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Twelve testable hypotheses on the geobiology of weathering

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ABSTRACT

Critical Zone (CZ) research investigates the chemical, physical, and biological processes that modulate the Earth's surface. Here, we advance 12 hypotheses that must be tested to improve our understanding of the CZ: (1) Solar-to-chemical conversion of energy by plants regulates flows of carbon, water, and nutrients through plant-microbe soil networks, thereby controlling the location and extent of biological weathering. (2) Biological stoichiometry drives changes in mineral stoichiometry and distribution through weathering. (3) On landscapes experiencing little erosion, biology drives weathering during initial succession, whereas weathering drives biology over the long term. (4) In eroding landscapes, weathering-front advance at depth is coupled to surface denudation via biotic processes. (5) Biology shapes the topography of the Critical Zone. (6) The impact of climate forcing on denudation rates in natural systems can be predicted from models incorporating biogeochemical reaction rates and geomorphological transport laws. (7) Rising global temperatures will increase carbon losses from the Critical Zone. (8) Rising atmospheric P_{CO2} will increase rates and extents of mineral weathering in soils. (9) Riverine solute fluxes will respond to changes in climate primarily due to changes in water fluxes and secondarily through changes in biologically mediated weathering. (10) Land use change will impact Critical Zone processes and exports more than climate change. (11) In many severely altered settings, restoration of hydrological processes is possible in decades or less, whereas restoration of biodiversity and biogeochemical processes requires longer

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timescales. (12) Biogeochemical properties impart thresholds or tipping points beyond which rapid and irreversible losses of ecosystem health, function, and services can occur.

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INTRODUCTION

The impact of humans on the Earth's atmosphere, water, sediments, soil, and biota is thought to be of such magnitude that a new geological epoch – *the Anthropocene* – has been proposed (Crutzen, 2002; Zalzsiewicz *et al.*, 2008). The pace of anthropogenic change threatens sustainable use of soil and water, and impairs critical ecosystem services (Vitousek *et al.*, 1997; DeFries & Eshleman, 2004; McNeil & Winiwarter, 2004; Foley *et al.*, 2005; Wilkinson, 2005; Wilkinson & McElroy, 2007; Holdren, 2008; Mann & Kump, 2008). Predicting changes in earth resources requires quantitative models to forecast – *Earthcast* – the behavior of the zone extending from the vegetation canopy to groundwater (Bachlet *et al.*, 2003; Yang *et al.*, 2003; Steefel *et al.*, 2005; Qu & Duffy, 2007; Minasny *et al.*, 2008; Goddéris *et al.*, 2009; Rasmussen *et al.*, 2010). This realm, where rocks meet life, has been named the Critical Zone (CZ; US National Research Council Committee on Basic Research Opportunities in the Earth Sciences, 2001). Within the CZ, biota – including humans – interact with earth processes to define the chemistry, texture, and topography of our surface habitat through weathering, element cycling, and erosion.

To describe the behavior of a system as multifaceted as the CZ, Earthcasting models need to be developed and parameterized from observations of the atmosphere, water, surface Earth materials, and biota, made over a range of spatial and temporal scales. It is not sufficient, for example, to focus only on rocks at depth if the goal is to solve problems related to human-land-air-water interactions. Likewise, if the goal is to understand the long-term implications of climate change, it is not sufficient to measure the short-term responses of vegetation, because nonlinear, highly complex responses can emerge over the long term, in strong contrast to more predictable, shorter-term linear responses (Swetnam *et al.*, 1999; Gunderson, 2000; Chadwick & Chorover, 2001; Bachlet *et al.*, 2003). One of the best time-integrated records of the CZ is the soil itself: soil horizons, thicknesses, texture, structure, composition, biological activity and their spatial patterns in landscapes integrate and record the flow of material, changes in climatic and tectonic forcing, and the influence of humans and other biota on the CZ (Dokuchaev, 1883; Jenny, 1941, 1980; Yaalon, 1983; Retallack, 1990; Richter & Markewitz, 2001). Indeed, humans ultimately depend on weathering and erosion processes to maintain the natural resources underlying society and ecosystems (McNeil & Winiwarter, 2004; Montgomery, 2007). Productive and sustainable agriculture, forestry, and aquatic resources are directly linked to CZ processes that transform rock into soil and sediment.

In this study, we pose 12 hypotheses developed by more than 30 scientists from a range of scientific disciplines (see Acknowledgements). The group sought to state *provocative*, *important*, and *testable* hypotheses that are related to the complex interactions among biology, weathering, and erosion. Although some of the hypotheses have been implicit in scientific research conducted since the late 1800s, we argue that new analytical, modeling, and field opportunities now allow advances that can test these hypotheses over the next decade.

EARLY DISCUSSIONS OF THE EFFECTS OF BIOLOGY ON WEATHERING AND EROSION

Understanding how biology interacts with earth materials to form the CZ has long been a subject of curiosity, scientific inquiry, and social necessity. Historically, numerous proposals were advanced to explain weathering, the process that breaks down and solubilizes rock components, leaving residual soil minerals and exporting solutes. Some of these early ideas match our current understanding; for example, in the early to mid-1800s, the decomposition of igneous rocks was attributed to the reactivity of water and carbonic acid (Fournet, 1833; Hartt, 1853) and landscape evolution was thought to be influenced strongly by the production of physically mobile soils (Gilbert, 1877, 1909). Furthermore, very early on, the role of vegetation was noted: for example, Belt (1874) wrote that 'the percolation through rocks of rain water charged with a little acid from decomposing vegetation' accelerated weathering. In roughly the same time period, Charles Darwin studied the effects of earthworms on soils, concluding that '… all the vegetable mold over the whole country has passed many times through, and will again pass many times through, the intestinal canals of worms' (Darwin, 1881). By the 1880s, the concept of soils as natural systems that are governed by the interaction of climate, living matter, parent material, relief, and time had been developed (Dokuchaev, 1883).

Perhaps the modern era of biota-weathering research began in the latter half of the 1900s as researchers began to explore the role of microbial communities in weathering of historic stone buildings (Ehrlich, 1990; Krumbein *et al.*, 1991). Today, a wide variety of researchers from many disciplines are focusing on the relationships between biota and weathering and erosion. Such efforts now focus on quantifying both the importance of microbial activity and plants in elemental cycling and rock weathering in natural systems (e.g. Banfield

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& Nealson, 1997; Berner *et al.*, 2003). Furthermore, researchers are also modeling the effects of fauna on weathering and erosion (e.g. Gabet *et al.*, 2003). Recent work on nutrient cycling and material flows within ecosystems also acknowledges the importance of rock weathering in structuring ecosystems (Banfield & Nealson, 1997; Buss *et al.*, 2005; Osterkamp & Hupp, 2010).

Despite the long history of inquiry, quantitative insights on many fundamental issues have been elusive. For example, the contribution of rock weathering to ecosystem-level biogeochemical cycling has rarely been measured directly and is typically calculated as the difference between atmospheric inputs and stream flow exports. Likewise, linking the role of biologic agents of erosion and climatic change to both short- and long-term denudation has been elusive. Fortunately, new isotopic techniques (Bourdon *et al.*, 2004; Johnson *et al.*, 2004; Von Blanckenburg, 2006) and advances in the use of molecular biological (Banfield *et al.*, 2005), elemental (Herrmann *et al.*, 2007), and organic (Johansson *et al.*, 2009) analyses now make it possible to quantify the rates of rock weathering and to define the role of organisms.

DEFINITIONS: TALKING ABOUT THE CZ

Although the CZ has been researched since the onset of science, the term itself is new. *CZ science* incorporates a holistic yet quantitative approach to understanding Earth surface processes, integrating across diverse scientific disciplines and a range of spatial and temporal scales. To promote communication across the CZ disciplines and to begin to achieve consensus about terminology, we present working definitions of key CZ terms that have been variously defined over the years by different groups.

Defining the CZ system

Beginning at the base of the CZ, we define *parent material* as earth material as it was before alteration by surface processes. In some cases, parent material is consolidated *bedrock*. In other cases, it can be unconsolidated *sediments*, or fragments of rocks and organic matter transported from elsewhere. Regardless of the nature of the parent material, its alteration causes the development of *regolith*, here defined as the mantle of unconsolidated and altered material that was generated from the parent material. In this context, *soil* is the surface sublayer within regolith where the parent material has been *extensively* altered, generally by chemical, physical, and biological transformations. Likewise, *saprolite* is the zone in regolith, if present, where parent material has weathered isovolumetrically in place. Saprolite generally retains evidence of parent material texture and fabric.

Biological, chemical, and physical alteration processes are important in both saprolite and soil, but soil is more affected by biology due to its shallow depth and proximity to the plant canopy, which is the source of chemical energy for much of the biological activity that drives weathering. Defined this way, soils are the surface-most zone of the regolith where biological, chemical, hydrological, and physical processes are most active, characteristically driving the evolution of layers known as *horizons*. Although CZ interactions between biology and weathering are most intense and dynamic in the soil, it should be emphasized that biological activity – both *in situ* and *ex situ* – is also an important feature of weathering processes in the saprolite and deeper zones of regolith.

Importantly, these definitions do not match those used in all the CZ disciplines. For example, some scientists define 'soil' to include saprolite. Also, geomorphologists describe regolith (Small *et al.*, 1999) or the mobile soil layer (Heimsath *et al.*, 1997) on hillslopes as the layer that is physically mixed and transported downslope. Clearly, the mobile layer and the chemically altered layer do not have to be coincident.

Lower limit of regolith

The bottom of regolith is defined here as the point where chemical and physical properties change from unaltered to altered. This leads to two operational definitions for the *parent–regolith interface*: (i) the physical interface where the underlying parent material has altered and can be easily sampled without drilling or hammering, or (ii) the chemical interface where regolith is chemically distinct from parent material. The first definition is useful for field work. Thus, the depth of refusal during augering or digging is often used to define the base of regolith. However, at this depth, the 'parent' may be both physically and chemically changed from the true parent and therefore the operational definition may be problematic. Furthermore, when parent is a deposit such as alluvium or colluvium, the physical base of regolith may not be easy to define using this criterion.

In addition, it is important to reiterate that geomorphologists often define the parent–regolith interface with a third operational definition: (iii) the interface between 'mobile' and 'immobile' material, generally identified in soil pits from grain size and textural relationships. The mobile layer is also sometimes denoted in the geomorphological literature as the 'soil' and the underlying material is referred to either as 'weathered bedrock' or as 'saprolite' depending on the degree of chemical weathering. Importantly, these geomorphological definitions may differ in many situations from definitions in this paper.

Whereas interfaces (i) and (iii) can be identified in the field, the chemical base of regolith (interface ii) requires measurements that can only be completed in the laboratory. Even with such laboratory analyses, an operational definition is still needed – e.g. 10% alteration – to define the distinction between regolith and parent. Such laboratory measurements can be used to define *weathering reaction fronts* for chemical reactions – zones of regolith across which a given chemical reaction for a given mineral occurs.

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Both regolith and parent material are often described with respect to their *lithology*. The term lithology refers to the rock type that includes information about composition and mineralogy. Also important is the rock *texture* – a term referring to the size and distribution of mineral grains and porosity, as well as the presence or absence of banding or other patterns.

CZ processes

The term *weathering* is used here to denote all processes that change the parent material to regolith. As discussed further below, some of these weathering processes result in net loss of material from a system whereas others represent alteration with little or no mass flux out. Here, we define *denudation* as the net loss of all material due to chemical, biological, and physical processes.

Although weathering is used here in a very general sense, we will define *chemical weathering* specifically to include only chemical reactions that transform the chemistry, mineralogy, or texture of a solid phase in the CZ. For example, the original minerals in the parent, i.e. the *primary minerals*, are often chemically weathered to produce *solutes* (dissolved species in the aqueous phase) that may precipitate as new *secondary minerals*. The driving force for weathering is the impulse to decrease the free energy of the system as primary minerals equilibrated to deep conditions re-equilibrate to the conditions at Earth's surface. Chemical weathering can release elements into water that are transported out of the system as solutes (*chemical denudation*), into the gas phase, or into ecosystem pools (*biological uptake*). Importantly, precipitation of secondary minerals is a crucial component of the chemical evolution of the CZ, but it is not included in the chemical denudation term.

