



Invited review

Expanding the role of reactive transport models in critical zone processes



Li Li ^{a,*}, Kate Maher ^b, Alexis Navarre-Sitchler ^c, Jenny Druhan ^d, Christof Meile ^e, Corey Lawrence ^f, Joel Moore ^g, Julia Perdrial ^h, Pamela Sullivan ⁱ, Aaron Thompson ^j, Lixin Jin ^k, Edward W. Bolton ^l, Susan L. Brantley ^m, William E. Dietrich ⁿ, K. Ulrich Mayer ^o, Carl I. Steefel ^p, Albert Valocchi ^q, John Zachara ^r, Benjamin Kocar ^s, Jennifer McIntosh ^t, Benjamin M. Tutolo ^u, Mukesh Kumar ^v, Eric Sonnenthal ^p, Chen Bao ^a, Joe Beisman ^c

^a Department of Civil and Environmental Engineering, The Pennsylvania State University, University Park, PA 16802, United States

^b Department of Geological & Environmental Sciences, Stanford University, CA 94305-2115, United States

^c Department of Geology and Geological Engineering, Colorado School of Mines, Golden, CO 80401, United States

^d Department of Geology, University of Illinois at Urbana Champaign, Urbana, IL 61801, United States

^e Department of Marine Sciences, The University of Georgia, Athens, GA 30602, United States

^f U.S. Geological Survey, MS 980, Box 25046, Federal Center, Denver, CO 80225, United States

^g Department of Physics, Astronomy, & Geosciences, Towson University, Towson, MD 21252, United States

^h Department of Geology, University of Vermont, Burlington, VT 05405, United States

ⁱ Department of Geography, University of Kansas, Lawrence, KS 66045-7613, United States

^j Department of Crop and Soil Sciences, University of Georgia, Athens, GA 30602, United States

^k Department of Geological Sciences, University of Texas at El Paso, Texas 79968, United States

^l Department of Geology and Geophysics, Yale University, New Haven, CT 06520-8109, United States

^m Earth and Environmental Systems Institute, Department of Geosciences, The Pennsylvania State University, University Park, PA 16802, United States

ⁿ Department of Earth and Planetary Science, University of California, Berkeley, CA 94720, United States

^o Department of Earth, Ocean and Atmospheric Sciences, University of British Columbia, Vancouver, BC V6T 1Z4, Canada

^p Earth Sciences Division, Lawrence Berkeley National Laboratory, 1 Cyclotron Road, Mail Stop 90-1116, Berkeley, CA 94720, United States

^q Department of Civil and Environmental Engineering, University of Illinois at Urbana Champaign, Urbana, IL 61801, United States

^r Physical Sciences Division, Pacific Northwest National Laboratory, Richland, WA 99352, United States

^s Department of Civil and Environmental Engineering, Massachusetts Institute of Technology, Cambridge, MA 0213, United States

^t Department of Hydrology and Atmospheric Sciences, University of Arizona, Tucson, Arizona 85716, United States

^u Department of Earth Sciences, University of Oxford, Oxford OX1 3AN, United Kingdom

^v Nicholas School of the Environment, Duke University, Durham, NC 27708-0328, United States

ARTICLE INFO

Article history:

Received 13 December 2015

Received in revised form 27 August 2016

Accepted 2 September 2016

Available online 30 September 2016

Keywords:

Critical Zone Processes
Reactive transport models
Chemical weathering
Hydrological cycles
Biogeochemical processes
Spatial heterogeneity
Root zone
Isotopes

ABSTRACT

Models test our understanding of processes and can reach beyond the spatial and temporal scales of measurements. Multi-component Reactive Transport Models (RTMs), initially developed more than three decades ago, have been used extensively to explore the interactions of geothermal, hydrologic, geochemical, and geobiological processes in subsurface systems. Driven by extensive data sets now available from intensive measurement efforts, there is a pressing need to couple RTMs with other community models to explore non-linear interactions among the atmosphere, hydrosphere, biosphere, and geosphere. Here we briefly review the history of RTM development, summarize the current state of RTM approaches, and identify new research directions, opportunities, and infrastructure needs to broaden the use of RTMs. In particular, we envision the expanded use of RTMs in advancing process understanding in the Critical Zone, the veneer of the Earth that extends from the top of vegetation to the bottom of groundwater. We argue that, although parsimonious models are essential at larger scales, process-based models offer tools to explore the highly nonlinear coupling that characterizes natural systems. We present seven testable hypotheses that emphasize the unique capabilities of process-based RTMs for (1) elucidating chemical weathering and its physical and biogeochemical drivers; (2) understanding the interactions among roots, micro-organisms, carbon, water, and minerals in the rhizosphere; (3) assessing the effects of heterogeneity across spatial and temporal scales; and (4) integrating the vast quantity of novel data, including “omics” data (genomics, transcriptomics, proteomics, metabolomics), elemental concentration and speciation data, and isotope data into our understanding of complex earth surface systems. With strong support from data-driven sciences, we are now in an exciting era where integration of RTM framework into other community models will facilitate process understanding across disciplines and across scales.

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* Corresponding author.

E-mail address: lili@engr.psu.edu (L. Li).

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1. Reactive transport models as a tool for integration and differentiation

Reactive transport models (RTMs) quantitatively evaluate coupling of physical, chemical, and biological processes that determine the formation, operation, and evolution of Earth surface systems. The coupling among processes plays a pivotal role in governing low-temperature biogeochemical systems, including the conversion of rock to soil, the release of nutrients from minerals for ecosystem vitality, the transport and bioremediation of reactive contaminants, and the biogeochemical cycling of important elements. RTMs are process-based models that allow both the integration and differentiation of distinct processes, thus providing a way to assess system response to external forcings. RTMs can be applied to optimize sampling campaigns; serve as a repository of knowledge within mathematical frameworks; and carry out numerical experiments under conditions where data are not available, thereby expanding forecasting capabilities beyond measurement limitations (assuming the forecast uncertainty can be addressed). From a practical point of view, RTMs could support decision making, risk assessment, and environmental stewardship, especially if data science approaches that address model sensitivity and uncertainty are developed.

Our goal here is to paint a broader picture of how RTMs could be useful to address outstanding biogeochemical questions, rather than to provide a comprehensive literature review and to discuss issues and methods. We aim to identify opportunities to integrate RTM framework into other relevant disciplines to advance process understanding, with the primary focus on the low-temperature (<100 °C) surface and near-surface environment termed the Critical Zone (CZ). The CZ is defined as the zone “from the outer extent of vegetation down to the lower limits of groundwater” (Brantley et al., 2007). We argue that RTMs can play an important role in understanding interactions between water, atmosphere, rock, soil, and life within the CZ. These interactions create complex coupling between chemical, physical, and biological processes that determine Earth system responses to external and anthropogenic forcings (Fig. 1).

The need for RTMs is in fact also driven by the vast growth of observation data documenting CZ processes, and specific hypotheses about solute chemistry and weathering processes suggested by these data (Brantley et al., 2013a; Kim et al., 2014; Perdril et al., 2015). By integrating processes of interests in different disciplines, RTMs allow integration between large, diverse, and complex data sets from disparate disciplines and scales, and can thus substantially advance cross-disciplinary research. For example, hydrologic models typically use a subset of observations for calibration, primarily water fluxes and

hydraulic heads. Elemental and isotopic concentrations and speciation of dissolved components can also provide constraints on water flow (Jin et al., 2011; Thomas et al., 2013). The use of these data in RTMs will enrich our understanding of critical zone systems by eliminating some model behaviors in favor of other model behaviors. RTMs can help discern such incongruities. RTMs therefore provide tools that synthesize understanding at a system level across disciplines while concurrently illuminate operative mechanisms and contributions of individual processes.

The major advance of modern RTMs was to couple flow and transport with a full geochemical thermodynamic and kinetic framework. RTMs are distinct from geochemical models that primarily calculate geochemical equilibrium, speciation, and thermodynamic state of a system (Wolery et al., 1990). RTMs also differ from reaction path models, which represent closed or batch systems without either diffusive or advective transport (Helgeson, 1968; Helgeson et al., 1969). Multi-component RTMs originated in the 1980s based on the theoretical foundation of the continuum model (Lichtner, 1985, 1988). RTM development advanced substantially in the 1990s with the emergence of widely-used RTM codes and their capabilities (see Steefel et al., 2015a for a review). Several early diagenetic models were developed at a similar time (Soetaert et al., 1996; Van Cappellen and Wang, 1996).

Reactive transport models have since been applied to understand biogeochemical systems for more than three decades in several earth system disciplines, including hydrogeology, geochemistry, and biogeochemistry (Beaulieu et al., 2011; Bethke, 1996; Brown and Rolston, 1980; Chapman, 1982; Chapman et al., 1982; Lichtner, 1985; Ortoleva et al., 1987; Regnier et al., 2013; Steefel et al., 2005; Steefel and Lasaga, 1994). RTMs are used across a diverse array of environments involving both porous and fractured media (as reviewed in MacQuarrie and Mayer, 2005; Steefel et al., 2005). They can simulate a wide range of processes, including fluid flow (single or multiphase), solute transport (advection, dispersion, and diffusion), geochemical reactions (e.g., mineral dissolution and precipitation, ion exchange, surface complexation), and biogeochemical reactions (e.g., microbe-mediated redox reactions, biomass growth and decay). Such models have been applied to understand a wide variety of systems and processes, including chemical weathering and soil formation (Brantley and Lebedeva, 2011; Godd ris et al., 2013; Lawrence et al., 2014a; Maher, 2011; Maher et al., 2009; Moore et al., 2012; Navarre-Sitchler et al., 2011), biogeochemical processes in coastal marine sediments (Dale et al., 2008; Krumins et al., 2013; Regnier et al., 1997), the role of spatial heterogeneity in determining mineral dissolution and precipitation reactions (e.g.,

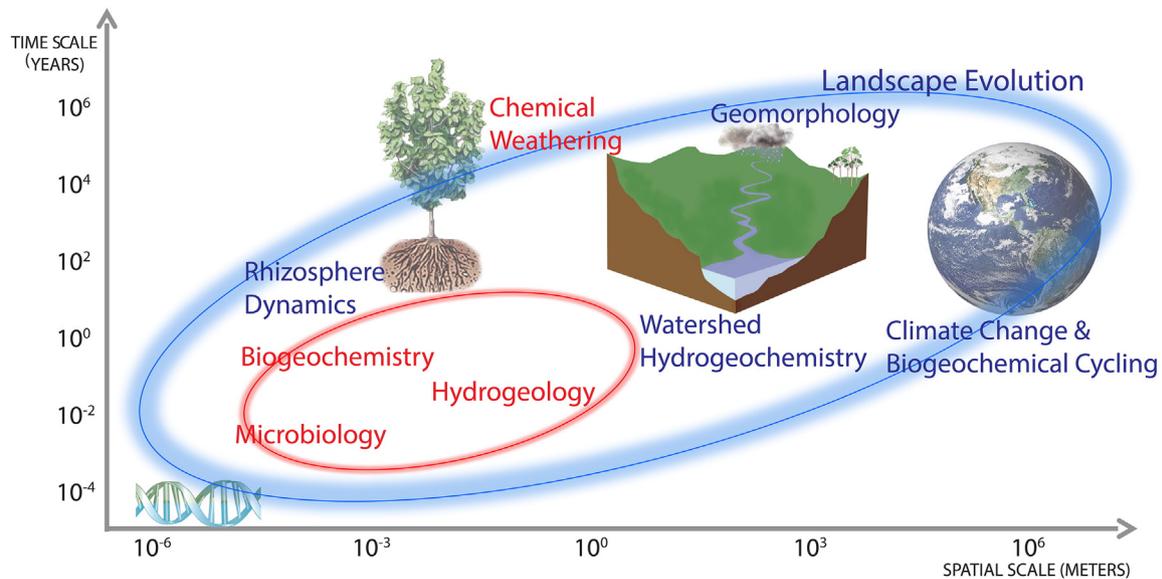


Fig. 1. RTMs are being used currently and will be used in the future at a wide range of temporal and spatial scales. The red color indicates disciplines where RTMs have been used most commonly in the past three decades. The blue color reflects potential opportunities for further RTM development and application.

