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Weathering and erosion of fractured bedrock systems

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ABSTRACT: We explore the contribution of fractures (joints) in controlling the rate of weathering advance for a low-porosity rock by using methods of homogenization to create averaged weathering equations. The rate of advance of the weathering front can be expressed as the same rate observed in non-fractured media (or in an individual block) divided by the volume fraction of non-fractured blocks in the fractured parent material. In the model, the parent has fractures that are filled with a more porous material that contains only inert or completely weathered material. The low-porosity rock weathers by reaction-transport processes. As observed in field systems, the model shows that the weathering advance rate is greater for the fractured as compared to the analogous non-fractured system because the volume fraction of blocks is < 1 . The increase in advance rate is attributed both to the increase in weathered material that accompanies higher fracture density, and to the increase in exposure of surface of low-porosity rock to reaction-transport. For constant fracture aperture, the weathering advance rate increases when the fracture spacing decreases. Equations describing weathering advance rate are summarized in the 'List of selected equations'.

If erosion is imposed at a constant rate, the weathering systems with fracture-bounded bedrock blocks attain a steady state. In the erosional transport-limited regime, bedrock blocks no longer emerge at the air-regolith boundary because they weather away. In the weathering-limited (or kinetic) regime, blocks of various size become exhumed at the surface and the average size of these exposed blocks increases with the erosion rate. For convex hillslopes, the block size exposed at the surface increases downslope. This model can explain observations of exhumed rocks weathering in the Luquillo mountains of Puerto Rico. Published 2017. **This article is a U.S. Government work and is in the public domain in the USA**

KEYWORDS: fractured bedrock; weathering; erosion; reactive transport modeling; homogenization

Introduction

As rocks weather in a given climate and tectonic regime, both their structural and chemical features affect the type and extent of weathering. One type of weathering profile consists of fresh unweathered rock that develops jointing. In this situation, joint-bounded bedrock blocks may be observed to gradually diminish in size upward as they weather until they become saprolite and soil (Ruxton and Berry, 1957; Fletcher and Brantley, 2010; Jamtveit *et al.*, 2011; Hewawasam *et al.*, 2013). A simple one-dimensional (1D) model of such a weathering profile has been considered previously (Fletcher and Brantley, 2010) in an attempt to analyze the distribution of corestone (block) sizes within a profile. In that previous work, the distribution of corestone size was analyzed to constrain how weathering and erosion were proceeding in the natural system (Brantley *et al.*, 2011; Buss *et al.*, 2013).

In contrast to the model by Fletcher and Brantley (2010), the jointed rock structure is largely ignored in quantitative models for chemical weathering and landscape evolution. The weathering column mostly is viewed as a mathematical continuum when in reality it is actually divided into a number

of cells by joint surfaces. For example, one researcher (Maher, 2010) treats weathering mostly from the point of view of residence time of the porewater in the weathering system. By definition, this assumes a rock matrix that can be considered as a continuum. In reality, joints in rocks can be filled with a material different from the rock material in the blocks and water flow in joints is different than in matrix material. Likewise, Reis and Brantley (2017) consider a parent rock consisting of blocks but they make the simplifying assumption that all the parent material has the same porosity everywhere, so that the block structure does not affect the weathering advance rate. Even when blocks are considered, previously published models of weathering nonetheless use governing equations that are formulated and solved for a continuous porous medium (Lichtner, 1985; Balashov, 1986; Merino *et al.*, 1993; Soler and Lasaga, 1998; Lebedeva *et al.*, 2007; Maher, 2011). Here, we begin the process of considering how weathering of such a continuous medium might differ from weathering of jointed blocks.

At the other extreme from studies treating the entire rock column as a continuum are studies that have modeled processes within a single fracture within a rock matrix (Steeffel

and Lichtner, 1994; Robinson *et al.*, 1998; Steefel and Lichtner, 1998a, 1998b; MacQuarrie and Mayer, 2005; Pacheco and Alencao, 2006; Spiessl *et al.*, 2008; MacQuarrie *et al.*, 2010). For example, a similar model for a system with parallel equidistant fractures was considered (DePaolo, 2006). Once again, however, such an approach does not take into account the whole system of fractures. Further development of numerical methods has allowed solutions for more complex problems. For example, one method (Neretnieks and Rasmuson, 1984) simplified the problem for a system of different sized blocks to yield an equivalent 1D calculation. The method of Multiple Interacting Continua (MINC) for modeling fluid and heat flow in fractured-porous media has also been developed (Pruess and Narasimhan, 1985). While for some problems an explicit discretization of all matrix blocks leads to an extremely fine grid and requires a large amount of computational resources, the MINC-method is practical in that it simplifies the space discretization. However, the method requires an analysis of its applicability for any given flow problem. The numerical program TOUGHREACT is another step in the development of this method by including reactive chemistry (Xu and Pruess, 2001). Nonetheless, numerical solutions of such a set of model equations set up for each fracture and for each part of a rock matrix would be possible only for a limited spatial domain.

Instead, this problem can be solved by large-scale (~100 m) averaging of the governing equations over the whole region for a heterogeneous porous medium consisting of joints and blocks. Depending on parameters, this averaging leads either to a dual-porosity type model or to a single porosity model with so-called 'effective coefficients' (Barenblatt *et al.*, 1960; Goncharenko *et al.*, 2000; Amaziane *et al.*, 2005). Specifically, the first porosity is defined as the porosity of the matrix, and the second porosity is determined by the 'concentration' of joints or fractures. Such dual-porosity models have been used to analyze hydrology in large heterogeneous regions (Warren and Root, 1963).

In this paper, we apply the technique of averaging to model a weathering profile within a system consisting of joint-bounded bedrock blocks and obtain a single porosity 'macro-model'. We consider some examples of two-dimensional (2D) reactive transport models for a ridgetop and a hillslope. The technique of homogenization is applied to a so-called meso-scale (~ 0.01–10 m) model which describes processes within blocks and in the space between them. The resulting macro-model treats an averaged medium as a continuum.

We use the term 'meso-scale' here to distinguish this intermediate level of modeling from micro- and macro-scale modeling. In the literature (Hornung, 1997), the mesoscopic description is defined as the Darcy-scale description that explicitly models flow within the fractures and matrix. The meso-scale equations result from averaging the micro-scale (~ 10–1000 μm) equations. This approach is necessary precisely because weathering involves multiphase and multiscale systems, i.e. interfacial regions within both weathering blocks and the material between them (Zachara *et al.*, 2016). Any part of a weathering system consists of a solid rock material composed of several minerals. The texture of the rock includes pores – holes in the rock filled with water, gas, or both, depending on the degree of water saturation. Generally, theoretical modeling of the processes in such systems must include equations for the mechanics of the continuous media with mass, energy, and momentum transfer described for each phase (Sahimi, 1995). We need to solve the equations within each phase under boundary conditions located at the phase interfaces. So if pores are small and numerous, direct simulations become computationally very intensive. This

situation therefore prompts us to search for average governing equations for averaged quantities. Thus, the meso-scale equations are the first step in a hierarchical averaging procedure (Whitaker, 1986; Auriault, 1991). Currently, we are not pursuing the full hierarchical procedure; rather, we assume that for a given range of parameters, the averaged meso-scale equations adequately describe reactive-transport processes at the scale of a single block and then we focus on the large-scale averaging problem.

For the meso-scale model, we also solve some examples numerically to compare these solutions with the solutions of a macro-model which we derive here via homogenization. Finally, we perform analysis and simulations for this new homogenized medium. Such large-scale homogenized equations allow modeling for domains larger than a single weathering column.

This theoretical treatment is developed here as a way to think about the complexity of natural weathering systems (Buss *et al.*, 2013). Basically, we are considering the 'roughness' of a weathering front on a scale of a soil column or a watershed (Navarre-Sitchler and Brantley, 2007), but we are developing a rigorous mathematical treatment of this idea while simultaneously treating the problem as a geochemical system. In our final section, we discuss some of the implications of this averaging in terms of understanding natural rates of weathering.

Models

Meso-scale modeling

We consider a 2D weathering column that contains bedrock blocks embedded in an inert or weathered material – for example, already weathered saprolite that has been transported downward from above or inert quartz that has sloughed off the block surfaces. Alternately, the saprolite in fractures could have formed as primary mineral grains sloughed off during fracturing that has long ago interacted with infiltrating fluids, leaving no albite to be weathered. Observations and measurements document that porosity in general increases during weathering (Buss *et al.*, 2013). So we assume the inert material has greater porosity than unweathered bedrock. The bedrock blocks are assumed to be squares or rectangles. Initially all of them are equal in dimension. In Figure 1, the blocks are shown as blue squares and the inert material as red background.

The geochemical treatment is based on our previous four-mineral multicomponent reactive transport model in 1D (Lebedeva *et al.*, 2007). That model included the initial reactions that started bedrock alteration (dissolution of the ferrous iron in the ferrous oxide (FeO) component in the bedrock) and the transformation of a primary mineral to a secondary mineral, i.e. albite feldspar to kaolinite. The model bedrock also contained quartz, treated as inert to weathering. In this way, the model included the essential features of isovolumetric weathering, i.e. a material that reacted with oxygen (FeO), a material that reacted with acid (albite), and a material that maintained the structure of the rock (quartz).

In the model, components in the pore fluid included oxygen (O_2), sodium ion (Na^+), silicon dioxide (SiO_2), aluminum hydroxide ($\text{Al}(\text{OH})_3$), hydrogen ion (H^+), hydroxide ion (OH^-), ferrous ion (Fe^{2+}), ferric ion (Fe^{3+}) and chloride ion (Cl^-). Here this model is simplified according to the analysis of the numerical solutions of the model derived previously (Lebedeva *et al.*, 2007). First, we split the initial complex multi-component reaction scheme into the two independent one-component reactions: dissolution of the ferrous component and

Figure 1. The meso-scope domain (characteristic length L) consisting of blocks and joints (fractures). Here the characteristic length of the periodic cell, i.e. one block and adjacent fractures, is equal to ℓ . The coordinate system is normalized by L . Blue squares represent intact bedrock blocks subtended by fractures or joints that are filled with weathered material (red). Initially, the extent of reaction is zero, i.e. $\eta=0$, within squares and $\eta=1$ in the space between them because fractures contain weathered material. [Colour figure can be viewed at wileyonlinelibrary.com]

transformation of albite. Secondly, we focus on the last reaction, noting that the thickness of the zone with goethite formed in the first reaction is negligible compared to the kaolinite zone in weathering profiles developed on granitic rocks. So instead of the full reaction system we can write the following main reaction equation:

Here, we note albite ($NaAlSi_3O_8$) as *ab*, and kaolinite ($Al_2Si_2O_5(OH)_4$) as *kao*. We also combine all aqueous species in Equation (1) into one thermodynamic component, $\frac{1}{2}Na_2O \cdot \frac{1}{2}H_2O \cdot 2SiO_2$, denoting it as $NaSi_2$ (Lebedeva *et al.*, 2007). Comparison of the numerical solutions of the full and approximate models allows derivation of the approximate kinetic functions and calculation of the effective kinetic constants.

By focusing on Equation (1), we are emphasizing weathering of feldspar, the most abundant mineral in igneous rocks (Brantley and White, 2009). We present this model noting that albite is just an example of any abundant rock-forming mineral that reacts quickly with pore fluids.

