Weathering dynamics reflected by the response of riverine uranium isotope disequilibrium to changes in denudation rate

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ABSTRACT

The ratio between the activity of dissolved ^{234}U and ^{238}U in river water, $(^{234}U/^{238}U)_{Riv}$, shows promise for tracing weathering processes. It has been suggested that preferential ^{234}U release generates a high $(^{234}U/^{238}U)_{Riv}$ under low weathering intensity while congruent weathering, as expected for high weathering intensity, would release uranium with a secular equilibrium $(^{234}U/^{238}U)_{Riv}$ of 1. However, weathering intensity depends on the combination of exposure age of weathering interfaces and dissolution rate, complicating the use of $(^{234}U/^{238}U)_{Riv}$ as a tool in weathering studies. This work attempts to resolve the weathering dynamics reflected by $(^{234}U/^{238}U)_{Riv}$ using catchment scale denudation rate (D) as a first order approximation for the age of weathering interfaces. A global dataset ($n = 653$), including 132 new measurements from Chinese catchments, indicates changing responses of $(^{234}U/^{238}U)_{Riv}$ to D. Higher values (>1.5) and larger variability of $(^{234}U/^{238}U)_{Riv}$ are observed in catchments both with high (>3 mm/yr) and low D (<0.1 mm/yr). In contrast, the lowest values (approaching secular equilibrium) and the least variable $(^{234}U/^{238}U)_{Riv}$ are associated with catchments of medium to high D (0.3–2 mm/yr). The observed pattern can be explained by a model that involves competing uranium release from active- and inactive-weathering interfaces in response to a shifting weathering regime, from kinetically-limited to supply-limited. $(^{234}U/^{238}U)_{Riv}$ decreases with decreasing D under a kinetically-limited weathering regime due to the increasing contribution of congruent weathering relative to the preferential dissolution of ^{234}U from radioactively damaged sites as D decreases. In contrast, $(^{234}U/^{238}U)_{Riv}$ increases with decreasing D under a supply-limited weathering regime because the minerals that remain under these conditions continue to release ^{234}U to solution by recoil, while contributing little to the dissolved ^{238}U because of their slow dissolution rate. A much deeper depth of the weathering interface is suggested for catchments with high D due to higher weathering contribution from deep fractures relative to the poorly developed surface regolith. A young age of ~10 kyrs is constrained by the model for complete dissolution of exposed weathering-active minerals, which implies a rapid shifting from kinetically-limited to supply-limited weathering regime and limited influence of weathering on the calculation of comminution age based on $(^{234}U/^{238}U)$ in sediments. A site-specific dissolution rate that is consistent with those estimated from weathering profiles is also constrained, which suggests that the discrepancy between field and laboratory weathering rate may largely be controlled by the difference in chemical affinity associated with stagnant micro-pores, low permeability, and high rock/fluid ratios rather than the passivation of weathering interfaces.

1. Introduction

The significant roles that weathering plays in the Earth system, such as supplying nutrients to terrestrial and marine ecosys-

tems (Cermeño et al., 2015), regulating the long-term balance of the global carbon cycle and geothermostat (Berner et al., 1983), and triggering climatic changes associated with tectonic uplift (Raymo et al., 1988), require a deep understanding of the factors that control weathering flux (e.g., Bluth and Kump, 1994; Jacobson et al., 2003; Li et al., 2016; Maher and Chamberlain, 2014; Riebe et al., 2004). The uranium isotope activity ratio of dissolved weathering products has been used to better understand weathering processes (e.g., Bourdon et al., 2009; Chabaux et al., 2001; Dosseto et al., 2006; Maher et al., 2006). Natural waters are enriched in ^{234}U relative to bedrock (Chabaux et al., 2003; Dunk et al., 2002) that is typically characterized by a secular equilibrium where the activity of ^{234}U ($\lambda_{234}{}^{234}$U, λ_{234} is decay constant) is equal to that of ^{238}U ($\lambda_{238}{}^{238}$U), such that the activity ratio (^{234}U/^{238}U) is 1. Laboratory experiments indicate that the enrichment of ^{234}U in natural waters can be attributed to both (1) the direct recoil ejection of the ^{234}U precursor during alpha decay of ^{238}U and (2) the preferential dissolution of radioactively damaged lattice sites that hold the ^{234}U nucleus (Andersen et al., 2009; Fleischer, 1980; Kigoshi, 1971). The relative contribution of recoil ejection and preferential dissolution is high when the supply of fresh mineral surfaces is abundant, resulting in preferential loss of ^{234}U to solution. On the other hand, congruent weathering would generate weathering products with a uranium isotope activity ratio approaching secular equilibrium (e.g., Maher et al., 2006; Pogge Von Strandmann and Henderson, 2015; Robinson et al., 2004a; Vigier, 2001). It is thus expected that the dissolved riverine uranium isotope activity ratio, $(^{234}$U/^{238}U$)_{Riv}$, is controlled by the age of the weathering interface (i.e., the weathering front) and the weathering rate that collectively determine weathering intensity.

