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Using a mathematical model of a weathering clast to explore the effects of curvature on weathering

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ABSTRACT

For the first time, we show that rind thicknesses developed on surfaces of a clast with different values of curvature can be used to estimate the duration of clast weathering. To obtain an analytical expression for the velocity of the curvilinear weathering front on a clast of arbitrary shape, we approximate our previous multi-mineral reactive-diffusion model and explore a simplified 2-D model numerically and analytically.

Our analysis documents that with increasing curvature of the weathering front, the mathematical description of weathering advance is equivalent to that derived for advection as the dominant solute transport mechanism, even for the case where transport is occurring by diffusion only. Specifically, for a curvilinear weathering front with constant curvature $K < 0$, diffusivity (D), and porosity (ϕ), the normal component of the weathering advance rate can be calculated using an advection-like term where the advection velocity v can be expressed as $v = D\phi|K|$. Therefore, at points along the rind–core interface with $K < 0$, rind thickness is directly proportional to the absolute value of the curvature of the core–rind interface. The reaction front thickness also increases with K. These inferences are in agreement with field observations. This quantitative analysis allows an assessment of the duration of weathering if certain parameters are known. For example, using the difference in curvature observed at two positions for a clast that weathered in Guadeloupe (0.12 mm^{-1} and 0.018 mm^{-1}) and the corresponding rind thickness difference (35.8 mm and 20.6 mm), we estimated the duration of weathering to be about 118 ky, which is consistent with the weathering ages previously determined by U-series isotope disequilibrium.

1. Introduction

Weathering rinds have been described on clasts since at least the 1960s (Cernohouz and Solc, 1966), and the rates of formation of these rinds have been used to assess the duration of weathering (Colman and Pierce, 1981; Colman, 1982; Kirkbride, 2005; Kirkbride and Bell, 2010). For example, Sak et al. (2004) measured weathering rind thicknesses on basaltic clasts from terraces of constrained geologic age to evaluate the rate of weathering rind advance, i.e. the velocity (distance/time) of advance of the interface between core and rind inward into the unaltered core of the clast. In that work, the rind was defined as the layer of clast material that enveloped the unaltered core protolith. They calculated the mean of observed rind thickness on clasts weathered for different exposure times and fitted these data to rate laws of weathering that are parabolic (i.e., the rind thickness $L = const \cdot \sqrt{t}$ where t is the time and *const* stands for a constant) or linear (rind thickness $L = const \cdot t$). For the low-porosity (basaltic) clasts that were under study, reactive transport is dominated by solute diffusion (Neretnieks, 1980; Steefel and Lichtner, 1994), and such diffusion is not generally thought to be well explained with a linear transport law. Instead, diffusion is better described by a parabolic rate law (Lichtner, 1988). They nonetheless concluded on the basis of observations of weathered clasts that a linear law was adequate to describe the rind evolution. The growth-rate curve could also have been fit by a more complex law that is neither parabolic nor linear.

In general, most 1-D models used for modeling weathering clasts (Navarre-Sitchler et al., 2011) are based on the assumption of an infinite weathering domain whereas the size of an actual clast is finite. Moreover, observations of rind–core interfaces on basaltic–andesitic clasts (Sak et al., 2010; Ma et al., 2012) reveal that they are generally curved (or, in mathematical parlance, "curvilinear"). Importantly, curvature affects the rate of material alteration, i.e., the weathering advance rate (Ortoleva et al., 1987; Sak et al., 2010; Ma et al., 2012; Lebedeva and Brantley, 2013; Reeves and Rothman, 2014). Many researchers have investigated the rate of advance of weathering (Lichtner, 1988; Steefel and Lichtner, 1994; Wang et al., 1995; Soler and Lasaga, 1998; White, 2002; Zaraisky et al., 2002; Oguchi, 2004; Lebedeva et al., 2007; Sidborn and Neretnieks, 2007) but these authors have analyzed weathering advance rates for planar reaction interfaces, i.e., where the regolith–bedrock or rind–core boundary is characterized by a curvature equal to zero. For

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example, Oguchi (2004) analyzed a planar weathering interface for clasts and obtained a parabolic law for the time dependence of rind thicknesses.

We present here a quantitative investigation of the complex behavior of a curvilinear weathering front and how it affects the rate of weathering advance of the rind–core boundary over time. We seek to understand the thickness of the rind material (rind thickness), the rate of growth of the rind (weathering advance rate), and the thickness of the core–rind interfacial layer where the concentration of dissolving mineral changes (the weathering or reaction front). Our approach differs from a recent treatment (Reeves and Rothman, 2014) which was set up following our model (Lebedeva et al., 2010). For example, Eqs. (3)–(4) (presented later) were rewritten from our work (Lebedeva et al., 2010) by Reeves and Rothman (2014) in the spherical system of coordinates, i.e., transforming them to 1-D equations. To investigate the problem, Reeves and Rothman (2014) treated a version of the well-known spherical Stephan problem (Hill, 1987) assuming that the latter approximates the diffusion-reaction equations in the original model (Lebedeva et al., 2010). The Stephan problem formulated for spherical symmetry is a 1-D problem which has been treated in several publications from various fields (e.g. Entchev et al., 2001). Reeves and Rothman (2014) used an approximate solution of the symmetrical spherical problem (Hill, 1987) to calculate the time evolution of the thickness of the weathering rind on a spherical clast. Reeves and Rothman (2014) do not explore controls on weathering front thickness nor rind thickness as a function of curvature. In fact, their approach cannot treat an arbitrary, non-spherical, rind–core boundary — in other words, a real clast. Here, we present a full chemical treatment of a 2-D model of arbitrary clast based on our previous multi-mineral multicomponent reactive transport model in 1-D (Lebedeva et al., 2007).

