Reply to Comment on "A simple model for regolith formation by chemical weathering" by Braun et al. Contradictory concentrations and a tale of two velocities by Harman et al.

Jean Braun[1], François Guillocheau[2], and Cecile Robin[2]

[1]Helmholtz Centre Potsdam German Research Center for Geosciences (GFZ) Telegrafenberg, Potsdam, Germany, [2]Geosciences Rennes, Université de Rennes 1 CNRS, Rennes, France

Abstract The apparent contradiction evidenced by Harman et al. is, in our opinion, a consequence of them assuming that the concentration of the solute is at equilibrium value C_{eq}, an assumption that is not part of our model. We take this opportunity to more clearly demonstrate that under the assumptions the concentration of the solute is not at equilibrium, the rate of dissolution and consequently the rate of propagation of the weathering front are, to first order, proportional to the velocity of the fluid parallel to the weathering front and thus to the slope of the water table. The results we derive from this assumption are therefore valid.

Harman et al. suggest that our model leads to a contradiction because "The model is built on the assumption that the flow out of the weathering zone is everywhere C_{eq}" (lines 29–31 and 92–93). We do not make this assumption. In fact, our main assumption that the rate of propagation of the weathering front is controlled by the velocity of the fluid (and thus the geometry of the water table) is only valid if the concentration of the solute in the weathering zone is NOT at equilibrium. It is not because a system is transport limited that the solute concentration is at equilibrium. We briefly demonstrate this point below although we believe it is relatively well understood and used by many (including *Maher* [2010] which we refer to in our article) to demonstrate that dissolution rate along a weathering front is proportional to fluid velocity. Furthermore, assuming that the fluid in the weathering zone has not reached equilibrium is supported by many observations. Recent studies [*Godsey et al.*, 2009] have shown, for example, that for many rivers the concentration of solute produced by weathering varies by a factor of only 3 to 20, while discharge varies by several orders of magnitude. This chemostatic behavior is evidence that solute concentrations often do not reach equilibrium in natural systems and, consequently, that our assumption that the fluid velocity along the weathering front controls the rate of weathering front propagation is, to first order, appropriate to describe natural systems.

The concentration of solute, C, along the weathering front obeys the following equation (modified from *Maher* [2010]):

$$\frac{\partial C}{\partial t} + v\frac{\partial C}{\partial x} + w\frac{\partial C}{\partial z} = \frac{R}{\phi}\left(1 - \frac{C}{C_{eq}}\right), \tag{1}$$

where ϕ is porosity, v is the velocity along or within the weathering front (direction x), which we will assume here has a small but finite thickness δ, w is the velocity of the fluid across the upper boundary of the weathering front (direction z), i.e., coming from the regolith layer, and R is a constant that is proportional to the dissolution rate constant of the mineral. As done in *Maher* [2010], we neglect dispersion of the solute. Incompressibility implies that

$$\frac{\partial v}{\partial x} + \frac{\partial w}{\partial z} = 0. \tag{2}$$

Assuming that the concentration of solute is $C_0 < C_{eq}$ in the regolith, we can approximate the vertical gradient in solute across the weathering front by $(C_0 - C)/\delta$. Furthermore, assuming that any velocity gradient in a direction parallel to the front does not vary much with depth, we can write the following:

$$w = \int_0^\delta \frac{\partial u}{\partial x}\,dz \approx \delta\frac{\partial u}{\partial x}. \tag{3}$$
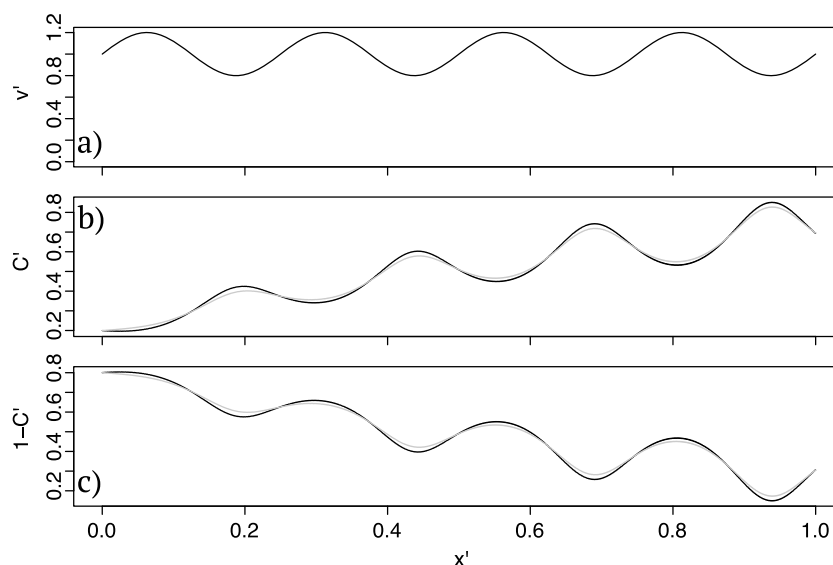
Figure 1. Numerical solution of equation (5). (a) Imposed normalized velocity field described by equation (7) where $\Delta = 0.2$ and $n = 4$; (b) normalized solute concentration; and (c) normalized dissolution rate. The black curves correspond to $C_0 = 0$ and the grey curve to $C_0 = 0.1$.