Physical weathering is defined here to include only processes that fracture, change the density, or reduce the grain size of the parent material without changing mineral chemistry. Thus, physical weathering does not change the chemistry but rather tends to increase the surface area per unit mass, or *specific surface area*, of parent material and thus increases its susceptibility to chemical weathering and denudation. By disrupting the coherence of the parent, physical weathering may also promote *physical denudation*, which is conceptually parallel to chemical denudation in that it denotes the net loss of regolith as solids rather than solutes. In this paper, *erosion* is defined as the sediment outflux minus the sediment influx for a given location and is thus identical to physical denudation. To some researchers, the term erosion connotes losses due to chemical, physical, and biological processes – a usage that we reserve for denudation. Here, we adopt the convention that *erosion* refers to material losses due to physical movement of earth material, without reference to losses of solutes from the system.

Critical Zone science aims to quantify rates and spatial distributions of these processes. The *rate* of *chemical* or *physical denudation* is defined as the net loss per unit time of solutes or sediments, respectively, from a given system. These rates are expressed in units of mass or moles or volume of material per unit time. To compare denudation rates among different watersheds or hillslopes typically requires normalization relative to the area in question. Thus, *chemical* and *physical denudation fluxes* are typically expressed as volume or mass per area per time ($m^3\ m^{-2}\ year^{-1}$ or $m\ year^{-1}$; $kg\ m^{-2}\ year^{-1}$). To transform from units of volume per area per time to mass per area per time requires knowledge of *bulk density* (mass per unit volume) of regolith or parent material.

Biological weathering refers to all the processes by which biota – including humans – change the chemical or physical properties of parent or regolith. Distinguishing biological from chemical and physical weathering is ambiguous: for example, the transformation of a primary mineral to a secondary mineral within a biofilm that releases solutes to bulk porefluid might be described as both chemical and biological weathering. Similarly, plant roots and burrowing animals take advantage of existing pores and fractures in bedrock to advance physical weathering. The distinction between chemical and physical weathering can be ambiguous as well. For example, chemical reactions are thought to drive fracturing during weathering; conversely, opening of fractures promotes chemical weathering of new surfaces.

Water in the CZ

In general, *groundwater* is water in the *saturated zone*, where pore space is filled with water. In contrast, the *unsaturated* or *vadose zone* is the layer where pores are filled by both air and water. The original definition of the CZ stated that the bottom of the CZ is roughly the bottom of groundwater (US National Research Council Committee on Basic Research Opportunities in the Earth Sciences, 2001). However, the base of groundwater is not precisely defined. At some point at depth, water is no longer described as groundwater and is better described as *diagenetic water*, i.e. water that has been heated to a minor degree along the geothermal gradient. Diagenetic water may have been trapped during rock formation or it may consist of meteoric water circulated downward from the Earth's surface.

As the residence time and temperatures of diagenetic waters increase, the water chemically equilibrates with higher-temperature assemblages of minerals at depth. In contrast, in some locations at the land surface, water may be in equilibrium with low-temperature assemblages of minerals. However, most of the CZ is characterized by water that is present at ambient temperature and that is not chemically equilibrated: shallowly circulating meteoric waters are not hot enough nor have they experienced long enough residence times to be everywhere chemically equilibrated. The CZ is the zone defined by the gradient from mineral assemblages equilibrated to above-ambient temperatures at depth to mineral assemblages equilibrated

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to ambient temperatures at Earth's surface. The CZ, the zone that is largely at near-ambient temperatures and that has not attained chemical equilibrium, is therefore the zone that hosts organisms living off energy derived from chemically non-equilibrated rocks and from the sun.

Evolution of the CZ

It is also important to note that some landscapes are experiencing active erosion while others are relatively stable, without significant erosion. *Stable landscapes* may be characterized by soil profiles that deepen with time and whose characteristics change with time. Sets of soils on the same lithology and in the same climate that have developed on such stable landscapes over different exposure periods are referred to as *chronosequences.* In contrast, the thickness of soils developed on actively eroding landscapes may reach steady state such that the rate of *weathering advance* downward into parent material is roughly equal to the rate of erosive loss of material at the surface. The weathering advance rate can be used to describe the rate of transformation of bedrock to saprolite (saprolite advance rate) or saprolite to soil (soil production rate).

In both actively eroding and stable landscapes, the CZ is an example of a *complex, non-equilibrium dynamical system* owing to its existence in a thermodynamic gradient, over which it dissipates energy and may exhibit emergent properties (Prigogine, 1980; Corning, 2002). As an *open system*, the CZ experiences inputs and outputs of energy and matter. Although the properties of a dynamical system generally vary with time, they may under certain conditions remain at *steady state*. For an open system, this requires the inputs and outputs across the system's boundaries to balance one another. Under steady-state conditions, it is possible to define the *mean residence time* or *turnover time* of a set of particles or elements as the mass of particles or elements in the system divided by the rate of throughput. The term residence time is usually applied to physical, chemical, and biological constituents of the CZ. The application of the concepts of residence time and steady state requires a careful definition of the system's boundaries and the timescale of interest.

THE HYPOTHESES

The complex interplay of weathering and biota in the CZ poses challenges for advancing research on how Earth's surface evolves in response to biological processes and other factors. Essential to overcoming these challenges is the use of an interdisciplinary approach. Using such an approach, we developed 12 provocative hypotheses that can be tested today, without regard for whether one or more may turn out to be untenable or whether some elements of the different hypotheses are contradictory. The goal in advancing these hypotheses is to stimulate important research at the nexus of weathering and biology.

Understanding the CZ

Hypothesis 1. Solar-to-chemical conversion of energy by plants regulates flows of carbon, water, and nutrients through plant-microbe soil networks, thereby controlling the location and extent of biological weathering

The fossil record documents that, for more than 400 million years, the majority of land plants have formed symbiotic associations with mycorrhizal fungi (Taylor *et al.*, 2009). In the Devonian, the evolution of land plants with mycorrhizal associations coincided with an order of magnitude decrease in atmospheric CO_2. This was followed by a more gradual decline in P_{CO2} from the middle Cretaceous that has been linked to increased continental weathering of Ca and Mg from silicate minerals and their re-precipitation in marine carbonates (Berner, 2006). Increasing evidence implicates plant–mycorrhizal fungal co-evolution as a key driver of these processes (Taylor *et al.*, 2009).

Plants and their mycorrhizal fungi form an integrated network transporting carbon, water, and nutrients through the CZ, with organic carbon flowing down from the top of the vegetation canopy to the tips of the deepest roots and mycorrhizal mycelia in soil, whereas in return water and nutrients are taken up and transported through the organisms back to the canopy (Fig. 1). Flows of soil water and dissolved nutrients into mycorrhizal fungi and roots (Fig. 1, Box B) are largely controlled by the photosynthetic activity of plants. As stomata open in leaves to allow CO_2 uptake and fixation, loss of water is promoted to the atmosphere (Fig. 1, Box A). This, in turn, serves to draw replacement water from elsewhere in the soil through the network of interconnected plant and fungal tissues. Biotic networks can affect geochemical processes at considerable distances beyond the site of biological origin due to transport of metabolic products (e.g. carbon and acids generated by biota) to significant depths where they stimulate reactions (Oh & Richter, 2005).

Roots and their mycorrhizal fungal associates are the major conduits for transport of the chemical energy fixed by plant photosynthesis into the soil. Mycorrhizal fungi are supported by 10–30% of the sugars synthesized by their host plants, enabling these fungi to develop extensive mycelial networks, often exceeding 200 m cm^{-3} of soil (Leake *et al.*, 2004). These fungal networks selectively absorb nutrients that are required by the host plants. The networks also contribute to labile C pools by actively secreting organic acids, siderophores, and enzymes (Landeweert *et al.*, 2001; Finlay *et al.*, 2009). Such organic molecules provide carbon sources to communities of associated bacteria and archaea, promoting the dissolution and uptake of mineral nutrients by the fungi (Fig. 1, Box C). Mycorrhizal fungal networks proliferate on the surfaces of some minerals due to strong physical bonding, secretion of organic compounds and protons, and active, selective, ion uptake, thereby directing the solar-to-chemical energy converted by the plant shoots into intense localized

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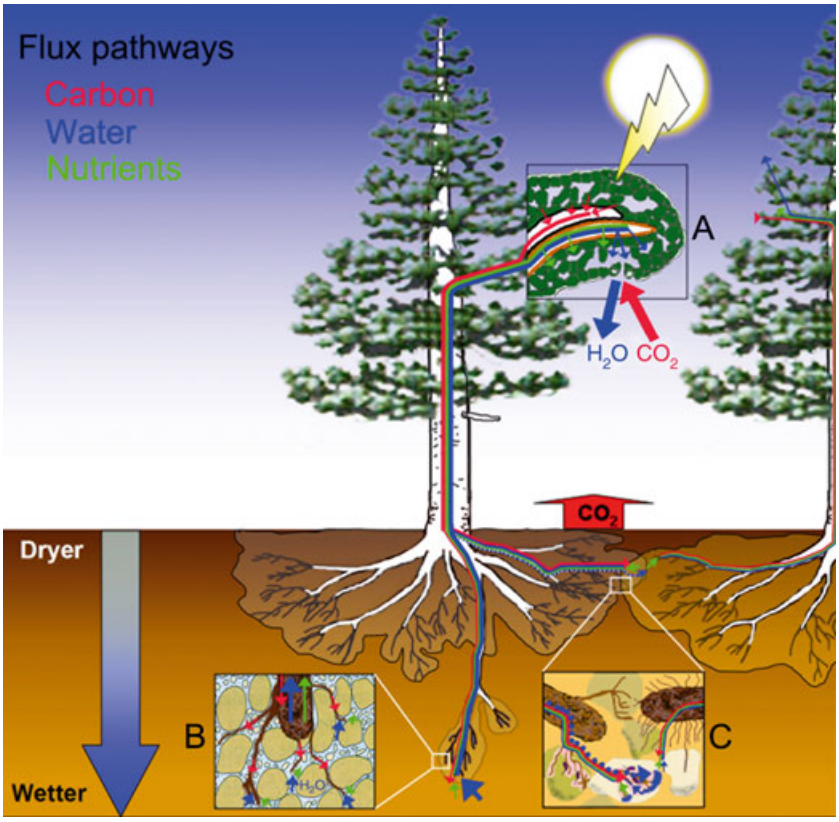

Fig. 1 A conceptual model of chemical energy in the form of organic carbon formed by photosynthesis driving carbon, water, and element flows in the CZ through a networked community of plants, mycorrhizal fungi, bacteria, and archaea. Plant roots and their associated mycorrhizal fungal networks are supported by substantial fluxes of recent photosynthate (red) fixed in plant shoots from atmospheric carbon dioxide. They use this energy to play a pivotal role in the uptake of water (blue) and nutrients (green) from soil. There is strong inter-dependency between these dynamic flux pathways that act synergistically to enhance biological weathering. (Box A) Water flow and nutrient fluxes are driven by transpiration losses associated with open stomata to allow carbon dioxide uptake into the leaves. The main demand for nutrients is in the leaves that provide the photosynthate carbon flux to roots and into mycorrhizal fungi for acquisition of nutrients. (Box B) Water uptake from the wetter deeper soil layers via mycorrhizal hyphal networks and roots includes the uptake of elements in soil solution and is supported by recent photosynthate provided by the plant. The mycorrhiza-root network can also contribute to hydraulic redistribution of soil water (dotted blue lines in main figure and Box C). (Box C) Mycorrhizal fungi release substantial amounts of carbon through respiration and exudation that promote biofilm development on mineral surfaces (pink areas) facilitated by specialized mycorrhizosphere bacteria and archaea (purple cells). Localized moisture films (blue patches) provided by hydraulic redistribution (dotted blue lines) may enable the fungi and associated micro-organisms to actively weather minerals during dry soil conditions and to capture and transport essential nutrients to the plant. Mycorrhizal networks of multiple species connect between adjacent plants, so they can transport some of the hydraulically redistributed soil water and the released nutrients into other plants (right side).

weathering of selected soil minerals (Leake *et al.*, 2008; Bonneville *et al.*, 2009). In addition, the associated bacteria and archaea form biofilms around the mycelial network (Fig. 1, Box C). This biofilm may also enhance weathering and may reduce the loss of weathered products to bulk soil water (Balogh-Brunstad *et al.*, 2008).