Bolton et al., 1996, 1997, 1999; Li et al., 2007). RTMs have played a key role in understanding and predicting coupled water and chemical mass transfer in environmentally relevant applications, including: bioremediation (Druhan et al., 2012; Li et al., 2009; Steefel et al., 2014; Yabusaki et al., 2011; Zachara et al., 2013); natural attenuation (Chen et al., 2001; Liu et al., 2008; Mayer et al., 2001); geological carbon sequestration (Apps et al., 2010; Atchley et al., 2013; Brunet et al., 2016; Carroll et al., 2016; Navarre-Sitchler et al., 2013; Tutolo et al., 2015; Xu et al., 2003); and nuclear waste storage (e.g., Saunders and Toran, 1995; Soler and Mader, 2005).

Microbial processes have been included in RTMs since the mid-1980s. Early applications included groundwater substrate dynamics and microbial growth (Molz et al., 1986); transport of bacteria and viruses with surface attachment and detachment (Yates et al., 1987); and multispecies interactions between oxygen, nitrate, organic carbon, and bacteria that regulate denitrification (Kinzelbach et al., 1991). New generation RTM codes have adopted more complex and flexible formulations including the kinetic degradation of microbial biomass and biogeochemical byproducts (Bao et al., 2014; Prommer et al., 2006). With the expanded use of isotopes as tracers of mineral-fluid and biologically mediated reactions, recent advances include the explicit treatment of isotopic partitioning due to both kinetic and equilibrium processes (Druhan et al., 2012; Johnson and DePaolo, 1994; Lehmann et al., 2007; Maher et al., 2006b; Van Breukelen et al., 2005; Van Breukelen and Rolle, 2012; Wanner et al., 2015).

A broad range of scales has been considered in reactive transport modeling. RTMs have been applied to understand subsurface processes in single pores (Kang et al., 2006; Li et al., 2008; Molins et al., 2012, 2014) and single cells (10^{-6} to 10^{-3} m) (Fang et al., 2011a; Scheibe et al., 2009), pore networks and columns (10^{-2} to 10^{-1} meters) (Druhan et al., 2014; Knutson et al., 2005; Li et al., 2006; Meile and Tuncay, 2006; Yoon et al., 2012), field scales (10^0 to 10^1 m) (Li et al., 2011; Liu et al., 2008; Maher et al., 2009), and more recently watershed or catchment scales (10^2 to 10^3 m) (Atchley et al., 2014; Beisman et al., 2015; Navarre-Sitchler et al., 2013). Recent weathering studies have linked regional scale reactive transport models to global vegetation models to investigate the role of climate change in controlling weathering over periods of 10^0 to 10^3 years (Godd eris et al., 2013, 2006, 2010; Roelandt et al., 2010). Models that include a full coupling between subsurface reactive transport processes and surface hydrology,

land-surface interactions, and meteorological and climatic processes are to be developed; interests in improving process representation are stimulating these types of efforts.

RTMs are complex, physically based models that represent “pragmatic reality” and are similar to distributed hydrologic models. RTMs therefore suffer similar limitations with the problems “of nonlinearity, of scale, of uniqueness, of equifinality, and of uncertainty” (Beven, 2001a, 2001b; Ebel and Loague, 2006). Here we are not advocating that complex models are better than parsimonious models. That accomplish a desired level of explanation or prediction power with as few variables as possible (Basu et al., 2010). Both types of models are useful. Parsimonious models can provide good conceptual frameworks. However, to derive and test parsimonious models in nonlinear natural systems, process-based models such as RTM are required to tease apart the importance of individual processes, to test the nonlinear coupling, and to identify controlling processes or parameters that need to be further investigated (Fatichi et al., 2016). In fact, we argue that complex models are a way toward developing conceptual framework for parsimonious models.

We present seven hypotheses in four different topical areas that highlight important questions and needs in understanding Critical Zone processes that can be uniquely addressed by application of existing RTMs or through the development of new RTM capabilities. We do not provide a comprehensive review of RTM applications, or a detailed discussion of concerns surrounding model use and evaluation. Instead, we aim to identify opportunities to integrate the RTM framework into other relevant disciplines to advance process understanding. The primary focus is in the CZ where interactions between water, atmosphere, rock, soil, and life create complex coupling between chemical, physical, and biological processes that determine system responses to external forcings (Fig. 1). The hypotheses have the potential to elucidate a broad range of earth surface processes at different spatio-temporal scales and to address long-standing questions regarding processes that ultimately sculpt the Earth’s surface and drive shallow subsurface evolution. While our list of hypotheses is by no means inclusive of all outstanding questions (cf. Steefel et al., 2005), these hypotheses focus on a broad cross-section of current research areas and illustrate where transformative scientific advances could be made through RTMs.

2. Testable hypotheses

2.1. Chemical weathering

Weathering of fresh bedrock generates soil and releases solutes to streams and groundwater, thus providing nutrients essential for terrestrial ecosystem productivity (e.g., Carey et al., 2005; Huntington, 2000; Moulton et al., 2000) and controlling chemical composition of natural waters (Malmstrom et al., 2000; Williams and Melack, 1997). At the global scale, silicate and carbonate weathering together consume about 0.3 Gt of atmospheric CO₂ per year (Gaillardet et al., 1999). Weathering and CO₂ levels are closely coupled through the dependence of weathering rates on temperature, pH, and water flux. This coupling maintains habitable Earth surface conditions over time scales of ~10⁵–10⁶ years for silicate weathering and over time scales of ~10³ years for carbonate weathering (Berner et al., 1983; Roelandt et al., 2010; Sundquist and Visser, 2003; Walker et al., 1981).

A process-based understanding of the controls on chemical weathering remains a central challenge for Earth surface studies. These processes include feedbacks between chemical reaction rates and variations in environmental conditions, particularly the availability of water. The introduction of chemically aggressive water in disequilibrium with bedrock drives weathering. Water serves as a medium for transporting weathering reactants and products, setting mineral-water contact area, and affecting concentrations of reactive gases (e.g., CO₂, O₂). In hydrologically saturated systems with low flow rates, O₂ can be consumed faster than it is replenished via diffusion, resulting in anoxic conditions. In contrast, in unsaturated systems, oxygen diffusion is often sufficient to drive oxidative degradation of organic matter in soils (Bolton et al., 2006). Likewise, rock chemistry can affect the presence or absence of O₂ and CO₂ as a function of depth (Brantley et al., 2013b).

Organisms can control the rates and extent of weathering by transferring water and nutrients among the solid, aqueous, and biological reservoirs in the CZ through root growth and exudation, and through associated fungal and microbial organisms. The availability of reactive gases is tightly coupled to biological processes that are notoriously difficult to resolve. The partial pressure of soil CO₂ (P_{CO2}) controls the formation of carbonic acid, which plays a major role setting the acidity of soil pore waters (Drever, 1989, 1997). The presence of O₂ can drive oxidative weathering of Fe(II)-bearing minerals such as biotite, which may create fractures and porosity that allow water infiltration and weathering of other minerals (Bazilevskaya et al., 2013; Buss et al., 2008; Molins and Mayer, 2007). Oxidation of pyrite can also produce sulfuric acid, which can enhance mineral weathering and create permeable pathways for water and solutes (Brantley et al., 2013b). Much remains to be learned about feedbacks among weathering, transport, and biologically-mediated processes with realistic subsurface structures at spatial scales of micrometers to meters. Despite advances in modeling these processes, their coupling to the long-term evolution of the critical zone and to climate cycles at the global scale have only begun to be explored. In the next sections we present two hypotheses that are ripe for testing with observations and RTMs.

Hypothesis 1. Under humid conditions where precipitation (*P*) exceeds potential evapotranspiration (*PET*), the rate of chemical weathering for a given mineral assemblage is controlled by the concentration and distribution of reactive gases; in contrast, in arid systems, water is the primary control on chemical weathering rates.

Motivation

We suggest that water availability determines the extent to which reactive gases control the rates of chemical weathering. For example, under humid conditions—such as those in tropical forests (*PET/P* < 1)—water-rock contact area is large and water flow is fast such that reaction

products are quickly transported away. The weathering rates are therefore determined by the concentration and spatial distribution of the reactive gases (Fig. 2). Conversely, under relatively dry conditions—such as those in semi-arid environments (*PET/P* > 1)—water-rock contact area is small and water flow is slow compared to gas diffusion through the vadose zone, creating water-limiting situations where water controls weathering rates (Perdrial et al., 2014). These fundamentally different controls on rates of chemical weathering should ultimately result in unique and different physical and chemical architectures (i.e., structure) within the regolith.

Current status

The hypothesis about the importance of water availability versus gas concentrations in different systems arises, in part, from previous RTM work on chemical weathering. Modeling of chemical weathering has thus far focused primarily on one-dimensional (1-D) systems at time scales typical of soil development and bedrock weathering. These models emphasize complex reaction networks among primary and secondary minerals, aqueous complexes and adsorbed species (Sidebar 1). They have illustrated key controls of Earth's surface evolution, namely fluid transport and reaction thermodynamics and kinetics in regulating both the advance rate and thickness of weathering fronts.

One of the long-standing puzzles in quantifying chemical weathering rates is the five to six orders of magnitude discrepancy between rates of mineral reactions as measured in laboratory versus field contexts (Blum and Stillings, 1995; Drever and Clow, 1995; Richards and Kump, 2003; Sverdrup et al., 1995; White, 1995; White and Brantley, 1995, 2003). This rate discrepancy has been attributed to two major categories of factors that operate at different spatial scales. One category includes processes and conditions that directly affect the amount and “reactivity” of mineral surfaces. Examples include mineral surface roughness or fractalness (Navarre-Sitchler and Brantley, 2007), passivation or armoring layers as a result of clay coating or secondary mineral precipitation (Helgeson, 1971; Maher et al., 2009; Nugent et al., 1998), leached layers that act as diffusion barriers (Luce et al., 1972), and water films between grains that vary under different temperature and pressure conditions (Renard et al., 1997). The second category includes factors that regulate fluid compositions. For example, water flow controls reaction rates by regulating the extent of deviation from equilibrium (Maher, 2010; Salehikhoo et al., 2013). The amount of

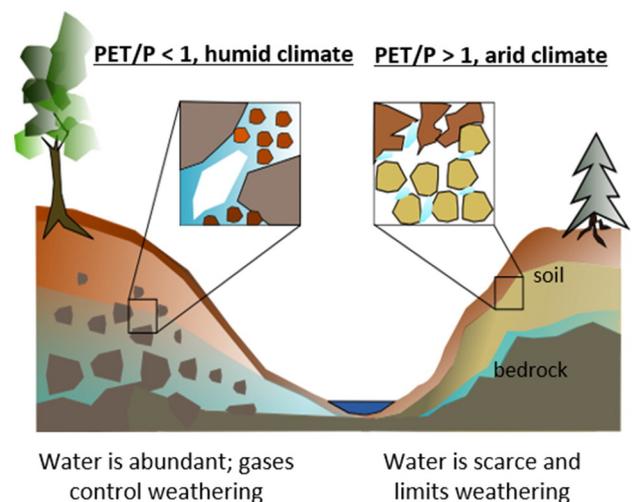


Fig. 2. A conceptual diagram expressing the role of water and gases in driving weathering in different climatic zones: gas (white) transport is likely to be rate-limiting for weathering under humid conditions where water is abundant and precipitation (*P*) exceeds potential evapotranspiration (*PET*) (*PET/P* < 1); water availability (blue) is likely to be rate-limiting for weathering in arid ecosystems where water is scarce and gases can rapidly diffuse through unsaturated pore spaces. The blue/green layer indicates the saturated zone.

Sidebar 1: A One-dimensional RTM for chemical weathering.

