallel to the cleavage plane at the rindlet edges (Fig. 3d). Also, the dissolution of

plagioclase (Fig. 3a,c) and exfoliation of biotite (Fig. 3b,d) make these grains easy to detach physically.

Figure 4 exemplifies some of these characteristics. Elemental compositions of plagioclase grains in corestones plot on the mixing line of sodium-rich and calcium-rich plagioclase, showing no chemical weathering (Fig. 4). In contrast, the chemical compositions of plagioclase grains located at the exterior of rindlets span a wide range from unaltered plagioclase to kaolinite and gibbsite, and more than half of the grains are altered. These altered compositions approach that of seep sediments (Fig. 4). We infer that the seep sediments likely originated from the fracture surfaces.

Some of these observations may explain previous geophysical observations at Río Icacos. Ground penetrating radar (GPR) surveys indicated that eroding channels in the hillside leading to the river are usually co-located with vertical zones of enhanced GPR reflection. These were interpreted as deep fracture zones filled with rindletted corestones (Comas *et al.*, 2019). Field measurements across these fracture zones showed coincident decreases in terrain conductivity and increases in magnetic susceptibility (Comas *et al.*, 2019). To test what might cause this, we conducted magnetic susceptibility (MS) measurements in the laboratory and observed that the MS values decreased from corestones \approx rindlets $>$ seep sediments $>$ soils (Table S-1). The decrease of MS is likely due to depletion of magnetite during weathering as documented by XRD (Supplementary Information); these measurements also showed that clay minerals (known to generally show relatively high electrical conductivity, EC (Palacky, 1987)) are enriched in seep sediments (Table S-2). These new data therefore show that the low EC in fracture zones could be caused by loss of particles like the clay-rich seep sediments while the high MS could be caused by retention of magnetite in the corestones and rindlets as seep sediment-like particles are removed.

Another geomorphological characteristic, amphitheatre-shaped headwalls throughout the Río Icacos, provides additional evidence of seepage erosion (Harrison *et al.*, 2020). For example, the steep slopes of headwalls around the sampled seep (27–60°) should provide a sufficient hydraulic gradient for subsurface particle flow. Hydrologic calculations also suggest that the size of fracture apertures is large enough to accommodate the size of seep sediments (Supplementary Information). In fact, during drilling in the quartz diorite, movement of particles in the subsurface between boreholes separated by 1 m has even been noted (Orlando, 2014).

Fracture Surfaces are Hot Spots for Weathering and Erosion

The chemical weathering rate of silicates as indicated by the riverine flux at Río Icacos is among the highest reported for granitoid watersheds (White and Blum, 1995). However, the high weathering rate at Río Icacos cannot be fully explained by the humid tropical climate since the rate is 4 to 20 times higher than other granitoid watersheds in tropical areas with high precipitation (Edmond *et al.*, 1995; von Blanckenburg *et al.*, 2004; Braun *et al.*, 2012). The high weathering flux at Río Icacos has previously been attributed to the interconnected fractures that allow fast infiltration of oxygenated meteoric water that can accelerate weathering at multiple depths (e.g., Fletcher *et al.*, 2006). Our study suggests that the transport of sand-sized particles through fractures at Río Icacos is an under-appreciated mechanism that exposes fresh particle surfaces to weathering fluids. Subsurface particle transport has not been previously invoked to explain the 10 fold discrepancies between short term denudation rates