Generally, this model describes the 2D reactive transport within the blocks as well as within the joints using equations for each part of the weathering column:

$$\frac{\partial(\phi C)}{\partial t} = \frac{\partial}{\partial x} \left(D\phi \frac{\partial C}{\partial x} \right) + \frac{\partial}{\partial y} \left(D\phi \frac{\partial C}{\partial y} \right) - \frac{\partial(Cu)}{\partial x} - \frac{\partial(Cv)}{\partial y} + j \quad (2)$$

$$\frac{\partial \eta}{\partial t} = \frac{j}{Q^0} \quad (3)$$

Here, C (mol/m³) is the concentration of component $NaSi_2$ in pore fluid. The extent of reaction for albite, η , is defined as:

$$\eta = 1 - Q/Q^0 = 1 - \phi_{ab}/\phi_{ab}^0, \quad (4)$$

where Q (in mol/m³) and Q^0 are the concentration of albite in the weathering material and in bedrock, respectively;

$\phi_{ab} = Q\bar{V}_{ab}^0$ is the volume fraction of albite in the rock, $\bar{V}_{ab}^0$ (in m³/mol) is its specific volume, ϕ_{ab}^0 is the initial volume fraction of albite in rock, and ϕ is porosity. In Equations (2) and (3), j (in mol/m³ s) is the reaction rate, D (in m²/s) is the diffusion coefficient for solutes in the aqueous pore solution reduced by tortuosity, v and u (in m/s) are the vertical and horizontal component of the Darcy velocity of a porefluid, respectively. As shown later, we consider the case of unidirectional advection, which can be either vertical or horizontal, depending upon the orientation of the system. The reaction rate, j , was derived in our previous work (Lebedeva *et al.*, 2007):

$$j = k(1 - \eta)(C^e - C), \quad k = 2k_{ab}s_{ab}\phi_{ab}^0\Psi \quad (5)$$

Here k (in s⁻¹) is an effective rate constant, k_{ab} is the dissolution rate constant for albite (in mol/m² s) as derived from published laboratory experiments (see discussion in Lebedeva *et al.*, 2007), s_{ab} is the specific surface area of albite (in m²/m³) calculated using a geometric model for particles, C^e is the concentration of $NaSi_2$ in porefluid in equilibrium with albite + quartz + kaolinite. The Ψ (in m³/mol) is a correction factor. This factor is necessary because we are only simulating albite dissolution whereas in reality other minerals are present in rocks that will buffer the pH and other solute concentrations (Lebedeva *et al.*, 2007). For example, the effect of pH changes along the flow path during albite dissolution was explored previously (Brantley *et al.*, 2008). In addition, the geometric surface area differs from the Brunauer–Emmett–Teller (BET) surface area used in mineral dissolution and this correction for roughness must be made. In our model, it follows from Equation (1) that the reaction rate is described by the non-linear

function of the form $j = k_{ab}f(s) \left(1 - \frac{C_{Na^+}^2 C_{SiO_2}^4}{C_{H^+}^2 K_{ab}} \right)$ where K_{ab} is the equilibrium constant for Equation (1), the function f describes the dependence on the mineral surface area, s , and C_i is concentration of aqueous species i (in mol/kg in this expression for j). So generally, we have a non-linear system of equations similar to Equation (2) describing each concentration C_i . It follows from the theory of non-linear differential equations (Vol'pert and Hudjaev 1985) that if the non-linear function j_i in the equation for the variable C_i satisfies the condition $K_1(C_i^e - C_i) \leq j_i \leq K_2(C_i^e - C_i)$ where K_1 and K_2 are constant, then the solution for the variable C_i can be approximated by the solution of a linear equation with some effective parameters. Solving the full non-linear system of equations as published previously (Lebedeva *et al.*, 2007), we estimated the non-linear function j in Equation (2) and calculated the correction factor Ψ . We assume that $f(s) = s_{ab}\phi_{ab}$.

We assume that the species in the pore fluid are in equilibrium with albite + quartz + kaolinite initially:

$$t = 0: \quad C = C^e \quad (6)$$

i.e. initially the weathering in Equation (1) does not occur.

Therefore, at the start of the simulation, the extent of reaction, η , is set equal to zero within bedrock blocks but set to unity between blocks where the albite has been completely dissolved.

Several sets of boundary conditions were considered. They are described for each simulated example. For vertical advection, the concentration at the upper boundary is maintained constant and equal to $C^R < C^e$. At the left and right boundaries as well as at the bottom of the column, the concentration gradient of the Na_2Si component in the porefluid was held equal to zero to maintain symmetry with respect to

the vertical axis or in recognition of the large distance from the top to the bottom of the column, respectively.

Finally, we assume isovolumetric weathering and calculate porosity ϕ as a function of volume fractions of minerals considered in the model:

$$\phi = 1 - \phi_{in} - \phi_{ab} - \phi_{kao} \quad (7)$$

Here, ϕ_j is the volume fraction of the inert material (subscript 'in'), albite (subscript 'ab') and kaolinite (subscript 'kao'). Porosity is a function of the extent of reaction, η , according to Equation (4) and the stoichiometric relationship between albite and kaolinite in Equation (1):

$$Q_{kao} = \frac{\phi_{kao}}{\bar{V}_{kao}^0} = \frac{Q_{ab}^0 - Q_{ab}}{2} = \frac{\phi_{ab}^0 - \phi_{ab}}{2\bar{V}_{ab}^0} \quad (8)$$

Here Q_{kao} is the concentration of kaolinite in weathering material, and $\bar{V}_{kao}^0$ is its specific volume. We assume that initially kaolinite is not present inside the (unweathered) blocks. Using Equations (4), (7), and (8) we obtain

$$\phi = \phi_{init} + \eta \phi_{ab}^0 \left(1 - 0.5 \left(\bar{V}_{kao}^0 / \bar{V}_{ab}^0 \right) \right) \quad (9)$$

where $\phi_{init} = 1 - \phi_{in} - \phi_{ab}^0$ is the initial porosity of the intact rock without kaolinite.

Using COMSOL Multiphysics software (COMSOL, 2008), we solved the 2D problem (Equations (2) and (3)) numerically. Figures 2–4 show some results of simulations for some test values of parameters. Figure 2 demonstrates that during

Figure 2. Weathering (without erosion) of blocks at a ridgetop experiencing vertical downward advection of a fluid shown at $t = 11200$ yr initially containing a constant equilibrium concentration of reactants: solution of the meso-equations shows that the blocks diminish in size at shallow depths. At the regolith-air boundary, i.e. the land surface, the concentration of the solute released to the solution during dissolution, C^R , was held constant in space and time at a value beneath the equilibrium value. At $x=0$ and $x=1$ ($\partial C/\partial x = 0$ for $0 \leq y \leq 1$; at $y=0$ ($\partial C/\partial y = 0$ for $0 \leq x \leq 1$). The Darcy velocity was set equal to 0.25 m/yr. This velocity is used to describe the average rate of advance of the solute into the weathering column. Colors indicate extent of reaction as shown in the bar at the right. Blue is unweathered and red is 100% weathered. It follows from the model that $0 \leq \eta \leq 1$. But the color legend presents a larger interval because the values of η in some singular points are taken into account. The deviation occurs at the boundaries where the variable η is discontinuous. It is a result of the approximation by continuous functions. Analysis of cross-sections shows that there are a few such points only. It does not affect simulations. [Colour figure can be viewed at [wileyonlinelibrary.com](#)]

Figure 3. Simulation similar to Figure 2 (no erosion) except calculated under the condition of unidirectional horizontal advection at 0.25 m/yr, shown for $t = 12000$ yr. The boundary conditions are: $C^R = 0$ at $x=0$, $0 \leq y \leq 1$ and zero-flux conditions at other boundaries: $(\partial C/\partial y) = 0$ at $y=0$, $y=1$, $0 \leq x \leq 1$ and $(\partial C/\partial x) = 0$ at $x=1$, $0 \leq y \leq 1$. Colors indicate extent of reaction as shown in the bar at the right. Blue is unweathered and red is 100% weathered. [Colour figure can be viewed at [wileyonlinelibrary.com](#)]

weathering the (unweathered) block size changes as a function of depth during vertical advection. We interpreted the change of the size as a reduction of unweathered core from initial joint-bounded bedrock block so that the weathering profile consists of weathering-reduced relicts of initial blocks decreasing in size upward. Such a model with unidirectional vertical advection cannot model the natural system where fluid flow is described by both vertical and horizontal components depending on a pressure gradient and permeability: it likely includes a vertical component if the column is largely water-unsaturated, but also includes a horizontal component because of the large differences in permeability of weathered and unweathered rock. To explore another limiting case of flow, Figure 3 shows weathering for the case of horizontal advection. In this simulation, a constant porefluid concentration of Na_2Si was assumed at $x=0$ for all depths whereas zero flux conditions ($\nabla C = 0$) were assumed at the upper, lower, and right boundaries. For this case, the size of blocks changes with the

Figure 4. A simulation with the same parameters as in Figure 3 (no erosion) except for the boundary condition at $x=0$: $C = (-0.952y/L + 1)C^e$ where L is the depth of the weathering column. Thus, at the bottom of the column, i.e. at $y=0$, the porefluid is in equilibrium with the dissolving mineral: $C = C^e$. At the air-regolith boundary $y=L$ (dimensionless vertical coordinate is equal to 1) the porefluid is dilute, i.e. $C = C^R = 0.008C^e < C^e$. Here, $t = 14400$ yr. Colors indicate the extent of reaction as shown in the bar at the right. Blue is unweathered and red is 100% weathered. [Colour figure can be viewed at [wileyonlinelibrary.com](#)]

horizontal coordinate x . As the final exploration of the impact of both vertical variation in boundary conditions and horizontal 1D flow, Figure 4 depicts weathering for the case of horizontal advection with non-constant boundary conditions (see discussion later) at the inlet of the column at $x=0$: $C = (-0.952y/L + 1)C^e$ where L is the depth of the weathering column. For this case, block size changed along both the vertical (depth) and the horizontal coordinate. Although this model case includes unidirectional, horizontal, advective water flow (while the diffusion transport occurs in both directions), the simulation allows us to consider how blocks might change in size and extent of weathering in a system where water flows by advection both vertically and horizontally.

The model solution to Equations (2) and (3) can also be considered with the imposition of erosion. In this case, the material at the upper boundary of the weathering column is removed during weathering. Depending on the degree of block alteration at the regolith surface, we can determine weathering regimes (Lebedeva *et al.*, 2010). Previously we defined the local equilibrium regime as the regime when the chemical profile through the regolith is characterized by complete depletion of albite ($\eta = 1$) and the regolith thickness varies with the erosion rate. In contrast, in the kinetic regime, the variation of the regolith thickness with erosion rate is negligible, albite depletion is not complete ($\eta < 1$), and the fraction of albite remaining at earth's surface increases with increasing erosion rate and decreasing weathering reaction rate. These features are consistent with several observations that have been made previously in the literature for transport-limited versus weathering-limited regimes.

Therefore, we expect an erosional local-equilibrium (we have also referred to this as erosive transport-limited) and an erosional weathering-limited (i.e. kinetic) regime in the model of fractured bedrock systems. In the first case, when the extent of reaction at the land surface is equal to unity, $\eta = 1$, no blocks are present at the surface because they have weathered completely. In the second case, $\eta < 1$, i.e. weathered blocks are exposed at the land surface. An increase in reaction rate constant causes an increase in the extent of reaction at the land surface; correspondingly, η increases and exposed blocks diminish in size. Such an analysis allows the weathering rates to be estimated. However, it is difficult to perform accurate simulations for the system of Equations (2) and (3) in the presence of erosion. A similar problem arises for models of the weathering of bedrock blocks along an eroding hillslope such as described by Fletcher and Brantley (2010). However, this problem, as well as the problem of numerical analysis of large heterogeneous regions, can be solved after rigorous homogenization of the weathering domain.

Here, we term the model written in Equations (2) and (3) as the 'meso-scale model,' (scale ~ 0.01 – 10 m) even though it is often also called a macro-scale model (Auriault, 1991). Here we reserve the term 'macro' for the models describing the large-scale domains (~ 100 m) where the weathering blocks are the small elements, i.e. the 'bricks' building the whole structure. As mentioned in the Introduction, the model for Equations (2) and (3) itself is already the product of averaging – averaging of the equations written at the scale of single pores and mineral grains, i.e. micro-scale equations. Therefore, the model in Equations (2) and (3) is referred to here as the meso-scale model. Importantly, treatment of systems at different spatial scales lies at the heart of what geochemists do when they analyze weathering systems (Navarre-Sitchler and Brantley, 2007). For example, it is common to look at weathering of one system at the scale of a single block of rock

(Buss *et al.*, 2008), a pedon (Chabaux *et al.*, 2013), or a watershed (McDowell and Asbury, 1994).

