



Originally published as:

Bouchez, J., Gaillardet, J. (2014): How accurate are rivers as gauges of chemical denudation of the Earth surface? - *Geology*, 42, 2, 171-174

DOI: 10.1130/G34934.1

# How accurate are rivers as gauges of chemical denudation of the Earth surface?

Julien Bouchez<sup>1,2</sup> and Jérôme Gaillardet<sup>2</sup>

<sup>1</sup>GFZ German Research Centre for Geosciences, Helmholtz Centre Potsdam, Telegrafenberg, 14473 Potsdam, Germany

<sup>2</sup>Institut de Physique du Globe de Paris, Université Paris Diderot, Sorbonne Paris-Cité, 1 rue Jussieu, 75238 Paris cedex 05, France

## ABSTRACT

Examination of the behavior of oxygen and hydrogen during weathering reactions shows that river dissolved load, although widely used, is an imperfect tracer of chemical denudation. At the current state of knowledge, none of the metrics for river total dissolved loads (such as the silicate-derived total dissolved solids,  $TDS_{sil} = Ca^{2+} + Mg^{2+} + Na^+ + K^+ + SiO_2$ , converted or not to equivalent oxides) account, in a mechanistic manner, for the transfer of oxygen and hydrogen between the solid and fluid phase during weathering reactions. We assess that chemical denudation derived from  $TDS_{sil}$  will significantly overestimate the true chemical denudation for weathering of Ca-feldspar to kaolinite, whereas weathering of water-rich sedimentary rocks will be characterized by an underestimation of chemical denudation by  $TDS_{sil}$ . For a handful of field sites, we estimate that the bias is lower than  $\pm 10\%$ . The sign and extent of the bias depends on the nature of bedrock and on weathering conditions. Altogether, our analysis questions the broadly accepted concept of chemical denudation rate.

## INTRODUCTION

Chemical weathering is the major geological and geochemical process leading to mass transfer from the upper continental crust to the ocean. Chemical denudation of the Earth surface occurs through a global reaction involving elements present in rocks of the continental crust, and species from the atmosphere and hydrosphere. The water molecule and protons permit the hydrolysis of chemical bonds, which releases major rock constituents such as Si, Na, K, Mg, and Ca, and leads to the incorporation of hydrogen into secondary weathering products such as oxyhydroxides, amorphous aluminosilicates, and clay minerals. Protons provided by the dissociation of  $H_2CO_3$  (derived from  $CO_2$ ),  $H_2SO_4$ , HCl, or  $HNO_3$  are neutralized during release of major rock-forming base cations. Dioxide acts as the chief electron donor for oxidation of reduced elements present in rocks, such as Fe, Mn, and S. Therefore, not only does silicate weathering remove chemical elements from the continental crust, but also entails a two-way transfer of matter between the solid and the fluid components of the Earth surface. The influence of this two-way transfer on the quantification of chemical denudation has been hitherto completely overlooked, and deserves better scrutiny.

Weathering and erosion processes express themselves in the chemical composition of the so-called “Critical Zone” extending from the unweathered bedrock through soils to the atmosphere (Brantley and Lebedeva, 2011). At larger spatial scales, rivers are natural integrators of these weathering and erosion processes and fluxes over their drainage areas (Lyell, 1853). Clarke (1924) was the first to use river dissolved loads to appraise the rate of solute delivery from continents to oceans. Later, several authors refined these estimates (Livingstone, 1963; Holeman, 1968; Garrels and Mackenzie, 1972; Martin and Meybeck, 1979) and introduced a series of corrections to the river solute load to discard contributions of rainwater-derived solutes and anthropogenic and biogenic inputs.

Accordingly, more recent studies (e.g., Meybeck, 1987; Edmond et al., 1995; Gaillardet et al., 1999) argued that chemical denudation of the Earth surface can be quantified from river dissolved loads. For example, in the case of rivers draining exclusively silicate rocks, the chemical denudation rate,  $C$  (typically in  $kg\ m^{-2}\ y^{-1}$ , which can be converted to  $mm\ yr^{-1}$ ), would be:

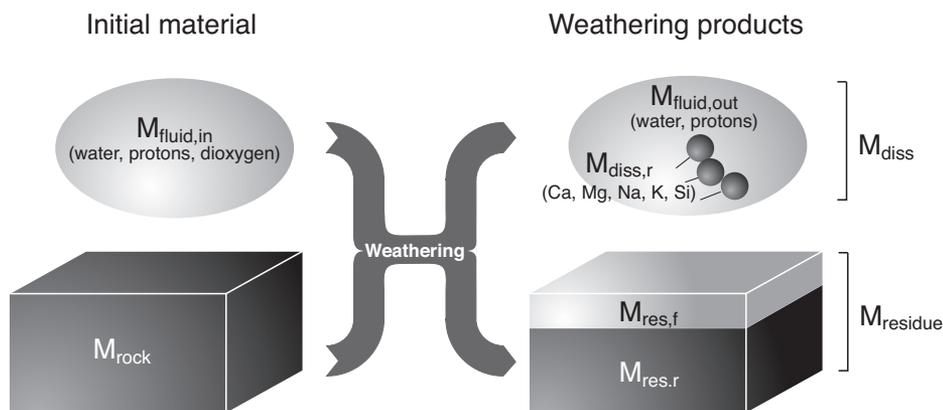
$$C = \frac{Q_{riv} \cdot TDS_{sil}}{A_{riv}} = \frac{Q_{riv}}{A_{riv}} \cdot \left( M_{Na} \cdot [Na^+]_{sil} + M_K \cdot [K^+]_{sil} + M_{Mg} \cdot [Mg^{2+}]_{sil} + M_{Ca} \cdot [Ca^{2+}]_{sil} + (M_{Si} + 2 \cdot M_O) \cdot [SiO_2] \right), \quad (1)$$

where  $Q_{riv}$  is the time-integrated water discharge of the river (in  $m^3\ y^{-1}$ ),  $A_{riv}$  is its drainage area (in  $m^2$ ), and  $TDS_{sil}$  quantifies the amount of total dissolved solids sourced from silicate rocks (in  $kg\ m^{-3}$ , or equivalently  $g\ L^{-1}$ ).  $TDS_{sil}$  is calculated from the silicate-derived dissolved major cation concentrations (called  $[X]_{sil}$ , with  $X = Na^+, K^+, Mg^{2+}$ , and  $Ca^{2+}$ ), and total concentration of  $SiO_2$ , which in general is derived only from silicate weathering. Concentrations (in  $mol\ L^{-1}$ ) are weighted by the molar mass of the corresponding compounds ( $M_X$ , in  $g\ mol^{-1}$ ). It is assumed here that the dissolved load of other elements such as Fe, Al, P, or Mn is too low to contribute significantly to  $TDS_{sil}$ . For a large river draining mixed lithologies, the contributions of different rock types have to be taken into account into the calculation of  $C$ . For rivers draining evaporites, anions released by rock weathering shall be accounted for, and in the case of rivers draining carbonate rocks, half the bicarbonate concentration has to be included in the definition of  $TDS$ , the other half being derived from the atmosphere. If only chemical denudation associated with silicate weathering is sought, and if sulfate derived from the oxidative weathering of pyrite can be neglected, these anion concentrations can be ignored in Equation 1, as bicarbonate is only derived from atmospheric and soil  $CO_2$ . Bearing in mind these additional complexities at the large river scale, here we focus primarily on chemical denudation associated with silicate weathering.

While  $C$  as defined in Equation 1 clearly quantifies the specific export of major dissolved species from the catchment, its broad acceptance as a measure of chemical denudation of continents is questionable. Indeed, the concept of chemical denudation suffers from the lack of a clear definition with respect to the fate of chemical elements supplied by the fluid phase during weathering reactions. We propose here that chemical denudation is defined as the net mass loss from crustal rocks as a result of chemical weathering reactions (Fig. 1). It is thus the net effect of (1) mass loss from the lithosphere by solubilization of chemical elements, and (2) mass gain by the solids through incorporation of chemical elements (oxygen and hydrogen) derived from the atmosphere and hydrosphere. As  $TDS_{sil}$  does not necessarily account for the transfer of oxygen and hydrogen between rocks and fluids, chemical denudation cannot be quantified accurately by Equation 1. To avoid confusion, we suggest that the flux of matter quantified by  $TDS_{sil}$  should be rather called the chemical weathering rate. In the present contribution, we set out to quantify the difference between chemical denudation and chemical weathering rates.