As transpiration draws water up through roots and mycorrhizal mycelia, the surface soil often becomes relatively dry although the deeper roots continue to access water (Fig. 1, Box B). Thus, water is hydraulically redistributed via roots from wetter to drier regions of the soil (Fig. 1, Boxes B and C). This process normally happens at night when transpiration is negligible. Hydraulically redistributed water (Warren *et al.*, 2008) can allow mycorrhizal fungi to remain active in dry soil. These processes can therefore lead to increases in localized concentrations of ligands, protons, and other secretions that may accelerate and enhance mycorrhizal weathering activity (Fig. 1, Box C). This may, in turn, enhance the supply of nutrients to host plants to enable greater growth and photosynthesis (Fig. 1, Box A), returning more chemical energy to weathering processes (Fig. 1, Box C).

The existence of functional connections between plant photosynthesis and mycorrhizal nutrient uptake are well established (Graustein *et al.*, 1979; Landeweert *et al.*, 2001; Finlay *et al.*, 2009), but only in the past decade have researchers begun to quantify the potentially major role played by mycorrhizal fungi and plants in weathering of minerals (Banfield & Nealson, 1997; Berner *et al.*, 2003; Taylor *et al.*, 2009) and in hydraulic redistribution of water (Brooks *et al.*, 2006). Advances in the use of isotope tracers to study the integrated

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transport pathways through mycorrhizal mycelia, roots, and shoots (Warren *et al.*, 2008), together with advances in methods to study mineral weathering at the scale of individual grains and fungal hyphae (Bonneville *et al.*, 2009), and molecular, microscopic, spectroscopic, and modeling techniques provide the necessary tools to test this hypothesis at appropriate spatial and temporal scales.

For example, chemical energy fixed by plants and allocated to support mycorrhizal mycelial networks in soil can be measured using ^{13}C- or ^{14}C-labeled CO_2 supplied to shoots (Leake *et al.*, 2004). These isotopes can be traced through mycorrhizal mycelia as exudates are taken up into associated bacteria and archaea. Pathways for hydraulic redistribution can similarly be studied using deuterium or tritium tracers. The absolute and relative magnitudes of hydraulic redistribution can be assessed through continuous monitoring of changes in the volumetric water content of deep and shallow soil layers (Warren *et al.*, 2008) and measurements of the direction and magnitude of sap flow in deep and shallow roots (Brooks *et al.*, 2006; Scholz *et al.*, 2008). Weathering can be measured by characterization of the alteration of natural minerals or by inserting mineral grains into regolith (Nugent *et al.*, 1998). Synthetic minerals labeled with rare earth or radioactive elements can also be used. These studies require an *interdisciplinary approach* that combines laboratory and field experiments and involves integrative studies across different bioclimatic regions.

Hypothesis 2. Biological stoichiometry drives changes in mineral stoichiometry and distribution through weathering

Stoichiometry is here used to refer to the quantitative ratio of elements in a phase or in a chemical reaction. The compositions of primary minerals such as quartz (SiO_2) or biotite ($K(Mg, Fe)_3AlSi_3O_{10}(OH)_2$), and secondary minerals such as goethite (FeOOH) are defined with respect to stoichiometry. Where reactants and products are known, the stoichiometries of mineral–water reactions that comprise chemical weathering are also well defined. Similarly, the stoichiometry of redox reactions that constitute plant and microbial respiration are also fairly well known. Even the stoichiometry of biota has been explored. In marine systems for example, the stoichiometry of marine phytoplankton is nominally defined by the ratios of C:N:P = 106:16:1 (Redfield, 1958; Redfield *et al.*, 1963). Relatively recently, ratios for other elements in phytoplankton – K, Mg, Fe, Mn, Zn, Cu, Mo – have been shown to reflect the intrinsic metabolic requirements of specific species (Ho *et al.*, 2003; Quigg *et al.*, 2003). The concept of biological stoichiometry is also rooted in the terrestrial and limnological literature (for a comprehensive synthesis see Sterner & Elser, 2002). Ecological stoichiometry has generally (but not always, see Townsend *et al.*, 2007) proven to be a useful framework for examining the transfer of matter at scales ranging from cells to organisms to ecosystems to the globe.

The stoichiometries of organisms and minerals in the CZ are intrinsically coupled because most of the 30 or so bioessential elements are derived from soil minerals. However, plants do not always require elements in the same proportions at which they occur in the Earth's crust (Table 1, Fig. 2). As a result, biological uptake by plants and micro-organisms alters the composition and distribution of elements in soils. Although it has been shown that plants and micro-organisms affect such distributions (Hinsinger *et al.*, 1993; Markewitz & Richter, 1998; Jobbagy & Jackson, 2001; Street-Perott & Barker, 2008; Brantley & White, 2009), and conversely, that element distributions influence plant community composition (Lopez *et al.*, 2009), few studies explicitly link the stoichiometric requirements of biological processes to the changes

Table 1 Average elemental ratios in plants and in Earth's crust*

Element ratio†	Plant tissue	Crustal rock
C:N	37	8.0
C:P	650	0.6
N:P	18	0.07
Al:P	0.08	90
Si:P	1.8	293
Fe:P	0.04	27
Cu:P	0.002	0.03
Si:Al	23	3.3
Fe:Al	0.50	0.30
P:Al	13	0.01
Cu:Al	0.02	0.0003
Mo:Al	0.0002	0.000005

*Data from J. R. Leake.
†Greater Si:Al, P:Al, and Fe:Al ratios in plants compared with the crust suggest that plants extract and retain Si, P, and Fe from earth materials.

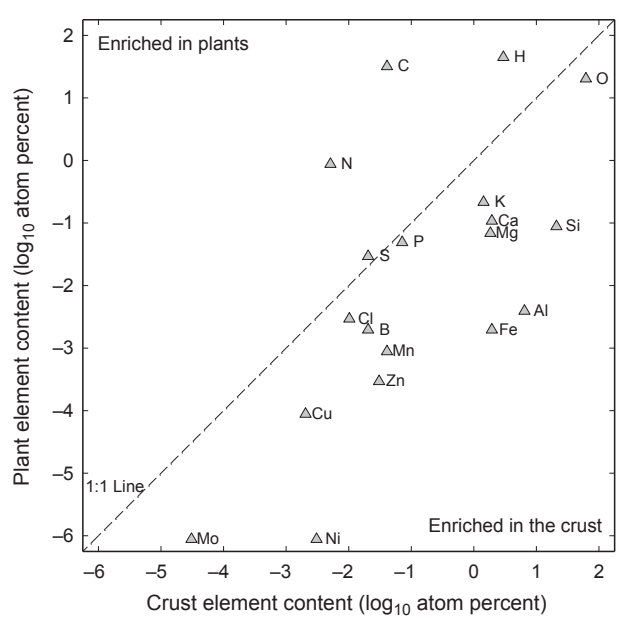

Fig. 2 Abundance of elements in Earth's crust compared with abundance in plant tissues. Data compiled by J. R. Leake.

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these processes exert on soil mineralogy. Furthermore, the range of 'typical' stoichiometries for biological systems reflects many different organisms, life strategies, and metabolisms. The stoichiometric effects of these processes have yet to be fully explored (Sterner & Elser, 2002).

A corollary to this hypothesis is the idea that abiotic chemical weathering would generate a substantially different set of mineral compositions for a given set of conditions, one that reflects equilibrium thermodynamics and abiotic reaction kinetics that are not affected by biological stoichiometry. For example, geologic evidence suggests the rise of land plants was responsible for the shift from predominantly mechanically derived sediments to the phyllosilicate-rich pedogenic clay minerals found in the Neoproterozic (Kennedy *et al.*, 2006). Despite such arguments, we currently have a limited mechanistic understanding of how mass and energy transfer by plants and micro-organisms alter mineralogy (see Fig. 1), and even less about the role of stoichiometric constraints on these processes.

Intriguingly, because many enzymatic reactions require redox-sensitive metals such as Fe or Mo, organisms may extract these metals and leave behind metal-depleted minerals (Kemner *et al.*, 2005; Liermann *et al.*, 2005; Tang & Valix, 2006). In fact, in arid-land systems, trace elements that are present in minerals are strongly depleted in biological soil crusts relative to uncrusted soils (Beraldi-Campesi *et al.*, 2009). Nutrient and metal limitation studies suggest that the N_2-fixing cyanobacteria that form these crusts have specific requirements for Mo that are satisfied via microbial alteration of soil minerals (H. Hartnett, unpubl. data).

The role of biological stoichiometry in weathering and its potential control on soil mineralogy is amenable to investigation via field studies and laboratory experiments at a variety of spatial scales. For example, high-resolution chemical mapping (Carlson *et al.*, 1999; Fenter *et al.*, 2001; Ketcham & Carlson, 2001) could reveal how micro-organisms associate with minerals containing bio-essential elements and what minerals remain after micro-organisms have extracted those elements. At larger scales, soils have a characteristic bio-architecture (Fierer *et al.*, 2003) wherein organisms exist in discrete zones; e.g. phototrophs at the soil surface, fungi at locations associated with plant roots, and heterotrophs at specific redox fronts or depths that are protected from exposure to UV radiation. At watershed or regional scales, the range of soil types encompassed by observatory networks enables the investigation of patterns along gradients in soil chemistry and biology.

Hypothesis 3. On landscapes experiencing little erosion, biology drives weathering during initial succession, whereas weathering drives biology over the long term

The interplay between weathering and biology is clearly evident in relatively stable landscapes where erosion is insignificant compared with the rates of weathering advance. In such landscapes, when soils are young and rich in nutrients, the net primary productivity is not limited by inorganic nutrient supply (Fig. 3). As summarized previously in Fig. 1, organisms increase mineral dissolution rates through a variety of processes such as providing organic acids (Drever & Stillings, 1997). Organisms also remove weathering products from solution (Berner & Cochran, 1998), a process that is influenced by the hydrological flux (Velbel, 1993; White *et al.*, 1996; Bhatt & McDowell, 2007; Brantley & White, 2009). As nutrients are removed from the system or incorporated into the biota over time, the net primary productivity can become limited by the inorganic nutrients derived from mineral weathering; this evolution is clearly observed in some chronosequences (Wardle *et al.*, 2004). Where such chronosequences are developed on stable landscapes, we hypothesize that weathering is at first controlled by biological processes, but later is controlled by physical processes that determine the contents and accessibility of nutrients in the CZ. The timing of this transition is dictated by climate, lithology, and denudation.

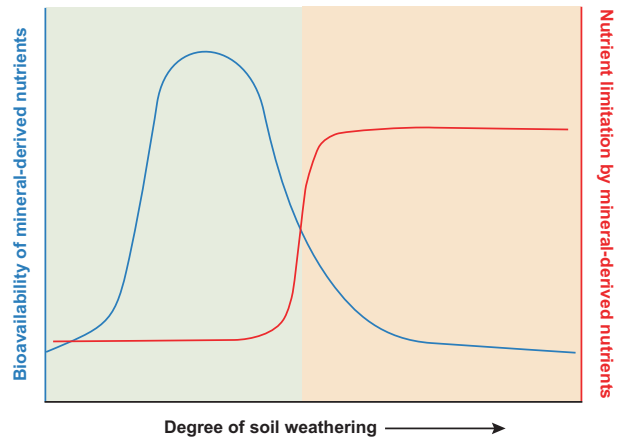

Fig. 3 A conceptual figure illustrating the hypothesized shift in the relationship between weathering and the biosphere for stable landscapes as discussed in Hypothesis 3. Soon after biota become established at a given location, the bioavailability of mineral-derived nutrients increases due to biotic stimulation of chemical weathering rates (see Fig. 1). Over time, as the degree of soil weathering progresses and nutrients are lost at a slow rate due to leakage from the system, biotic demand will eventually exceed the supply of mineral-derived nutrients, causing the system to shift into a state of nutrient limitation.