Homogenization: Macro-scale modeling

Although we can perform detailed simulations such as described in the previous section at the scale of the entire weathering column or a single hillslope, they would be very intensive mathematical calculations when extended to the scale of a catchment. Besides, often the data necessary to parametrize such simulations are unavailable. Hence, we explore techniques of averaging. There are many methods available to derive the macroscopic average equations and the effective transport properties. For example, the methods of volume averaging (Whitaker, 1986) and homogenization (Hornung, 1997) are available for these cases. These methods are based on consideration of two length scales – one associated with the mesoscopic (ℓ) and one associated with the macroscopic (L) phenomena – under the condition that $\varepsilon = (\ell/L) < 1$. Both methods proceed smoothly from the initial heterogeneous problem to an averaged problem. To determine the effective parameters it is necessary to solve some auxiliary problems. These problems are different for each method. We will focus on the mathematically rigorous method of homogenization (see Appendix A). The ratio ε is the same term that was used previously (Navarre-Sitchler and Brantley, 2007) to describe the roughness of the natural systems over a broad range in scale. Roughness, λ , has been defined by geochemists as the ratio of true surface area (including all deviations from the Euclidean plane) to geometric surface area (based on calculations of surface area using the assumption of Euclidean solid geometries): $\lambda = (A_{ext} + A_{pore})/A_{geom}$ (Hodson *et al.*, 1997) where A_{ext} is the surface area due to the topography of grain surfaces, A_{pore} is the surface area due to connected internal porosity, A_{geom} is the surface area determined by geometric calculations. This parameter (λ) when discussed at the grain scale correlates well with mineral microtexture (Hodson *et al.*, 1997). But there are studies of roughness using Euclidean models (Power and Tullis, 1991) where roughness is determined as the departure from the Euclidean ideal (for example, a difference between a stepped surface and a plane). In those cases, the less the surfaces of mineral grains depart from the more smooth step-poor analogue, the smaller their external surface area and the smaller the parameter λ . So the geochemical definition correlates with that in Euclidean models. In this paper, roughness is considered at the scale of fractured systems (see discussion in Navarre-Sitchler and Brantley [2007] for roughness at different scales). Roughness at this scale is a measure of heterogeneity in our model systems because the weathering front is not continuous but is truncated by fractures infilled with pre-weathered material.

Note that the ratio of the block size, $\sim \ell$ (for example, ~ 1 m), to a characteristic catchment size L (for example, the scale of observation of the system ~ 100 m), is small, i.e. $\varepsilon = (\ell/L) < 1$. This is a requirement for the use of the homogenization procedure to obtain averaged governing equations for averaged quantities to understand weathering of blocks for a catchment. The upshot is that we solve the continuous averaged equations, i.e. equations with continuous variables and parameters, instead of equations describing heterogeneous domains like in Figure 1 where some variables may be discontinuous. For example, discontinuous variables in a system such as Figure 1 include porosity, diffusivity, and the extent of reaction. With this approach, the distribution of block size can be obtained as a function of depth at the scale of a catchment.

A detailed description of the homogenization method for porous media has been presented in many publications (see, for example, Bakhvalov and Panasenko, 1989; Hornung, 1997). Therefore, here we only summarize it briefly in Appendix A. In natural systems, fractures or joints can be periodically distributed (Li *et al.*, 2014a). So here we focus on the case when a medium is composed of recurrent cells, noting that homogenization methods are not restricted to periodic problems. In general, we seek to describe systems where heterogeneities separate regions of homogeneity. For such systems, a 'cell' is defined as consisting of the homogeneous part of the system, i.e. the block, as well as its surrounding heterogeneity, i.e. the material of the joints. Thus, in the parent material, the cells are only slightly larger than the blocks for small-aperture joints and fractures. For example, Figure 1 depicts such cells, each of which includes a block with initially low porosity surrounded by fractures or joints with larger porosity. Under this assumption we can consider processes described by equations with periodic coefficients and periodic internal boundary conditions. A solution is sought in the form of a series in powers of the small parameter ε with coefficients depending both on the macroscopic space variables x, y (usually referred to as slow variables) and the re-cast variables $\xi = x/\varepsilon, \zeta = y/\varepsilon$ (usually referred to as fast or mesoscopic variables). The two sets of variables are needed because the slow variables correspond to the global structure of the models and the fast variables to the local structure. For example, we seek a solution of Equations (2) and (3) that is a function of these variables in the form:

$$\begin{aligned} C(x, y, \xi, \zeta) &= c_0(x, y, \xi, \zeta) + \varepsilon c_1(x, y, \xi, \zeta) + \varepsilon^2 c_2(x, y, \xi, \zeta) + \dots \\ \eta(x, y, \xi, \zeta) &= \eta_0(x, y, \xi, \zeta) + \varepsilon \eta_1(x, y, \xi, \zeta) + \varepsilon^2 \eta_2(x, y, \xi, \zeta) + \dots \end{aligned} \quad (10)$$

Such a series is substituted into the original Equations (2) and (3). In each equation we obtain a sum of ε^i multiplied by some expression for the functions c_i, η_i $i=0, 1, 2, \dots$, i.e. the coefficients, for the left- and right-hand sides of the equation. By equating the coefficients of the powers ε in the left-hand and right-hand sides to each other, we get equations for the functions c_i, η_i . Solving them we can also obtain effective parameters such as the effective diffusion coefficient and the effective reaction rate constant. This procedure is shown in Appendix A.

In this work, our goal is to investigate the simplified macro-model, i.e. the model where the functions c_0, η_0 and the coefficients in corresponding equations turn out to be independent of the fast variables, i.e. the local structure. We call these equations the averaged equations. The numerical treatment of the averaged problem is less difficult than treatment of the original problem. Using this standard homogenization technique we get the following macro-model:

$$\frac{\partial(\phi_0 c_0)}{\partial t} = \frac{\partial}{\partial x} \left(D^{\text{eff}} \frac{\partial c_0}{\partial x} - u c_0 \right) + \frac{\partial}{\partial y} \left(D^{\text{eff}} \frac{\partial c_0}{\partial y} - v c_0 \right) + k(C^e - c_0)(1 - \eta_0) \quad (11)$$

$$\frac{\partial \eta_0}{\partial t} = \frac{k}{Q^0} (1 - \eta_0)(C^e - c_0) \quad (12)$$

$$\phi_0 = \phi_{\text{init}0} + \eta_0 \phi_{ab}^0 \left(1 - 0.5 \left(\bar{V}_{kao}^0 / \bar{V}_{ab}^0 \right) \right), \quad D^{\text{eff}} = D \phi_0 \quad (13)$$

The averaged model is obtained under the assumption of a

constant Darcy velocity in the fractures and joints and the assumption that the transition zone between weathered and unweathered parts of a block is narrow, i.e. the extent of reaction is approximately equal to zero within the unweathered core of the block whereas it is equal to unity within the other part of the elementary cell. These assumptions essentially simplify the model. The assumptions can be adequate for some natural systems experiencing unidirectional advection and weathering in the local-equilibrium regime. But generally, the averaged problem has a more complex form (Hornung, 1997). Particularly, when advective transport is not unidirectional, homogenization may result in macro-equations like Equations (11) and (12) that have additional terms on the right-hand side which depend on the micro-porosity domains – the blocks (Ngoc *et al.*, 2011). So we avoid this problem by the assumption about advection which is reasonable near ridgetops.

The second problem on the meso-scale level arises for the effective diffusivity D^{eff} . As discussed in Appendix A, D^{eff} can be calculated as a function of the solution of an auxiliary problem (Equations (A15), (A24)–(A26) in Appendix A) considered for the elementary cell. The parameters of this problem depend on both macroscopic and mesoscopic variables. Thus, generally, the averaged system for Equations (11) and (12) is a coupled system of the macroscopic equations for the macroscopic variables $c_0(x, y, t)$ and $\eta_0(x, y, t)$ and the mesoscopic system described in Equations (A15), and (A24)–(A26) for the local variable depending on the mesoscopic variables (ξ, ζ) . But the mesoscopic system, in turn, includes parameters depending on the macroscopic variables (x, y) . So the coupling is in both directions. Such a system of equations is called distributed micro (meso)-structure model (Hornung, 1997). Using the second assumption we decoupled the macro- and meso-systems and obtained Equation (13) for the effective diffusivity.

Thus, generally, we need to solve auxiliary meso-scale equations describing the corresponding periodic cell located at each point (x, y) of the macroscopic problem. It may not be apparent that the macroscopic description has any advantage in comparison with the mesoscopic description. Nonetheless, as discussed previously (Hornung, 1997), even the distributed models require far less computational effort than the mesoscopic models.

Variables $\phi_0, \phi_{\text{init}0}, c_0$, and η_0 in Equations (11) and (13) are averaged over the unit cell (see, Figure 1) so that, for example

$$\eta_0(x, y, t) = \frac{1}{|\Omega|} \int_{\Omega} \eta(x, y, \xi, \zeta, t) d\Omega \quad (14)$$

where $|\Omega| = |\Omega_B| + |\Omega_F|$ is the size of the elementary cell, i.e. its volume if we conceptualize the 2D model in Figure 1 as a three-dimensional (3D) model. This volume consists of the volume of the block, $|\Omega_B|$, and the volume of the weathered inert material $|\Omega_F|$. Therefore, if the initial value of the extent of reaction is equal to zero within the blocks and equal to unity between the blocks, then the initial value of the averaged extent of reaction $\eta_{0, \text{init}}$ is equal to.

$$\begin{aligned} \eta_{0, \text{init}} &= \frac{1}{|\Omega|} \left(\int_{\Omega_B} \eta(x, y, \xi, \zeta, 0) d\Omega + \int_{\Omega_F} \eta(x, y, \xi, \zeta, 0) d\Omega \right) \\ &= \frac{|\Omega_F|}{|\Omega|} = \phi_F \end{aligned} \quad (15)$$

Here, ϕ_F is the volume fraction of joints in the rock, i.e. the volume fraction of pre-weathered material. It follows from Equation (15) that the initial extent of reaction for the averaged model is equal to the volume of space between the blocks divided by the volume of cell. Therefore, the initial averaged rock is ‘weathered’ even if the extent of reaction is still equal to zero within the blocks: this is essentially because each fracture contains weathered material only.

Figure 5 shows solutions of the model for Equations (2) and (3) (the meso-scale model) and the model for Equations (11)–(13) considered for a ridgetop experiencing downward unidirectional advection. Figure 5 shows that the approximation is satisfactory. Note that in the unweathered zone, the averaged value of the extent of reaction is not equal to zero. This is the result of the assumption that the joints are distributed homogeneously in the rock at all depths and because each joint contains weathered material even upon initiation of the simulation. Actually, in natural systems, the volume of inert material between the blocks would diminish with increasing depth, and the averaged value of the initial extent of reaction would tend toward zero at larger depths because $\phi_F \rightarrow 0$. Then the dashed curve in Figure 5 would also tend toward zero at greater depths.

Figure 5. Comparison of the solutions of the meso-scale model $C(x, y, t)$ (normalized by C^0) and $\eta(x, y, t)$ (set up similar to the model in Figure 2 (no erosion) except with a smaller distance between blocks) and the macro-scale model, $(C_0(x, y, t)/C^0)$ and $\eta_0(x, y, t)$ (vertical axis). As required by the condition of homogenization, the ratio of the size of the cell, $\sim \ell$, to the length of the weathering column L , is small: $\varepsilon = 0.2$. The cross-section at $x = 0.5$ is presented. Therefore, the solutions are shown as a function of elevation, y . Elevation $y = 1$ corresponds to the surface (note that the vertical direction depicted in Figure 2 is here shown as horizontal). Only vertical advection (along the y -axis) is simulated, with a Darcy velocity equal to 0.05 m/yr. The meso-scale solution is depicted by solid curves (the black curve = the concentration of dissolved component in porefluid; the red curve = the extent of reaction). The macroscopic solution is depicted by similar dashed curves (black for the averaged concentration in porefluid, red for the averaged extent of reaction). Curves of solute concentration are almost identical. The meso-scale model depicts the extent of reaction as a step function in the unweathered zone ($\eta = 0$ within the blocks, $\eta = 1$ between the blocks). In the weathering zone, the meso-scale extent of reaction is presented by a continuous function (solid red curve). This curve is approximated by the continuous dashed curve calculated for the averaged solution. In the unweathered zone, the macroscopic extent of reaction tends to the initial value of the averaged extent of reaction equal to the volume fraction of the inert material ϕ_F (here $\phi_F = 0.088$). [Colour figure can be viewed at wileyonlinelibrary.com]