## MONOMINERALIC WEATHERING REACTIONS

In order to demonstrate that  $TDS_{sil}$  is not an accurate measure of chemical denudation, we first examine the transfer of chemical elements in a series of simple examples of weathering reactions affecting one single mineral (Table 1). All these reactions are independent of the acid species providing the protons, such as carbonic, sulfuric, or nitric acid. This simple approach helps in setting boundaries to the bias associated with  $TDS_{sil}$  as a measure of chemical denudation. For each of these reactions, we count the net release of oxygen ( $\Delta O$ ) and hydrogen ( $\Delta H$ ) from the solid phase during the weathering reaction, for each mole of initial mineral. For example, each mole of K-feldspar contains 8 atoms of oxygen and can be hydrolyzed to



**Figure 1.** Schematic representation of transfers of mass during weathering.  $M_{\text{rock}}$  is mass of initial rock affected by weathering. During weathering, chemical elements initially present in rock (Si, Ca, Mg, Na, and K, but also O and H) are partitioned between residual solid ( $M_{\text{res,r}}$ ) and dissolved phase ( $M_{\text{diss,r}}$ ). The residual product ( $M_{\text{residue}}$ ) is formed of  $M_{\text{res,r}}$ , but also of oxygen and hydrogen ( $M_{\text{res,f}}$ ) initially present in fluid phase ( $M_{\text{fluid,in}}$ ).

TABLE 1. SILICATE MINERAL WEATHERING REACTIONS

Equation	$O_{\text{TDS}}$	$\Delta O$	$\Delta H$	$TDS_{\text{sil}}$ ( $\text{g mol}^{-1}_{\text{min}}$ )	$\Phi$ (%)
(R1) $\text{KAlSi}_3\text{O}_8 + \text{H}^+ \rightarrow \frac{1}{2}\text{Al}_2\text{Si}_4\text{O}_{10}(\text{OH})_2 + \text{K}^+ + \text{SiO}_2$	2	+2	-1	99.2	1.0
(R2) $\text{KAlSi}_3\text{O}_8 + \frac{2}{3}\text{H}^+ \rightarrow \frac{1}{3}\text{KAl}_3\text{Si}_3\text{O}_{10}(\text{OH})_2 + \frac{2}{3}\text{K}^+ + 2\text{SiO}_2$	4	+4	-0.66	146.0	0.45
(R3) $\text{KAlSi}_3\text{O}_8 + \text{H}^+ + \frac{1}{2}\text{H}_2\text{O} \rightarrow \frac{1}{2}\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4 + \text{K}^+ + 2\text{SiO}_2$	4	+3.5	-2	159.3	6.3
(R4) $\text{KAlSi}_3\text{O}_8 + \text{H}^+ + \text{H}_2\text{O} \rightarrow \text{Al}(\text{OH})_3 + \text{K}^+ + 3\text{SiO}_2$	6	+5	-3	219.4	8.6
(R5) $\text{CaAl}_2\text{Si}_2\text{O}_8 + 2\text{H}^+ + \text{H}_2\text{O} \rightarrow \text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4 + \text{Ca}^{2+}$	0	-1	-4	40.1	49.9
(R6) $\text{Mg}_5\text{Al}_2\text{Si}_3\text{O}_{10}(\text{OH})_8 + 10\text{H}^+ \rightarrow \text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4 + 5\text{Mg}^{2+} + \text{SiO}_2 + 7\text{H}_2\text{O}$	2	+9	+4	181.6	-59.5
(R7) $\text{FeSiO}_3 + \frac{1}{6}\text{O}_2 \rightarrow \frac{1}{3}\text{Fe}_3\text{O}_4 + \text{SiO}_2$	2	+1.66	0	60.1	9.0

Note:  $O_{\text{TDS}}$ —oxygen atoms present in dissolved  $\text{SiO}_2$  released and hence “counted” by  $TDS_{\text{sil}}$  (in mole per mole of initial mineral weathered);  $\Delta O$  and  $\Delta H$ —oxygen and hydrogen transfers (in mole per mole of initial mineral weathered) between the fluid and the solid phase, where a positive value means a net release of oxygen (or hydrogen) to the fluid phase;  $TDS_{\text{sil}}$ —mass of  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$ , and  $\text{SiO}_2$  released by the reaction (in grams of dissolved species released per mole of initial mineral weathered);  $\Phi$ —bias in estimating denudation rates using  $TDS_{\text{sil}}$  (in %; see text Equation 2). A positive value of  $\Phi$  means that  $TDS_{\text{sil}}$  overestimates the actual chemical denudation rate. Reactions: K-feldspar to (R1) montmorillonite, (R2) illite, (R3) kaolinite, and (R4) gibbsite; (R5) Ca-feldspar to kaolinite; (R6) chlorite to kaolinite; (R7) Fe-pyroxene to magnetite.