An example of this general phenomenon is the idea that terrestrial ecosystems shift from N- to P-limitation over the course of ecosystem development as weathering and denudation deplete biologically available P pools in the regolith (Walker & Syers, 1976; Wardle *et al.*, 2004). Once P in regolith is depleted, the only P available is from underlying parent minerals or incoming dust (Derry & Chadwick, 2007). This idea of a shift from N- to P-limitation has been around for decades, yet it has generally been confirmed only for extremely old and chemically weathered soils in tropical settings (Tanner *et al.*, 1990; Herbert & Fownes, 1995; Vitousek & Farrington, 1997; Cleveland *et al.*, 2006). Furthermore, the

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availability of elements other than N and P (e.g. Ca, Fe, K, Mn, Cu, Mo) must also be considered as discussed above in Hypothesis 2 (Clarkson & Hanson, 1980).

Intriguingly, limitation can also be due to multiple elements (Bern *et al.*, 2005; Elser *et al.*, 2007; Barron *et al.*, 2009). The interpretation of multinutrient limitation and how it might affect ecosystems must be carefully considered with respect to the spatial and temporal scale of observations (Wiens, 1989; Hunter *et al.*, 1998). The spatial controls on soil ecosystems (Ettema & Wardle, 2002) and how stable ecosystem states are controlled by environmental drivers (Beisner *et al.*, 2003) is of great current interest.

Variations in lithology represent additional complexity. The elemental composition of bedrock sets the size of the nutrient pool, whereas the weatherability of the minerals affects how quickly the pool is made biologically available. Therefore, different bedrock types may sustain different degrees of ecosystem development or succession depending on the abundance and susceptibility of minerals to weathering. Additionally, soils develop a number of other properties such as Eh, pH, porosity, clay content, and cation exchange capacity that all depend at least partly upon their parent material (Oh & Richter, 2005), which in turn strongly influence elemental cycling between biota and minerals. Lithology also affects the spatial variation in biotic activity (Fierer *et al.*, 2003, Philippot *et al.*, 2009).

One corollary to this hypothesis is the growing consensus that denudation replenishes inorganic nutrients that otherwise become depleted (e.g. Porder *et al.*, 2007). The means by which this occurs is likely a part of complex feedbacks among tectonics, climate, and lithology (Anderson *et al.*, 2007). For example, climate may be particularly important in controlling chemical weathering rates in systems with high denudation rates (West *et al.*, 2005). Thus, the residence time of minerals within soils may be sensitive to physical denudation rates in geomorphically dynamic landscapes (Almond *et al.*, 2007; Yoo & Mudd, 2008a). Unraveling long-term changes in biological availability of inorganic nutrients in physically dynamic landscapes will require greater understanding of how (if at all) the propagation of weathering fronts are coupled with ground surface denudation (Hypothesis 4).

Hypothesis 4. In eroding landscapes, weathering-front advance at depth is coupled to surface denudation via biotic processes

In stable landscapes (Hypothesis 3), regolith development depends on rates of weathering front advance and the progressive depletion of parent material by chemical denudation (Yoo & Mudd, 2008b). In contrast, regolith development in eroding landscapes reflects the balance between advance of weathering at depth and lowering of the surface by chemical and physical denudation. Unlike chemical denudation, which encompasses losses due to weathering reactions over all depths in the regolith profile, erosion removes material preferentially from the near surface, without leaving behind any secondary minerals or chemically depleted rock fragments (Fig. 4). Hence, physical denudation tends to keep soils relatively fresh, compared with those developed in stable settings. Note that if erosional renewal of regolith is fast enough, it could preclude development of the latter stages of ecosystem succession identified in Hypothesis 3. To obtain a comprehensive understanding of how biological processes interact with regolith development, it is important to quantify relative rates of regolith production and removal in eroding landscapes. Cosmogenic radionuclide (CRN) measurements in samples of soil, sediment, and rock permit quantitative study of landscape denudation (Granger & Riebe, 2007) and soil production (Heimsath *et al.*, 1997). Over the last two decades, we have learned much about the CZ from CRN studies of surface processes in diverse settings (Von Blanckenburg, 2006). In contrast, we know comparatively little about how climate and biological stoichiometry (see Hypothesis 2) influence the advance of weathering into parent material at depth. Recent studies of weathering of clasts of known age have provided clues about how weathering initiates and advances into geologic materials (Sak *et al.*, 2004) but it is not clear how this scales to understanding weathering in eroding, soil-mantled watersheds (Navarre-Sitchler & Brantley, 2007). Important progress has been made in studies of root wedging, faunally induced bioturbation (Gabet *et al.*, 2003) and the grain-scale processes discussed in Hypothesis 1. Yet, linkages between biological processes and weathering in the subsurface remain qualitative at best. Theoretical considerations

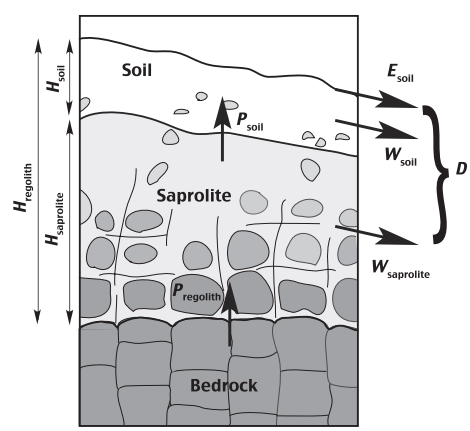

Fig. 4 Schematic showing regolith with thickness $H_{regolith}$ (here equal to the combined thickness of the soil, H_{soil}, and saprolite, $H_{saprolite}$) overlying unweathered parent material (labeled bedrock). Upward arrows denote fluxes of solid Earth materials across horizons; diagonal arrows denote fluxes out of the system. Chemical and physical weathering of parent material results in a flux of 'fresh' minerals into the regolith ($P_{regolith}$). Chemical denudation in saprolite ($W_{saprolite}$) prepares it for conversion into soil (P_{soil}). Physical and chemical denudation of soil (E_{soil} and W_{soil}, respectively) removes it from the landscape. The sum of the denudational fluxes is the total denudation rate (D). Aeolian fluxes (not shown) may be an important additional source of mass in the CZ. Adapted from Riebe *et al.* (2003, 2004) and Dixon *et al.* (2009).

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(Dietrich *et al.*, 1995) and field data (Heimsath *et al.*, 1997) imply that variations in production rates of the mobile soil layer may often be driven by biotic processes. This raises the question of whether a similar coupling exists between biota at the surface and the processes that control regolith production at depth. If this is the case, then it would provide a mechanism for equilibrating rates of surface lowering and weathering front advance. By extension, this would provide a means to keep regolith thickness roughly stable over time. Steady-state regolith thickness is an *a priori* assumption in many studies of weathering (Yoo & Mudd, 2008b). Although recent modeling efforts suggest that steady-state regolith can prevail in some landscapes (Fletcher *et al.*, 2006; Lebedeva *et al.*, 2007), we lack empirical evidence for it in nature and furthermore do not understand how biota might contribute to (or disrupt) any tendency toward development of steady state. Hypothesis 4 addresses this knowledge gap head-on, proposing that weathering-front advance is coupled to surface erosion via biotic processes. In the limit of very tight coupling, the regolith production rate should be equal to the total (physical plus chemical) denudation rate (Fig. 4), and, by extension, the surface lowering rate should be equal to the weathering advance rate.

To test whether surface denudation is coupled to weathering-front advance via biotic processes, we need reliable, widely applicable methods for quantifying rates of weathering front advance in landscapes. To date, no such method has been available. However, recent advances in multicollector inductively coupled plasma mass spectrometry promise to yield quantitative understanding of the initiation of weathering from measurements of weathering-induced fractionations in non-traditional stable isotopes (Johnson *et al.*, 2004) and U-series disequilibrium dating (DePaolo *et al.*, 2006; Maher *et al.*, 2006; Dosseto *et al.*, 2008). These approaches may allow quantification of the time elapsed since weathering began (i.e. the regolith residence time; Dosseto *et al.*, 2008). For example, if the production rate of regolith (P_{regolith}) equals the denudation rate of the landscape (Fig. 4), the regolith thickness (H_{regolith}) would be at steady state and we could write expressions (1) and (2):

$$H_{\text{regolith}} = P_{\text{regolith}}\tau_{\text{regolith}} \tag{1}$$

and

$$P_{\text{regolith}} = P_{\text{soil}}[Zr]_{\text{saprolite}}/[Zr]_{\text{parent}}. \tag{2}$$

Here P_{soil} is the production rate of soil (measured from CRN), τ_{regolith} is the residence time for material in the regolith (for example, estimated from U-series disequilibrium dating), and $[\text{Zr}]_{\text{saprolite}}$ and $[\text{Zr}]_{\text{parent}}$ are the concentrations of an immobile element such as zirconium (i.e. an element which is relatively insoluble and thus cannot be chemically denuded away) in saprolite and parent material, respectively.

If the regolith is in steady state, regolith thicknesses predicted from expressions (1) and (2) should be equal to thicknesses observed from cores or shallow geophysical images, suggesting that landscape lowering is quantitatively coupled with weathering front advance. Discrepancies between observed and predicted values of H_{regolith} would imply departures from steady state. Hence, the comparison of predicted and observed thicknesses should shed light on linkages between or decoupling of surface and subsurface processes. To the extent that surface and subsurface processes are coupled, we should be able to explore *how* the coupling works, using results from expressions (1) and (2) from many points on the landscape.

Such observations could then be combined with measures of biotic parameters to address questions about the geobiology of weathering and erosion. For example, do differences in vegetation and other biota (e.g. the mycorrhizal networks discussed in Hypothesis 1) help regulate the advance of the weathering front? If so, we should see correlations between regolith depth and the penetration depth of the process in question. If tree roots and associated mycorrhizal networks regulate the depth of bedrock – as part of the interchange of water and nutrients outlined in Hypothesis 1, for example – then depth of rooting may correspond systematically to the depth of fractured rock, where weathering advance is focused. On the other hand, if vegetation has changed over the timescales of regolith formation due to ecosystem succession factors discussed in Hypothesis 3, we might observe disagreement between regolith thickness and the penetration depths of biota, even in systems that have nominally steady thickness over the long term. In any case, we are poised to make significant advances in documenting how biological, chemical, and physical processes interact across depth, from the surface to the regolith-rock interface in the CZ.

Hypothesis 5. Biology shapes the topography of the Critical Zone

In some ways, coming to grips with the importance of life on the Earth's air, water, and land is simply a matter of recognizing the obvious: life in all shapes and forms mantles most of the planet's surface. Hypotheses 1 through 4 emphasize the phenomena that control elemental distributions and thickness of regolith. As such, investigations driven by these hypotheses could provide answers to the question, *what would this planet – any planet – look like without life?* One important aspect of this question is not addressed by the previous hypotheses however: can life also affect macro-scale topography of Earth's surface?

Quantitatively connecting CZ processes to landscape evolution is a broadly studied topic (Amundson *et al.*, 2007; Anderson *et al.*, 2007) that even has implications for the search for extraterrestrial life. The ways that biota may, or may not, shape topography is of critical importance for extraterrestrial exploration for two very simple reasons. First, if there is a distinct topographic signature of life, then explo-

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ration for life beyond Earth could focus on searching for such topography. Second, topographic metrics can be remotely sensed. Therefore, it remains an exciting possibility that topographic evidence of life might be discerned with remote measurements.