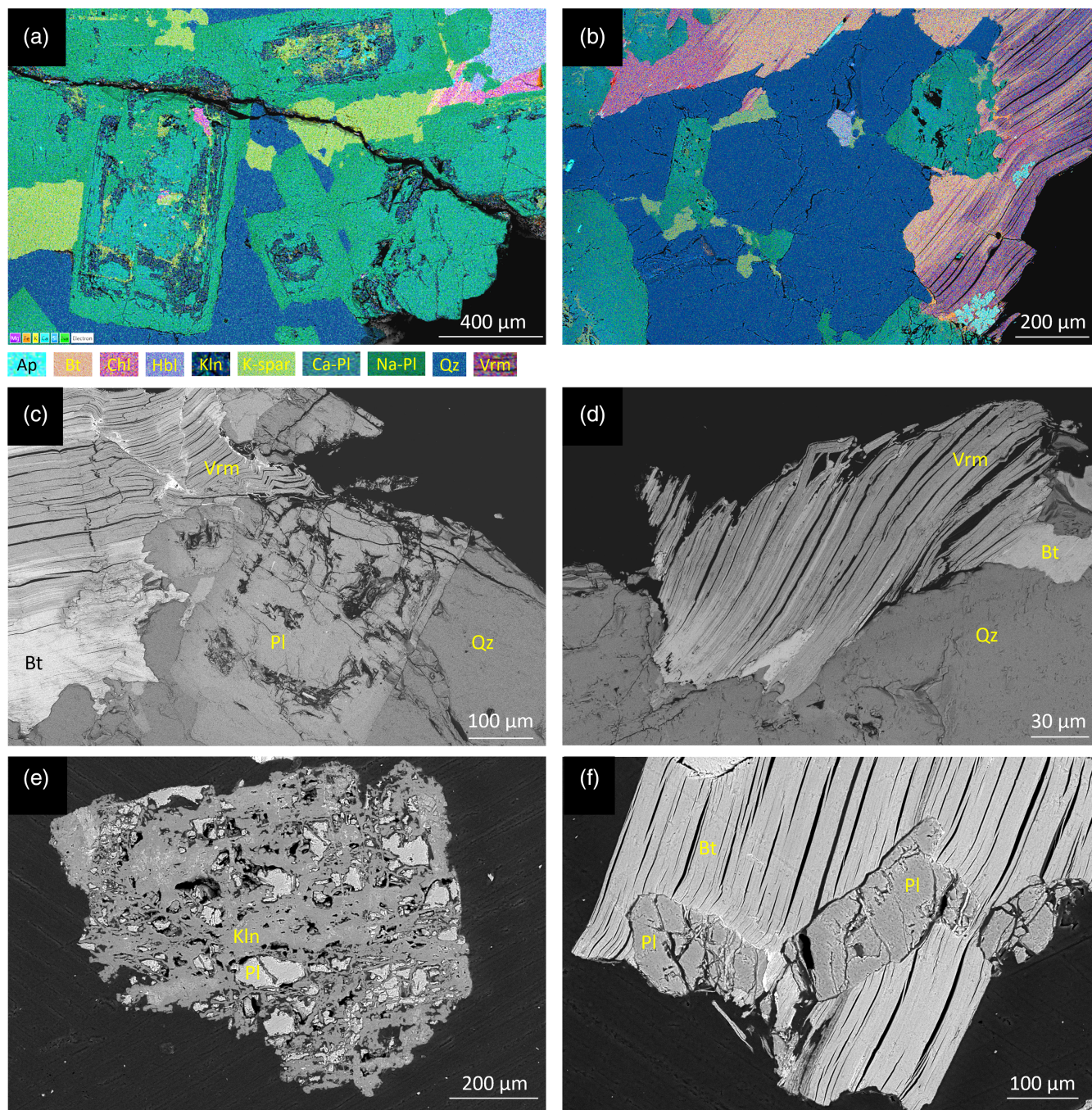


Figure 3 (a, b) Elemental maps and (c–f) backscattered electron images of the edge of rindlets (a–d) and seep sediments (e, f). The rindlet sample is from borehole LGW1 at 5.38–5.40 metres below land surface (LGW1 1–20) and the seep sediments were collected during August 9–16, 2016 (0.85–2.56 mm size fraction). Ap: apatite, Bt: biotite, Chl: chlorite, Hbl: hornblende, Kln: kaolinite, K-spar: K-feldspar, Pl: plagioclase, Qz: quartz, Vrm: vermiculite.

inferred from solid loads at stream gages (Stallard, 2012) and the long term denudation rates inferred from cosmogenic ^{10}Be (Brown *et al.*, 1995). The stream sediments of Río Icacos are enriched in cosmogenic ^{10}Be from soils, but also contain seep sediments that do not contain ^{10}Be due to delivery from depth. Whether this means that denudation rates are underestimated remains to be explored.

Chemical weathering in fractured rocks has been relatively well studied. However, our understanding of particle transport through fractures is very limited because it is based on only a few studies such as those in carbonate (Levenson and

Emmanuel, 2017) or carbonate-rich shale lithologies (Deng *et al.*, 2017). The significance of subsurface particle transport depends on disaggregation related to weathering of the fracture surface, the size of the particles relative to the fracture apertures, the fracture connectivity, and the hydraulic gradient. Subsurface particle transport is an under-appreciated process that likely shapes the deep critical zone and promotes chemical and physical weathering in mountainous areas with well developed fracture networks like the Luquillo Mountains. More investigations are needed to characterise particle transport by subsurface flow through different fracture geometries, in different lithologies, and at different temporal and spatial scales.

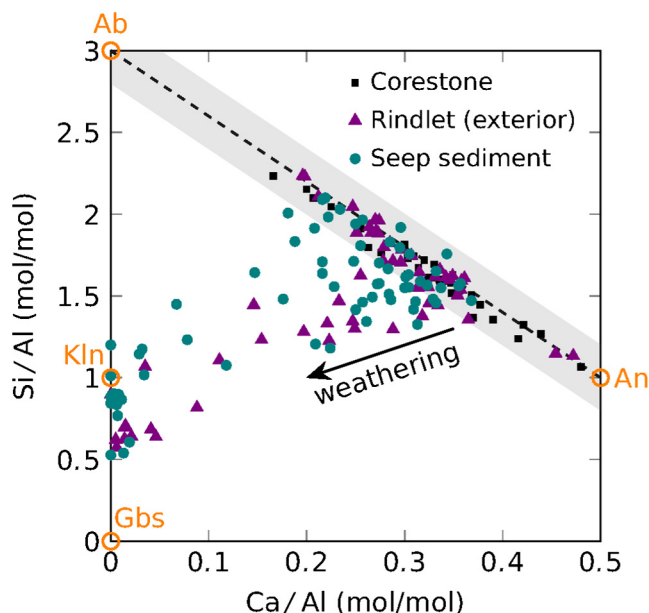


Figure 4 Si/Al and Ca/Al molar ratios determined by scanning electron microscopy energy dispersive X-ray spectroscopy (EDS) on individual plagioclase grains from different solid end members (corestone, rindlet and seep sediment). The orange circles represent sodium-rich (albite, Ab) and calcium-rich (anorthite, An) plagioclase and typical weathering products of plagioclase such as gibbsite (Gbs) and kaolinite (Kln). The dashed line represents solid solution mixing of Ab and An. Shaded zone shows one standard deviation of uncertainty in Ca/Al molar ratios assuming the relative error of EDS measurement is 5 %. Therefore, the points within the shaded zone are considered as unaltered plagioclase.

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Additional Information

Supplementary Information accompanies this letter at <https://www.geochemicalperspectivesletters.org/article2127>.



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