Results

Block size

Using the macro-model we can obtain a simulated distribution of averaged block sizes with depth. As mentioned earlier, the block size is defined as the size of the unweathered core of the initial joint-bounded bedrock blocks. So if the weathering profile is capped with corestone-free saprolite the size of the blocks at the surface is equal to zero, i.e. in our model the initial elementary cell consisting of unweathered (block) and weathered (joint) material becomes homogeneous (see, for example the upper part of the column in Figure 2). First, we derive expressions for the block size for the meso- and macro-models. Let us consider the cell Ω which is the sum of the domains Ω_B (block) and Ω_F (inert material). We denote $|\Omega_{BW}|$ and $|\Omega_{UW}|$ as the volume of the weathered part of the block where $\eta > 0$ and the volume of the unweathered part with $\eta = 0$, respectively. Therefore,

$$|\Omega_B| = |\Omega_{BW}| + |\Omega_{UW}| \quad (16)$$

Under the assumption that $\eta = 1$ in the domain Ω_F and $\eta = 0$ in the domain Ω_{UW} and taking into account that $|\Omega| = |\Omega_B| + |\Omega_F| = |\Omega_{BW}| + |\Omega_{UW}| + |\Omega_F|$, we obtain the average over the elementary cell extent of reaction, η_0 , from Equations (14) and (16) using the mean value theorem to calculate the integral:

$$\begin{aligned} \eta_0 &= \frac{1}{|\Omega|} \int_{(\Omega_{BW} + \Omega_{UW} + \Omega_F)} \eta d\zeta = \frac{1}{|\Omega|} \left(\int_{\Omega_{BW}} \eta d\zeta + |\Omega_F| \right) \\ &= \frac{|\Omega_{BW}| \bar{\eta} + |\Omega_F|}{|\Omega|} \\ &= \frac{|\Omega_{BW}| (\bar{\eta} - 1) + |\Omega| - |\Omega_{UW}|}{|\Omega|} \quad (17) \end{aligned}$$

where $\bar{\eta}$ is calculated in some point in the domain Ω_{BW} . Assuming that the transition zone between weathered and unweathered domains is narrow, i.e. $\eta = \bar{\eta} = 1$ in the domain Ω_{BW} we obtain that the volume of the unweathered block $|\Omega_{UW}|$ is equal to

$$|\Omega_{UW}| = |\Omega| (1 - \eta_0) \quad (18)$$

Then for the model in Figure 1, Equation (18) takes the form

$$|\Omega_{UW}| = \ell^2 (1 - \eta_0) \quad (19)$$

where ℓ is the size of the square cell, i.e. the sum of spacing of initial fractures in the bedrock and its aperture.

For the meso-scale model, the volume of the unweathered block is calculated as follows:

$$|\Omega_{UW \text{ meso}}| = |\Omega_B| - |\Omega_{BW}| \approx |\Omega_B| - \int_{\Omega_B} \eta d\Omega \quad (20)$$

The approximation in Equation (20) is correct for a thin reaction front on a block scale, i.e. if $\eta = 1$ almost everywhere within the weathered part of the block Ω_{BW} . This condition is satisfied for our model and for natural weathered blocks where weathering occurs in the transport-limited regime. A good example has been described in the literature (Buss *et al.*, 2013). Figure 6 demonstrates that the macro-model yields a simulation that is a good approximation of the meso-model.

Thus, we can obtain the time evolution and spatial distribution of the block size solving Equations (11)–(13) and (19)

Figure 6. The distribution of block size as a function of hillslope elevation (both in dimensionless units) at a ridgetop as a solution of macro-equations in the absence of erosion ($\varepsilon=0.125$; for example, the initial block size + aperture is equal to $l=1.25$ m, the column length $L=10$ m). The continuous curve represents the solution of the macro-equations; black circles correspond to the solution of the meso-equations. The figure shows a relatively narrow reaction front for the blocks between 0.4 and 0.6 where weathering occurs. Vertical advection velocity $v=0.05$ m/yr, $\phi_F=0.36$, and fracture spacing is equal to 1 m.

for the homogenized media. For such a system, we can perform simulations within complex 2D domains such as hillslopes considered in earlier studies (Fletcher and Brantley, 2010; Lebedeva and Brantley, 2013), and we can include erosion. Our preliminary simulations showed that including erosion is rather difficult mathematically for the meso-scale system (Equations (2) and (3)). To our knowledge, there are not yet published papers on this subject.

Effect of roughness of the weathering profile on weathering advance rate

To understand the role of joints in reaction front advance we consider first the expression for the front velocity for the case of unidirectional advection in a homogeneous media, for example for vertical advection (see Appendix B). For this case, we consider a 1D version of Equations (2) and (3) with an advection term, $\partial(Cv/\partial y)$, which we take with a positive sign because we consider the positive direction as that of the vertical axis y upward toward the air–soil interface. These equations describe a 1D front when the variables C and η do not depend on the coordinate x . For example, such a front will develop when the solute gradient is equal to zero ($\nabla C=0$) at all boundaries except the air–soil surface. As shown in Appendix B, the advance rate of the reaction front, ω , is calculated as follows

$$\omega = \frac{v(C^e - C^R)}{\phi_{init}C^e - \phi^RC^R + Q^0(1 - \eta_{init})} \approx \frac{v(C^e - C^R)}{Q^0(1 - \eta_{init})} \quad (21)$$

Here ϕ_{init} and η_{init} are the initial porosity and extent of reaction (i.e. far ahead of the moving weathering front where solute is in equilibrium with mineral), and ϕ^R is porosity at the air–regolith boundary. The approximation (the second equality in Equation (21)) holds when $|\phi_{init}C^e - \phi^RC^R| \ll Q^0(1 - \eta_{init})$. The latter condition is generally satisfied for processes of mineral alteration (Lebedeva *et al.*, 2007). For homogeneous intact rocks where $\eta_{init}=0$, the expression in Equation (21) takes the form (Ortoleva *et al.*, 1987; Lichtner, 1988; White, 2002; Lebedeva *et al.*, 2010):

$$\omega = \frac{v(C^e - C^R)}{Q^0} \quad (22)$$

Let us assume that initially the weathering column consists of a large number of rows of intact blocks (i.e. $\eta=0$) embedded in 100% weathered material, i.e. $\eta=1$ (Figure 1). Then the averaged extent of reaction ahead of the weathering front, $\eta_{0,init}$ is equal to ϕ_F (Equation (15)), i.e. it is equal to the volume fraction of the material-filled joints. According to Equation (21) the advance rate of the weathering front can be expressed as

$$\omega = \frac{v(C^e - C^R)}{Q^0(1 - \phi_F)} = \frac{v(C^e - C^R)}{Q^0} \cdot \frac{|\Omega|}{|\Omega_B|} \quad (23)$$

Equation (23) documents that the rate of advance depends on the ratio of the block volume to the total volume of the cell, $\phi_B=1 - \phi_F$. In other words, it depends on the roughness at the scale of the weathering profile (Navarre-Sitchler and Brantley, 2007). So for the analysis of the field observations it is necessary to measure not only porosity within the blocks but also to calculate ‘the concentration of blocks’ i.e. the fracture spacing, and the extent of weathering of material in the fractures. Furthermore, according to Equations (22) and (23), the weathering advance rate is greater for the system consisting of blocks and joints than it is for the case of homogeneous non-fractured rocks because the ratio $(|\Omega|/|\Omega_B|) > 1$. Later we compare weathering advance rates for the separate blocks and the whole weathering column consisting of these blocks. Weathering advance rates across scales were compared previously (Navarre-Sitchler and Brantley, 2007) for the interface-limited weathering regime. There it was found that the largest variation in weathering advance rates across spatial scales is attributed to the inability to measure comparable surface areas at different scales and the scaling factor was defined as the roughness and related to the ratio of spacings of grain boundaries, fractures, faults, etc. Here we obtained a scaling factor affecting the weathering advance rate for the transport-limited regime as defined in a previous publication (Lebedeva *et al.*, 2010).

Discussion

Weathering advance rate for blocks and within columns

In this section we consider weathering blocks as elements of a weathering column. Various aspects of weathering blocks (clasts) are modeled by meso-scale models (Sak *et al.*, 2010; Navarre-Sitchler *et al.*, 2011; Ma *et al.*, 2012; Lebedeva and Brantley, 2013; Reeves and Rothman, 2014; Lebedeva *et al.*, 2015). Previously we obtained that the weathering advance rate of mineral alteration within blocks (known as clasts in our previous publication) can be calculated as follows (Lebedeva and Brantley, 2013; Lebedeva *et al.*, 2015):

$$\omega_n = \omega_{pl} - D\phi \frac{C^e - C^R}{Q^0} K = \frac{(C^e - C^R)(v - D\phi K)}{Q^0} \quad (24)$$

where ω_n is the normal component of the weathering advance rate, ω_{pl} is the velocity of the analogous planar front, and K is the curvature of the weathering front ($K < 0$ for weathering inward blocks in Figure 7). The second equality in Equation (24) holds if the velocity of the planar front is determined by Equation (22). Equations (22) and (23)

Figure 7. Weathering column without erosion. (a) A set of identical unweathered blocks (blue) weathering under the same boundary conditions. Blocks are embedded in homogeneous inert material (red) and homogeneous porefluid (not shown explicitly). The extent of weathering after dimensionless time 0.015 is color-contoured, with warmer colors showing the approach to 100% weathered. Solute concentrations at all the block-inert material boundaries remain the same through time: $C = C^R$. Here, solute transport within (unweathered) blocks and within joints is by diffusion only. If the simulation is continued until $t = 0.03$, the blocks weather completely. For (b), the identical weathering column as in (a) is weathered for $t = 0.03$, but with a different distribution of porefluid concentration. Here the inlet concentration at $y = 1$, $0 \leq x \leq 1$, is maintained equal to $C^R = 0$ and all other outer boundary conditions are zero-flux ($\nabla C = 0$). Solute transport occurs only by diffusion (like (a), fluid does not advect). After reaction, the extent of weathering of every block (contoured in color) varies only as a result of reaction–diffusion processes within the column. For these conditions, (b) shows that only the first row of blocks is about half-weathered. The first row will be completely weathered at $t = 0.065$. (c) A simulation showing the advance of the weathering front for a porous medium containing blocks like in (a) and (b), but experiencing unidirectional advection through fractures and blocks at a vertical velocity $v = 0.1$ m/yr. Boundary conditions are as in (b). According to Equation (23), the dimensionless front velocity within the weathering column is equal to 8.3. Therefore, the front location, L_{front} , at $t = 0.03$, is equivalent to $L_{front} = 1 - 8.3 \times 0.03 = 0.75$. So the ‘column-scale’ reaction front traveled a distance of about 0.25. In contrast, the weathering front within the first row of blocks traveled only a distance of about 0.15 (the vertical dimensionless size of the block). This is in accordance with Equation (22) which yields $\bar{\omega}_{block} \approx 4$ for $C^R = 0$, $(C^R/Q^0) = 5 \times 10^{-5}$, $L = 1$ m, $D = 0.8 \times 10^{-9}$ m²/s. (d) The column depicted in (c) at a dimensionless time $t = 0.06$. The second row of the blocks is now completely weathered. The dimensionless rate of the weathering advance at the block-scale, $\bar{\omega}_{block}$, is described by Equation (22) as in (c), while the dimensionless advance rate at the column-scale is equal to $\bar{\omega}_{col} = \bar{\omega}_{block} / (1 - \phi_F) = 8.3$ (Equation (23), $\phi_F = 0.52$). [Colour figure can be viewed at wileyonlinelibrary.com]

are obtained for planar weathering fronts where $K = 0$. Equations (22)–(24) show that the weathering advance rate depends on the structure of the weathering system, transport characteristics, geometry of the front, and boundary conditions at the surface, C^R . For the weathering blocks, the effects of the boundary conditions are illustrated by Figures 2–4 where the surface concentration C^R_{block} for each block depends on location of the block within the weathering column. Note that in Figures 3 and 4 where transport occurs by horizontal advection, weathering fronts within the blocks move inward into the block core from the upward and downward directions from the joint planes. A similar weathering scheme to calculate the total denudation rate was previously described (Turner *et al.*, 2003) for weathering of quartz diorite in the Rio Icaos basin, where those authors considered multiple parallel weathering fronts

moving upward and downward. The authors first analyzed the case when all the blocks weather identically under uniform steady-state conditions. They noted that under natural-system boundary conditions, the rate of advance of weathering fronts in blocks deep in the subsurface may be negligible compared to blocks nearest the ground surface (compare Figures 3 and 4). Figure 7a demonstrates a hypothetical situation where all the blocks within the column have the same boundary concentration ($C = C^R$ at all inner boundaries between block and inert material) and transport occurs only by diffusion. For this hypothetical case, for example, precipitation might be extremely high, maintaining C^R far from equilibrium throughout the fractures. In this case, the unweathered core of an originally rectangular block becomes elliptical, so, the role of the second term in Equation (24) is essential. Such rounding within

rectangular blocks has been observed (Jamtveit *et al.*, 2011). A pertinent example that may match aspects of Figure 7a was described by (Sak *et al.*, 2004) where weathering basaltic clasts in a soil in Costa Rica showed both rounding and also showed little difference in the extent of weathering as a function of depth.