The possible control of weathering intensity on $(^{234}$U/^{238}U$)_{Riv}$ (Pogge Von Strandmann and Henderson, 2015; Robinson et al., 2004a; Vigier et al., 2006) may help to resolve debates related to weathering limitation regimes and thus elucidate the relative importance of tectonics and climate on the global chemical weathering flux (Bluth and Kump, 1994; Ferrier et al., 2016; Hilley et al., 2010; Jacobson et al., 2003; Riebe et al., 2004; West et al., 2005). Under a low denudation rate (D), mineral residence time in the weathering zone is relatively long and weathering-active minerals can be completely dissolved before leaving the eroding surface. Under these conditions, it has been conceptually accepted that the chemical weathering rate (W) is limited by the supply of fresh minerals (supply-limited) and is thus linearly related to D (Riebe et al., 2004; West et al., 2005). Notably, such supply-limited weathering regimes provide the main premise for the "uplift-weathering" hypothesis which proposes that uplift-enhanced erosion promoted silicate chemical weathering and accelerated the drawdown of atmospheric CO_2 during the late Cenozoic (Raymo et al., 1988). In contrast, when ample fresh minerals are constantly produced under high D, W is limited by weathering reaction kinetics determined by factors such as rock type, temperature, supply of reactive fluid, and thus the flux becomes decoupled from D, i.e., "kinetically-limited" (West et al., 2005). A kinetically-limited weathering regime enables a negative feedback between atmospheric CO_2 concentration (and thus climate) and weathering rate, which is essential for silicate weathering to act as a geothermostat that maintains the balance of the carbon cycle and the habitability of the Earth (Berner et al., 1983; Li and Elderfield, 2013).

The proof of shifting weathering regimes, which generally relies on the relationship between W and D in modern weathering environments (Ferrier et al., 2016; Gabet and Mudd, 2009; West et al., 2005), is, however, elusive. Generally, a strong correlation can be observed between D and W under low D (West et al., 2005), but debate arises under high D. Results based on small granitic catchments show decoupling between D and W

at high D (West et al., 2005), while compilation of global soil data suggests that W retains a tight coupling with D even at extremely high D (Larsen et al., 2014), challenging the existence of a true kinetically-limited weathering regime. A pure supply-limited weathering regime would require strong control of climate on D in order to sustain a stabilizing geothermostat (Ferrier et al., 2016), yet evidence for a strong climate control on denudation remains incomplete (Perron, 2017). In threshold landscapes, mass wasting (movement) is the major agent of erosion (Li et al., 2017a), and rapid incipient weathering of fresh slope debris may contribute to the high W at high D (Emberson et al., 2016), though much of this flux may not be from the silicate sources that consume atmospheric CO_2 over geological timescales (Jacobson et al., 2003), complicating the interpretation and implications for the carbon cycle. It is also possible that D and W are spuriously correlated since the calculation of W from soils, which is based on the chemical depletion of regolith, involves D. Moreover, W and D deduced from the dissolved and suspended flux of rivers both depend on runoff. In both cases, there is the risk of false correlation (Ferrier et al., 2016).

To avoid spurious correlation between D and W, weathering intensity as measured by proxies such as chemical depletion fraction (Ferrier et al., 2016) and lithium isotopic compositions (Dellinger et al., 2015) can be used as alternative indicators for shifting weathering limitation regimes. Supply limitation implies total dissolution of weathering-active minerals so that the same high degree of chemical depletion would be expected, while kinetic weathering limitation predicts a lower chemical depletion fraction at higher D due to restricted weathering time. While chemical depletion can be measured at single locations in hillslope regolith (e.g., Larsen et al., 2014; Riebe et al., 2004), it is difficult to make these measurements over large spatial scales that integrate weathering across the Earth's surface. Given the limited tools to infer weathering regime at the scale of river basins, the question is whether the $(^{234}$U/^{238}U$)$ in the dissolved load can help to make this distinction and provide quantitative information about weathering conditions under each regime.

If measurements of $(^{234}$U/^{238}U$)_{Riv}$ can further be used to constrain weathering rates, the resulting site-specific rates may also help to explain the 3–6 order of magnitude discrepancy between observations of dissolution rates in the field versus the laboratory (White and Brantley, 2003; White and Buss, 2014). Despite the relatively well established kinetics of mineral dissolution in the laboratory (Brantley and Olsen, 2014), this large discrepancy inhibits extrapolation of experimentally-based kinetic laws to field settings, hampering efforts to quantify the strength of feedbacks between climate and silicate weathering (Li et al., 2016; Maher and Chamberlain, 2014). Both intrinsic and extrinsic processes have been invoked to explain the lab-to-field rate discrepancy (White and Brantley, 2003). The intrinsic factors could include overestimation of the active weathering surface caused by coating of secondary precipitates and consumption of energetically active surface. The extrinsic factors are related to differences in chemical affinity of the reacting fluid due to the stagnant micro pores, slow flow rate, and high rock/fluid ratio in the field. The site-specific dissolution rate constrained by uranium isotope disequilibrium, which is independent of estimated active surface area (Maher et al., 2006), may be used to differentiate between intrinsic and extrinsic factors because the intrinsic factors would not influence site-specific dissolution rates.

Though promising for untangling these complicated questions about weathering, dissolved riverine uranium isotope activity ratios vary widely, and their relationship with weathering intensity appears complex. High $(^{234}$U/^{238}U$)_{Riv}$ has been observed in some catchments flowing toward the east coast of the South Island, New Zealand, where a kinetically-limited weathering regime and associ-