This multi-mineral model was used to treat a model rock composition: it included reactions that initiated bedrock alteration (oxidative dissolution of FeO) and formed weathered material (transformation of albite to kaolinite) (see Appendix A). The model bedrock also contained quartz, treated as inert to weathering. In the model, components in the pore fluid included O_2, Na^+, SiO_2, $Al(OH)_3$, H^+, OH^-, Fe^{2+}, Fe^{3+} and Cl^-. Here, this model is simplified further and applied to a non-regular 2-D domain. We are unaware of other publications where a full model has been treated in 2-D domains.

The present paper builds on our previous work. We previously explored a simplified model which is based on an approximation of a numerical simulation of the complex model (Lebedeva et al., 2007). The simplified model was shown to satisfactorily reproduce the thicknesses of zones of mineral alteration, changes in porosity, and velocities of the reaction fronts. Therefore, we applied this model to preliminary 2-D modeling of weathered clasts (Sak et al., 2010) where mineral alteration occurred according to the hypothetical reaction $M_1 + A \rightleftarrows M_2$ between minerals M_1, M_2, and a reactant aqueous species A. Specifically, the model was based on the assumption that the rind increased in thickness as a result of reaction between M_1 and A. We compared our simulations with measurements of rind and reaction front thicknesses. Our simulations documented that both the thicknesses of the weathering rinds and weathering fronts (i.e. thickness of the transition zone where minerals dissolve between core and rind) increased when curvature of the weathering front increased. The first result about weathering rinds was consistent with observations while the latter (about reaction fronts) was not. Although we proposed a partial explanation, this question remained open. Simulations also revealed that the core–rind boundary of an idealized angular and irregularly shaped clast eventually approached the geometry of an ellipse. This was similar to modeled results from investigations of a different phenomenon — bubble contraction (Entov and Etingof, 1991) — and this similarity gave us the idea to analyze the similarity of the mathematical models describing these different systems.

We also used the simplified weathering model to investigate weathering across eroding convex-upward hillslopes (Lebedeva and Brantley, 2013). In the latter work we found that regolith became thickest on the hillslopes where the curvature approached a maximum. We compared this result with our preliminary simulations of weathering clasts and hypothesized that curvature-driven solute transport caused development of the thickest rind (on a clast) or thickest regolith (on a hillslope) precisely at the point where weathering fronts show the highest curvature. Here, we continue numerical investigations of weathering of clasts. Unlike the paper by Sak et al. (2010) we investigate the reaction of albite alteration. Although we considered this reaction previously (Lebedeva and Brantley, 2013), in the 2013 paper we focused on the effect of curvature for landforms, including the effect of advection and erosion. That system was not amenable to analytical investigation. Here we quantify the dependencies of the rind and front thicknesses on curvature. We pursue a simplified approach here that allows us not only to simulate weathering clasts of arbitrary geometry but also to obtain the analytical expressions for the velocity and thickness of the curvilinear weathering front. Thus we resolve the uncertainties described in the earlier paper with respect to how the front thickness depends on front curvature (Sak et al., 2010). Other than the treatments by Ortoleva et al. (1987), Sak et al. (2010), Ma et al. (2012), Lebedeva and Brantley (2013), and Reeves and Rothman (2014), analysis of the effect of curvature on weathering rate has not to our knowledge been previously presented in the geochemical literature.

Outside of geochemical studies, the effect of curvature has been analyzed for various reaction-diffusion systems. For more than a half of a century, scientists have investigated this effect, and for some systems it has been documented both experimentally and mathematically (Markstein, 1951; Knapp and Aris, 1972; Zykov, 1980; Zeldovich, 1981; Keener, 1986; Foester et al., 1988; Grindrod, 1991; Brazhnik and Tyson, 1999; Entchev et al., 2001). While these papers are devoted to different natural phenomena, the papers summarized differential equations that are similar to those in our model. Therefore, the properties of these solutions are similar. Here we apply some of the methods from these contributions to our simple 2-D model of the weathering clast and present numerical solutions to illustrate our results.

2. Model formulation

We developed the simplified model here from the observation that many of the important geochemical attributes of rock weathering are reproduced by simulating a model rock containing only one reactive and one inert mineral (Lebedeva et al., 2010). Previously (Lebedeva et al., 2010; Lebedeva and Brantley, 2013), we analyzed and simulated a parent rock containing reactive albite + inert quartz as it weathered to quartz + albite + kaolinite. We argued that the albite could be conceptualized as any abundant rock-forming mineral that reacts quickly with pore fluids. In fact, we have observed albite-rich feldspar is often the most abundant and reactive mineral during weathering of many igneous rocks (Brantley and White, 2009).

Thus, the model is based on the assumption that weathering can be described by albite (ab) transforming to kaolinite (kao) (Lebedeva et al., 2010):

$$2ab \xrightarrow{3H_2O} 2Na^+_{(aq)} + 2OH^-_{(aq)} + 4SiO_{2(aq)} + \text{kao}. \quad (1)$$

In the approximate model, we combine all aqueous species in the albite reaction (1) into one thermodynamic component, ½Na_2O ½H_2O 2SiO_2, denoting it as $NaSi_2$ (Lebedeva et al., 2007). We define the extent of reaction for albite dissolution as

$$\eta = 1 - Q/Q^0, \quad (2)$$

where Q (mol/m^3) and Q^0 are the concentration of albite in the weathering material and in the protolith, respectively. We also assume isovolumetric weathering. Notably, under this condition it can be shown that η equals $-\tau$ where τ is the mass transfer coefficient (Brimhall and Dietrich, 1987; Anderson et al., 2002).