half a mole of kaolinite (reaction R3, Table 1), which contains 4.5 atoms of oxygen and 2 atoms of hydrogen. Therefore, 3.5 moles of oxygen is transferred from the solid to the fluid phase, while 2 moles of hydrogen makes the inverse journey ( $\Delta O = 3.5$  and  $\Delta H = -2$ ). However, if one were able to measure the dissolved load of the corresponding leaching solution,  $TDS_{\text{sil}}$  would account for 4 moles of oxygen (as 2 moles of  $\text{SiO}_2$  is released) per mole of K-feldspar weathered. Therefore, in this case, chemical denudation calculated from Equation 1 is a slight overestimate of the actual chemical denudation. For any reaction, the relative bias (in %) made when estimating chemical denudation based on  $TDS_{\text{sil}}$  (Equation 1) is defined as:

$$\Phi = -\frac{\Delta O \cdot M_{\text{O}} + \Delta H \cdot M_{\text{H}} - 2 \cdot (\text{SiO}_2) \cdot M_{\text{O}}}{TDS_{\text{sil}}} \cdot 100, \quad (2)$$

where  $(\text{SiO}_2)$  is the number of moles of  $\text{SiO}_2$  released per mole of initial mineral weathered. Importantly,  $\Delta O$ ,  $\Delta H$ ,  $(\text{SiO}_2)$ , and  $TDS_{\text{sil}}$  can be expressed in various units such as moles per gram of mineral or weathered, moles per mole of mineral weathered, or moles per liter of water flushing

through the system, as long as the same units are used for all these parameters. With the definition of Equation 2, positive values of  $\Phi$  imply that  $TDS_{\text{sil}}$  leads to an overestimation of the actual chemical denudation rate.

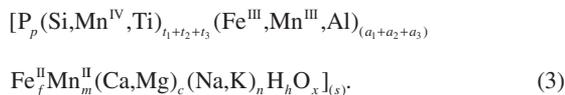
While for some reactions no significant bias is associated in using  $TDS_{\text{sil}}$  (K-feldspar to montmorillonite [R1] or to illite [R2],  $\Phi = 1.0\%$  and  $0.45\%$ , respectively; Table 1), in other cases,  $TDS_{\text{sil}}$  significantly overestimates chemical denudation (K-feldspar to kaolinite [R3] or to gibbsite [R4], and Fe-pyroxene to magnetite [R7],  $\Phi = 6.3\%$ ,  $8.7\%$ , and  $9.0\%$ , respectively). In the case of Ca-feldspar to kaolinite (R5), an important weathering reaction affecting granitic and basaltic rocks, chemical denudation is clearly overestimated by  $TDS_{\text{sil}}$  ( $\Phi = 49.9\%$ ). The reaction of chlorite to kaolinite (R6), typical of sedimentary rock weathering, is associated with a large negative bias ( $\Phi = -59.5\%$ ). Interestingly, some authors have suggested use of a modified definition of  $TDS_{\text{sil}}$  to account for the loss of oxygen from the rock during chemical denudation, whereby  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Na}^+$ , and  $\text{K}^+$  are all expressed in mass of equivalent oxides (Stallard, 1995, 2012; West et al., 2005; Calmels et al. 2011). In most cases, with this method “too many” oxygen atoms are assumed to be released from the mineral (Table DR1 in the [GSA Data Repository](#)<sup>1</sup>).

<sup>1</sup>GSA Data Repository item 2014047, bias  $\Phi_{\text{ox}}$  on chemical denudation rates from the use of  $TDS_{\text{sil}}$  converted into oxide mass; bias  $\Phi$  (Equation 5) from the chemistry of bedrock and topsoil in Critical Zone Observatories; Table DR1 (bias  $\Phi_{\text{ox}}$  for monomineralic weathering reactions); Table DR2 (weathering mechanisms affecting oxide components of a silicate mineral or rock); and Table DR3 (bias  $\Phi$  from Equation 5 and  $\Phi_{\text{ox}}$  for four Critical Zone Observatories), is available online at [www.geosociety.org/pubs/ft2014.htm](http://www.geosociety.org/pubs/ft2014.htm), or on request from [editing@geosociety.org](mailto:editing@geosociety.org) or Documents Secretary, GSA, P.O. Box 9140, Boulder, CO 80301, USA.

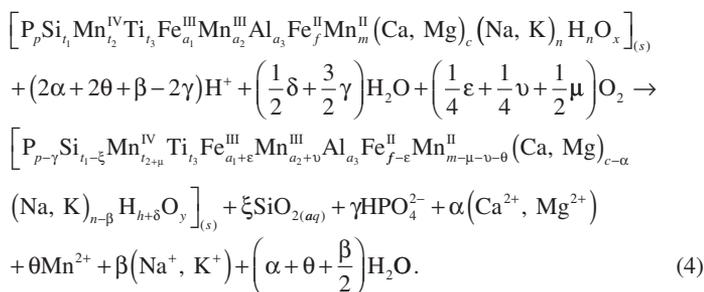
In the following, we proceed to derive a generic formulation of the bias  $\Phi$  as a function of the stoichiometry of the silicate weathering reaction, that can be applied to single minerals or to bulk rocks.