Of course, studies of life's role in shaping both micro- and macro-topography are extensive (Brady *et al.*, 1999; Buss *et al.*, 2002; Vanacker *et al.*, 2007; Bonneville *et al.*, 2009). However, no mathematical model has been proposed to define such shaping factors (Dietrich & Perron, 2006) at least partly because the effect of biological productivity is difficult to deconvolve from factors such as temperature and precipitation (Fig. 5). Life contributes to most surface processes both directly, by modulating the chemistry and transport of sediment and solutes as described in previous hypotheses, and indirectly, by influencing the climate and atmospheric boundary conditions that regulate erosion, weathering, and sediment transport (Gabet *et al.*, 2003; Berner *et al.*, 2003). It seems safe to say, therefore, that this planet's topography would be different if life on Earth had not evolved.

Interestingly, however, a recent review suggests that there may not be a topographic signature of life (Dietrich & Perron, 2006). Nonetheless, this hypothesis must be explored further. For example, well-designed physical experiments and coupled numerical models that integrate biogeochemical and hydrological processes such as those at Biosphere 2 in Arizona (Dontsova *et al.*, 2009; Huxman *et al.*, 2009) are needed. The connections between micro- and macro-organisms and their impact on Earth's surfaces must be studied explicitly when testing this hypothesis: thus, observations at the scale demanded by Hypotheses 1, 2, 3, and 4 must be related to observations at the larger scale demanded by Hypothesis 5.

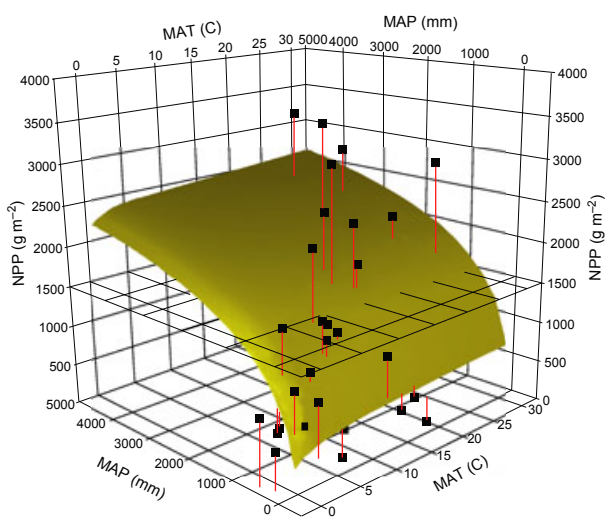

Fig. 5 A diagram illustrating the relationship between net primary production (NPP, grams of plant matter per square meter of land area), vs. mean annual precipitation (MAP, mm year^{-1}) and mean annual temperature (MAT, °C). Individual data points are shown as black cubes. A multivariable regression model used to fit the data is illustrated as a smooth surface. Data from Lieth (1973), figure made by R. Amundson.

Ironically, the most difficult aspect of deciphering the role of life on topography is identifying a control experiment where life does *not* exist. At the field scale, attempts to understand chemical-weathering processes in the absence of vascular plants and most organisms larger than micro-organisms are restricted to artificially designed 'sand boxes' (Gabet *et al.*, 2006), or observing recent volcanic flows and the like. All such approaches are characterized by unique initial conditions and short temporal scales (Berner *et al.*, 2003).

The most glaring gap in our current understanding of what shapes the Earth's surface (see Dietrich & Perron, 2006) is the lack of quantitative geomorphic transport laws necessary for landscape evolution models. In the absence of such mathematical models, it may be possible to set up physical (e.g. sandbox or shaking table), or numerical experiments to quantify how topography changes as a function of soil residence time. Experiments should be designed in concert with control experiments that are maintained abiotic. Furthermore, it may be possible to design experiments where biota are allowed to change and the consequent changes in topography are measured, providing initial tests of Hypothesis 5.

PROJECTED RESPONSES OF THE CZ TO FUTURE PERTURBATIONS

Hypothesis 6. The impact of climate forcing on denudation rates in natural systems can be predicted from models incorporating biogeochemical reaction rates and geomorphological transport laws

Perhaps because of the intimate coupling among chemical, physical, and biological processes, we cannot currently project how the shape and composition of the CZ evolves over time. If we could parameterize quantitative models for the evolution of natural Earth surfaces in the face of ongoing climate change, as well as other human impacts on the Earth's surface, we could calculate how the Earth's surface will change into the future. Some have referred to such predictions as *Earthcasts* (C. Paola, pers. comm.). Hypothesis 6 contends that such models can be built and parameterized based on simple laboratory and field observations and that they will be successful in projecting future changes, at least in natural systems that are not highly impacted by human land use. Eventually, we should be able to augment these models to also project anthropogenic impacts under different scenarios of human activity. The term 'biogeochemical' in this hypothesis is meant to include ecological phenomena that govern ecosystem responses, including community composition shifts and species that adapt to changing conditions.

To parameterize numerical models, extensive work in the laboratory over the last several decades has quantified the equilibrium states and the rate behavior of mineral–water–gas

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reactions and, to a lesser extent, microbiota–mineral–water reactions (White & Brantley, 1995; Palandri & Kharaka, 2004; Brantley *et al.*, 2008; Oelkers & Schott, 2009). Significant effort is also underway to identify appropriate geomorphic transport laws (Dietrich *et al.*, 2003). These mathematical laws express the mass flux caused by one or more processes and generally must be validated by field measurements. In addition to the availability of such data, many researchers are formulating numerical models to simulate CZ processes (Kang *et al.*, 2006; Steefel, 2008; Goddéris *et al.*, 2009).

Despite these developments, model testing against natural systems is still in its infancy and many problems remain to be resolved so that quantitative, accurate predictions can be made (White, 2008; Dixon *et al.*, 2009). For example, upon comparison of laboratory and field rates of mineral reactions, many researchers have discovered that laboratory rates are much faster than natural rates (Fig. 6). This observation has driven efforts to reconcile model simulations with field observations

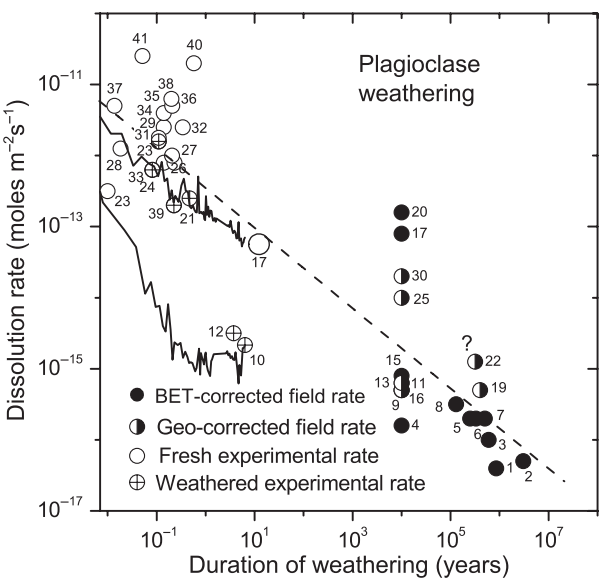

Fig. 6 A plot showing how the rate of dissolution of plagioclase feldspar varies as a function of the duration of observation (plotted in years on the *x*-axis). Measurements of this rate in the laboratory are orders of magnitude faster than the rates estimated in natural systems. Filled symbols represent rates measured in the field that have been normalized by the surface area of the feldspar measured by BET analysis. Half-filled data denote field rates corrected for geometric surface area. Open symbols represent rates measured in the laboratory for freshly ground unaltered samples; open symbols with crosses delineate laboratory rates measured for samples that were previously weathered in the field. The dashed line is a regression fit to the data. Solid lines indicate the measured laboratory rate of dissolution of pristine or previously weathered Panola granite as a function of time. Figure revised from the original publication: references for original data as indicated by numbers are found in the original reference (White & Brantley, 2003). Many explanations have been advanced for why rates vary with duration of observation, including the effects of changing soil structure with time, changing mineral surface chemistry with time, changing chemical affinity with time, the effects of biota, inadequacies in measurement of surface area, hydrologic factors, clay precipitation effects, etc.

(White & Brantley, 2003; Maher *et al.*, 2009; Zhu, 2009). In addition, geomorphological transport laws are not currently available for processes such as landslide formation, debris flows, surface wash, and glacial scour (Dietrich *et al.*, 2003).

Testing this hypothesis will require the development of new modeling approaches to allow projection from laboratory measurements to field observations for soils, sediments, and landscapes. Earthcasting approaches must allow delineation of climate variables as a function of time both in the past and forward into the future as drivers of denudation. Full coupling of climate and weathering models is currently not possible, and instead, climate model outputs must be used to drive the weathering or erosion models separately (Williams *et al.*, 2010). A rigorous test of Hypothesis 6 will require development of new coupled models of the climate-CZ system. Another frontier in modeling is the incorporation of biotic effects such as those discussed in Hypotheses 1 through 4 (Goddéris *et al.*, 2009).

Hypothesis 7. Rising global temperatures will increase carbon losses from the Critical Zone

The Earth is warming. Average air temperatures have increased 0.13 °C per decade globally (IPCC, 2007), and fivefold greater increases have been observed in the Arctic (up to 0.6 °C per decade north of 62°N; Polyakov *et al.*, 2002). Projections based on six emission scenarios suggest warming could reach 1.8–4.0 °C per decade by 2100 (IPCC, 2007). Positive feedbacks operating on CZ carbon pools – both plants and soils – have the potential to accelerate these temperature increases.

Importantly, because most CZ processes respond to temperature, warming can have complex effects on the CZ carbon balance (e.g. Norby & Luo, 2004). Warming has the potential to increase decomposition of soil organic matter and the resultant export of dissolved organic carbon (DOC; e.g. Rustad *et al.*, 2001; Knorr *et al.*, 2005; Davidson & Janssens, 2006), but the extent to which this potential is realized is regulated downward by changes in composition, activity, and density of soil microbial communities and roots (e.g. Luo *et al.*, 2001; Carney *et al.*, 2007; Strand *et al.*, 2008). While increases in DOC fluxes from some temperate watersheds experiencing warming have recently been identified, these increases have been attributed to decreases in sulfate deposition (Evans *et al.*, 2006; Monteith *et al.*, 2007). On the other hand, increased DOC export has been observed, possibly in response to warming, in other regions that have historically received little atmospheric S deposition (Freeman *et al.*, 2004). Finally, for the few studies where changes in soil organic carbon have been documented over time, the effects of land use change must be considered as an alternative to climate change (Bellamy *et al.*, 2005).

The net, temperature-driven change of the CZ carbon pool will represent the summation of all the net changes in individual soil and plant carbon pools. Model and observational stud-

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ies of plant responses to elevated temperature tend to predict there will be an increase in net primary production (Rustad *et al.*, 2001), but the range of responses is large and in some systems plant growth may decline with increasing temperature. In addition, the effects of temperature on plant growth or NPP (see Fig. 5) result from interactions controlled by many other factors such as the partial pressure of CO_2 and annual precipitation (e.g. Norby & Luo, 2004; Bradley & Pregitzer, 2007).

Global feedbacks will depend on the sign and magnitude of CZ responses to warming, most of which are difficult or impossible to project for specific regions (Fig. 7). For example, decreased DOC concentrations from the Yukon have been attributed to destabilization as warming increases soil CO_2 fluxes (Striegl *et al.*, 2005). Conversely, it has been suggested that Siberian DOC exports will increase nonlinearly with warming (Frey & Smith, 2005). The effects of increased C export – solid, liquid, or gas – will depend not only on the net effect of fluxes related to the organic carbon pools but also relative to changes in C sinks such as silicate weathering (Hypothesis 8) and upon changes in discharge (Fig. 7). Furthermore, changes in soil erosion (Harden *et al.*, 1999; Smith *et al.*, 2001) will also affect organic carbon pools (Van Oost *et al.*, 2007). Importantly, small changes in soil carbon content can exert a disproportionate effect on the global C cycle because soils contain more than double the C in the atmosphere and vegetation combined (Bajtes, 1996; Houghton, 2007).