In many soil profiles, primary minerals such as plagioclase are depleted over time via chemical weathering. The relative depletion of minerals in relation to their original concentrations in parent materials is characterized by τ values. The τ values represent a fractional loss (or accumulation of minerals) where 0 is equivalent to the parent, -1 is 100% loss relative to the parent and 0.25 is 25% gain relative to the parent (Anderson et al., 2002; Brimhall and Dietrich, 1987). RTMs offer a valuable tool for understanding processes controlling chemical weathering. RTMs require information on the parent rock such as mineralogy, porosity, and mineral surface areas; climate information such as rainfall and evapotranspiration (to determine average flow rates through soil profiles) and atmospheric CO_2 concentrations over geological time. Reaction thermodynamics (equilibrium constants) and kinetics are also needed for such simulations, where mineral dissolution and precipitation rates are often represented by the Transition State Theory (TST) rate laws with rate dependence on aqueous chemistry. Fig. S1 shows the use of an 1D RTM (FLOTTRAN) to understand and quantify the role of environmental conditions (flow, pCO_2) and mineral properties (e.g., reactive surface area) in controlling plagioclase weathering, e.g., plagioclase τ values for a 250 ka granitic alluvium soil profile from Merced, CA, USA (circles, Fig. S1). Such RTMs can be developed with constraints from field data and can be extrapolated to different geochemical conditions to help elucidate reaction mechanisms and identify key controls of chemical weathering. RTMs can also be used to quantify weathering rates, casting the evolution of relevant properties over geological time scales (Navarre-Sitchler et al., 2011, 2009).

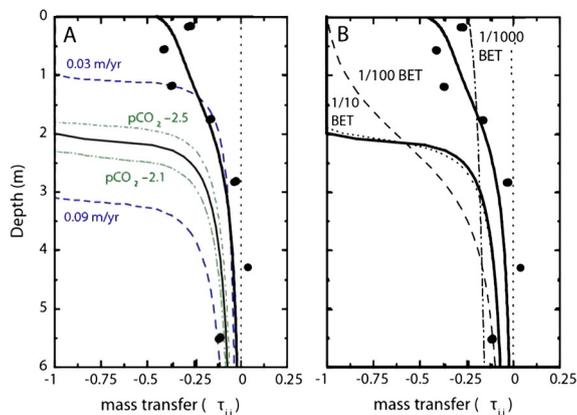


Fig. S1: Field (circles) and modeled plagioclase reaction fronts (lines) as τ values versus depth for different (A) flow rates or pCO_2 , and (B) reactive surface areas for a Merced chronosequence profile (250 ka). The best fit model (thicker black solid line) compares well with the plagioclase field data (dots). The figure shows that the reaction front advance rate could be altered by flow and pCO_2 (A) while the thickness of the front could only be changed by reducing the reactive surface area relative to BET surface area (B) (modified from Moore et al. (2012)).

wetted surface under unsaturated conditions, as well as concentrations of catalyzing or inhibiting aqueous species, also play a significant role (Lawrence et al., 2014a; Oelkers et al., 1994). Both of these categories of factors have been explored using RTMs together with field observations.

Porous medium characteristics—the particular details of pore structure and heterogeneous spatial distribution of porous medium properties (e.g., permeability and mineral abundance)—can lead to large spatial variations in flow rates and deviations from equilibrium, therefore modifying the overall “effective” reaction rates at large scales (Bolton et al., 1996, 1999; Malmstrom et al., 2004; Meile and Tuncay, 2006; Molins et al., 2012; Salehikhoo and Li, 2015). For example, a mineral that does not have any coating can be bathed in a fluid at equilibrium in the low permeability zone of a heterogeneous medium and therefore is not effectively dissolving. In essence, any factors that influence the reaction kinetics (surface area, concentrations of catalyzing or inhibiting species, and distance from equilibrium) can contribute to the rate discrepancy. In natural systems, all these factors can operate simultaneously resulting in much smaller effectively-dissolving surface areas than the measured Brunauer–Emmett–Teller (BET) or imaged surface area, although the dominance of different factors may vary under

different conditions (e.g., Jin et al., 2011; Nugent et al., 1998; White and Peterson, 1990; Zhu, 2005; Li et al., 2014).

Modeling studies have also probed the effects of time and climate on weathering rates using chronosequences and climosequences (i.e. soils of different age or soils of similar age and different climate regimes, respectively) (Godd ris et al., 2013, 2010; Lawrence et al., 2014a; Maher et al., 2009; Moore et al., 2012). The advance rates of weathering fronts may be limited by the accumulation of weathering products (Maher et al., 2009; Moore et al., 2012) and by the drainage rate of groundwater from the fresh bedrock (Rempe and Dietrich, 2014). RTMs have also helped place constraints on conversion of rocks to regolith at the weathering front, including basalt clasts and carbonates (Brantley et al., 2013b; Hausrath et al., 2008; Hausrath and Olsen, 2013; Navarre-Sitchler et al., 2011, 2009). Compared to water availability, the role of reactive gases has been explored to a much lesser extent, although modeling studies have emphasized the importance of including soil CO_2 in quantifying weathering rates (Brantley et al., 2013b).

Future directions

With a process-based framework, RTMs are uniquely suited to evaluate the competition between reactive gases and water availability under otherwise similar weathering conditions. Brantley et al. (2013a, 2013b) hypothesize that the soil O_2 to CO_2 ratio in different landscape positions (ridgetop versus valley) is related to the depths of weathering fronts for different mineral phases, but this has not yet been tested using a fully coupled model framework. Current RTMs include capabilities of multiphase flow that are required to simulate fluid dynamics under different water availability (wet and dry) conditions, as well as the generation or consumption of reactive gases by microbial processes (Molins and Mayer, 2007). Modeling capabilities need to be expanded to include root processes in order to test hypotheses regarding how plants affect weathering. In addition to the traditional measurement of thermodynamic equilibrium constants and kinetic rate formulations of mineral reactions, coupled measurements of reactive gases and water chemistry at depth are also needed (Hasenmueller et al., 2015). Time-series measurements of mineral and hydrologic properties, including surface area, porosity, permeability, and unsaturated flow parameters, are rare although they are critical to constrain RTMs (Jin et al., 2010; Navarre-Sitchler et al., 2009; Takagi and Lin, 2011).

Hypothesis 2. *At the global scale, variations in water availability induced by climate change exert more control over chemical weathering than increased CO_2 levels and temperature.*

Motivation

At the global scale, various forcing and feedback loops work together in regulating the ultimate consequences of increasing CO_2 levels and resulting climate change. Insights into critical feedbacks between climate change and chemical weathering, however, are limited (Beerling and Berner, 2005; Berner and Caldeira, 1997; Godd ris et al., 2013; Roelandt et al., 2010). There has been debate about whether climate change and global warming will lead to positive or negative feedbacks between atmospheric CO_2 levels, plants, and weathering (Beerling and Berner, 2005) as both rising CO_2 level and temperature can enhance chemical weathering. Climate change can also have profound impacts on the hydrological cycle, including changes in evapotranspiration, rainfall abundance, precipitation patterns, shifts in snow and ice melting, and a change in the frequency of extreme events (Barnett et al., 2005; Bindoff et al., 2013; Chattopadhyay and Hulme, 1997; Jung et al., 2010; Rosenzweig and Neofotis, 2013). As mentioned in Hypothesis 1, water is a key driver for biogeochemical processes (Kump et al., 2000; Maher and Chamberlain, 2014). Changes in water cycles likely trigger shifts in plant response and soil CO_2 levels (Bond-Lamberty and Thomson, 2010), therefore regulating chemical

weathering to a more significant extent than increasing atmospheric CO₂ level and temperature alone. In addition, changes in the timing and intensity of precipitation can alter recharge rates, which influence groundwater residence times, flow paths, and mineral weathering fluxes. The need to consider the sensitivity of weathering rates to flow paths, water availability, reactive gases, and temperature presents a classical reactive transport problem. However they have only begun to be explored using RTMs.

Current status

Our limited understanding of the relationship between climate change, CO₂ regulation mechanisms, and chemical weathering exists partly due to the lack of tools that explicitly couple relevant processes at the global scale. Many global models developed to understand the feedbacks between CO₂ level and chemical weathering are zero-dimensional (Berner and Kothavala, 2001; Edmonds and Edmond, 1995) and hence represent global average conditions. The Rock Geochemical Model (RokGeM) was developed for incorporation into the Global Environmental and Ecological Simulation of Interactive Systems (GENESIS) to understand the sensitivity of weathering to temperature and run-off (Colbourn et al., 2013). A recent advance has been coupling the rock weathering models with Earth System models to understand the interactions between terrestrial weathering, CO₂ levels, and climate change. For example, the weathering model WITCH has been coupled with the Lund-Potsdam-Jena (LPJ)—a Dynamic Vegetation Model (DVG)—to examine the role of vegetation in affecting chemical weathering at the continental scale (Roelandt et al., 2010). Sensitivity analysis shows that in tropical environments, plants control weathering by introducing roots with organic acids that increase mineral-water contact and dissolution rates. When atmospheric CO₂ increases, decreases in evapotranspiration enhance infiltration, biosphere productivity, and soil acidity, promoting CO₂ consumption by mineral weathering by an estimated 2.4%–5% increase per 100 ppmv rise in CO₂ (Beaulieu et al., 2010). These estimates however are highly contingent upon climatic, ecohydrological, lithological, and biological conditions. Most of these models are executed with steady-state CO₂ levels and hydrologic scenarios and do not consider transient precipitation patterns that accompany

climate change. In addition, existing models do not consider weathering rate response to human activities such as land use change and fertilizer utilization (Guo et al., 2015; Perrin et al., 2008; Raymond et al., 2008). Only a few studies have used RTMs to forecast future weathering (Godd ris and Brantley, 2013; Godd ris et al., 2013).

Future directions

Multi-component RTMs with spatially explicit representations of precipitation patterns and biosphere and geosphere characteristics can advance our predictive understanding of process coupling at continental and global scales (Sidebar 2). Model development along these lines, however, faces major challenges. Existing models of continental weathering typically have large grids [e.g., spatial resolution of 0.5° × 0.5° latitude–longitude in (Beaulieu et al., 2012)], whereas our understanding and measurements of multicomponent reactive transport processes currently focus on much smaller scales (micrometers to meters). Translating mechanistic understanding of complex reaction networks at small scales (10⁻³ to 10¹ m) to a few key reaction mechanisms at continental and global scale models (10³ to 10⁵ meters) presents a daunting task. Such cross-scale understanding, however, is key for advancing not only model development but also conceptual understanding of which processes are important at large scales. Such understanding will reduce computational cost and facilitate explicit incorporation of two-way feedback schemes among processes, instead the current use of cascade or one-way simulation schemes that lack feedbacks.

2.2. Carbon cycling

Soil represents the largest terrestrial pool of organic carbon (C) (Stockmann et al., 2013). Soil C decomposition and stabilization play a key role in determining the atmospheric CO₂ concentrations and global C cycles (Davidson and Janssens, 2006). Although the complexity of soil C partitioning has long been recognized (von L utzow et al., 2007), soil C is currently conceptualized and modeled as pools of different decomposition rates and turnover times (Ostle et al., 2009; Thornton et al., 2009). For example, a typical three-pool soil C model includes a readily

Sidebar 2: CO₂ consumption by chemical weathering at the regional scale.

According to predicted future anthropogenic emission scenarios, atmospheric CO₂ concentration is expected to double before the end of the 21st century, which will promote changes in hydrological cycles and vegetation cover. Although typically considered unimportant at the century scale, recent studies have demonstrated that chemical weathering can be highly sensitive to climate changes. A recent modeling study demonstrates that doubling CO₂ level will likely alter CO₂ consumption rates significantly for the Mackenzie River Basin, one of the most important Arctic watersheds (Beaulieu et al., 2012). The prediction was made using B-WITCH, a code that couples the dynamic global vegetation model LPJ with a process-based continental weathering model (Fig. S2). Using spatially explicit data on lithology, vegetation cover, soil properties, and climate conditions, the model reproduced field data of river chemistry (Beaulieu et al., 2010). Two simulations were carried out at the CO₂ levels of 355 and 560 ppmv to quantify the effects of carbon doubling. With an average CO₂ consumption rates of 0.06 mol/m²/year, the predicted CO₂ consumption rates in the south (red area) that sits on carbonaceous shale increase by more than three times responding to the carbon doubling. In contrast, the northeastern watershed sees no change or up to a maximum of one time decrease. This emphasizes the importance of including chemical weathering in understanding the evolution of global carbon cycle under changing climate conditions.