## GENERALIZATION

Monomineralic silicate weathering reactions such as those listed in Table 1, as well as bulk rock weathering reactions, can be written in a generic way. To this aim, we decompose silicate weathering into several mechanisms, each affecting one of the major components of silicates (Table DR2). Silicates contain as major oxides  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{FeO}$ ,  $\text{Fe}_2\text{O}_3$ ,  $\text{TiO}_2$ ,  $\text{MnO}$ ,  $\text{Mn}_2\text{O}_3$ ,  $\text{MnO}_2$ ,  $\text{P}_2\text{O}_5$ ,  $\text{CaO}$ ,  $\text{MgO}$ ,  $\text{K}_2\text{O}$ ,  $\text{Na}_2\text{O}$ , and  $\text{H}_2\text{O}$ , and therefore can be described following the stoichiometric formula:



In order to balance the positive charges of the mineral, the number of oxygen moles is  $x = 2.5p + 2(t_1 + t_2 + t_3) + 1.5(a_1 + a_2 + a_3) + f + m + c + 0.5(n + h)$ . During weathering reactions,  $\text{Al}_2\text{O}_3$ ,  $\text{Fe}_2\text{O}_3$ ,  $\text{Mn}_2\text{O}_3$ ,  $\text{MnO}_2$ , and  $\text{TiO}_2$  are essentially immobile and their role in chemical denudation can be neglected in the present analysis. The other oxide components are affected by various weathering mechanisms. Any silicate weathering reaction is then a linear combination of the mechanisms affecting oxide components, as listed in Table DR2, applied to the silicate material of Equation 3:



In order to satisfy electroneutrality, the number of oxygen moles in the weathered solid product is  $y = 2.5(p - \gamma) + 2(t_1 + t_2 + t_3 - \xi + \mu) + 1.5(a_1 + a_2 + a_3 + \epsilon + \nu) + f + m + c - \epsilon - \mu - \nu - \theta - \alpha + 0.5(n + h - \beta + \delta)$ , or equivalently  $y = x - 2.5\gamma - 2(\xi - \mu) + 1.5(\epsilon + \nu) - \epsilon - \mu - \nu - \theta - \alpha + 0.5(\delta - \beta)$ .

From Equation 4, it can be inferred that the net number of oxygen moles solubilized during the reaction is  $\Delta\text{O} = x - y = 2.5\gamma + 2\xi + \alpha + \theta - \mu + 0.5(\beta - \delta - \epsilon - \nu)$ . Similarly, it is straightforward that  $\Delta\text{H} = -\delta$ . If  $TDS_{\text{sil}}$  were measured in the leaching solution resulting from this weathering reaction, only  $2\xi$  moles of oxygen would be counted via dissolved  $\text{SiO}_2$  for each mole of initial silicate weathered. Therefore, the bias (Equation 2) when using river load to estimate chemical denudation is

$$\Phi = - \frac{[2.5\gamma + \alpha + \theta - \mu + 0.5(\beta - \delta - \epsilon - \nu)] \cdot M_0 - \delta \cdot M_H}{TDS_{\text{sil}}} * 100. \quad (5)$$

Because of the small value of the molar mass of hydrogen as compared to that of oxygen, the sign of  $\Phi$  is mainly controlled by the term between brackets. Therefore, Equation 5 shows that river loads will lead to an overestimation of chemical denudation (positive values of  $\Phi$ ) if rock hydration ( $\delta$ ) and/or oxidative weathering ( $\epsilon$ ,  $\nu$ , and  $\mu$ ), which add oxygen to the solids, are important. By contrast, an underestimation of chemical denudation will be obtained if solubilization of base cations ( $\alpha$ ,  $\beta$ ,  $\theta$ , and  $\gamma$ ) is the major process, as it removes oxygen from the source rock. Each of these coefficients is *a priori* independent of the others. These coefficients will most likely depend on the type of source

mineral and/or rock, and on the weathering regime that will condition the type of secondary phase precipitating (Table 1). In the next section, we estimate the value of  $\Phi$  in several natural settings, using reported data on the chemistry of soil profiles.