In contrast to the model in Figure 7a, when the boundary conditions at the block surface vary with depth due to reaction–diffusion processes within the weathering column according to Equations (2) and (3), then blocks weather at different rates at different depths. For the case shown in Figure 7b, for example, the weathering advance rate is slower than that shown in Figure 7a. The simulation in Figure 7a documents complete weathering at a dimensionless time $\tau = (tDL^{-2}C^e/Q^0) = 0.03$ ($L = 1$ m here): in contrast, the first row of blocks is only half-weathered in Figure 7b at $\tau = 0.03$. The dimensionless time necessary to achieve complete weathering of the first row in Figure 7b is equal to 0.065.

Figures 7c and 7d illustrate the application of Equations (22) and (23). Weathering is simulated for the case of unidirectional vertical advection. The weathering front moves with a constant velocity at the weathering column scale: after a dimensionless time interval equal to 0.03, a successive row of the blocks weathers completely. As shown in Figure 7c, the weathering front within the blocks is almost planar (this is the result of the boundary conditions), only exhibiting roughness at the scale of the fracture spacing. So we can estimate the velocity of the front within the blocks using Equation (22). For the parameters shown in the figure caption, the dimensionless front velocity for the block, $\bar{\omega}_{block}$, is equal to $\bar{\omega}_{block} = \omega L Q^0 / (DC^e) = 4$ while the weathering front within the column moves with dimensionless velocity $\bar{\omega}_{col} = (\bar{\omega}_{block} / (1 - \phi_F)) = (\bar{\omega}_{block} \phi_B) = 8.3$ at $\phi_F = 0.52$ (Equation (23)). Thus, the weathering front described at the column scale in this example moves faster than the rate described for the block scale: it moves with the velocity ω_{block} within every block but it ‘jumps’ to the next row when the previous one is weathered. Such behavior is described by Equations (22) and (23). Although this example exaggerates the effect of roughness (the joint concentration ϕ_F is very large), it is clear that the volume fraction of material between the blocks, ϕ_F , and properties of this material must be taken into account in estimating the weathering advance rate when considered at the column scale. A similar dependency on the structure of the system was obtained previously for a 1D approximate model (Fletcher and Brantley, 2010):

$$\omega_{col} = \frac{6L^* \omega_{block}}{S_0} = \frac{\omega_{block}}{\varepsilon \sqrt[3]{\phi_B}} \quad (25)$$

where S_0 was defined as the maximum size of the initial bedrock blocks, $\varepsilon = (\ell/6L^*)$, $\phi_B = (S_0^3/\ell^3)$, and $3L^*$ is the column depth.

Given these considerations, the column-scale weathering advance rate is predicted to be larger than the block-scale rate, a result also observed in natural systems (Navarre-Sitchler and Brantley, 2007). If there were a system where the column-scale weathering advance rate appears slower than a block-scale rate, it is possible to explain this by invoking differences in the boundary and transport conditions such as described in Figures 7a and 7b.

Using the macro-model (Equations (11)–(13)) we can investigate the effect of fracture spacing on weathering advance rate. Figure 8 demonstrates how the weathering advance rate increases when the fracture spacing, δ , decreases while the fracture aperture, d , is constant over time and space. For the

Figure 8. Dependence of the weathering advance rate on fracture spacing for the two-dimensional (2D) model depicted in Figure 1 in the absence of erosion. The weathering advance rate is calculated by solving macro-equations (Equations (11)–(13)). In these simulations, the fracture spacing, i.e. the initial block size, δ , and the periodic cell size, ℓ , were varied while the fracture thickness, $d = \ell - \delta$ remained constant ($d = 0.02$ m for column size $L = 1$ m). The fracture spacing values are equal to 0.15, 0.2, 0.25, and 0.3 m and normalized by L . The vertical advection velocity was set equal to 0.1 m/yr. The solid curve shows the theoretical dependence as described by Equation (26). The dimensionless value of the weathering advance rate in the absence of fractures, $\bar{\omega}_0$, equals 4. It corresponds to the dimensional front velocity $\omega_0 = -\omega_0 DC^e(Q^0 L)^{-1} = 5 \times 10^{-6}$ m/yr.

simple structure shown in Figure 1 where the cell and the block volumes are calculated in 2D as areas of the corresponding squares, it follows from Equation (23) that the weathering advance rate depends on fracture spacing as follows:

$$\omega = \omega_0 \left(1 + \frac{d}{\delta} \right)^2 \quad (26)$$

Here, ω_0 is the weathering advance rate in non-fractured media and the cell length is equal to $\ell = d + \delta$. For a 3D-model using the same assumptions, the parenthetical expression in Equation (26) is replaced by $(1 + d/\delta)^3$. The exact nature of this correction factor (i.e. the parenthetical) varies with the geometry of the block and the extent of alteration in the initial fracture material.

We can also extrapolate to the micro-scale from our meso-scale model. We infer from our models that on the micro-scale, the weathering advance rate within a single grain differs from the weathering rate of a system of grains. The difference is determined by the structure of this system as shown by this example.

The spatial structure affects also the kinetics of dissolution of minerals which in turn, affects the weathering advance rate. This effect was investigated previously in experimental columns (Salehikhoo *et al.*, 2013; Li *et al.*, 2014b). The authors found that the rates of dissolution depend not on the total mineral surface area – for example the surface area measured by BET sorption analysis – but on an effective surface area. The latter is a function of both flow rate and the pattern of spatial structure. For the experimental columns from that research, the effective surface area was related to the distribution of reactive phases in the porous material. The

techniques in this paper could also be used to analyze those experiments.

Simulations of weathering columns with erosion at a constant rate

When erosion occurs at a constant rate, i.e. the velocity of lowering the air-regolith boundary is constant in time and space, then under some conditions the system tends toward a steady state (Lebedeva *et al.*, 2010). In the steady state, the thicknesses of all layers of regolith are constant in time and the system moves downward with the velocity of erosion, E . If the system depicted in Figure 1 weathers under a constant erosion rate, for example, then in the steady state, the thickness of the weathered zone and the average size of blocks at each depth both remain constant.

As previously shown by Fletcher and Brantley (2010) in an analogous but less generalized model, if the rate of erosion is small, blocks will never become exposed at the surface. Instead, they weather completely at some depth because the upward moving blocks spend enough time in the weathering regime to weather to saprolite completely. Extending our terminology for a homogeneous column of unfractured rock (Lebedeva *et al.*, 2010), we call such a profile ‘completely developed’ and such a regime ‘erosional transport-limited’. Figure 9 shows the distribution of block sizes with elevation at a ridge top for the system presented in Figure 1. Calculations are performed for the homogenized system (Equations (11)–(13)):

Figure 9. Distribution of block size for regimes that are erosional transport-limited (curve 1) and erosional weathering-limited (curve 2). Calculations are performed for the averaged model (Equations (11) and (12)) describing the weathering profile depicted in Figure 1. The dimensionless elevation $y=1$ corresponds with the air-regolith (land) surface. The bottom of the profile corresponds with the elevation $y=0$. Unidirectional vertical advection with a Darcy velocity equal to 0.025 m/yr is modeled. The transport-limited regime is obtained at an erosion rate of $3 \times 10^{-6}\text{ m/yr}$. At the surface, no blocks are exhumed because they completely weather during their transit through the weathering zone (as observed for weathering volcaniclastic rocks in the Luquillo Mountains of Puerto Rico (Fletcher and Brantley, 2010)). In contrast, at an erosion rate equal to $2.4 \times 10^{-5}\text{ m/yr}$, blocks are exhumed at the land surface (as observed for weathering metavolcaniclastic rocks in the Luquillo Mountains of Puerto Rico [Orlando, 2014]). Data for the former system are not shown but for the latter system are shown in Figure 10. Unlike Figure 10, calculations presented in this figure are illustrative and do not take into account the observed length of the profile and sizes of blocks.

the block size is calculated using Equation (19) where the dimensionless value of the original block size is equal to 0.04 ($\ell=0.25$) and the initial volume fraction of weathered material in the rock, ϕ_F (see Equation (15)), is equal to 0.36. For the erosional transport-limited regime, the block size distribution is shown by curve 1. No weathered blocks are present at the air-regolith interface, while at the elevation $y=0$, i.e. at the bottom, the size of the blocks is dictated by fracture spacing.

When the erosion rate increases, eventually blocks of diminished size reach the surface – indicating the column-scale extent of reaction is larger than zero but less than one. Note that because the reaction front is thin, the reduced blocks that emerge at the surface are entirely unweathered – the column-scale extent of reaction is actually the volume fraction of weathered material in a ratio to the original material in each cell, i.e. $\eta_0 = (|\Omega| - |\Omega_{UWL}|)/|\Omega|$ as follows from Equation (18). The average value of this extent is constant in time. For example, curve 2 in Figure 9 depicts the distribution of block size in this erosional weathering-limited regime. In this case, the blocks that emerge at the land surface are only on average about half the original block size defined by fracture spacing.

The block size distribution data from Fletcher and Brantley (2010) are good examples of this type of system. In that example of a volcaniclastic sedimentary rock weathering in the Luquillo Mountains in the rain forest of Puerto Rico, the distribution of blocks versus elevation in the weathering column showed evidence for diffusion-limited weathering (and a very thin reaction front around each block) and decreasing block size as a function of elevation in the weathering column (Fletcher and Brantley, 2010). In that system, the block size decreased to zero at the top of the column under the hillcrest and the upper part of the column was filled with weathered material, i.e. a completely developed profile describing an erosive transport-limited regime.

We do not show fits to the data already described by Fletcher and Brantley (2010). Instead, we present another dataset for a similar system from the same rainforest, albeit at higher elevation (Figure 10). In this case, the rock type is much more resistant to erosion and thus defines the ridges of the mountains. The lithology is the same rock as described by Fletcher and Brantley (2010) except that it was metamorphosed to hornfels-facies, i.e. the rock is characterized by an even lower porosity and a metamorphic mineral assemblage. Like the volcaniclastic rocks described by Fletcher and Brantley (2010), the hornfels forms angular blocks and weathers to form thin weathering rinds that slough off as described by Buss *et al.* (2013). Block sizes were measured in the same way they were measured by Fletcher and Brantley (2010), i.e. by measuring blocks exposed at the land surface along a hillslope (Orlando, 2014) (Figure 10). According to previously reported data (Orlando, 2014), we estimated the size of the periodic cell and set it equal to $\ell = 114.6\text{ cm}$. The corresponding value of the fracture aperture was set to 10^{-3} m (Klimczak *et al.*, 2010). Taking into account the range of erosion rates estimated previously (Fletcher and Brantley, 2010) and personal unpublished communication (S. Hynek, 2016) we analyzed the weathering profile observed by Orlando (2014) at the erosion rates, E , from the interval $1.7\text{--}4 \times 10^{-6}\text{ m/yr}$. Finally, to model albite dissolution we used parameters obtained previously in our work (Lebedeva *et al.*, 2007). Thus, we solved the model Equations (11) and (12) at the erosion rates from the estimated interval and the ratio $(C^e/Q^0) = 5 \times 10^{-5}$ and sought values for the remaining parameters to fit our observation of a steady-state weathering column of length 134 m and a block size distribution as

Figure 10. Block size measured on volcanoclastic sedimentary rocks metamorphosed to hornfels facies and exhumed in the Luquillo Mountains of Puerto Rico (Orlando, 2014). At every elevation, the three cross-sectional dimensions of the five largest exposed blocks were measured and the average dimension was calculated as described previously (Fletcher and Brantley, 2010). This hornfels lithology is the ridge-forming unit of the mountains: angular hornfels corestones are exposed at all elevations along ridges. The hornfels is a metamorphic aureole around a quartz diorite pluton. The contact occurs at approximately 747 m above sea level (a.s.l.). Exhumation of unweathered blocks at the land surface is evidence that weathering is occurring in the weathering-limited regime as described in the text. To check reproducibility, various investigators repeated the measurements up and down the elevation transect and data are shown as different colors with numbers. The solid curve presents the solution of the model Equations (11), (12), and (19). The latter was modified for three dimensions so that the block size was calculated from the equation $\delta = \ell \sqrt[3]{1 - \eta_0}$. Values of the parameters were varied to produce the curve: $E = 3 \times 10^{-6}$ m/yr, $(C^0/Q^0) = 5 \times 10^{-5}$, $\phi_{ab}^0 = 0.4$, and the vertical Darcy velocity $v = 0.06$ m/yr. The dissolution rate constant was chosen as the effective kinetic constant $k = 1.8 \times 10^{-10}$ 1/s for albite dissolution ($k_{ab} = 5.4 \times 10^{-13}$ mol/m² s, $s_{ab} = 3.5 \times 10^4$ m²/m³, $\Psi = 0.012$ m³/mol). The size of the periodic cell is equal to $\ell = 114.6$ cm, and the fracture aperture is equal to 0.1 cm. The fact that the fit estimate of the infiltration rate in these mountains (0.06 m/yr) is much lower than the mean annual precipitation at the mountain top (> 4 m/yr) is consistent with very little infiltration reaching this relatively unfractured bedrock in the subsurface. Note that a few outlier measurements were ignored in the fit. [Colour figure can be viewed at [wileyonlinelibrary.com](#)]

observed (Orlando, 2014). With this fit we obtained at the erosion rate $E = 3 \times 10^{-6}$ m/yr a weathering-limited regime using a vertical Darcy velocity for infiltrating water of 0.06 m/yr and an effective weathering constant of $k = 1.8 \times 10^{-10}$ 1/s (see the figure caption). This successful use of the model to understand an observed size distribution of exposed blocks suggests that measurement of block sizes exposed at ridgelines could be useful in understanding such weathering systems.