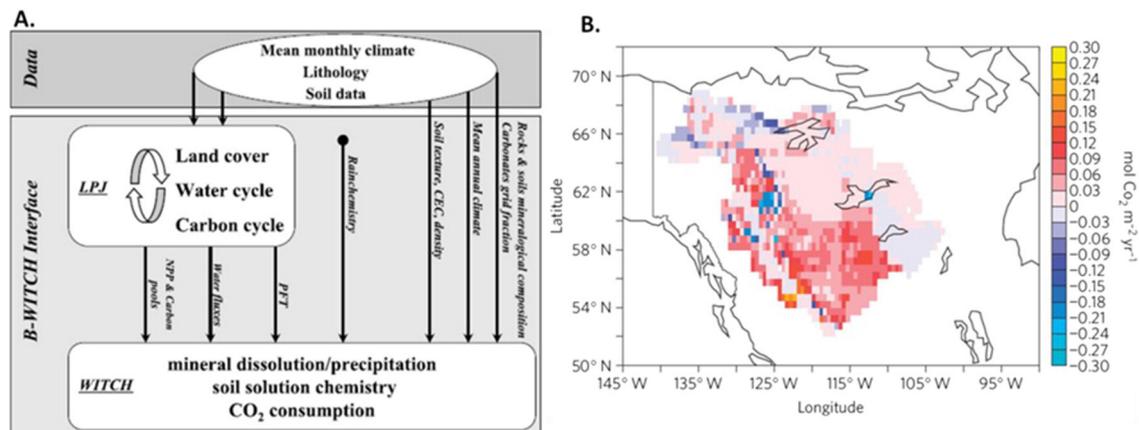


Fig. S2. A. B-WITCH LPJ takes climate, lithology, and soil data to calculate the land cover and water and carbon cycles, the output of which is further fed into WITCH, a geochemical model that simulates mineral weathering and CO₂ consumption through transition state theory rate laws (Roelandt et al., 2010); B. Predicted spatial distribution of differences in CO₂ consumption rates when atmospheric CO₂ rises from 355 to 560 ppmv (Beaulieu et al., 2012).

degradable C pool with residence times less than 5 years; a slowly degrading pool with residence times of decades; and a relatively stable pool with residence times between 10^3 – 10^5 years (Marin-Spiotta et al., 2009; Trumbore, 1993; Trumbore et al., 1995).

One of the grand challenges is to understand mechanisms and quantify rates of C decomposition and stabilization under different environmental conditions (Conant et al., 2011; Lehmann and Kleber, 2015). Carbon decomposition is primarily biologically driven. Microbes transform C (e.g., leaves, roots) in the presence of multiple electron acceptors including O_2 , nitrate, sulfate, as well as solid phases such as iron-containing and manganese-containing minerals (Dunn et al., 2006; Fierer et al., 2003; Philippot et al., 2009). Carbon stabilization, however, is both biotic and abiotic (Eusterhues et al., 2003; Guggenberger and Kaiser, 2003; Kleber et al., 2015; Lalonde et al., 2012; Mikutta et al., 2006, 2009; Rasmussen et al., 2007, 2008; Rumpel et al., 2004). Plant roots and mycorrhizal fungi influence soil properties including physical structure, hydrological and biogeochemical gradients and, as a result, are integral controls on soil structure and water availability (Fierer and Schimel, 2002; Lawrence et al., 2009; Roy et al., 2013). A change in soil properties can limit organic matter degradation through physical separation from microbes and water (Manzoni et al., 2014) affect organic matter-mineral associations (Mikutta et al., 2006; Schmidt et al., 2011). These physiochemical conditions are likely more important controls on stabilized or passive C than biological activities (Schmidt et al., 2011; Torn et al., 1997).

The competing effects of biotic and abiotic factors can be understood through the development of RTMs that simulate water dynamics, physical stabilization, and microbial growth conditions with biological processes and biogeochemical reaction networks (e.g., Riley et al., 2014). A detailed mechanistic understanding of the root zone will enable modeling approaches that elucidate the types of processes and the scales required to accurately capture subsurface C cycling, and the derivation of general principles for C stabilization/decomposition. Such mechanism-based principles have yet to be incorporated into earth system models, however hold promise for elucidating the feedbacks that govern the C cycles and climate system at the global scale.

Hypothesis 3. As soil moisture increases, the fraction of C stabilized through mineral association increases, while the fraction of C stabilized through physical separation decreases.

Motivation

Soil C stabilization occurs through two general groups of mechanisms: (1) physical separation of the organic C from reactants or enzymes required for mineralization via occlusion, movement of C to depth, isolation of C in zones without suitable electron acceptors; and (2) movement of organic C into an unavailable form, for instance through association with mineral surfaces or through chemical recalcitrance (Conant et al., 2011; Kleber et al., 2015; Lehmann and Kleber, 2015). Soil moisture governs partitioning between these two general mechanisms (Fig. 3). As conditions become drier, we hypothesize that the physical separation-based mechanisms will become dominant due to the lack of water. Conversely, an increase in soil moisture and the wetting of new surface area will instead promote additional C–mineral associations and C stabilization.

Soil mineral composition varies significantly with climate (e.g., temperature and rainfall), parent rock, and weathering stage. Weathered soils often have minerals with high surface areas and large cation exchange capacities, which promote soil C stabilization through enhanced mineral–organic matter association and reduce soil C decomposition and CO_2 efflux (Denef et al., 2007; Eusterhues et al., 2003; Guggenberger and Kaiser, 2003; Lalonde et al., 2012; Mikutta et al., 2006, 2009; Rasmussen et al., 2007, 2008; Rumpel et al., 2004). Soil mineralogy therefore can play an important role in determining soil C–climate change feedback. Rising CO_2 levels and climate change can in turn

impact soil mineralogy by changing chemical weathering rates via shifts in water content, temperature, plant and microbial physiology, and the composition of plant community (Banwart et al., 2009; Berner, 2006) (Hypothesis 2). The codependence of mineral composition, weathering, and CO_2 concentration forms a coupled regulatory system for the C cycle at human-life time scales. Under all conditions, soil mineral and plant composition in the weathering zone will determine the system response and feedback to climate change. Such feedbacks however are not well understood (Trumbore and Czimczik, 2008).

Current status

The dependence of soil C stabilization and decomposition on soil mineral composition has not been considered in models until recently (Sulman et al., 2014; White et al., 2014). Carbon decomposition is commonly described with first-order dependence on soil moisture and/or temperature (Manzoni and Porporato, 2009; Parton et al., 1987), possibly with an extra Michaelis–Menten term to account for microbial processes (Wieder et al., 2013). The first order dependence on soil moisture can reproduce C behavior under steady-state moisture conditions, but not under dynamic conditions such as pulsed rewetting perturbations (Lawrence et al., 2009). Recent studies have recognized this inadequacy in the representation of complex soil C processes, especially when predicting the soil C–climate feedbacks. For example, limited representation of physical and chemical processes under varying hydrological (soil moisture), geochemical (pH, O_2 , nutrient supply), and biological (e.g., microbe physiology and efficiency) conditions has been shown to introduce large uncertainties in estimating the temperature sensitivity of soil C decomposition under warming conditions (von Lütow and Kögel-Knabner, 2009). A recent comparison between predictions from 11 ecosystems models and free-air CO_2 enrichments (FACE) data indicate the prediction uncertainty is dominated by the poor representation of C turnover time (De Kauwe et al., 2014). A model explicitly linking soil C decomposition with microbial and mineral surface sorption has predicted weaker soil C–climate feedbacks than models without these processes (Tang and Riley, 2015).

Given the importance of representing soil C process in future models (Georgiou et al., 2015), we need to evaluate the functional relationships

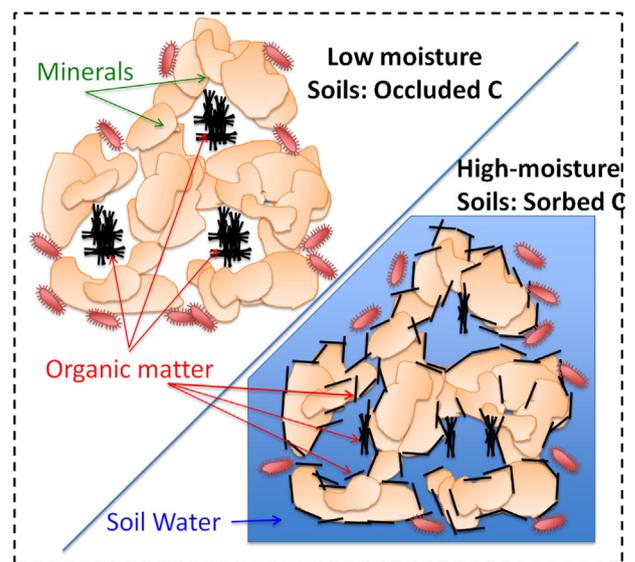


Fig. 3. The primary mechanism for carbon stabilization likely differs in high and low moisture soils. In low moisture soils, physical separation dominates because the lack of water may separate microbial enzymes from readily degradable carbon in particles or micro-clusters. In high moisture soils, C stabilization may be dominated by organic carbon sorption onto wetted mineral surfaces. High moisture soils also can facilitate microbial degradation because microbial enzymes will more likely be in contact with the C.

between soil C decomposition rates and key soil properties including mineral composition as well as other relevant variables. The recent development of CORPSE (Carbon, Organisms, Rhizosphere, and Protection in the Soil Environment) offers a promising framework for modeling soil C dynamics (Sulman et al., 2014). CORPSE considers the proportion of protected and unprotected soil C pools as a function of clay content, with each pool including a mixture of compounds with different tendency toward decomposition (labile, resistant, and recalcitrant). A dynamic microbial biomass pool controls soil C transformation with rate dependence on the abundance of microbial biomass and concentration of degradable organic C through Michaelis-Menten formulation, in addition to the typical temperature and soil moisture dependence. The biomass can grow based on the amount of C assimilated, which allows simulation of processes such as priming, where simple C input greatly increases the overall soil C transformation (Dungait et al., 2012; Finzi et al., 2015; Fontaine et al., 2007; Kuzyakov and Blagodatskaya, 2015). Riley et al. (2014) presents soil C cycling model that includes a comprehensive treatment of microbial and fungal activity, stabilization mechanisms and representation of C via polymeric and monomeric carbon substrate groups. Although the model adequately reproduced C turnover times across a variety of sites, there are not yet sufficient measurements to fully evaluate such a complicated model.

Future directions

Existing RTM capabilities include multiphase flow and gas transport, preferential flow, and microbe-mediated redox reactions by different functional microbial groups. These capabilities can be used to track soil moisture, the evolution of microbial community composition and C decomposition in the presence of roots and mycorrhiza. In particular, multiphase flow dynamics (i.e., air and water in vadose zone) can help understand transitions between dry and wet conditions, transformations between degradable and stabilized C, as well as important mechanisms for C stabilization under different physiochemical conditions. One challenge in soil C modeling is representing the complex chemistry of organic matter (Allen-King et al., 2002; Chen et al., 2003; Hedges et al., 2000). Molecular-scale representation of soil C chemistry in RTMs is not likely because of the computation cost associated with capturing the diversity of organic components (Tang and Riley, 2015, 2013). The advent of more sophisticated tools for characterization of organic matter chemistry offers an opportunity to devise new approaches for representing the functional diversity and reactions of organic matter.

Highly mechanistic representations of soil C have yet to be explicitly included in global scale earth system models such as the Community Earth System Models (CESM) due to observational and computational constraints. Moving from small scale, mechanistic understanding to large-scale earth system modeling presents a major challenge. Simple parameters representing mineralogy (e.g., clay content) and organic matter reactivity (e.g., C pool structure) may not adequately reflect C cycling under changing conditions or across broad spatial scales. Nevertheless, highly resolved models of soil C are necessary to determine the importance of spatial scale and the level of details needed to represent the carbon systematics at larger scales, and could thus be viewed as a critical component in the continued development of earth system models. Overall, RTMs provide a useful framework for assessing rate-limiting processes and system conditions or thresholds.