## APPLICATION TO NATURAL SETTINGS

We now estimate the error associated with chemical denudation rates calculated from river dissolved chemistry. This can be done provided that the stoichiometric coefficients and  $TDS_{\text{sil}}$  of Equation 5 are measured. A first possibility would be to use published river dissolved loads to estimate both  $TDS_{\text{sil}}$  and the coefficients of Equation 5. However, it is not straightforward, if not impossible, to determine the coefficients  $\epsilon$  and  $\delta$  (associated with Fe and Mn oxidation and OH incorporation, respectively) from river dissolved loads. A second option is to compare the chemical composition of source rock and solid weathering products. While it is virtually impossible to determine the coefficients  $\delta$  and  $\epsilon$  from the chemistry of river-borne solids (as the available data usually does not comprise hydrogen content, oxidation state of Fe), this approach can be performed using data on soil chemistry and associated bedrock for a handful of well-characterized weathering profiles, such as Critical Zone Observatories. In these cases,  $TDS_{\text{sil}}$  in Equation 5 can be predicted from the amount of soluble cations (Si, Ca, Mg, Na, K) lost between bedrock and soil (per kilogram of bedrock weathered, for example), rather than measured in the dissolved compartment. Such a predicted value of  $TDS_{\text{sil}}$  characterizes a dissolved load that is the chemical complementary of the soil over the time scale of the formation of the weathering profile. Therefore, the predicted  $TDS_{\text{sil}}$  value will match the measured  $TDS_{\text{sil}}$  in the water draining the weathering profile only if the considered weathering system is operating at steady state. Nevertheless, the present approach only requires the predicted  $TDS_{\text{sil}}$  value in order to estimate  $\Phi$ , and does not require that the system is actually operating at steady state (the latter being one of the central concepts in weathering and erosion studies). We identified four Critical Zone Observatories for which the required data to estimate  $\Phi$  from Equation 5 is reported: Luquillo (Rio Icacos watershed, Puerto Rico; White et al., 1998), Panola (Georgia, USA; White et al., 2001), Nsimi (Cameroon; Braun et al., 2012), and Susquehanna Shale Hills (Pennsylvania, USA; Jin et al., 2010).

Details on the calculations are provided in the Data Repository, and the results are listed in Table DR3 and plotted in Figure 2. In Luquillo and Panola, values for  $\Phi$  of  $-5\%$  are calculated, while in Nsimi,  $\Phi = 4\%$ . However, in Shale Hills, a value of  $\Phi = -11\%$  is obtained and is mainly driven by  $\text{H}_2\text{O}$  loss from the metasedimentary bedrock (Table DR3; Fig. 2). The bias resulting from the use of dissolved load to estimate chemical denudation was also calculated based on  $TDS_{\text{sil}}$  expressed as oxides (e.g., West et al., 2005). In most cases, this calculation results in an overestimate of chemical denudation, as “too many” oxygen atoms are accounted for by  $TDS_{\text{sil}}$  (Table DR3).

## CONCLUSION

Following our findings, at the current state of knowledge the main concern on the validity of reported chemical denudation rates is likely not the behavior of oxygen and hydrogen. Uncertainties on solute sources (atmosphere, human activities, carbonates, evaporites, or silicate rocks) and hydrological fluxes are certainly larger. Regarding estimates of total (i.e., including both physical and chemical) denudation rates from river loads, particulate fluxes are the main source of uncertainty. However, the definition of physical denudation also deserves examination. Indeed, if physical denudation is defined as the mass or volume of upper crust eventually exported as solids, this number is different from the mass of sediment exported from a weathering system (soil profile or river basin), as this sediment mass also contains oxygen and hydrogen atoms originally supplied by the fluids and not by the rock (Fig. 1). A viable alternative to retrieve accurate estimates of total denudation rates from river dissolved loads is

Schott, R.F. Stallard, J. Viers, and A.J. West. The participation in the poll, "What is chemical denudation?," was much appreciated.