Simulation of a hillslope

We also consider weathering of a hillside consisting of joint-bounded blocks, as shown in Figure 11. Here we consider a dynamical steady-state hill where the hill lowers due to erosion but the regolith thickness is maintained constant in time. We consider a pre-existing jointed rock structure, i.e. the rock is previously jointed at all depths with constant joint spacing. Alternately, new joints of the same aperture and spacing could

Figure 11. Model simulations depicting a hillslope weathering under a constant erosion rate $E = 2 \times 10^{-5}$ m/yr: (a) mineral concentrations are depicted where green represents unweathered material and the orange domain represents completely weathered material; (b) concentration of the Na_2Si component dissolved in the porefluid where blue corresponds to the concentration at the air-regolith surface and red corresponds to the concentration at chemical equilibrium; (c) same as (a) except for the model uses an advection velocity and kinetic constant less than those used to calculate (a) and (b). In (a) and (b) no blocks are exhumed at the land surface and the system is therefore operating in the erosive transport-limited regime. In (c), blocks are present at the regolith surface and the system is therefore best described as operating in the weathering-limited regime. Black square contours show the original location of blocks. In the moving system of coordinates, the hillslope does not move while the bedrock and blocks move toward the surface at a constant erosion rate. The model simulation is set up with joint spacing everywhere held constant: as discussed in the text, this could be because of pre-existing conditions or because fractures form at constant spacing during weathering. The parameters are: $(C^0/Q^0) = 5 \times 10^{-5}$, $D = 0.8 \times 10^{-9}$ m²/s, $\phi_{ab}^0 = 0.4$, $s_{ab} = 3.5 \times 10^4$ m²/m³, $\Psi = 0.012$ m³/mol, $\phi_F = 0.36$, $\ell = 2$ m, $L = 20$ m. For (a) and (b): $k = 6.5 \times 10^{-8}$ 1/s, $k_{ab} = 1.9 \times 10^{-10}$ mol/m² s, $v = 0.4$ m/yr; for (c): $k = 6.5 \times 10^{-9}$ 1/s, $k_{ab} = 1.9 \times 10^{-11}$ mol/m² s, $v = 0.2$ m/yr. [Colour figure can be viewed at [wileyonlinelibrary.com](#)]

be continuously forming at the bottom of the column. For the latter system, a feedback is needed to couple the fracturing, erosion, and weathering (Molnar *et al.*, 2007). For example, fracturing is likely to enhance erosion and be associated with

Figure 12. The calculated distribution of the average block size exposed at the ridge top of the hill in Figure 11 (black curve) and downslope (red curve). At the same depth (as measured normal to the slope) block size is larger downslope than at the ridge top. Curvature of the hillslope is also larger at the ridge top than downslope. Parameters are as in Figure 11 except for $E=0$, $k_{ab}=2.4 \times 10^{-12}$ mol/m²s, $v=0.01$ m/yr. [Colour figure can be viewed at wileyonlinelibrary.com]

steeper hillslopes with greater curvature. However, hillslope-derived blocks emerging onto the land surface could retard river incision and affect hillslope curvature (Shobe *et al.*, 2016). Similar to the simulation we presented previously for a homogeneous (non-jointed) hill where we observed that the weathering rate depends on hill curvature (Lebedeva and Brantley, 2013), we found that the block size depth distribution also depends on hill curvature (Figure 12). In addition, Figure 12 shows that the average size of blocks is greater along the hillslope than at the ridge top.

Although these models do not incorporate a mechanism for jointing, they do show that the block size distributions observed and described in the literature (Fletcher and Brantley, 2010) along hillslopes in the Bisley watershed of Puerto Rico may not have been formed in an earlier weathering regime, as described by the original authors, but could have formed in the hill itself during weathering and erosion. Note that in our model we considered initially identical blocks, i.e. all the blocks are the same at time=0 but Buss *et al.* (2013) observed that fracture spacing is larger under ridges than under valleys. This could mean that either fractures are more closely spaced *a priori* under valleys or that more dense fracturing occurs under valleys as compared to ridges during weathering and erosion.

Conclusions

We present a detailed numerical solution of a reactive-transport model of albite weathering within a regolith column and within a hill. We compare weathering in a homogeneous column to a column containing bedrock blocks embedded in inert material to understand the importance of fracture spacing in weathering systems. We document first that the distribution of block sizes depends on the direction of advection of porefluid and on the boundary conditions of porefluid chemistry. For example, blocks diminish in size upward toward the land surface or along a horizontal direction depending upon whether the flow regime is vertical or

horizontal, respectively. Second, we observed that weathering rounds the blocks but the rate of weathering advance into the blocks generally is slower than the rate of weathering advance in the whole column. The latter follows explicitly from the model because the extent of pre-weathering in the fractured parent material is not equal to zero in comparison with the unfractured material. In addition, the network of vertical and horizontal fractures leads to the increase in exposure of surface of low-porosity rock to reaction-transport processes. Here we assumed a constant unidirectional Darcy velocity in the fractured system. Our recent unpublished simulations with a variable in space and time Darcy velocity show that this assumption is reasonable under conditions near the ridge top. When both vertical and horizontal fractures are present, advective transport is not negligible and affects the weathering advance rate. So these systems differ from the systems with parallel fractures (only vertical or only horizontal) where advective transport is neglected within low-porosity rock.

These simulations were performed using a so-called 'meso-scale' model describing every part of the heterogeneous porous medium. Specifically, different properties of the weathering medium – within blocks and within joints – were taken into account. The meso-scale simulations require a very fine spatial mesh and are limited by small spatial domains. The macro-equations are obtained from the meso-scale equations via a homogenization method. The macro-scale equations (i) describe weathering within an averaged homogeneous porous medium and allow modeling of large domains; (ii) describe the block size distributions within the complex weathering domains; and (iii) document that the weathering advance rate increases when the volume fraction of bedrock blocks (the fracture spacing) decreases.

This model is a powerful new tool to understand scaling relationships in weathering systems and to understand the relationship between weathering and erosion. In a weathering hillside experiencing a constant erosion rate, for example, the weathering can attain a steady state if the joint spacing is constant with depth or if joints continuously form at constant spacing at the regolith-bedrock boundary by a mechanism that shows a feedback with weathering or erosion. In the erosional transport-limited regime, bedrock blocks are never exhumed at the air-regolith boundary because they completely weather as they transit through the weathering zone. In the erosional weathering-limited regime, blocks of various sizes can be exhumed at the land surface. At a constant erosion rate, the average size of blocks at the surface remains constant in time, and will increase with increasing erosion rate. For convex hillslopes, block size on the surface increases downslope due to the effect of curvature as described previously (Lebedeva and Brantley, 2013). We present examples of these end members from the Luquillo Mountains in Puerto Rico: volcanoclastic rocks weather in the erosive transport-limited regime while these same rocks metamorphosed to hornfels facies mineral assemblages with lower fracture densities weather in the weathering-limited regime.

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Appendix A: Application of the Homogenization Method to the Meso-scale Model

We briefly outline here the homogenization method for the meso-scale model (Equations (2) and (3)). More details and aspects of this method for different models are described in the literature (see, for example, Hornung, 1997). For mathematical reason, we rewrite Equations (2) and (3) in the form:

$$\frac{\partial(\phi^{(k)} C_k)}{\partial t} = \frac{\partial}{\partial x_i} \left(D_k \phi^{(k)} \frac{\partial C_k}{\partial x_i} \right) - \frac{\partial(C_k v_{ki})}{\partial x_i} + j^{(k)} \quad (A1)$$

$$\frac{\partial \eta^{(k)}}{\partial t} = \frac{j^{(k)}}{Q_k^0} \quad (A2)$$

where index $k=1, 2$ denotes the domains of the periodic cells (Figure 1): $k=1$ denotes a weathering block with an initial area (volume) $|\Omega_B|$ and $k=2$ relates to the domain which is filled by inert material with an initial area $|\Omega_F|$. The total volume of the cell is equal to

$$|\Omega| = |\Omega_B| + |\Omega_F| \quad (A3)$$

Here we denote the spatial variables (x, y) as (x_1, x_2) and the components of advective velocity (u, v) as (v_1, v_2) . This notation allows us to simplify the mathematical presentation

$$\begin{aligned} \frac{\partial(\phi_{k0} C_{k0} + \varepsilon \phi_{k1} C_{k1} + \varepsilon^2 \phi_{k2} C_{k2} + \dots)}{\partial t} &= \frac{\partial}{\partial x_i} \left(D(\phi_{k0} + \varepsilon \phi_{k1} + \dots) \frac{\partial(C_{k0} + \varepsilon C_{k1} + \dots)}{\partial x_i} \right) + \\ &\frac{1}{\varepsilon} \left[\frac{\partial}{\partial \xi_i} \left(D(\phi_{k0} + \varepsilon \phi_{k1} + \dots) \frac{\partial(C_{k0} + \varepsilon C_{k1} + \dots)}{\partial x_i} \right) + \frac{\partial}{\partial x_i} \left(D(\phi_{k0} + \varepsilon \phi_{k1} + \dots) \frac{\partial(C_{k0} + \varepsilon C_{k1} + \dots)}{\partial \xi_i} \right) \right] + \\ &\frac{1}{\varepsilon^2} \frac{\partial}{\partial \xi_i} \left(D(\phi_{k0} + \varepsilon \phi_{k1} + \dots) \frac{\partial(C_{k0} + \varepsilon C_{k1} + \dots)}{\partial \xi_i} \right) - v_i \frac{\partial(C_{k0} + \varepsilon C_{k1} + \dots)}{\partial x_i} - \frac{v_i}{\varepsilon} \frac{\partial(C_{k0} + \varepsilon C_{k1} + \dots)}{\partial \xi_i} + \\ &j_{k0} + \varepsilon j_{k1} + \dots \end{aligned} \quad (A10)$$

using a common convention: if the summation over several repeated indices is from 1 to n , the summation sign can be omitted.

Porosity is calculated according to Equation (9):

$$\phi^{(k)} = \phi_{init,k} + a_k \eta^{(k)} \quad (A4)$$

$$n_i \left(D_1 \phi^{(1)} \frac{\partial C_1}{\partial x_i} - v_{1i} C_1 \right) \Big|_{\Gamma} = n_i \left(D_2 \phi^{(2)} \frac{\partial C_2}{\partial x_i} - v_{2i} C_2 \right) \Big|_{\Gamma} \quad (A6)$$

$$\bar{n} \cdot \bar{v}_1 \Big|_{\Gamma} = \bar{n} \cdot \bar{v}_2 \Big|_{\Gamma} \quad (A7)$$

where $\bar{n} = (n_1, n_2)$ is the unit outward vector normal to the boundary. In our treatment we consider only unidirectional advection so we assume that either $v_{11} = v_{21} = v_1$, $v_{21} = v_{22} = 0$ or $v_{11} = v_{21} = 0$, $v_{21} = v_{22} = v_2$. We also assume that $D_1 = D_2 = D$, $Q_1^0 = Q_2^0 = Q^0$, $a_1 = a_2 = a$.