The resulting equation governing the steady state concentration of the solute along the weathering front is therefore

$$v\frac{\partial C}{\partial x} - \frac{\partial v}{\partial x}(C_0 - C) = \frac{R}{\phi}\left(1 - \frac{C}{C_{eq}}\right). \tag{4}$$

Here we will assume that C_0 is a constant although we recognize that it is likely to vary spatially but should remain smaller than the concentration in the weathering front. By introducing the length scale λ that characterizes any gradient in velocity (and in concentration as we will show later from the solution of this equation) in a direction parallel to the weathering front, we can write the following dimensionless form of the same equation:

$$v'\frac{\partial C'}{\partial x'} - \frac{\partial v'}{\partial x'}(C_0' - C') = \frac{R\lambda}{v_0 C_{eq}\phi}(1 - C') \tag{5}$$

where

$$x' = x/\lambda, C' = C/C_{eq}, v' = v/v_0. \tag{6}$$

The first term corresponds to the advection of solute by the flow, the second term to the dilution caused by recharge from the overlying regolith by a fluid of concentration C_0, and the third term to the dissolution along the weathering front. The ratio $R\lambda/v_0 C_{eq}\phi$ is dimensionless, and we will call it G. This derivation is similar to the one proposed by *Maher* [2010], although, in their study, they apply it to the vertical flow of the fluid through the weathering zone.

If the concentration in the weathering front is at or near equilibrium, the second term of this equation dominates and we are in a situation described by Harman et al. where recharge controls dissolution. If, however, the fluid is not at equilibrium, the first term dominates and the weathering rate is controlled by the fluid velocity. To further demonstrate this point, we will assume an arbitrary periodic velocity field superimposed on a background, constant value:

$$v'(x') = 1 + \Delta\sin(2n\pi x'/\lambda') \tag{7}$$

and solve equation (5) numerically (by finite difference) taking a value of $G = 10^{-3}$ that results in a mean concentration that is approximately half the equilibrium concentration and imposing $C'(x' = 0) = 0.2$. In this way, the mean concentration is not at equilibrium, but not radically far from it either. The solution is shown in Figure 1. We see that the periodic variation in velocity results in a variation in concentration and dissolution rate of similar relative amplitude ($\Delta = 20\%$ in the example shown in Figure 1). We note that the dissolution

rate is in phase with the velocity, i.e., higher velocity leads to enhanced dissolution rate, as expected in systems where the solute is not at equilibrium concentration. This result holds, regardless of the value of G, as long as the concentration of the solute remains below equilibrium. This demonstrates that under the assumption that solute concentration is not at equilibrium (but potentially not being far from it), the velocity of the fluid along the weathering front controls the local rate of dissolution. Note that we have assumed $C'_0 = 0$. The results are independent of the value of C_0 as long as C_0 is smaller than the concentration in the weathering front (the grey curves in Figure 1 correspond to $C_0 = 0.1$). This is likely to be the case under our assumption that most of the weathering takes place in the weathering front. There is also a quasi-monotonous increase in concentration along the profile that leads to a similar progressive decrease in dissolution. Both are related to the advection of solute dissolved upstream as argued by Harman et al.

It is easy to show (from the differential equation (5) or its numerical solution shown in Figure 1) that the constant of proportionality between the dimensionless rate of dissolution $1 − C'$ and the dimensionless velocity v' is G and, consequently, that the constant of proportionality between the dissolution rate and the velocity is $C_{eq}\phi/\lambda$. From this, we can derive the rate of propagation of the weathering front, w, following and using *Maher*'s [2010] notation, for example:

$$\frac{\partial M}{\partial t} = w\frac{\partial M}{\partial z},\tag{8}$$

where M is the change in volume fraction of the mineral due to chemical weathering. Introducing V_m, the molar volume of the mineral, we have

$$\frac{\partial M}{\partial t} = V_m R(1 − C/C_{eq}) \approx \frac{V_m C_{eq}\phi}{\lambda}v_0 \tag{9}$$

while

$$\frac{\partial M}{\partial z} \approx \frac{M_p}{\delta} \tag{10}$$

assuming that the mineral has been progressively and completely dissolved during the weathering process in the weathering front of thickness δ. This leads to

$$w = \frac{\partial B}{\partial t} \approx \frac{\delta}{\lambda}\frac{V_m C_{eq}\phi}{M_p}v_0 = \frac{\delta}{\lambda}\frac{V_m C_{eq}}{M_p}q_0, \tag{11}$$

where q_0 is the darcy velocity. The ratio of length scales δ/λ is difficult to estimate and we have assumed in our model that it is equal to unity to obtain equation (8). This ratio is likely to be smaller than unity and, possibly, by several orders of magnitude. In our model, this variability is implicitly included in the factor F that we also made proportional to the ratio of hydraulic conductivities between the weathering front and the regolith.

We acknowledge having been careless in using the term "velocity" where we should have used flow rate (velocity times porosity) in equations (9) and (10) of BMGR. As noted by Harman et al., this is of no consequence for our further derivations and results. We apologize also for the missing sign in the expression relating the velocity to the geometry of the water table. It is of no consequence for the rest of the paper as it is the amplitude of the velocity of the fluid that matters for the propagation of the weathering front, not its direction.

References

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