## REFERENCES CITED

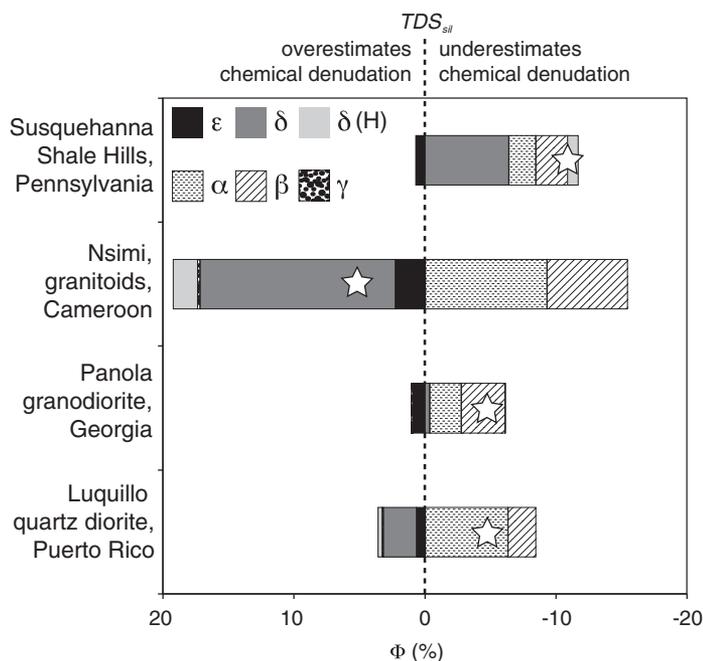
- Brantley, S.L., and Lebedeva, M., 2011, Learning to read the chemistry of regolith to understand the Critical Zone: Annual Review of Earth and Planetary Sciences, v. 39, p. 387–416, doi:10.1146/annurev-earth-040809-152321.
- Braun, J.-J., Maréchal, J.-C., Riotte, J., Boeglin, J.-L., Bedimo Bedimo, J.-P., Ndam Ngoupayou, J.R., Nyeck, B., Robain, H., Sekhar, M., Audry, S., and Viers, J., 2012, Elemental weathering fluxes and saprolite production rate in a Central African lateritic terrain (Nsimi, South Cameroon): *Geochimica et Cosmochimica Acta*, v. 99, p. 243–270, doi:10.1016/j.gca.2012.09.024.
- Calmels, D., Galy, A., Hovius, N., Bickle, M., West, A.J., Chen, M.-C., and Chapman, H., 2011, Contribution of deep groundwater to the weathering budget in a rapidly eroding mountain belt, Taiwan: *Earth and Planetary Science Letters*, v. 303, p. 48–58, doi:10.1016/j.epsl.2010.12.032.
- Clarke, F.W., 1924, Data of geochemistry (fifth edition): U.S. Geological Survey Bulletin 770, 716 p.
- Edmond, J.M., Palmer, M.R., Measures, C.I., Grant, B., and Stallard, R.F., 1995, The fluvial geochemistry and denudation rate of the Guyana Shield in Venezuela, Colombia, and Brazil: *Geochimica et Cosmochimica Acta*, v. 59, p. 3301–3325, doi:10.1016/0016-7037(95)00128-M.
- Gaillardet, J., Dupré, B., Louvat, P., and Allègre, C.J., 1999, Global silicate weathering and CO<sub>2</sub> consumption rates deduced from the chemistry of large rivers: *Chemical Geology*, v. 159, p. 3–30, doi:10.1016/S0009-2541(99)00031-5.
- Garrels, R.M., and Mackenzie, F.T., 1972, A quantitative model for the sedimentary rock cycle: *Marine Chemistry*, v. 1, p. 27–41, doi:10.1016/0304-4203(72)90004-7.
- Holeman, J.N., 1968, The sediment yield of major rivers of the world: *Water Resources Research*, v. 4, p. 737–747, doi:10.1029/WR004i004p00737.
- Jin, L., Ravella, R., Ketchum, B., Bierman, P.R., Heaney, P., White, T., and Brantley, S.L., 2010, Mineral weathering and elemental transport during hillslope evolution at the Susquehanna/Shale Hills Critical Zone Observatory: *Geochimica et Cosmochimica Acta*, v. 74, p. 3669–3691, doi:10.1016/j.gca.2010.03.036.
- Livingstone, D.A., 1963, Chemical composition of rivers and lakes: Data of geochemistry: U.S. Geological Survey Professional Paper 440-G, 63 p.
- Lyll, C., 1853, Principles of geology (ninth edition): Boston, Little, Brown and Co., 835 p.
- Martin, J.-M., and Meybeck, M., 1979, Elemental mass-balance of material carried by major world rivers: *Marine Chemistry*, v. 7, p. 173–206, doi:10.1016/0304-4203(79)90039-2.
- Meybeck, M., 1987, Global chemical weathering of surficial rocks estimated from river dissolved loads: *American Journal of Science*, v. 287, p. 401–428, doi:10.2475/ajs.287.5.401.
- Mortatti, J., and Probst, J.-L., 2003, Silicate rock weathering and atmospheric/soil CO<sub>2</sub> uptake in the Amazon basin estimated from river water geochemistry: Seasonal and spatial variations: *Chemical Geology*, v. 197, p. 177–196, doi:10.1016/S0009-2541(02)00349-2.
- Stallard, R.F., 1995, Relating chemical and physical erosion: *Reviews in Mineralogy*, v. 31, p. 543–564.
- Stallard, R.F., 2012, Weathering, landscape equilibrium, and carbon in four watersheds in Eastern Puerto Rico, in Murphy, S.F., and Stallard, R.F., eds., *Water quality and landscape processes of four watersheds in eastern Puerto Rico*: U.S. Geological Survey Professional Paper 1789, 304 p.
- Turner, B.F., Stallard, R.F., and Brantley, S.L., 2003, Investigation of in situ weathering of quartz diorite bedrock in the Rio Icacos basin, Luquillo Experimental Forest, Puerto Rico: *Chemical Geology*, v. 202, p. 313–341.
- West, J.A., Galy, A., and Bickle, M.J., 2005, Tectonic and climatic controls on silicate weathering: *Earth and Planetary Science Letters*, v. 235, p. 211–228, doi:10.1016/j.epsl.2005.03.020.
- White, A.F., Blum, A.E., Schulz, M.S., Vivit, D.V., Stonestrom, D.A., Larsen, M., Murphy, S.F., and Eberl, D., 1998, Chemical weathering in a tropical watershed, Luquillo Mountains, Puerto Rico: I. Long-term versus short-term weathering fluxes: *Geochimica et Cosmochimica Acta*, v. 62, p. 209–226, doi:10.1016/S0016-7037(97)00335-9.
- White, A.F., Bullen, T.D., Schulz, M.S., Blum, A.E., Huntington, T.G., and Peters, N.E., 2001, Differential rates of feldspar weathering in granitic regoliths: *Geochimica et Cosmochimica Acta*, v. 65, p. 847–869, doi:10.1016/S0016-7037(00)00577-9.