From affordable, networked, and miniature datalogging sensor grids to coupled, remotely sensed data products, large

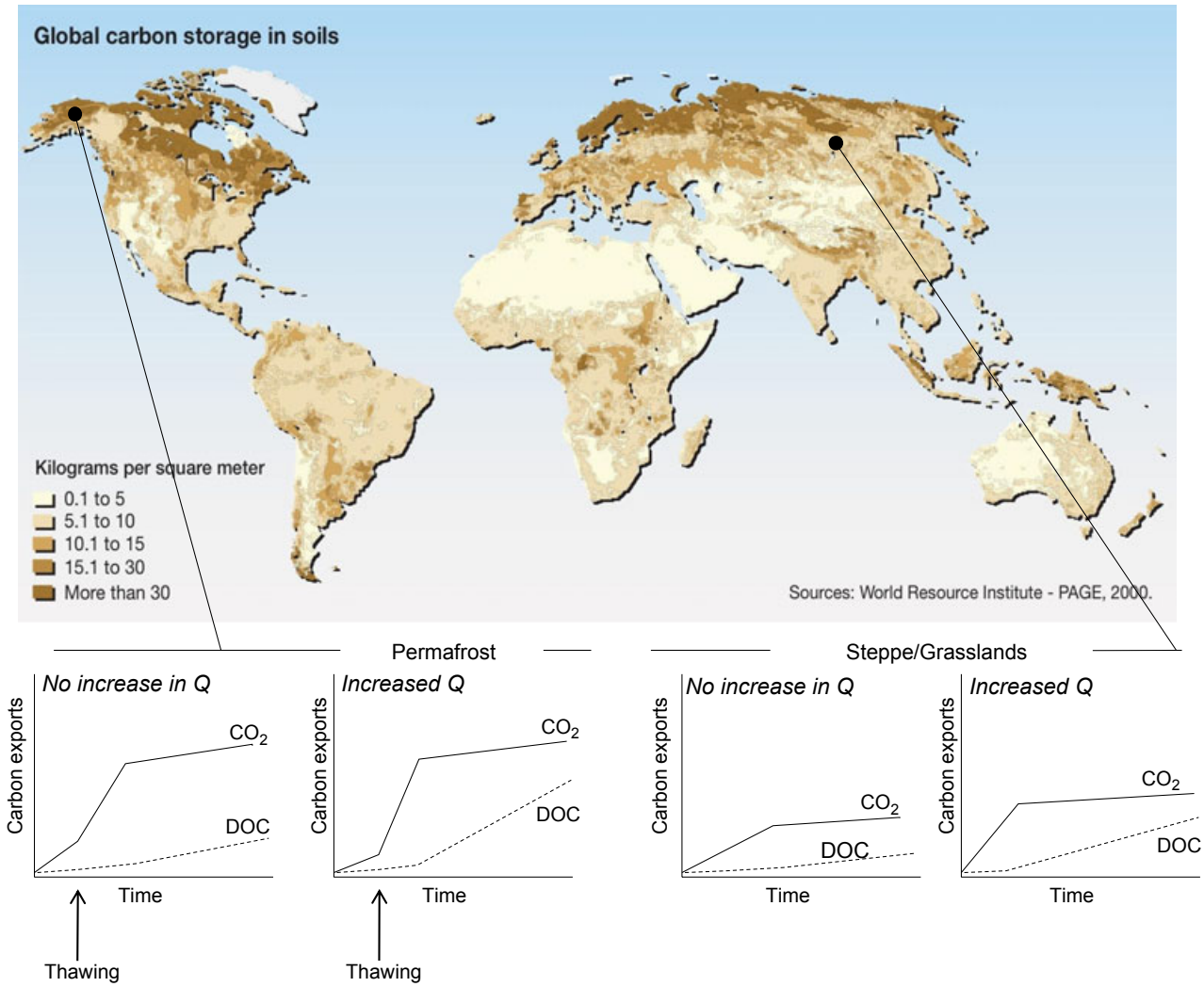

Fig. 7 Predictions of carbon export (CO_2 and DOC) under a warming climate, with and without increases in discharge (Q). The two examples chosen are from northern latitudes which are expected to see the largest temperature increases. The difference in magnitude of the carbon exports is meant to reflect the difference in carbon storage between the regions. There are a variety of factors affecting carbon exports including those that affect net primary productivity and therefore total carbon stocks (e.g. climate, fertility, species composition) and those that affect the decomposition and export of those carbon stocks (e.g. temperature, water, substrate quality, oxygen). Base map is from the UNEP/GRID-Arendal Maps and Graphics Library (2009).

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data sets are now being collected that will allow us to test how ecosystem C fluxes respond to temperature and moisture changes (e.g. Baldocchi *et al.*, 2004). Various modeling approaches are increasingly being used to model data-rich systems at single scales. In the future, powerful models will be parameterized by real-time data and compared with results from warming experiments across multiple scales. Experiments that manipulate temperature, moisture, nutrient, and CO_2 concentrations are starting to provide insights into the sign and magnitude of potential ecosystem responses to warming. From this information we will eventually predict how carbon fluxes will respond (e.g. Fig. 7; UNEP/GRID-Arendal Maps and Graphics Library, 2009). Necessarily, these models will be parameterized using observations over short timescales but will be used to predict longer term effects.

Three interrelated research areas of great importance should be targeted: (i) analysis and modeling of CZ carbon fluxes in solid, liquid, and gases across a matrix of experimentally manipulated sites or in locations along natural gradients; (ii) ongoing observations on Arctic ecosystems with special focus on the greenhouse gas CH_4; and (iii) multifactor experiments designed to identify tipping points (see Hypothesis 12) in ecosystem responses to warming. These latter experiments could allow, for example, investigation of the inter-relationships of temperature, moisture, ozone, and elevated CO_2, or the inter-relationship of N deposition fluxes and elevated CO_2.

Hypothesis 8. Rising atmospheric P_{CO2} will increase the rates and extents of mineral weathering in soils

The accelerating rate of increase in atmospheric CO_2 concentrations (Canadell *et al.*, 2007) is expected to impact the CZ in many ways, as discussed in the previous hypothesis. For example, elevated CO_2 causes changes in plant physiology that can cause 'top-down' perturbations of the CZ. In this regard, plants are transducers that sense changes in the atmosphere and actuate changes in the CZ (Bradley & Pregitzer, 2007). Changes in CO_2 are causing alterations in the type, distribution, respiration rates, and growth rates of plants (Ainsworth & Long, 2005; Norby *et al.*, 2005, McMahon *et al.*, 2010), but these effects may be species-specific (Fransson *et al.*, 2007), short term (Oren *et al.*, 2001), or subject to change as elevated CO_2 interacts with other global change factors (Langley and Megonigal, 2010). The sum effect of all these factors on primary mineral weathering is currently unknown. However, given the discussion in Hypothesis 1 that emphasizes plants as a source of the inorganic and organic compounds that enhance chemical weathering, we hypothesize here that elevated CO_2 will cause significant increases in the rate and extent of primary mineral weathering over much of Earth's surface (Fig. 8). Importantly, this increase in weathering could furthermore feedback to alter the primary productivity (Fig. 5) and could potentially impact aquatic resources downstream. Altered rates of mineral weathering could even affect the flux of solutes to drinking water (Natali *et al.*, 2009).

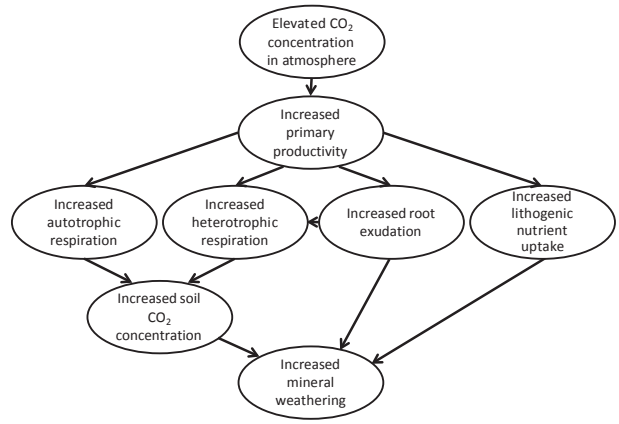

Fig. 8 Conceptual diagram for Hypothesis 8 that reflects a hypothesized relationship between elevated CO_2 in the atmosphere and rate and extent of mineral weathering. Length of the arrows and size of the pools do not indicate magnitude of the response or the reservoirs, as these are largely unknown, especially in different ecosystem types.

Soil CO_2 concentrations are naturally elevated well above atmospheric concentrations due to biological activity. Elevated atmospheric CO_2 accelerates biological activity directly by stimulating primary productivity (Ainsworth & Long, 2005; Norby *et al.*, 2005), indirectly increasing microbial respiration and decomposition (Pendall *et al.*, 2004; Carney *et al.*, 2007). Increased plant and microbial respiration dictates an increase in overall soil respiration (King *et al.*, 2004; Comstedt *et al.*, 2006), resulting in higher soil CO_2 and dissolved inorganic carbon concentrations (Andrews & Schlesinger, 2001; Karberg *et al.*, 2005). These latter changes can then supply more protons for dissolution reactions (Goddéris *et al.*, 2006). Elevated atmospheric CO_2 may also accelerate weathering through an increase in plant production of root exudates that contain organic acids and organic polyphenolic compounds (see Hypothesis 1). In addition, increases in ecosystem productivity could increase the size of the sink for products of mineral dissolution. The magnitude of these responses and the responses of different ecosystems are largely unknown (Fig. 8).

To investigate these many factors, a few free-air CO_2 enrichment (FACE) studies have examined the effects of elevated CO_2 on mineral weathering. Andrews & Schlesinger (2001) observed higher soil P_{CO2}, a 271% increase in soil solution cation concentration, a 162% increase in alkalinity, and a 25% increase in Si over only 2 years of elevated CO_2 in soil plots located in a loblolly pine plantation in North Carolina (USA). However, a longer-term (5-year) data set from the same experiment revealed a more complex pattern, including years that showed significant effects of the treatments on soil CO_2 concentrations, but no differences in chemical weathering rates (Oh *et al.*, 2007). Elevated atmospheric CO_2 has also

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been observed to increase soil gas CO_2 and dissolved inorganic carbon concentrations during the growing season by 14% and 22%, respectively, whereas total alkalinity increased by 210%, likely due to enhanced chemical weathering (Karberg *et al.*, 2005). In addition, a significant decrease in soil pH and higher surface soil trace metal concentrations were observed with CO_2 enrichment (Natali *et al.*, 2009). These limited studies highlight the variability of responses to elevated CO_2 and the need to study the effects across all biomes.

Although some of the published studies to date provide strong indications that elevated CO_2 can increase weathering rates (Karberg *et al.*, 2005), there is no conclusive evidence in the form of increased fluxes of rock-forming elements or changes in mineral mass balance to prove this hypothesis. For example, depending on the initial soil mineralogy, an increase in P_{CO2} could cause the base cation content of the soil to either decline due to accelerated export (chemical denudation) or remain relatively unchanged due to increased rates of mineral weathering accompanied by secondary mineral precipitation.

At this time we cannot project how weathering will respond to changing CO_2. Small-scale mesocosm studies under controlled conditions and field-based elevated CO_2 experiments using standardized CO_2 enrichment methodologies and state of the art characterization techniques are needed. At the field scale, investigators should fully sample existing elevated CO_2 studies (e.g. FACE sites) and initiate new elevated CO_2 field studies that encompass the full range of ecosystem and CZ types. In addition, to predict decadal and centennial changes across landscapes will require implementing field experiments using observatories sited along environmental gradients and using models to predict chemical denudation fluxes as a function of changing CO_2 (e.g. Banwart *et al.*, 2009; Goddéris *et al.*, 2009). Finally, Fig. 8 only emphasizes the short term impacts: we also need models that are written to incorporate how vegetation modulates or responds to the important long-term feedbacks between weathering and climate (e.g. Berner, 2006).