2.3. Spatial complexity across scales

Natural systems are heterogeneous with large spatial variations in properties and fluxes. The geoscience community has long recognized the importance of spatial heterogeneity in determining earth processes. As an example, the hydrogeology community has studied the role of spatial variation in porosity and permeability in regulating subsurface flow and solute transport since the 1970s. Large-scale tracer experiments have been carried out at field sites with varying degrees of spatial

complexity. These include, the low and intermediately heterogeneous aquifers in Cape Cod, Massachusetts (LeBlanc et al., 1991) and the Borden aquifer in Ontario, Canada (Woodbury and Sudicky, 1991), as well as the highly heterogeneous Macrodispersion Experiment (MADE) aquifer in Columbus, Mississippi (Boggs et al., 1992), where the Advection-Dispersion-Equation (ADE) has been significantly challenged (Zheng et al., 2011). The field of stochastic groundwater hydrology was charged with a primary goal of understanding and quantifying the impacts of spatial variability on solute transport and representing this spatial complexity through effective parameters (Adams and Gelhar, 1992; Dagan et al., 2013; Fiori et al., 2010; Gelhar and Axness, 1983; Kang et al., 2015; Pedretti et al., 2013; Sudicky, 1986; Sudicky et al., 2010). Effective, upscaled models were developed to capture anomalous behavior (Neuman and Tartakovsky, 2009), including the dual porosity model (Gerke and Van Genuchten, 1993), multi-rate mass transfer model (Haggerty and Gorelick, 1995), non-local methods including Continuous Time Random Walk (Berkowitz et al., 2006), and Fractional Advection Dispersion Equation (fADE) (Benson et al., 2000a, 2000b).

Challenges arising from understanding spatial heterogeneity are universal across all earth disciplines. The past decade has witnessed leaps in understanding spatial complexity in subsurface biogeochemical processes. The long-standing puzzle in the geochemistry field, i.e., the five to six orders of magnitude lower rates of weathering observed in natural systems compared to those in well-mixed batch reactors, has inspired the use of RTMs in examining the role of spatial heterogeneity in controlling chemical weathering rates (Bolton et al., 1996; Li et al., 2006; Malmstrom et al., 2004; Meile and Tuncay, 2006). RTMs simulating field scale remediation experiments also highlighted the significance of spatial heterogeneity in determining biogeochemical processes (Li et al., 2010; Liu et al., 2013; Tang et al., 2013; Yabusaki et al., 2011; Zachara et al., 2013) along with carefully designed laboratory-scale column or flow cell experiments (Miller et al., 2013; Rolle et al., 2009; Wang and Li, 2015; Willingham et al., 2008).

RTMs have not yet been utilized to understand many systems characterized by extensive and multi-scale heterogeneity. This is an area ripe for advance because geochemical and geobiological data are now being analyzed in well-instrumented field sites. These data can constrain RTMs over spatial and temporal scales that have not been possible previously. For example, the root zone represents an example of such extreme heterogeneity. The hyporheic zone, i.e., the interface between river, land and subsurface, is another zone where hydrological and biogeochemical complexities collectively influence biogeochemical processes. The topography, vegetation type, lithological variation, and river network geometry impose spatial heterogeneity that plays a pivotal role in partitioning energy, water, and biogeochemical fluxes across different compartments in watersheds. RTMs are well suited to study how reactions and fluxes scale in these highly heterogeneous systems.

Hypothesis 4. *Rhizosphere activities shaped by spatial structure of roots dominate soil formation and functioning.*

Motivation

Roots represent structural, biogeochemical and hydrological interfaces of key importance in generation of soil. Root-soil-water-microbe interactions couple abiotic and biotic processes, including chemical weathering and soil C processes discussed in previous hypotheses. The spatial configuration of a root system – the Root system architecture (RSA) – anchors and mechanically supports plants, facilitating uptake of water and nutrients (Garré et al., 2012). The RSA varies by plant species, adapts to unevenly distributed resources (Bouma et al., 2001; Lynch, 1995), and is responsive to changing soil conditions (Jung and McCouch, 2013; Pacheco-Villalobos and Hardtke, 2012; Tron et al., 2015).

Root structures also impact soil physical properties and generate macro pores that act as highly permeable conduits for water (Beven and Germann, 1982), profoundly impacting water flow and solute transport. Roots control soil chemistry by modulating soil moisture, pH, sorption capacity, and extent of aqueous complexation (Hinsinger et al., 2011, 2003; Lucas et al., 2011) (Fig. 4). Chemicals released from mineral weathering and C decomposition are taken up by roots (Banwart et al., 2011; Brantley and White, 2009; Lopez et al., 2009), while root exudates and other products—often organic acids and CO₂ gas—can accelerate mineral weathering and soil C processes (Hinsinger et al., 2003; Oh et al., 2007). Bacteria and fungi are closely associated with roots and affect soil processes (Drever, 1994; Landeweert et al., 2001; Thorley et al., 2015). Root structures therefore dictate the spatial distribution of water, reactive species, and biogeochemical reaction rates.

Current status

Root models have been developed extensively by plant scientists to describe water and nutrient uptake (e.g., Diggle, 1988; Lynch et al., 1997; Smithwick et al., 2014; Warren et al., 2014). Agricultural scientists have developed crop models, which typically simulate soil water dynamics, soil-plant nitrogen and phosphorus cycling, crop canopy and root growth, plant dry matter production, yield, plant residue production and decomposition, and erosion (Bassu et al., 2014; Camargo and Kemanian, 2016; Stöckle et al., 2003; White et al., 2014). However, soil and water biogeochemical dynamics—including soil composition evolution and export of dissolved organic carbon—are typically not considered mechanistically in crop models. Early biogeochemical models employed either discrete soil layers with different physical and chemical properties (Veen and Paul, 1981) or continuous descriptions of soil organic matter and nutrient dynamics (O'Brien and Stout, 1978). Most existing models consider multiple soil layers with advection and diffusion processes (Maggi and Porporato, 2007; Miller et al., 2008; Raynaud et al., 2006; Walter et al., 2003), sometime considering the statistical characteristics of root structure (Porporato et al., 2003). Explicit representation of biogeochemical processes associated with spatially heterogeneous roots has been rare, with only a few exceptions (Schnepf et al., 2012; Wu et al., 2007). Effective models have been developed to represent heterogeneous soil systems with averaged and lumped properties (Manzoni et al., 2008). At larger scales, roots are rarely represented explicitly in soil production and landscape evolution models (Lifton and Chase, 1992; Minasny and McBratney, 1999, 2001, 2006; Pelletier and Rasmussen, 2009; Yoo and Mudd, 2008). Increasingly, field evidence from some settings suggests that large tree roots could achieve substantial penetration (up to 3 m) into shallow bedrock, therefore accelerating weathering processes (Roering et al., 2010). Key parameters for roots include those relating root depth and root density to macropore permeability and size, all of which are important in distributing water.

Recent incorporation of root functions in large-scale hydrological, ecological, and climate modeling have improved model simulation of latent heat fluxes (Zheng and Wang, 2007), soil moisture dynamics (Ren et al., 2004), and seasonal climate (Barlage and Zeng, 2004). Although vegetation types have been well classified and parameterized in these models, RSA has not been differentiated among vegetation types. For example, water flow between different soil layers via root systems occurs in different ecosystems and plant species throughout the world (Neumann and Cardon, 2012). This water movement is driven by gradients in water potential at the soil-root interface and is regulated by root structure, which is believed to have significant impacts on water budget, plant transpiration rate, and temperature at both local scale and ecosystem scale (Prieto et al., 2012). To date, land surface models generally consider rooting depth and fine root density in soil layers (Ryel et al., 2002), but do not account for the role of root structure in determining local soil and climate conditions. The lack of representation of root structure in biogeochemical models limits our ability to simulate seasonal water and biogeochemical cycling (e.g., C, N) and potentially

increase the model biases relative to dynamic soil moisture, plant transpiration rate, and gross ecosystem productivity data (Zheng and Wang, 2007). Few RTMs have included the chemical effects of roots as a function of depth (Goddéris and Brantley, 2013; Goddéris et al., 2010).

Future directions

Understanding the role of root structure is challenging using experimentation alone, largely because of the complexity of biotic and abiotic interactions, the stochastic and evolving nature of root architecture and the expenses associated with obtaining realistic root structures. RTMs can go beyond measurement limitations and have been used to numerically describe the dynamics of microbial populations, mineral composition, and sorption/desorption processes in heterogeneous, multiphase subsurface systems (Yabusaki et al., 2011). To mechanistically represent intricate interactions among roots, microbes, and minerals, RTMs need to incorporate dynamic root growth as a function of water and/or nutrient concentrations and the effects of soil organisms, root exudates, and the above and below ground linkages that in turn influence soil properties and vegetation composition (Wardle et al., 2004). Incorporation of these dynamic biological structures and spatial complexities into RTMs will allow prediction of soil biogeochemical processes and ecosystem response to environmental perturbation. The role of root structure on biogeochemical processes could be evaluated at the soil profile scale by comparing measurement data versus modeling output regarding weathering rates and the development of redoximorphic mottling with soil heterogeneity generated from stochastic or resource driven root distributions (e.g., Schulz et al., 2016). Such complex models could be used to pinpoint processes of key importance through global sensitivity analysis (Fenwick et al., 2014; Neuman et al., 2012), and ultimately compared with simple models that only include parameters

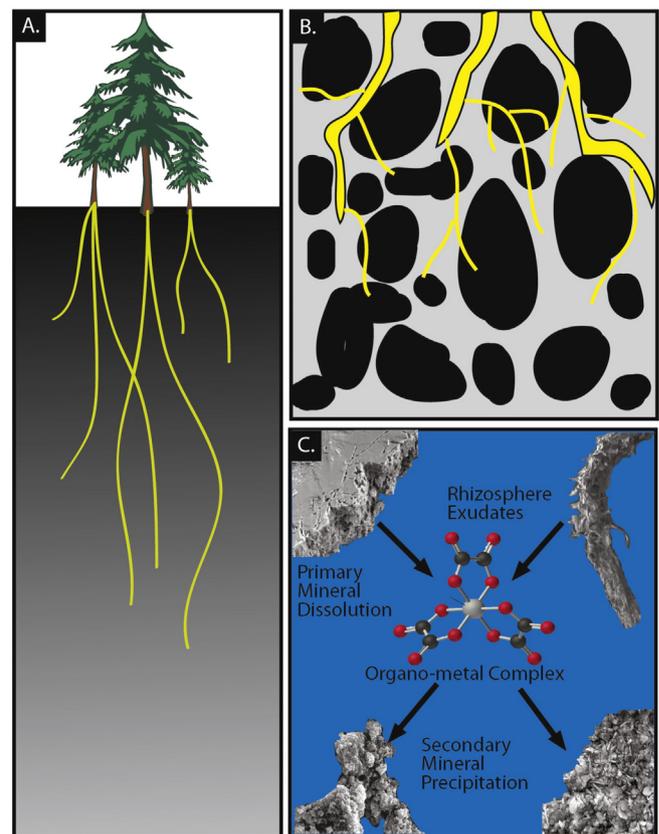


Fig. 4. Rhizosphere processes influence the development of biogeochemical gradients at a range of spatial scales including: (a) soil profile scale (b) pore scale and (c) mineral surface scale. Representation of these processes in RTMs requires consideration of how rhizosphere processes vary over the spatial and temporal scales of interest (Figure is adapted from Lawrence et al. (2014b) and is used with permission).

representing root function (e.g., root depth and density). This would allow the distinction between parameters that are critical to the processes of interest and those that are not essential. In other words, RTMs should be used to guide measurement and experimentation by highlighting the most important processes and parameters through sensitivity analysis or data assimilation.

Hypothesis 5. RTMs can be used to identify and quantify critical interfaces that control large-scale biogeochemical reaction rates and ecosystem functioning.