Manuscript received 12 July 2013

Revised manuscript received 27 October 2013

Manuscript accepted 3 November 2013

Printed in USA



**Figure 2. Relative bias associated with estimates of chemical denudation based on river dissolved load ( $\Phi$ ; see Equation 5 in text) for four natural settings: Luquillo (Puerto Rico), Panola (Georgia, USA), Nsimi (Cameroon), and Shale Hills (Pennsylvania, USA). Calculations were achieved from chemistry of topsoil and local bedrock (see text and Data Repository [see footnote 1] for details). Net bias  $\Phi$  is represented by white stars. This net bias results from several contributions (Equation 4 in text; Table DR3 in the Data Repository):  $\alpha$  and  $\beta$  reflect oxygen loss from rock to solution during solubilization of Ca or Mg and of Na or K, respectively;  $\gamma$  is related to loss of oxygen during P solubilization;  $\epsilon$  reflects incorporation of oxygen into solid phase during Fe oxidation;  $\delta$  represents hydration or dehydration of solid phase during weathering.**

to divide the dissolved flux of a given soluble element not incorporated in solids by its concentration in bedrock (Turner et al., 2003; Mortatti and Probst, 2003; Stallard, 2012).

Extrapolating this analysis, weathering of basalts and granitic rocks under fast denudation, during which weathering of Ca-feldspar to kaolinite should prevail, will be characterized by an underestimation of chemical denudation by  $TDS_{sil}$  (Table 1). By contrast, chemical denudation in river basins underlain by water-rich meta-sedimentary rocks will have much higher denudation than suggested by their river dissolved loads alone (Table 1; Table DR3), because the release of the water molecule from the rock is not accounted for by  $TDS_{sil}$ . In the case of organic-rich sedimentary rocks, oxidation of organic carbon and pyrite will lead to an additional mass loss from the solid that is not measurable using  $TDS_{sil}$ . Conversely, addition of water to the residual solid via clay swelling will lead to a mass gain of the solid phase, again invisible to  $TDS_{sil}$ . These observations are of particular significance at the global scale as shales represent such a large portion of the continental crust undergoing denudation.

Our analysis has fundamental implications on the way denudation rates should be defined, and on the concept of chemical denudation itself. Many important scientific challenges are related to these findings, such as the oxygen and hydrogen geological cycles, the role of weathering in Earth's surface lowering, or the intimate mechanisms of chemical weathering.

## ACKNOWLEDGMENTS

This study greatly benefited from comments from R.A. Berner, D. Calmels, C. Dessert, A. Galy, Y. Goddérès, F. Guyot, P. Louvat, M. Lupker, E. Tipper, J.