We introduce the mesoscopic (fast) variables $\xi = (\xi_1, \xi_2)$:

$$\xi_i = \frac{x_i}{\varepsilon}, \quad \varepsilon = \frac{\ell}{L}, \quad i = 1, 2 \quad (A8)$$

and seek a solution for the Equation (A1), (A2), and (A4)–(A6), i.e. the functions $C_k(x, \xi, t)$, $\eta^{(k)}(x, \xi, t)$ in the form of Equation (10). We assume that these functions are ℓ -periodic, i.e. for example, $C_k(x, \xi, t) = C_k(x, \xi + \ell, t)$. We substitute the sums of Equation (10) into Equations (A1), (A2), and (A4)–(A6), and apply the chain rule

$$\frac{dF(x, \frac{x}{\varepsilon})}{dx_i} = \left(\frac{\partial F}{\partial x_i} + \frac{1}{\varepsilon} \frac{\partial F(x, \xi)}{\partial \xi_i} \right) \Big|_{\xi=\frac{x}{\varepsilon}} \quad (A9)$$

As a result we have

$$\frac{\partial(\eta_{k0} + \varepsilon \eta_{k1} + \dots)}{\partial t} = \frac{j_{k0} + \varepsilon j_{k1} + \dots}{Q^0} \quad (A11)$$

$$(C_{10} + \varepsilon C_{11} + \dots) \Big|_{\Gamma} = (C_{20} + \varepsilon C_{21} + \dots) \Big|_{\Gamma} \quad (A12)$$

$$\begin{aligned} n_i \left(D(\phi_{10} + \varepsilon \phi_{11} + \dots) \left(\frac{\partial(C_{10} + \varepsilon C_{11} + \dots)}{\partial x_i} + \frac{1}{\varepsilon} \frac{\partial(C_{10} + \varepsilon C_{11} + \dots)}{\partial \xi_i} \right) - v_{1i}(C_{10} + \varepsilon C_{11} + \dots) \right) \Big|_{\Gamma} \\ = n_i \left(D(\phi_{20} + \varepsilon \phi_{21} + \dots) \left(\frac{\partial(C_{20} + \varepsilon C_{21} + \dots)}{\partial x_i} + \frac{1}{\varepsilon} \frac{\partial(C_{20} + \varepsilon C_{21} + \dots)}{\partial \xi_i} \right) - v_{1i}(C_{20} + \varepsilon C_{21} + \dots) \right) \Big|_{\Gamma} \end{aligned} \quad (A13)$$

where $a_k = \text{constant}$. The boundary conditions describing the boundary between blocks and inert material, Γ , (the sides of the squares in Figure 1) are as follows:

$$C_1 \Big|_{\Gamma} = C_2 \Big|_{\Gamma} \quad (A5)$$

We equate the terms of orders ε^{-2} , ε^{-1} , ε^0 , ... to zero and obtain the problems to determine the functions C_{k0} , η_{k0} , C_{k1} , η_{k1} , ... Thus, first we have the problem:

$$\frac{\partial}{\partial \xi_i} \left(D \phi_{k0} \frac{\partial C_{k0}}{\partial \xi_i} \right) = 0 \quad (A14)$$

$$\frac{\partial \eta_{k0}}{\partial t} = \frac{j_{k0}}{Q^0} = \frac{k(1 - \eta_{k0})(C^e - c_{k0})}{Q^0} \quad (A15)$$

$$c_{10}|_{\Gamma} = c_{20}|_{\Gamma} \quad (A16)$$

$$n_i D \phi_{10} \frac{\partial c_{10}}{\partial \xi_i} \Big|_{\Gamma} = n_i D \phi_{20} \frac{\partial c_{20}}{\partial \xi_i} \Big|_{\Gamma} \quad (A17)$$

It follows from Equations (A14)–(A17) that the function c_{k0} does not depend on the fast variables ξ :

$$c_{10}(x, t) = c_{20}(x, t) = c_0(x, t) \quad (A18)$$

Using Equation (A15) and taking into account Equation (A18) we obtain Equation (12) for the averaged extent of reaction η_0 defined by Equation (14). Equation for the averaged porosity ϕ_0 follows from Equation (A4):

$$\begin{aligned} \phi_0(x, t) &= \frac{1}{|\Omega|} \left(\int_{\Omega_B} \phi_{10}(x, \xi, t) d\Omega + \int_{\Omega_F} \phi_{20}(x, \xi, t) d\Omega \right) \\ &= \phi_{init0} + a\eta_0(x, t) \end{aligned} \quad (19)$$

where

$$\phi_{init0} = \frac{1}{|\Omega|} \int_{\Omega} \phi_{init}(\xi) d\Omega, \quad \eta_0(x, t) = \frac{1}{|\Omega|} \left(\int_{\Omega_B} \eta_{10}(x, \xi, t) d\Omega + \int_{\Omega_F} \eta_{20}(x, \xi, t) d\Omega \right).$$

Taking into account Equations (A18) and (A19), we obtain the problem for the function $c_{k1}(x, \xi, t)$ from Equations (A10), (A12), and (A13):

$$\frac{\partial}{\partial \xi_i} \left(D \phi_{k0} \frac{\partial c_{k1}}{\partial \xi_i} \right) = - \frac{\partial}{\partial \xi_i} \left(D \phi_{k0} \frac{\partial c_0}{\partial \xi_i} \right) \quad (A20)$$

$$c_{11}|_{\Gamma} = c_{21}|_{\Gamma} \quad (A21)$$

$$\begin{aligned} n_i \left(D \phi_{10} \left(\frac{\partial c_0}{\partial x_i} + \frac{\partial c_{11}}{\partial \xi_i} \right) - v_i c_0 \right) \Big|_{\Gamma} \\ = n_i \left(D \phi_{20} \left(\frac{\partial c_0}{\partial x_i} + \frac{\partial c_{21}}{\partial \xi_i} \right) - v_i c_0 \right) \Big|_{\Gamma} \end{aligned} \quad (A22)$$

We seek the solution of Equations (A20)–(A22) in the form:

$$c_{k1} = \chi_k^1 \frac{\partial c_0}{\partial x_1} + \chi_k^2 \frac{\partial c_0}{\partial x_2} \quad (A23)$$

where χ_k^i is some auxiliary function. Substituting Equation (A23) into Equations (A20), (A21), and (A22) we obtain equations for this function:

$$\frac{\partial}{\partial \xi_i} \left(D \phi_{k0} \frac{\partial \chi_k^j}{\partial \xi_i} \right) = - \frac{\partial}{\partial \xi_j} (D \phi_{k0}) \quad (A24)$$

$$\chi_1^j \Big|_{\Gamma} = \chi_2^j \Big|_{\Gamma} \quad (A25)$$

$$n_i \left(D \phi_{10} \frac{\partial \chi_1^j}{\partial \xi_i} - D \phi_{20} \frac{\partial \chi_2^j}{\partial \xi_i} \right) \Big|_{\Gamma} = n_j (D(\phi_{20} - \phi_{10})) \Big|_{\Gamma} \quad (A26)$$

At the next order ε^0 we obtain from Equation (A10) the problem for c_{k2} :

$$\begin{aligned} \frac{\partial (\phi_{k0} c_0)}{\partial t} &= \frac{\partial}{\partial x_i} \left(D \phi_{k0} \frac{\partial c_0}{\partial x_i} \right) + \frac{\partial}{\partial \xi_i} \left(D \phi_{k0} \frac{\partial c_{k1}}{\partial x_i} + D \phi_{k1} \frac{\partial c_0}{\partial x_i} \right) + \\ &\frac{\partial}{\partial x_i} \left(D \phi_{k0} \frac{\partial c_{k1}}{\partial \xi_i} \right) + \frac{\partial}{\partial \xi_i} \left(D \phi_{k0} \frac{\partial c_{k2}}{\partial \xi_i} + D \phi_{k1} \frac{\partial c_{k1}}{\partial \xi_i} \right) - v_i \frac{\partial c_0}{\partial x_i} - \\ &v_i \frac{\partial c_{k1}}{\partial \xi_i} + j_{k0} \end{aligned} \quad (A27)$$

The boundary conditions follow from Equations (A12) and (A13):

$$c_{12}|_{\Gamma} = c_{22}|_{\Gamma} \quad (A28)$$

$$\begin{aligned} n_i \left(D \phi_{10} \left(\frac{\partial c_{11}}{\partial x_i} + \frac{\partial c_{12}}{\partial \xi_i} \right) + D \phi_{11} \left(\frac{\partial c_0}{\partial x_i} + \frac{\partial c_{11}}{\partial \xi_i} \right) - v_i c_{11} \right) \Big|_{\Gamma} = \\ n_i \left(D \phi_{20} \left(\frac{\partial c_{21}}{\partial x_i} + \frac{\partial c_{22}}{\partial \xi_i} \right) + D \phi_{21} \left(\frac{\partial c_0}{\partial x_i} + \frac{\partial c_{21}}{\partial \xi_i} \right) - v_i c_{21} \right) \Big|_{\Gamma} \end{aligned} \quad (A29)$$

We integrate Equation (A27) over the periodic cell Ω , use the divergence theorem, the periodicity, the boundary conditions of Equations (A28) and (A29), and expressions in Equation (A23) to obtain the averaged equation for the first term in Equation (10) c_0 :

$$\begin{aligned} \frac{\partial (\phi_0(x, t) c_0(x, t))}{\partial t} &= \frac{\partial}{\partial x_i} \left(D_{ij}^{eff}(x, t) \frac{\partial c_0(x, t)}{\partial x_j} - v_i c_0(x, t) \right) \\ &+ k(C^e - c_0(x, t))(1 - \eta_0(x, t)) \end{aligned} \quad (A30)$$

where D_{ij}^{eff} is the effective diffusivity determined by the solution of the Equations (A24)–(A26). The effective diffusion tensor is defined as follows

$$D_{ij}^{eff} = \frac{D}{|\Omega|} \sum_{k=1}^2 \int_{\Omega_k} \phi_{k0} \left(\delta_{ij} + \frac{\partial \chi_k^j}{\partial \xi_i} \right) d\Omega \quad (A31)$$

Here $\delta_{ij}=1$ at $i=j$ and $\delta_{ij}=0$ at $i \neq j$. As it follows from Equations (A4) and (A15) generally, the component of the diffusion tensor, D_{ij}^{eff} , depends on both macroscopic (x_1, x_2) and mesoscopic (ξ_1, ξ_2) variables. So the averaged system of Equations (11), (12), and (A15) is a coupled system of the global Equations (11) and (12) for the global variables $c_0(x, t)$, $\eta_0(x, t)$ and the local Equation (A15) for the local variable $\eta_{k0}(x, \xi, t)$. To calculate the effective diffusivity in Equation (11) we need to solve Equation (A15) and the problem described in Equations (A24)–(A26) whereas the solution of the local Equation (A15) depends on the global variable $c_0(x, t)$. This problem can be essentially simplified if we assume that the transition zone between weathered and unweathered parts of a block is narrow, as expected in the local-equilibrium regime. Then taking into account that $\eta_{10}=0$ within the unweathered part and $\eta_{10}=\eta_{20}=1$ within the weathered part of the block and the joint, we obtain from Equations (A24)–(A26) the

components of the effective diffusion tensor: $D_{12}^{eff} = D_{21}^{eff} = 0$, $D_{11}^{eff} = D_{22}^{eff} = D\phi_0 = D(\phi_{init} + a\eta_0)$.

Note that the error of approximation depends not only on ε but also on other parameters of the problem of interest. For example, the comparison of the original and averaged solutions for the problem of thermal conductivity described by (Bakhvalov and Panasenko, 1989) shows that for some values of the parameter, say p -parameter, describing the property of a composite medium, the relative error of approximation varies from 0.1 at $\varepsilon = 0.5$ to 0.028 at $\varepsilon = 0.125$. So if from the practical point of view, the error 0.1 is acceptable, then the medium with $\varepsilon = 0.5$ is homogenizable. But when this p -parameter decreases and becomes about a thousand times smaller, the error increases, and it becomes equal to 0.56 at $\varepsilon = 0.5$ and 0.049 at $\varepsilon = 0.125$.