Motivation

Life thrives at interfaces characterized by large gradients in water content, redox, nutrient, and/or pH conditions and organic C availability (Prommer et al., 2006). Here we define critical interfaces as the interacting boundaries between zones of distinct hydrological, biogeochemical, and topographic properties. Reaction rates at these interfaces are often orders of magnitude higher than the rest of the domain. These discrete interfaces can in some cases dominate reactions within an entire watershed. These interfaces include, for example, interfaces defined by internal domains in porous media (IDPM) (Zachara et al., 2016), biofilms on rock surfaces, surface water-ground water mixing zones, discrete reaction fronts within soil pedons (Brantley et al., 2013a, 2013b), and hyporheic zones at riverland- subsurface interfaces (Hefting et al., 2013; Hester and Gooseff, 2010; McClain et al., 2003; Stonedahl et al., 2010) and contrasts between low- and high-permeability zones (Fig. 5). Biogeochemical processes and biodiversity at these interfaces often outsize the rest of the domain and dictate ecosystem functioning and reaction rates at larger scales. For example, interfaces between different soil zones have been observed to have 2–20 times higher microbe density than the bulk soil (Kuzyakov and Blagodatskaya, 2015). In engineered bioremediation systems, microbe-mediated redox reactions dominate at the interface between the high permeability zone—where organic carbon is injected—and the low permeability clay zone—which is rich in electron acceptors (e.g., iron-containing minerals) (Li et al., 2011). Nitrate removal in the shallowest hyporheic zone (<4 cm) can be substantial enough to account for total nitrate removal of the whole stream (Harvey et al., 2013). Respiration rates at the land-river-sediment interface have been found to be 16 times more than those within the alluvial reach (Argerich et al., 2011).

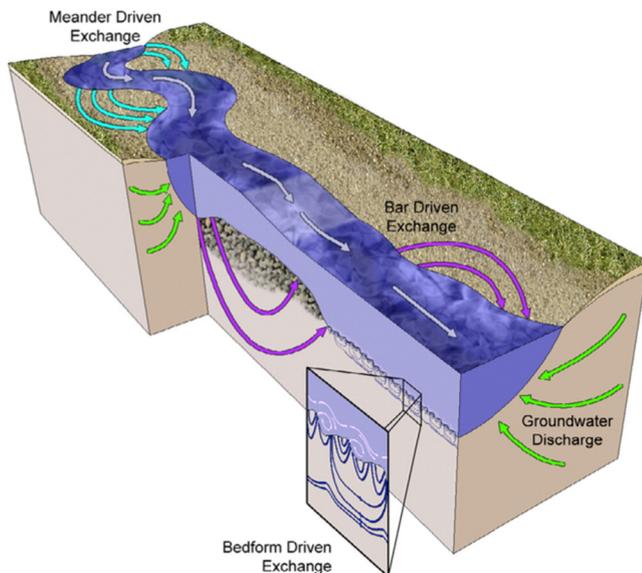


Fig. 5. Hyporheic processes that occur at various interfaces at different scales. (Figure from Stonedahl et al. (2010), use with permission).

Growing evidence has demonstrated that watershed topography governs spatial distribution of flow converging areas (Takagi and Lin, 2011; Li et al., 2017), leading to high C decomposition rates (Andrews et al., 2011) and high soil CO₂ concentrations (Hasenmueller et al., 2015) at critical interfaces. Extensive studies have shown that solute transport into and out of these interfaces—often determined by transverse mixing or diffusive fluxes—plays a key role in reaction extent (Janot et al., 2016; Jose and Cirpka, 2004; Luo and Cirpka, 2008; Werth et al., 2006). The complexity of the hyporheic zone has continued to inspire many open research questions (Boano et al., 2014; Harvey and Gooseff, 2015). Based on field observations we support the idea that critical interfaces dominate overall behavior and reaction rates at larger scale. In a world with advanced RTM we can explore this idea with the integration of data and numerical simulations. Identification of critical interfaces and quantification of rates at the critical interfaces using RTMs can guide experimental and field campaigns on where, what, and how intensive measurements should occur. We also argue that understanding and quantifying the critical interface is key to upscale from detailed representation at small scales to relatively simplified, large scale representation of salient process dynamics.

Current status

The subsurface community has used multi-component RTMs to understand the role of spatial heterogeneity in determining microbe-mediated redox reactions (Bao et al., 2014; Cirpka et al., 1999; Cirpka and Valocchi, 2007; Scheibe et al., 2011; Zhang et al., 2010b), adsorption-desorption reactions (Deng et al., 2012; Liu et al., 2013, 2008; Sassen et al., 2012; Szecsody et al., 1998a, 1998b), and mineral dissolution and precipitation reactions (Atchley et al., 2014; Meile and Tuncay, 2006; Navarre-Sitchler et al., 2013; Werth et al., 2010; Willingham et al., 2008; Zhang et al., 2010a). Various studies have emphasized the importance of connectivity, transverse mixing, and reactive interfaces of heterogeneous porous media in regulating solute transport (Pedretti et al., 2013; Renard and Allard, 2013; Rolle and Kitanidis, 2014) and reactions (Anna et al., 2013; Chiogna et al., 2011; Jin et al., 2011; Rolle et al., 2009; Salehikhoo and Li, 2015; Wang and Li, 2015).

Biogeochemical reactions have begun to be integrated with complex flow dynamics to explore heterogeneity in the hyporheic zone (Bardini et al., 2012). At the watershed scale, RTMs need to be coupled with surface hydrological models that have spatially-explicit representations of surface characteristics such as topography, river network, and vegetation types. The surface hydrology community has utilized distributed models for more than five decades to understand processes including rainfall, infiltration, runoff, surface water and subsurface water interactions, and river hydrodynamics (Abbott et al., 1979, 1986; Beven, 1989; Freeze and Harlan, 1969; Gan et al., 2006; James, 1972; Jarboe and Haan, 1974; Kumar et al., 2009; McDonnell et al., 2007a; Qu and Duffy, 2007b; Quinn et al., 1991; Singh, 1995; Therrien et al., 2010; VanderKwaak and Loague, 2001; Shen and Phanikumar, 2010). Solute and water quality models have been developed as add-ons to hydrological models to understand environmental impacts of contaminants (Arnold and Soil, 1994; Donigan et al., 1995; Santhi et al., 2001). These models use empirical and simplified correlations and do not incorporate physics-based multi-component reaction network and rigorous thermodynamics and kinetics representations (Davison et al., 2014). Model development that integrates surface hydrology model and reactive transport model has recently started (Yeh et al., 2006; Beisman et al., 2015). Similarly, recent model development has coupled hydrological, land-surface interactions, and reactive transport processes at the watershed scale (Bao et al., 2017; Duffy et al., 2014).

Future directions

Although it is conceptually obvious that critical interfaces regulate biogeochemical reaction rates, it remains unclear how to quantitatively relate critical interfaces to process representation and biogeochemical rates at larger spatial scales. *How large are the critical interfaces? What*

are the general principles and quantitative function that relate small-scale spatial organization to the formation of and fluxes at critical interfaces? Answers to these questions lie at the heart of developing larger scale predictive models using salient small-scale characteristics. Challenges remain partly due to difficulties and uncertainties in characterizing complex, hierarchical spatial patterns across scales. In this context, process-based models that explicitly incorporate spatial complexity present a powerful and cost-effective tool in querying heterogeneity controls of biogeochemical processes.

Models developed for processes across hydrology and biogeochemistry can be used as virtual laboratories for numerical experiments, whether they focus on the hyporheic zone or at the watershed scale. Although computationally expensive, these models can reveal rich information that would allow analysis of ecohydrological and biogeochemical processes at the grid block (local) scale and their key controls, as well as those at large scales through the mass balance of the system. Output from a watershed hydrobiogeochemistry model will reveal the temporal and spatial distribution of variables, including temperature, soil moisture, chemistry of gases, groundwater, and stream flow, and quantities derived from these variables such as rates of soil weathering and carbon decomposition. Their relationships with key characteristics at the watershed scale, including the dynamic connectivity, critical interface areas, and topographic features, can be explored. Such exercise can potentially “discover” general principles across scales, as well as emergent zones or critical interfaces which are not identified by spatially scarce measurements. As an example, the sediment transport modeling of Chesapeake Bay identified a persistent zone of high particle concentrations formed due to convergent flow, which was later confirmed by field survey that showed maximum abundance of plankton groups in this zone (Hood et al., 1999). Advances along these lines will ultimately allow the fundamental underpinning of dominant processes at different spatial scales and will foster the development of relationships between large-scale rates, reactive interfaces, and key spatial complexity metrics, therefore moving toward predictive understanding across scales.

2.4. Integration of novel data

The past decades have witnessed rapid advances in technology and the generation of novel data at scales as small as nanometers to those as large as the globe (i.e., remote sensing from satellites). Advanced observation techniques have expanded our visual capabilities from a relatively narrow range (10^{-3} – 10^1 meters) to a much wider spectrum (10^{-9} – 10^7 meters). Our insight into microbial processes has been revolutionized by the ability to broadly query microbial communities through genomics and the development of techniques to measure gene expression, proteins and metabolites (transcriptomics, proteomics, metabolomics) (Sharon and Banfield, 2013)—together referred to as “omics” data. New analytical capabilities have rapidly expanded the use of isotopes to elucidate key processes where multiple reaction and transport pathways may obscure the interpretation of solute concentrations alone (Albarede, 2004; Anbar, 2004; Johnson et al., 2004; Williams and Hervig, 2005). The field of hydrogeophysics has grown enormously with the development of non-destructive imaging to allow glimpses into complex subsurface processes (Binley et al., 2015; Parsekian et al., 2015; St. Clair et al., 2015). Advances in field characterization methods have provided high-resolution data to identify bioreactive fringes, mixing zone, and “hot spots” in the subsurface (Haberer et al., 2011). Imaging techniques such as X-ray Computed (micro)tomography have enabled unprecedented visualization of pore-scale details, allowing fundamental conceptualization and direct simulation at the scale of microns (Blunt et al., 2013; Bultreys et al., 2016; Hapca et al., 2015; Molins et al., 2012; Steefel et al., 2015b; Wen et al., 2016). In addition, the collection of different data types have started to be coordinated through large research community networks such as the Critical Zone Observatories (CZOs), the Long-Term

Ecological Research (LTER), the Great Lake Ecological Observatory Network (GLEON), and the USGS Hydrologic Benchmark Network (HBN), and the National Ecological Observatory Network (NEON). Large and diverse data from these networks allow integrated understanding of the interactions among processes that are traditionally done in disparate disciplines (Brantley et al., 2016; Brooks et al., 2015; Clark et al., 2015).

The growth in data type and intensity presents a major advantage for the use of models such as RTMs that typically represent complex processes and require a large number of parameters (Duffy et al., 2014). The incorporation of these novel data into RTM frameworks, however, introduces additional challenges. Many of the new data do not directly relate to solute or solid concentrations that RTMs calculate. Comparison of data and model output therefore requires further conceptualization, insights, and parameterization. For example, electrical geophysical methods typically measure properties such as electrical conductivity and chargeability, which reflect the overall changes induced by aqueous reactions and water-rock interactions such as surface complexation and ion exchange. Incorporation of geophysical data with RTMs has only recently begun (Singha et al., 2011; Wu et al., 2014). In general, the integration of novel data into RTM framework represents a development of broad and interdisciplinary potential.

Hypothesis 6. *The stable isotope partitioning of heterogeneous reactions in natural systems can range from dominantly irreversible to fully reversible, and requires detailed, spatially resolved description of both fluid and solid phase isotopic compositions at fluid-solid interfaces.*

Motivation

Isotopes have been extensively used as tools for hydrologic characterization, analysis of water-rock-life interactions, fluxes, and mixing between hydrologic and chemical reservoirs. Examples include the use of ^{13}C , ^{15}N and ^{14}C in soil and groundwater systems to unravel processes of C and N transformations (e.g. Dijkstra et al., 2008; Lawrence et al., 2015; Trumbore, 2009); the characteristic fractionations associated with redox reactions employed to analyze elemental cycling (Cheng et al., 2016; Dale et al., 2009; Druhan et al., 2012; Gibson et al., 2011; Hubbard et al., 2014); the growth and stability of secondary minerals (Mavromatis et al., 2014, 2015; Nielsen et al., 2012; Oelze et al., 2014, 2015; Schott et al., 2014; Watkins et al., 2013); transient isotope partitioning during the initial stages of mineral dissolution (Brantley et al., 2004; Chapman et al., 2009; Crosby et al., 2007; Kiczka et al., 2010; Weiss et al., 2014; Wiederhold et al., 2006; Wimpenny et al., 2010; Ziegler et al., 2005), and application to solute fluxes across landscapes (Dellinger et al., 2014, 2015; Louvat et al., 2014; Noireaux et al., 2014; Rive et al., 2013; Tipper et al., 2012a, 2012b; von Blanckenburg and Bouchez, 2014; von Blanckenburg and Schuessler, 2014).

