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Controls on rind thickness on basaltic andesite clasts weathering in Guadeloupe

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ABSTRACT

A clast of low porosity basaltic andesite collected from the B horizon of a soil developed on a late Quaternary volcaniclastic debris flow in the Bras David watershed on Basse-Terre Island, Guadeloupe, exhibits weathering like that observed in many weathered clasts of similar composition in other tropical locations. Specifically, elemental profiles measured across the core–rind interface document that primary minerals and glass weather to Fe oxyhydroxides, gibbsite and minor kaolinite in the rind. The earliest reaction identified in the core is oxidation of Fe in pyroxene but the earliest reaction that creates significant porosity is plagioclase dissolution. Elemental loss varies in the order $Ca \approx Na > K \approx Mg > Si > Al > Fe \approx P \gg Ti$, consistent with the relative reactivity of phases in the clast from plagioclase ≈ pyroxene ≈ glass > apatite > ilmenite. The rind surrounds a core of unaltered material that is more spherical than the original clast. The distance from the core–rind boundary to a visually prominent rind layer, L, was measured as a proxy for the rind thickness at 36 locations on a slab cut vertically through the nominal center of the clast. This distance averaged 24.4 ± 3.1 mm. Maximum and minimum values for L, 35.8 and 20.6 mm, were observed where curvature of the core–rind boundary is greatest ($0.12\ mm^{-1}$) and smallest ($0.018\ mm^{-1}$) respectively. Extrapolating from other rinds in other locations, the rate of rind formation is estimated to vary by a factor of about 2 (from ~4 to $7 \times 10^{-14}\ m\ s^{-1}$) from low to high curvature. The observation of a higher rate of rind formation for a higher curvature interface is consistent with a diffusion-limited model for weathering rind formation. The diffusion-limited model predicts that, like rind thickness, values of the thickness of the reaction front (h) for a given reaction, defined as the zone over which a parent mineral such as plagioclase completely weathers to rind material, should also increase with curvature. Values of h were quantified as a function of interface curvature using bulk chemical analysis ($500 < h < 2000$ µm). Values of h were also quantified by measuring loss of matrix glass and increase in porosity as a function of curvature. In contrast to rind thickness, h shows no consistent increase with curvature. This contradiction is attributed to the mm-scale roughness of the interface which is related to phenocryst grain size. Therefore, the overall rind formation rate is strongly affected by curvature measured at the scale of the clast, while mineral reaction rates documented by reaction front thickness are strongly affected by curvature at the scale of phenocrysts. Similarly, the weathering advance rate ($m\ s^{-1}$) for the entire Bras David watershed can be extrapolated from the clast weathering rate if roughness at the watershed scale equals values of approximately 400–800.

1. Introduction

The weathering of silicate rocks plays a significant role in regulating atmospheric CO_2 (Walker et al., 1981; Berner et al., 1983), cycling nutrients in soil (Hyman et al., 1998; Chadwick et al., 1999; Derry et al., 2005; Starr and Lindroos, 2006; Amundson et al., 2007) and shaping landscapes (i.e., Dethier, 1986; Pavich, 1986; Pope et al. 1995; Dixon and Thorn, 2005; Dixon et al., 2008). As the most abundant silicate rock in the Earth's crust, basalt is of special interest because it accounts for 30–35% of the rate of atmospheric CO_2 drawdown that has been attributed to silicate weathering globally (Dessert et al., 2003).

Basalt weathering rates have been measured in laboratory dissolution experiments (i.e., Gislason and Eugster, 1987; Eick et al., 1996; Gislason and Oelkers, 2003), modeled using reactive transport codes (i.e., Hausrath et al., 2008; Steefel, 2008; Sitchler, 2008), and

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measured in soil profiles and watersheds (i.e., Louvat and Allegre, 1997; Dessert et al., 2001; Gaillardet et al., 2003; Zakharova et al., 2007). Generally, weathering rates are normalized to mineral surface area to facilitate comparisons between rates measured at different scales (i.e., laboratory- vs. field-measured rates) and under different conditions. Laboratory-derived rates are consistently 2–5 orders of magnitude greater than field-derived rates (White and Brantley, 2003).

The discrepancy between laboratory and field rates has, in part, been attributed to differences between the laboratory and field setting including duration of weathering (White and Brantley, 2003; Maher et al., 2004), hydrologic regime (Velbel, 1993; Pacheco and Alencoao, 2006) factors related to clay precipitation (Maher, 2010), and methods used to measure surface area or the presence of surface coatings (Nugent et al., 1998; Maher et al., 2006; Navarre-Sitchler and Brantley, 2007), as well as the influence of organic acids (Wasklewicz, 1994; Drever and Stillings, 1997). Comparisons between laboratory and field settings can also be complicated by the ongoing removal of weathered materials by physical erosion (i.e., Bluth and Kump, 1994; Millot et al., 2002; Dupre et al., 2003; Anderson, 2005; West et al., 2005).