Hypothesis 9. Riverine solute fluxes will respond to changes in climate primarily due to changes in water fluxes and secondarily through changes in biologically mediated chemical weathering

Riverine export of terrestrial elements mobilized by chemical weathering, i.e. chemical denudation, is an important flux in global elemental cycles. Models have shown that weathering processes exert a negative feedback to atmospheric CO_2 levels and global climate over very long timescales (Ridgwell & Zeebe, 2005; Berner, 2006). It is less clear, however, how riverine export will respond to climate change over the coming decades. Understanding this is critical to our ability to predict future changes in river quality, ecosystem sustainability, mobility of pollutants, and response of coastal systems to climate change.

The solute export of a watershed (F_i) is calculated from the product of the river discharge (Q in $m^3\ s^{-1}$) and the concentration of solute i (C_i in mol L^{-1}). Recent studies have demonstrated that the export of weathering products scales with discharge for watersheds (Fig. 9) representing a range in climate and lithology (Raymond & Cole, 2003). Figure 9 suggests that biota exert little to no control on the decadal timescale of riverine export of weathering products. Therefore, we hypothesize that factors that alter discharge rates, namely precipitation and evapotranspiration, will be the major source of change to riverine chemical export in the coming decades.

Of course, this hypothesis may in fact contradict several of the preceding hypotheses that were largely addressing observations made at the scale of a pedon or smaller (e.g. Hypothesis 8). Perhaps, observations made at different scales lead to different conclusions. Clearly such contradictions must be investigated. Why might biota-facilitated chemical weathering play only a minor role in changing riverine fluxes? This could be because, although chemical weathering in topsoil is biologically mediated, its kinetics is controlled by the interplay of several factors (White & Blum, 1995; Brantley & White, 2009). For example, concentrations of dissolved weathering products, C_i, are often diluted with increases in discharge (Q), as hydrology alters weathering regimes by changing the residence time and the relative contribution from deep groundwater vs. shallow porewaters (Kirchner, 2003; Raymond *et al.*, 2008). Watersheds rarely show an increase in the concentration of cations during periods when a large volume of water moves through the watershed because the weathering signals are diluted by the water inputs. Nonetheless, the dilution of C_i is small compared with the increase in Q during wet years, and the overall flux therefore increases with Q. One inference from such observations is that C_i in many watersheds is always at or near the maximum in concentration as dictated by mineral solubility. Such solubility-controlled

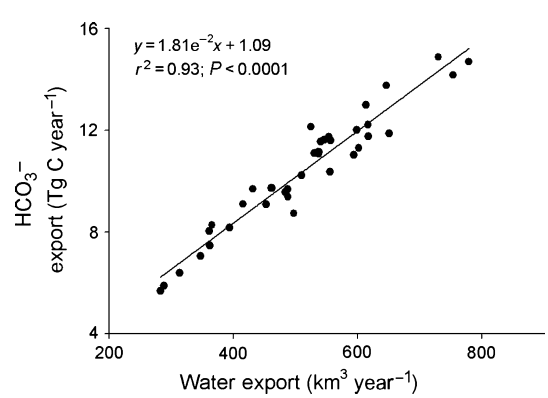

Fig. 9 Annual export of water and bicarbonate from the Mississippi River. Data are from Raymond *et al.* (2008) for 1900–1950. The main source of the bicarbonate is soil-weathering processes.

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weathering has been commonly observed in watersheds dominated by carbonate minerals (Williams *et al.*, 2007) or those with low precipitation (Raymond *et al.*, 2008).

It is possible that biological processes maximize weathering intensities so that the relative changes in concentrations of the dissolved loads in response to climate-induced changes are insignificant, especially on the century to decade timescales. Furthermore, despite the arguments in the preceding hypothesis, although elevated P_{CO2} levels are commonly observed in soil atmospheres, a small rise of atmospheric CO_2 may not lead to significant increases in weathering if such changes do not affect the solubility limitations of weathering. It may also be important to point out that biologically facilitated weathering is highest during the growing season, when discharge is typically low due to high rates of evapotranspiration.

Of course, variation in biologically mediated chemical weathering may become important in some instances such that the impact of climate change on C_i is more significant than impact on Q. The thawing and decomposition of peats in northern latitudes will expose soils with a very high weathering potential to solutions with DOC (Striegl *et al.*, 2007) and may therefore show enhanced chemical denudation (see Fig. 7). Similarly, periods of low sea level during glacial periods expose carbonate-rich continental shelf that are then susceptible to weathering (Foster & Vance, 2006). Also, farming – another example of a biotic process– can alter bicarbonate production and export from watersheds through processes such as liming (Hamilton *et al.*, 2007). Recent studies have demonstrated that suburban growth and urbanization can also increase chemical denudation rates due to organic matter loading (Barnes & Raymond, 2009).

The impacts of climate change on watershed-scale chemical weathering rates and denudation fluxes will undoubtedly be governed by a complex interplay between changing water delivery and alterations in stream chemistry (C_i). In most areas of the globe, however, alterations in the water budget will precede large-scale land-cover changes. It is our contention that, in the short term (decades to a century), the alteration of water throughput will trump changes in biologically mediated chemical weathering. This argument is buttressed by the fact that examination of contemporary watershed data has not revealed any significant biologically driven variation on river fluxes.

Data required to test this hypothesis are available due to advances in remote sensing techniques, data compilation, and real-time measurements (Raymond & Cole, 2003). For example, the US Geological Survey has discharge and riverine water chemistry data for most watersheds in the USA, with different climate, vegetation, and land use history, and these records often cover many decades. These databases allow identification of changes due to anthropogenic forcing. With such data, process-based models can be parameterized to forecast the response of riverine element export to climate change in the coming decade (e.g. Goddéris *et al.*, 2006). Such reactive-transport models should be linked to terrestrial ecological models to take into consideration the impacts of biological activity on water budget, C cycles, soil erodibility, and mineral dissolution.

Hypothesis 10. Land use change will impact Critical Zone processes and exports more than climate change

The fluxes of matter and energy from the CZ are sensitive to the effects of human activities (Vitousek *et al.*, 1997; Yang *et al.*, 2003; Green *et al.*, 2004; Montgomery, 2007; Alexander *et al.*, 2008), perhaps most evidently in the direct effects of road building, timber harvesting, and agriculture on erosion of the Earth's surface (Cronin *et al.*, 2003; Wilkinson, 2005). The evidence, which includes degraded soils, altered patterns of ecological succession, and accelerated sedimentation in streams, rivers and floodplains, hails from innumerable studies of agricultural erosion, fertility loss in soils, logging, deforestation, and urban development that span a wide range of geographic settings.

Human activities have modified landscapes and land-cover types over such a massive scale (Cronin *et al.*, 2003; Barnes & Raymond, 2009) that these effects have been more important than climate effects in determining changes in CZ fluxes to date. For example, Fig. 10 shows that sediment accumulation rates increased in Chesapeake Bay (USA) coincident with land use changes associated with European settlement and farming in the watershed. Because erosion originating from agricultural lands and construction sites is often high compared to forests (Swaney *et al.*, 1996) – the dominant vegetation type in the absence of significant disturbance – it is unlikely that climate change alone could have caused the significant increase in erosional fluxes into the Bay.

Although climate change may not have been the biggest driver to date in determining changing erosion patterns, this hypothesis probes whether ongoing changes in temperature and precipitation (Canadell *et al.*, 2007; IPCC, 2007) will be more or less important to CZ fluxes than changes in land use and cover. Human-induced land-use change has been drastic in both developed and developing regions, and is likely to stay high for decades to come if the standard of living rises in the latter localities. At the same time, the effects of climate change on the CZ will be increasing with time globally and will impact landscapes regardless of human population density for long durations of time (Yang *et al.*, 2003). Moreover, climate change will also modulate ecosystem composition and CZ function in ways that will likely increase fluxes associated with chemical and physical weathering (Banwart *et al.*, 2009). Rising soil temperatures and changing precipitation regimes will also shift rates and spatial distributions of biogeochemical processes (see Hypotheses 7 through 9). Understanding the relative importance of forcing due to changes in land use and climate is needed for

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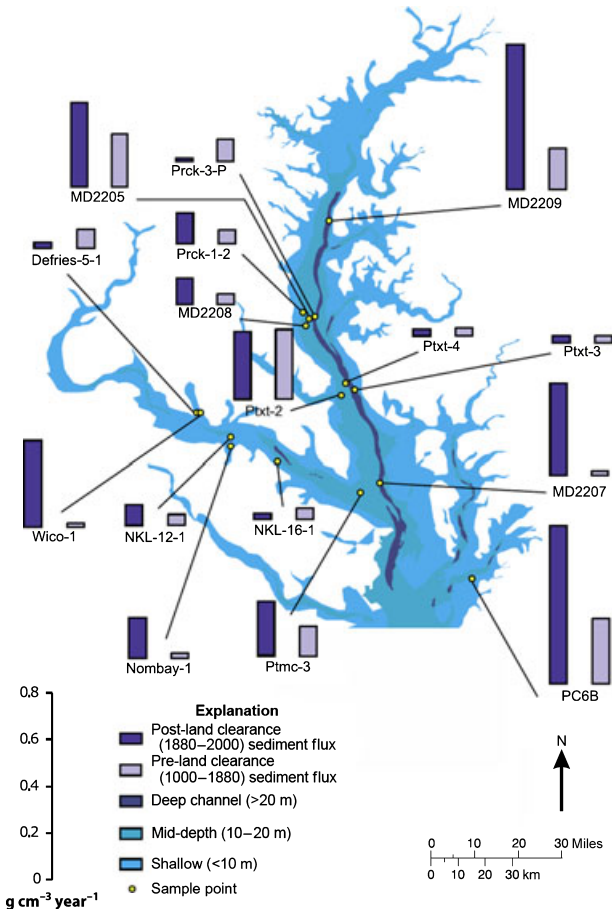

Fig. 10 Long-term sediment fluxes estimated between 1000 C.E. and 1880 C.E. and post-1880 based on sediment cores in the Chesapeake Bay. Of the 16 core sites, 10 show marked increases in sediment fluxes post-land clearance when compared with the long-term averages (Cronin *et al.*, 2003). Figure reproduced with permission.

reliable prediction of changes in ecosystem services. As discussed in Hypothesis 12, it will be important to determine whether changes in climate and land use might push landscapes across tipping points into undesirable states of ecosystem function.

Addressing this hypothesis will require an array of approaches from observational field studies conducted at multiple scales to the analysis of historical databases of human effects on the CZ (Walter & Merritts, 2008). By examining how land use has affected the susceptibility of the CZ to denudation in the past, we should be able to place constraints on how it will respond as human influence changes in the future. For example, analyses of sediment loadings in rivers can be related to climate fluctuations (Rossi *et al.*, 2009), as well as to areal changes in highly erodible cultivated lands following establishment of programmatic change such as the USDA Conservation Reserve Program in 1962 (Amelung *et al.*, 2001). Geographic information system and remote sensing technologies are now available to facilitate regional-scale assessments (Cronin *et al.*, 2003). Moreover, there is much to learn from paleosols, which document effects of significant climate changes in the geologic past (Retallack, 1990).

MANAGING THE CZ

Hypothesis 11. In many severely altered settings, restoration of hydrological processes is possible in decades or less, whereas restoration of biodiversity and biogeochemical processes requires longer timescales

Although advances have been made in restoring and maintaining agriculturally impacted topsoils and in restoring CZs associated with stream channels and riparian zones, less is known about how systems-level interactions influence the response of CZs to perturbations and restoration efforts. Hypothesis 11 proposes that restoring CZ function is possible for degraded systems, but the timescales of restoration of the hydrologic system is faster than that of the biogeochemical system (Fig. 11). A corollary to this hypothesis is the inference that restoring hydrologic pathways is a prerequisite to re-establishing biodiversity and biogeochemical processes.