Current status

Isotope-specific analytical expressions for the combined effects of transport and reactivity have been derived and applied to a variety of stable (Bouchez et al., 2013; Fantle and DePaolo, 2007; Fantle et al., 2010; Jacobson and Holmden, 2008) and radiogenic systems (DePaolo, 2006; Johnson and DePaolo, 1994, 1997; Lemarchand et al., 2010; Maher et al., 2006a; Tricca et al., 2001). However, more often approximations using either the Rayleigh distillation model or simple mixing models are applied to interpret stable isotope data in soils and rivers and groundwater systems, although the assumptions of these models are usually violated. Most of these systems could be incorporated into a multi-component reactive transport description that considers a suite of parameters that influence observed reaction rates (Maher et al., 2006b) or fractionation factors (Druhan et al., 2013). As a result, the recent expansion of stable isotope measurements has been accompanied by increased isotope-specific capabilities in RTM (Sidebar 3). Some models consider transport-based fractionation (Eckert et al.,

Sidebar 3: Using isotopes to identify key biogeochemical processes in marine sediments

Here a 1D RTM constrained by a comprehensive dataset (C , ^{32}S , ^{34}S , N , Fe) allows the identification of the complex reaction network associated with sulfur cycling in the organic-rich mud underlying the Namibian shelf waters (Dale et al., 2009). The sulfur dynamics are influenced by the bacterium *Thiomargarita namibiensis* that oxidizes H_2S to SO_4^{2-} using nitrate as the electron acceptor. The oxidized sulfate can further oxidize organic carbon (G) or methane (Fig. S3). Detailed quantification of reaction rates indicate sulfate reduction (SR) and H_2S oxidation by nitrate (>6.0 mol/S/m²/year). As a result, only a small fraction (~ 0.3 wt.%) of total H_2S production is trapped as sedimentary pyrite (FeS_2) and organic sulfur (S_{org}). A fractionation approaching 100‰ was observed, far higher than laboratory-based estimates for these processes. Mass balance calculations argue against the commonly believed view that this is caused by disproportionation of autochthonous elemental sulfur. Instead, the model indicates that repeated multi-step sulfide oxidation and intracellular disproportionation by *Thiomargarita* could, in principle, generate the measured isotopic fractionation.

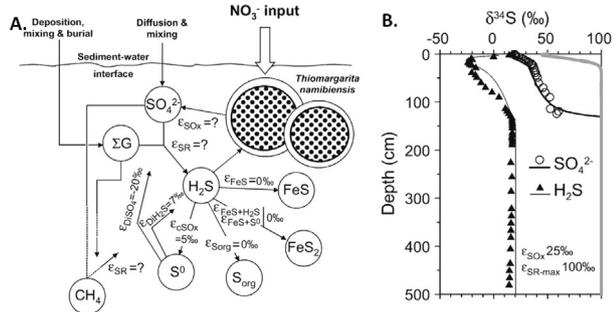


Fig. S3. A. Reaction network and fractionation (ϵ); B. measured (symbols) and predicted (lines) fractionation of SO_4^{2-} and H_2S using indicated ϵ values. The thick gray line shows the rate-dependent fractionation for sulfate reduction (modified from Dale et al. (2009), use with permission).

2012; Rolle et al., 2010; Van Breukelen and Rolle, 2012), or addition of individual isotopic ‘species’ in existing models that are necessary to describe contaminant degradation and sorption reactions (Hunkeler et al., 2009), including the transformation through multiple reaction pathways (Jin and Rolle, 2014). Others incorporate isotope-specific rate laws for mineral dissolution and precipitation that impact radiogenic and radioactive isotopes (Maher et al., 2006b), stable isotope fractionation associated with mineral growth (Druhan et al., 2013), abiotic redox reactions (Jamieson-Hanes et al., 2012; Wanner et al., 2014) and Monod kinetics (Cheng et al., 2016; Druhan and Maher, 2014; Gibson et al., 2011). A key advantage of these approaches is that the major element compositions are directly associated with the isotopic fractionation, enabling more rigorous evaluation of the transformations than could be obtained by considering the elemental or isotopic data in isolation (Sullivan et al., 2016). Currently, parameterization of existing RTMs is often limited by a lack of information on the processes that lead to differential isotope partitioning.

Future directions

There are two aspects of isotope-enabled RTMs that provide an array of interesting future research directions. The first is the use of isotopes to provide additional constraints on subsurface biogeochemical reactions. In many systems, major elements may participate in multiple reactions whereas the isotopic fractionation may be strongly determined by one reaction. Examples include Ca isotope fractionation due to calcite precipitation (Druhan et al., 2013), Li isotope fractionation during weathering (Bouchez et al., 2013) and metal isotope fractionation due to redox transformations (Druhan et al., 2014). The application of RTMs to interpret multiple isotopic profiles in tandem with the elemental variations may offer new insights into the isotopic system and reactions over space and time.

Nevertheless, to fully exploit the power of isotopes as tracers of biogeochemical processes, much more information about the processes that control fractionation is required. Although decades of research have focused on determining the causes and magnitudes of isotope

fractionation for reactions with a continuum of departures from equilibrium (or a mixture of kinetic and equilibrium fractionation), the description of this fractionation remains incomplete. There is thus a pressing need to determine fractionation factors defined as the ratio of either the rate constants (kinetic fractionation) or the equilibrium constants (equilibrium fractionation) for two isotopologues of the same species. This definition is compatible with the existing structure of RTMs and is in stark contrast to the empirical, condition-specific fractionation factors. Ultimately, the rigorous mass balance provided by RTMs may enable us to determine fractionation factors in the field using multi-element approaches to constrain the isotope partitioning. In addition, as diffusive fractionation and apparent fractionation due to mixing processes are widespread in subsurface systems, better understanding of the kinetic and equilibrium fractionation factors would enable RTM applications to separate the effects of transport (i.e., diffusion and mixing) from biogeochemical processes.

An additional challenge involves treatment of the solid phase during heterogeneous reactions. Continuum-scale RTMs describe the mineralogical composition of each grid block as a collection of mineral phases. The stable isotope composition of each mineral must then be incorporated and secondary minerals formed in the simulation must be described as a mixture of isotopic end members with temporally variable or spatially zoned isotopic compositions. A consequence of describing heterogeneous isotope fractionation in current continuum-scale RTMs is that the growth of a mineral phase requires the use of a solid solution, while dissolution of a solid is accomplished by the use of a pre-specified isotopic composition (Druhan et al., 2013). As a result, this approach lacks the capability to describe stable isotopes across reversible saturation states. Current research using lattice-Boltzmann (Huber et al., 2013) and surface kinetic (Maher et al., 2016) or ion-by-ion (Nielsen et al., 2012) models offer more accurate descriptions of isotopic incorporation into solids. These methods have yet to be reconciled with continuum scale approaches. Future research on the reversibility of stable isotope fractionation factors needs to be developed at spatial scales appropriate to describe fluid-solid interfaces in order to support and validate model development. Grain-scale models with moving boundaries within a continuum grid cell could be adapted for isotopic composition

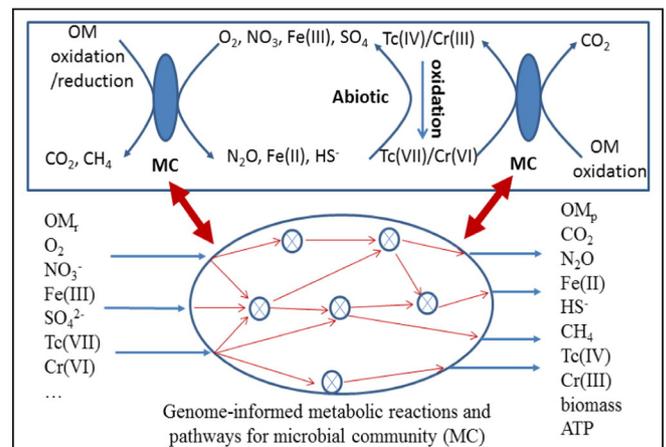


Fig. 6. Reaction network and metabolic pathway using natural organic matter (OM) and a wide range of available electron acceptors. The two blue cells schematically represent microbial communities (MC) consisting of many different organisms. The two red arrows expand the MCs, leading to the oval region schematically describing enzymatic pathways. The oval region describes collective enzymatic pathways, or reaction networks, for the microbial communities that may be elucidated by genomic or proteomic analyses. The effective concentrations of involved enzymes along with other parameters descriptive of enzyme kinetics may be used to drive reaction-based calculations in RTM (courtesy of Chongxuan Liu, Pacific Northwestern National Laboratory).

evolution as has been done for trace element mineral compositions during recrystallization (Neogi et al., 2014).

Hypothesis 7. *The incorporation of “omics” data into RTMs will enable predictive understanding of the emergent behavior of dynamic biogeochemical systems.*

Motivation

Biogeochemical systems are complex, internally interactive, and fundamentally nonlinear. Dynamically evolving microbial communities shape the distribution of biogeochemical processes in earth surface environments (Fig. 6). The advent of omics data in recent decades had motivated the rapid advances in developing metabolic models to understand bacterial cell signal-transduction proteins, regulators, and metabolic and respiratory subsystems (Fredrickson et al., 2008; Reed and Palsson, 2003). The integration of omics data into RTM development, however, has not kept pace (Fang et al., 2011b; King et al., 2009; Vallino, 2003; Zhuang et al., 2011). The development of omics-enabled RTMs is challenging for several reasons. First, it requires expertise in microbial ecology and geochemical modeling along with omics methods and bioinformatics (Feist et al., 2009). Only recently have we begun to train scientists to effectively bridge these fields. Second, the nature of omics data differs from concentration, geochemical speciation, or direct rate measurements that traditionally have been integrated with RTMs. Such data is not *directly* comparable to the output of the current generation of RTMs. Third, and most importantly, the complexity of the microbial community revealed by omics data needs to be reduced to a level that is practical and can be parameterized, but yet inclusive of system-determining biogeochemical processes for integration into RTMs.

Current status

The incorporation of microbial activity in RTMs has mostly been limited to bulk biomass growth (Barry et al., 2002; Tartakovsky et al., 2009) and the indirect effects of microbial activity on electron acceptors and organic C concentrations using Monod or Michaelis-Menten rate laws (Li et al., 2010; Tartakovsky et al., 2013). These model formulations aim at simulating the impact of environmental conditions (e.g., substrate availability) on microbial activity, which then feedback on the environment (by community growth, for example). With careful simulation construction, numerical models have been used successfully to discriminate between various microbial functions and to predict the microbial community response to biostimulation conditions where microbial populations respond to an overwhelming abundance of a known C source (e.g. Druhan et al., 2012; Li et al., 2011; Yabusaki et al., 2011). Conversely, there are functional genes that code for specific microbial activities. One example is nitrogen cycling where genes are known for each enzymatic step. The transcription of these functional genes therefore can tell us the limiting steps/processes in nitrogen cycling in soils, even though the data do not yield rates directly (Wallenstein and Vilgalys, 2005; Yan et al., 2003). A key challenge is to predict feedbacks between the microbial community and environmental conditions (Bouskill et al., 2012). For example, nutrient limitation is likely to affect the emergent behavior and is difficult to predict. To date, the effects of nutrient limitation are only coarsely accounted for and only within the context of a generally limited, *a priori* defined reaction network (Bethke et al., 2008; Jin et al., 2012; King et al., 2010).

Future directions

It is timely to consider how omics information can be used to develop functional-gene or protein-based models that include key enzymatic reactions (metabolic groups) controlling system behavior and response to environmental or geochemical change (Fig. 6). To keep computational burden manageable, a limited number of microbial actors capable of carrying out biogeochemically significant reactions could be selected as the model core with steady state concentrations assumed for

intracellular metabolites. Such a model would explicitly consider the dynamics of biomass, genes, enzymes, substrates, as well as the community control strategy (e.g., maximizing energy yield and/or biomass growth (Jin et al., 2012)), and could be used to explore hypotheses on the role of dynamic microbial community membership and interactions on the functioning and resilience of biogeochemical systems. In addition, the integration of omics data into RTMs can take place through the establishment of quantitative relationships between the fundamentally measurable biological characteristics and model parameters, such as growth yields under varying environmental conditions (e.g., Vieira-Silva and Rocha, 2010). Complementary to the use of molecular biology data to inform the model structure or parameterization *a priori*, rich data sets also offer strong constraints on RTMs. This includes the insights offered on active pathways through, e.g., transcriptomics and proteomics, or the use of concentrations of a wide range of chemicals (e.g., metabolomics) in the calculation of bioenergetics differentiating between thermodynamically feasible and infeasible processes.