The comparison of weathering rates from laboratory to field is just one example of a comparison that crosses both temporal (White and Brantley, 2003) and spatial scales (Navarre-Sitchler and Brantley, 2007). Navarre-Sitchler and Brantley (2007) assumed that the rate of weathering of basalt was constant when compared across scales from the laboratory to hand samples (clasts) to soil profiles to watersheds, as long as the rate was normalized accurately by the basalt surface area experiencing weathering ($A_{weathering}$). However, at each scale, the weathering rate is more often reported as a rate normalized by the interfacial area assessed at that scale, A: for example, the geographic area of a watershed ($A=A_{watershed}$) or the surface area of a clast ($A=A_{clast}$). Navarre-Sitchler and Brantley (2007) defined the ratio of $A_{weathering}$ divided by A as the roughness of the weathering interface at each scale. By collating basalt weathering rates from the literature after correcting the rates for roughness at each scale, Navarre-Sitchler and Brantley (2007) showed that much of the laboratory-field discrepancy can be solved, leaving only about two orders of magnitude in variation of rates. This residual variation was attributed to variations in factors such as rock composition, temperature, biota, erosion, etc., that vary from location to location.

In this study, we investigate the importance of roughness of one weathering interface at the clast scale. This study therefore isolates the importance of interfacial curvature on weathering (e.g., Colman, 1982a; Sak et al., 2004; Navarre-Sitchler et al., 2009). Visually, a weathered clast can be seen to be comprised of two parts, the core and the weathering rind. The rind is defined as a crust that is enriched in relatively immobile oxides (TiO_2, Fe_2O_3, and Al_2O_3) that envelops the unweathered core (e.g., Colman, 1982a; Sak et al., 2004). The *in situ* formation of rinds on basaltic clasts weathering in surficial deposits provides a simple, well-constrained field-based analogue to landscape-scale or soil profile-scale weathering.

Many authors have recognized that the thickness of rinds on weathered clasts vary with curvature of the weathering interface (i.e., Cernohouz and Solc, 1966; Colman and Pierce, 1981; Oguchi, 2004; Sak et al., 2004; Kirkbride, 2005; Kirkbride and Bell, 2010). On nonspherical clasts, rind thickness is often thicker near angular corners producing more rounded cores. The progressive rounding of corners led Cernohouz and Solc (1966) to suggest that the blunting of clast corners could be used as a chronometer. Following along those lines, Kirkbride and Bell (2010) proposed a relative dating scale based on clast shape.

In contrast to these treatments of clast shape, most studies have used 1-D models when investigating the formation of weathering rinds (e.g. Oguchi, 2004, Sak et al., 2004; Sitchler, 2008). However, in some cases, 1-D models are unable to account for observed variations in rind thickness related to clast curvature. Here we compare predictions based on a simple 2-D diffusion model to observed variations in rind thickness as a function of curvature.

To understand the effects of curvature at the clast scale, we analyze a single basaltic andesite clast collected from the B horizon of a weathered volcaniclastic debris flow on Basse-Terre Island, Guadeloupe (Fig. 1). Measurements of weathering rind thickness and curvature of the core–rind boundary are combined with petrographic, bulk chemical, and electron microprobe analyses from around the clast. We use these measurements to quantify variations in the reaction front thickness and weathering rind advance as a function of curvature of the core–rind boundary.

2. Geologic setting

One representative clast collected from the B horizon of a soil profile developed on Quaternary volcaniclastic debris flows was analyzed. The exposure that we describe and sampled is an outcrop located within 30 m of the ridgetop of a moderately sloping (<10°), west-facing slope within the Bras David watershed on Basse-Terre Island, Guadeloupe. The slope is vegetated with grasses and widely dispersed trees. The watershed has a warm and wet climate with a mean annual temperature of 25 °C and a mean annual precipitation of 4500 mm yr^{-1} (Météo-France, 2008, unpublished data). At the sample site, recent excavation due to housing construction exposed a >10 m-thick section of the debris flow. While the debris flow have not been dated, volcanic flows in the immediate vicinity were emplaced 900 ka before present, based on Ar/Ar dating (Samper et al., 2007). Exposure age for weathering is thus ≤900 ka.

The excavation exposes a well-developed (2–8 m) thick weathering profile developed on volcaniclastic debris flows. Within this exposure, two debris flows were distinguished in the field by color, texture, and abundance of rock fragments. The lower debris flow is a ≥5 m thick, dark yellowish brown (Munsell Color Company notation 10YR), clayey unit with <5% small volcaniclastic blocks. The boundary between this debris flow and the overlying debris flow is marked by an abrupt low relief surface. The exposed debris flows have experienced pedogenesis: the upper debris flow is a dark reddish brown (Munsell Color Company notation 5YR). This upper debris flow is a sandy clay loam containing ~30% matrix-supported volcaniclastic blocks of variable composition. The upper debris flow becomes progressively more weathered toward the surface (≥3 m depth). The clast analyzed in this paper (Fig. 2) was collected from the upper debris flow at 0.8 m depth below the base of the O horizon.

3. Methods

3.1. Field sampling

The clast, which was distinguished from the surrounding soil matrix by texture and color, was oriented and measured prior to removal from the outcrop (clast shown in position in outcrop in Fig. 2). The weathering rind was distinguished from the surrounding soil by a difference in color: the rind is brownish yellow (Munsell Color Notation 10YR) in contrast to the yellowish red (Munsell Color Notation 5YR) matrix of the upper debris flow. As shown in the figure, the major axis of this oblate clast was oriented vertically, and the minor axis is oriented horizontally. The highest curvature of the core-rind boundary that was analyzed is situated along the lower side of the clast.

During removal of the clast from the matrix a narrow (<0.5 cm thick) portion of the outer rind disaggregated from the clast. The amount of rind material remaining in the outcrop after clast removal was measured in the field in several different orientations: the amount of rind left behind varies with position. In the field, the clast and attached rind were wrapped in plastic and masking tape to