Thus, the limits of application of the method of homogenization are determined by the order of error in a particular approximation.

Also there is a mathematical reason for a non-homogenizable situation. It is connected with solvability of the auxiliary problems. These problems determine effective parameters. It could happen that at some values of parameters these problems do not have a solution. For example, such a situation arises in the problem of homogenization of the reactive transport equations on the micro scale at some values of kinetic and transport parameters.

The auxiliary problems considered in Appendix A are solvable.

Appendix B: Weathering Advance Rate According to the Meso-scale Model

We describe briefly the derivation of the expression for the front velocity in the case of unidirectional advection such as, for example, vertical advection (Ortoleva *et al.*, 1987). To do this, we consider the 1D version of Equations (2) and (3) with the advection term $\partial(Cv/\partial y)$ which we take with positive sign because we consider the vertical axis y values to increase in this example toward the air–soil interface. We are seeking a constant front velocity ω in the moving system of coordinates

$$z = y + \omega t \quad (B1)$$

$$t_1 = t \quad (B2)$$

In the new system of coordinates the Equations (2) and (3) take the forms

$$\frac{\partial(\phi C)}{\partial t_1} + \omega \frac{\partial(\phi C)}{\partial z} = \frac{\partial}{\partial z} \left(D\phi \frac{\partial C}{\partial z} \right) + \frac{\partial(Cv)}{\partial z} + j \quad (B3)$$

$$\frac{\partial \eta}{\partial t_1} + \omega \frac{\partial \eta}{\partial z} = \frac{j}{Q^0} \quad (B4)$$

In the steady state $(\partial(\phi C)/\partial t_1) = 0$ and $(\partial \eta/\partial t_1) = 0$. We multiply Equation (B4) by Q^0 and subtract it from Equation (B3):

$$\omega \frac{d(\phi C - \eta Q^0)}{dz} = \frac{d}{dz} \left(D\phi \frac{\partial C}{\partial z} \right) + \frac{d(Cv)}{dz} \quad (B5)$$

We assume that the reaction front is far enough from the inlet at the land surface boundary so that we can neglect the derivative (dC/dz) at $z \rightarrow \infty$, i.e. at the surface, and suppose that far ahead of the front, i.e. at $z \rightarrow -\infty$, a zero flux boundary condition, $-D\phi(\partial C/\partial z) = 0$ can be assumed. Then by integrating Equation (B5) over the axis z we can obtain:

$$\omega(\phi^R C^R - Q^0 - \phi_{init} C^e + Q^0 \eta_{init}) = v(C^R - C^e) \quad (B6)$$

Here ϕ^R is porosity at the inlet of the system, ϕ_{init} and η_{init} are porosity and the extent of reaction at $z \rightarrow -\infty$. Therefore, the advance rate of the reaction front is calculated as follows

$$\omega = \frac{v(C^e - C^R)}{\phi_{init} C^e - \phi^R C^R + Q^0(1 - \eta_{init})} \approx \frac{v(C^e - C^R)}{Q^0(1 - \eta_{init})} \quad (B7)$$

The approximation holds when $|\phi_{init} C^e - \phi^R C^R| \ll Q^0(1 - \eta_{init})$. The latter condition is satisfied well enough for processes of mineral alteration.

Note that the front velocity, ω , does not depend on the parameter D . So the presence of dispersion affects only the value D in Equation (B3) and does not change the front velocity if the conditions of derivation of Equation (B7) hold.

List of Variables

A_{ext}	surface area due to the topography of grain surfaces (m ²)
A_{geom}	surface area determined by geometric calculations (m ²)
A_{pore}	surface area due to internal porosity (m ²)
a_k	constant in Equation (A4)
C	concentration of component NaSi ₂ in porefluid (mol/m ³)
C_i	concentration of aqueous species i (mol/kg)
C_k	concentration of component NaSi ₂ in porefluid in domain Ω_k ($k=1$ for block, $k=2$ for fracture) (mol/m ³)
C^e	concentration of component NaSi ₂ in porefluid in equilibrium (mol/m ³)
C^R	concentration of component NaSi ₂ in porefluid at the air–regolith boundary (mol/m ³)
C_{block}^R	concentration of component NaSi ₂ in porefluid at the block–fracture boundary (mol/m ³)
$c_0, c_1, c_2, \dots$	coefficients in formal asymptotic solution $C \sim \sum_{i=0}^{\infty} \varepsilon^i c_i$; c_0 is the averaged macroscopic concentration
$c_{k0}, c_{k1}, c_{k2}, \dots$	coefficients in formal asymptotic solution in domain Ω_k
D	diffusion coefficient for solutes in the aqueous pore solution (m ² /s)
D_k	effective mesoscopic diffusion coefficient for solutes in the aqueous solution in domain Ω_k ($k=1$ for block, $k=2$ for fracture) (m ² /s)
D^{eff}	macroscopic effective diffusion coefficient (m ² /s)
D_{ij}^{eff}	component of the macroscopic effective diffusion tensor (m ² /s)
d	fracture aperture (m)
E	erosion rate (m/yr)
j, j_i	rate of the reaction (mol/m ³ s)
$j^{(k)}$	rate of the reaction in domain Ω_k (mol/m ³ s)
j_{ki}	coefficient in the formal asymptotic expansion of the function $j^{(k)} \sim \sum_{i=0}^{\infty} \varepsilon^i j_{ki}$ in domain Ω_k
K	curvature

K_1, K_2	constants determining the lower and upper boundaries of the function j_i	ϕ_{ab}	volume fraction of albite in the weathering material
K_{ab}	equilibrium constant for albite dissolution	ϕ_{ab}^0	initial volume fraction of albite
k	effective rate constant (1/s)	ϕ_B	volume fraction of blocks in the parent material
k_{ab}	dissolution rate constant for albite (mol/m ² s)	ϕ_F	volume fraction of fractures in the parent material
L	characteristic macroscopic length (m)	ϕ_{in}	volume fraction of the inert material
ℓ	characteristic mesoscopic length, length of the elementary cell (m)	ϕ_{init}	initial porosity on the mesoscopic level
$\mathbf{n} = (n_1, n_2)$	normal vector on the block-fracture interface directed out of Ω_B	ϕ_{init0}	initial porosity on the macroscopic level
Q	concentration of albite in the weathering material (mol/m ³)	$\phi_{init, k}$	initial porosity on the mesoscopic level in the domain Ω_k
Q^0, Q_{ab}^0	concentration of albite in bedrock (mol/m ³)	$\phi^{(k)}$	porosity on the mesoscopic level in the domain Ω_k
Q_k^0	initial concentration of albite in domain Ω_k (mol/m ³)	$\phi_{k0}, \phi_{k1}, \phi_{k2}, \dots$	coefficients in formal asymptotic solution in domain Ω_k
Q_{kao}	concentration of kaolinite in the weathering material (mol/m ³)	ϕ_{kao}	volume fraction of kaolinite
s	mineral surface area (m ²)	ϕ^R	porosity at the air-regolith boundary
s_{ab}	specific surface area of albite (1/m)	χ_k^i	solution of the cell problem (Equations (A24)–(A26))
t, t_1	time (s)	Ψ	correction factor for the effective rate constant in Equation (5) (m ³ /mol)
u	horizontal component of the Darcy velocity of a porefluid (m/s)	$ \Omega $	volume of the elementary cell ($m^p, p=2, 3$)
$\bar{V}_{ab}^0$	specific volume of albite (m ³ /mol)	$ \Omega_B $	initial volume of the unweathered block in the cell ($m^p, p=2, 3$)
$\bar{V}_{kao}^0$	specific volume of kaolinite (m ³ /mol)	$ \Omega_{BW} $	volume of the weathered part of the block ($m^p, p=2, 3$)
v	vertical component of the Darcy velocity of a porefluid (m/s)	$ \Omega_{UW} $	volume of the unweathered part of the block ($m^p, p=2, 3$)
v_1, v_2	horizontal and vertical components of the Darcy velocity of a porefluid, respectively (m/s)	$ \Omega_F $	volume of the fracture (joint) in the cell ($m^p, p=2, 3$)
v_{k1}, v_{k2}	horizontal and vertical components of the Darcy velocity of a porefluid, respectively, in domain Ω_k (m/s)	ω	unidirectional weathering advance rate in a medium under consideration (m/s)
x, x_1	horizontal coordinate (m)	ω_0	unidirectional weathering advance rate in non-fractured media (m/s)
x_2	vertical coordinate (m)	ω_n	normal component of the velocity of the curvilinear weathering front in a 2D model (m/s)
y	vertical coordinate (m)	ω_{pl}	normal component of the velocity of the planar weathering front in a 2D model (m/s)
z	vertical coordinate in the moving system of coordinates (m)	$\omega_{block}, \bar{\omega}_{block}$	dimensional and dimensionless weathering advance rate within a block, respectively
Γ	interface between fracture and block	$\omega_{col}, \bar{\omega}_{col}$	dimensional and dimensionless weathering advance rate within a column, respectively
δ	fracture spacing (m)		
δ_{ij}	Kronecker symbol		
ε	small length scale parameter		
$\zeta = \frac{\gamma}{\varepsilon}$	mesoscopic variable		
η	extent of reaction		
$\eta^{(k)}$	extent of reaction in domain Ω_k		
$\eta_0, \eta_1, \eta_2, \dots$	coefficients in formal asymptotic solution		
	$\eta \sim \sum_{i=0}^{\infty} \varepsilon^i \eta_i$; η_0 is the macroscopic averaged extent of reaction		
$\eta_{k0}, \eta_{k1}, \eta_{k2}, \dots$	coefficients in formal asymptotic solution in domain Ω_k		
η_{init}	initial value of extent of reaction for homogeneous media		
η_0, η_{init}	initial value of the averaged extent of reaction		
$\bar{\eta}$	extent of reaction in the weathered block applied to calculation of integral by mean value theorem		
λ	roughness		
$\zeta = \frac{x}{\varepsilon}$	mesoscopic variable		
$\zeta_1 = \frac{x_1}{\varepsilon}, \zeta_2 = \frac{x_2}{\varepsilon}$	mesoscopic variables		
τ	dimensionless time		
ϕ	porosity on the mesoscopic level		
ϕ_0	averaged macroscopic porosity		

List of Selected Equations

1. Length scale parameter

$$\varepsilon = \frac{\ell}{L}$$

2. Macroscopic extent of reaction

$$\eta_0(x, y, t) = \frac{1}{|\Omega|} \int_{\Omega} \eta(x, y, \zeta, \zeta) d\Omega = \frac{|\Omega| - |\Omega_{UW}|}{|\Omega|} \quad (14, 17)$$

3. Initial volume fractions of blocks and fractures

$$\phi_B = \frac{|\Omega_B|}{|\Omega|}, \quad \phi_F = \frac{|\Omega_F|}{|\Omega|}, \quad |\Omega| = |\Omega_B| + |\Omega_F| \quad (15, 16, A3)$$

4. Averaged macroscopic porosity

$$\phi_0 = \phi_{init0} + \eta_0 \phi_{ab}^0 \left(1 - 0.5 \left(\bar{V}_{kao}^0 / \bar{V}_{ab}^0 \right) \right) \quad (13)$$

$$\phi_{init0}(x, y, 0) = \frac{1}{|\Omega|} \int_{\Omega} \phi_{init}(x, y, \xi, \zeta, 0) d\Omega \quad (A19)$$

5. Dimensionless time

$$\tau = \frac{DC^e}{Q^0 L^2} t \quad (\text{Fig.7})$$

6. Unidirectional velocity of the weathering front in a fracture medium for completely developed weathering profile

$$\omega = \frac{v(C^e - C^R)}{Q^0} \cdot \frac{|\Omega_B|}{|\Omega|} \quad (23)$$

7. Dependence of the unidirectional velocity of the weathering front on fracture spacing

$$\omega = \omega_0 \left(1 + \frac{d}{\delta} \right)^p \quad (26)$$

p=2,3 for 2-D and 3-D model, respectively

8. Dependence of the normal velocity of the curvilinear weathering front on curvature for 2-D model

$$\omega_n = \omega_{pl} - D\phi \frac{C^e - C^R}{Q^0} K = \frac{(C^e - C^R)(v - D\phi K)}{Q^0} \quad (24)$$

9. Dimensionless front velocity

$$\varpi = \omega \frac{LQ^0}{DC^e} \quad (\text{Fig.8})$$

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