As a new generation of molecular-biology enabled RTMs are developed, there is potential to describe and predict isotope partitioning as a function of the evolving relationship between multiple enzymatic reactions within an individual cell and their expression as a function of dynamic microbial community membership and interaction. Elements that are strongly influenced by biological cycling, such as iron and sulfur, record long-term variations in isotopic fractionation through the rock record that preserves information about climate, redox conditions and microbial dynamics (Sidebar 3). Stable isotope distributions therefore offer key means of validating a new generation of molecular-biology enabled RTMs in complement to direct metagenomic data, particularly where acquisition of these data is limited or precluded. This will be relevant particularly in applications beyond modern day systems, such as paleosols and chronosequences where direct metagenomic observables have been largely erased, but the characteristic partitioning of stable isotopes associated with past microbial communities is preserved. The combination of omics and isotope data will therefore enhance our interpretation of processes with relevance to short-term response (e.g. contamination or biostimulation) and in natural systems over geologic timescales. In fact, because of the long time scales involved in natural systems, we may be able to infer fractionation factors and reaction rate constants that are more accurate than those from laboratory systems, especially for those systems with small fractionation and rate constants.

3. Looking forward

Over the past three decades, researchers have demonstrated the usefulness of RTMs in understanding and predicting coupled physical, chemical, and biological processes in natural and engineered subsurface environments. We recognize that the use of RTMs can be expanded to understand various earth surface processes and to address some of the pressing research needs of other disciplines (Vereecken et al., 2016). However, RTMs alone are insufficient. Looking forward, we see many opportunities where the RTM framework can be integrated into existing models in related disciplines (Fig. 1). This becomes particularly important as the science community increasingly recognizes the significance of subsurface processes in influencing earth system functioning and formation. For instance, groundwater has been found to profoundly impact wetland formation and vegetation gradients (Fan, 2015; Fan et al., 2013). Soil C decomposition and stabilization influence global C cycle and climate change (Schmidt et al., 2011; Trumbore and Czimczik, 2008). The seven hypotheses outlined here are examples that can be tested with current capabilities or future development of RTMs. In particular, we envision advanced understanding by integrating RTMs into disciplines including hydrology, geochemistry, soil sciences, terrestrial ecosystem sciences, and geomorphology. Although coupling models across disciplines presents numerous challenges including upscaling, computational expenses and data availability, we believe this should be attempted. Otherwise, we will miss very important linkages and

feedbacks among processes that regulate different parts of earth surface systems (Faticchi et al., 2016). The current lack of models describing process-level coupling will significantly limit the use of large-scale models for forecasting global hydrology and biogeochemistry.

3.1. Challenges

RTMs are similar to distributed hydrologic models and therefore share their problems and limitations. Whereas hydrological models solve for water, hydraulic or pressure head and saturation, RTMs solve for a suite of chemical species, often in the order of tens. That leads to an additional level of reaction complexity with nonlinear laws of thermodynamic relationships and kinetics. The RTM approach therefore imposes a higher data demand for defining model domains, conditions, and constraints. For instance, a distributed hydrologic model domain needs information on topography, soil maps, and soil hydrological properties as a function of depth. Many of these data are available from national databases, including the USGS National Elevation Dataset (NED), the Soil Survey Geographic (SSURGO) database, and the National Land Cover Database (NLCD). An RTM will need an additional suite of biogeochemical properties including spatial distribution of mineralogy, specific surface area, ion exchange capacity, organic matter content, and microbial biomass. In constraining the model output, it would need not only water fluxes but also concentrations of reaction products including, major cations (e.g., Ca, Mg, Na, K), major anions (e.g., SO₄, NO₃, Cl), dissolved organic and inorganic carbon, nutrients (N, P), and pH. The use of these additional data in constraining RTM however will enrich our understanding of complex earth systems.

As models become more complex, new tools to evaluate them will need to be developed (van Griensven and Meixner, 2006; van Griensven et al., 2006). Uncertain parameters may range from categorical (e.g., boundary conditions), continuous (e.g., mean permeability or rate constants) to spatial (e.g., uncertainty on facies models). The problem of uncertainty in distributed models has been routinely addressed with the Generalized Likelihood Uncertainty Estimation (GLUE) in the hydrology community (Beven and Binley, 1992). Other approaches include, for example, distance-based global sensitivity analysis (Fenwick et al., 2014) and Maximum Likelihood Bayesian Model Averaging (BMA) framework (Neuman et al., 2012; Ye et al., 2004). These approaches, can aid in evaluating parameter sensitivity across multiple categories and assist in model reduction. Unfortunately, robust approaches are not yet routinely applied to RTM-based studies. Data assimilation, originated from numerical weather prediction (Daley, 1991), is another technique that has been used widely in recent decades to address the issue of parameter non-uniqueness or equifinality in atmospheric, geographic, oceanic, and hydrologic sciences (Beven, 2001b; Navon, 2009; Rabier, 2005). Data assimilation, however, has rarely been used in multi-component RTMs.

Upscaling represents another grand challenge in integrating RTMs into large scale hydrologic and earth system models that operate at much larger spatial scales than traditional RTMs. A similar challenge remains in upscaling from the hydrologic time of months and years to the landscape evolution timescale of millennia (Duffy et al., 2014). This challenge lies at the heart of Critical Zone science where one major goal is to understand measurements across systems operating at different time scales. As spatial and temporal scales increase, dominant processes might change due to the “averaging” and “aggregation”. This would require different mathematical formulation in representing large-scale processes, parameters, as well as boundary and initial conditions. Although theoretical upscaling frameworks such as volume averaging exist (Whitaker, 1999; Wood and Whitaker, 1998), these approaches fall short when dealing with complex biogeochemical systems that have a large number of species and highly nonlinear reaction thermodynamics and kinetics. A range of multi-scale hybrid modeling approaches have been reviewed and analyzed recently (Scheibe et al., 2015; Scheibe and Smith, 2015). Simple averaging however is not

possible due to the high nonlinearity and complex process coupling. Massive numbers of process-based model simulations can be run to derive general principles and performance patterns and can be used to translate small-scale processes and characteristics into large scale representations (McDonnell et al., 2007b).

3.2. Directions

The integration of RTM framework into the broader hydrologic sciences will be a powerful approach toward understanding complexity at large spatial scales. Hydrologic models at the catchment scale typically include surface hydrological processes (Brunner and Simmons, 2012; Kollet and Maxwell, 2006; Kumar et al., 2009; Maxwell, 2013; Qu and Duffy, 2007a) and recently have been coupled with atmospheric drivers and land-surface interactions (Clark et al., 2015; Maxwell and Miller, 2005; Shi et al., 2013). Indeed, most hydrologic models are underconstrained. The incorporation of RTM modules into hydrologic models offers the potential to constrain simulations by incorporating expressions for the wide array of solutes moving in surface and groundwaters. Coupling hydrologic models with RTMs will advance our understanding of watershed hydrobiogeochemistry with the potential to resolve long-standing puzzles including, for example, the observed concentration-discharge relationship at the watershed scale (e.g., Godsey et al., 2009; Kirchner, 2003; NRC, 2012). RTMs incorporating complex physical settings of hyporheic zones and water corridors can offer fundamental insights into intriguing interactions among flow, transport, and biogeochemical reactions, likely demystifying observations at these critical reactive interfaces (Harvey and Gooseff, 2015).

The root zone represents another focal point where mechanistic understanding can be obtained by extending current RTMs capabilities. Such understanding is of interest to an array of disciplines (biogeochemistry, soil sciences, microbiology, hydrology, and terrestrial ecosystem sciences). Integration of spatially-explicit RTMs into existing Earth System Models (ESMs) will capture interactions among atmosphere, biosphere, and geosphere under changing climate. Expansion of temporal scales into geological time scales will allow the integration of geochemical processes with geomorphic frameworks to understand chemical, physical, and biological coupling in landscape evolution. Landscape evolution models have been developed that can explain topography (e.g. slope, relief, channel density) (e.g., Chen et al., 2014; Goren et al., 2014; Zhang et al., 2016). Whereas soil production and thickness has been predicted in landscape evolution models (Dietrich et al., 1995), existing RTMs of chemical weathering have been developed mostly from the geochemical perspective. Initial steps have been taken to couple the modeling of chemical weathering and erosion (Lebedeva and Brantley, 2013; Maher, 2010). Such models predict the depth to fresh bedrock across hillslopes on the basis of simplifying assumptions, but other such models connecting hillslope development to the landscape scale are only now emerging (Anderson et al., 2013; Lebedeva and Brantley, 2013; Rempe and Dietrich, 2014; St. Clair et al., 2015). The incorporation of geochemical processes into long-timescale models of the spatial patterns of soil and weathered bedrock will increase our understanding of the co-evolution of climate, ecosystems, and landscapes (Dupré et al., 2003; Goddérís and Brantley, 2013; National Research Council, 2010).

Much like the fractured nature of data collection within separate disciplines (Brooks et al., 2015), model development also reflect fragmentation among disciplines. As data collection has been coordinated within networks of communities through joint platforms such as the Critical Zone Observatory (CZOs), Long Term Ecological Research (LTER) network, and United States Geological Survey (USGS), the Great Lake Ecological Observatory Network (GLEON), and the USGS Hydrologic Benchmark Network (HBN), and the National Ecological Observatory Network (NEON), we also emphasize the need for interdisciplinary model development and the integration of RTM capabilities into existing models in other communities (Duffy et al., 2014; Goddérís

and Brantley, 2013). For example, to understand the role of biotic processes in chemical weathering, root models from the plant community can be coupled with RTMs (DOE, 2015). In this context, flexible modular approaches are needed to advance modeling capabilities across disciplines. Several geoscience research communities have worked toward that direction, including the Community Surface Dynamics Modeling Systems (CSDMS) (<http://csdms.colorado.edu/>), where modeling infrastructure has been developed to minimize overlapping efforts. The US Department of Energy (DOE) Advanced Scientific Computing Research (ASCR) and Basic Energy Research (BER) have embarked on a pilot effort to re-factor existing High Performance Computing (HPC) software and develop new computational tools that can be scaled up to the next generation 'extreme-scale' platforms. Efforts are needed to identify common interests to leverage resources and push synergistic model development for multiple scientific communities.

We are now in an exciting era characterized by an unprecedented luxury of rich data (Fan et al., 2015). Comparisons between data and models will offer insights about the key data that are critical to improve understanding. Collaborative sciences are dissolving the boundaries that separate traditional disciplines. RTMs are acting as frameworks that quantitatively integrate across the fields of hydrology, geochemistry, geomorphology, plant physiology, and microbiology. Such interfacing will lead to greater understanding of the formation, evolution, and functioning of the Critical Zone (Fig. 1). While the era of numerical weather prediction by computers began about half a century ago, earth process forecasting will become possible with increasing observations and computational capabilities in the coming decades. Although large uncertainties and challenges will remain, we are ready to build numerical integrators for processes, data, disciplines, and scales to explore the evolution and functions of the critical zone.

Acknowledgement

This paper grew out of the workshop "Expanding the role of reactive transport modeling in biogeochemical sciences", held in Alexandria, Virginia on April 13–15, 2014 (Li et al., 2014) with support from the NSF Low Temperature Geochemistry and Geobiology (EAR 14-14558). EWB received support from NASA Astrobiology Institute's Virtual Planetary Laboratory under Cooperative Agreement number NNA13AA93A. SLB acknowledges funding from DOE OBES DE-FG02-OSER15675. LL acknowledges funding from DOE SBR DE-FOA-0000311. We acknowledge insightful feedbacks and careful editing from Jon Chorover and David L. Parkhurst, as well as stimulating and constructive comments from Olaf Cirpka and two anonymous reviewers that have significantly improved this paper. We appreciate Dr. Joan-Albert Sanchez-Cabeza for handling this manuscript.

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