It is common to note that ecosystem services are altered in soils and streams as hydrological processes are changed (Daily *et al.*, 2000; Rogers, 2006). However, we need metrics and techniques for identifying and quantifying such alterations in CZ systems so that we can learn how to reclaim, rehabilitate and restore function (Fig. 11c; Wallace, 2007; Heneghan *et al.*, 2008). Given the complexity of inter-relationships among chemical, physical, and biological factors endemic to the CZ (Fig. 11a), process-based models for soil erosion, soil carbon evolution, water quality evolution, and the evolution of ecosystem function must be developed and tested against field data (see, for example Hypothesis 6). Such tests will extend our ability to Earthcast at the spatial and temporal scales required by natural resource managers (e.g. hectares and years).

We suggest that addressing this hypothesis requires a three-stage approach. First, regionally meaningful metrics of both healthy and altered CZ systems must be developed and evaluated to ensure they are statistically robust, even in a changing environment. The choice of metrics will depend on needs of natural resource managers (namely, what they can feasibly measure), and also on the relevant CZ processes and ecosystem services in a range of disturbed landscapes. The second phase requires developing, implementing, and monitoring restoration projects to restore altered CZs. Such strategies should include: (i) taking account of past, present, and future land uses; (ii) conducting hydrological studies with attention to groundwater interactions; (iii) analysis of physical and biological properties of systems; (iv) study of how soil and water chemistry (both at the surface and at depth) influence water and soil quality (Mitsch & Jorgensen, 2004). These techniques will most likely include

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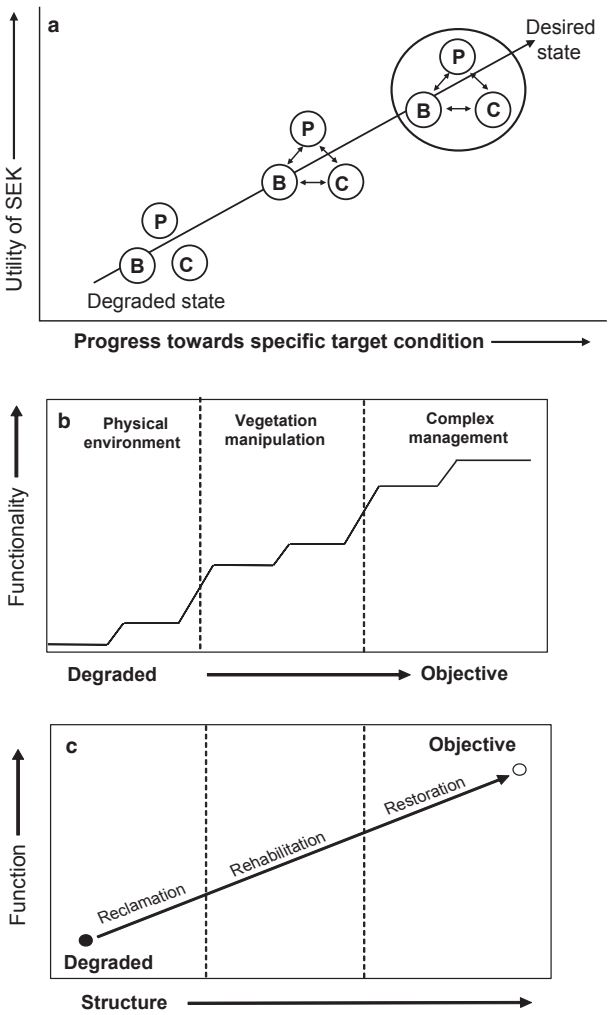

Fig. 11 Framework for integrating soil ecological knowledge (SEK) with theoretical models of ecosystem restoration. (a) When sites are heavily degraded, some improvement in soil function may be achieved by manipulations of either the chemical (C), physical (P), or biological (B) attributes of the soil. For greater progress toward a target condition, however, an increase in the degree of complex SEK is required, and there are more complex interactions among P, C, and B attributes. To achieve the desired state of restoration requires very high level understanding of P, C, and B processes. (b) Physical, biological, and management thresholds that must be overcome if restoration is to be successful. Hypothesis 11 is consistent with the likelihood of faster restoration of functionality with respect to physical processes such as hydrologic flow and slower restoration of biogeochemical processes. (c) The integral relationship between structural and functional attributes in ecosystem restoration (figure reproduced with permission from Heneghan *et al.*, 2008).

biotechnology, geo-engineering and landscaping, plantings, and species introductions. Both hydrologic fluxes and biogeochemical processes must be monitored along with the metrics used to define healthy and altered CZ's. Finally, both the societal and economic implications of these techniques must be evaluated with the help of resource managers. Such a long-term approach will allow both testing of this hypothesis and the development of efficient restoration strategies.

Hypothesis 12. Biogeochemical properties impart thresholds or tipping points beyond which rapid and irreversible loss of ecosystem health, function, and services can occur

A dynamical system may experience a *threshold* or *tipping point* when its state is such that even a small perturbation can cause an irreversible change in the system's functioning and properties. Ecosystems, deep ocean circulation, and earth's climate have all been previously suggested to exhibit threshold behavior (Lenton *et al.*, 2008). One common characteristic of systems with thresholds is that variables can be difficult or impossible to measure at the precision needed to predict changes around the threshold.

Here, we hypothesize that the CZ, as a dynamical system, most likely exhibits *tipping points*. These thresholds are presumed to be irreversible on timescales relevant to human life (decades to centuries), because, unlike in Hypothesis 11, once a tipping point is passed, restoration may not be possible to the previous state within those timescales. Although thresholds have been presumed to exist for the CZ, few have been precisely defined. As an example, Fig. 12 shows a CZ tipping point in which nutrient buffering collapses as fertilizer application increases beyond a threshold (Rabalais, 2002). Other CZ tipping points include thresholds for erosion by rill formation and landsliding (e.g. Favis-Mortlock, 1998). Tipping points for accelerated desertification, acidification, decline in carbon storage, collapse of nutrient buffering, or growth of harmful algal blooms could also be important (Millenium Ecosystem Assessment, 2005).

Given the increasing pressures on natural systems, it is critical to identify tipping points as quickly as possible. Furthermore, because the tipping point concept is relatively intuitive, it is a very useful concept for both policy makers and scientists. The term 'tipping point' is now being used by both groups to describe global challenges such as climate change (Post *et al.*, 2009; Russill & Nyssa, 2009), biodiversity losses (Pimm, 2009), and crop yields (Barley, 2009). However, policy can only be formulated appropriately if we identify where and when tipping points occur. Currently, thresholds are only recognizable after passing the threshold. As a result, one current focus of research is to identify early warning signals of change and threshold behavior in ecosystems as well as effective responses to such threats (Jordan *et al.*, 2006).

Many of the coupled biological, geological and hydrological processes are well enough understood to open the way to use models to explore tipping points in regolith or soil formation. To understand the biogeochemical resilience of soils with respect to acidification, nutrient depletion, drought, and erosion, however, we need to quantify the rates and mechanisms of chemical weathering, hydrology, erosion, and biotic processes in regulating biogeochemical resilience. With such knowledge, we can use models to explore tipping points as a function of variables such as climate, lithology, and vegetation as we attempt to propose regulatory frameworks. It is furthermore crucial to examine

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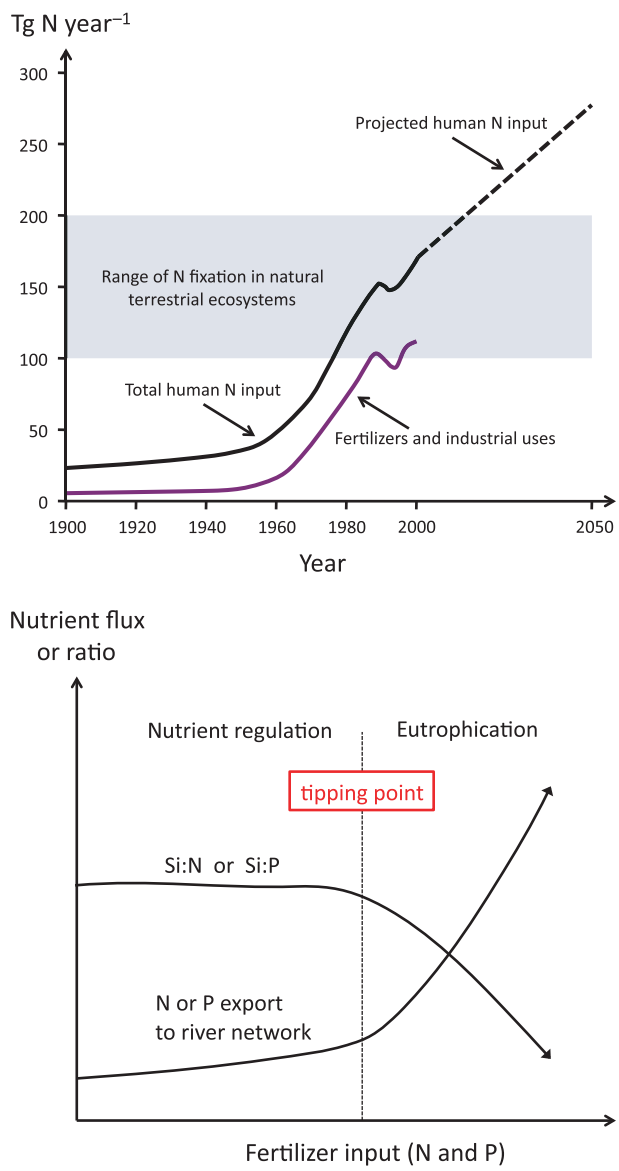

Fig. 12 Hypothetical response (lower figure) in buffering of nutrients by CZ processes as anthropogenic inputs of nitrogen (N) and phosphorus (P) via fertilizer application are increased (upper figure). At relatively low fertilizer loadings, processes such as denitrification that eliminate or processes such as sorption or plant uptake that retain N and P can limit the export fluxes from the soil environment. Beyond a threshold in fertilizer application, however, the natural buffering capacity of the soil is exceeded and there is a rapid transfer of bioavailable N and P to the stream network. If the export of bioavailable silicon (Si), primarily produced by chemical weathering of silicate minerals, remains constant, then the increase in N and P export fluxes is also accompanied by a drop in the Si:N and Si:P ratios. Both the absolute and relative changes in nutrient fluxes as the tipping point is crossed may cause significant downstream damage to in-stream ecosystems, freshwater reservoirs, and the coastal zone (Rabalais, 2002). Upper figure reproduced with permission from the Millenium Ecosystem Assessment (2005).

how the biogeochemical resilience and tipping points of soil environments relate to ecosystem services within watersheds.

Table 2 Variables and properties that contribute to biogeochemical tipping points in the Critical Zone

Population density, land use, water allocation, and economic development within a watershed
Minimum and maximum rainfall, air temperature, water table depth, and baseflow
% Vegetation cover, rooting depth, and % impervious cover
Regolith thickness, soil age, and maturity
Acid buffering capacity, clay content, cation exchange capacity, and organic matter content
Nutrient filtering capacity, internal nutrient recycling, and nutrient ratios
Functional and genetic diversity of microflora and microfauna
Textural threshold(s) and soil aggregates

Like the other hypotheses, methods by which research priorities for Hypothesis 12 can be addressed include experimental watershed studies as well as smaller-scale mesocosm experiments. However, to understand tipping points also requires modeling efforts to build conceptual understanding of biogeochemical resilience, allowing for scaling from the mesocosm to the watershed to the region to the globe. Examples of properties that are expected to be important in imparting thresholds to the CZ, and which should therefore be targeted in these studies, are listed in Table 2.

Finally, the geologic record may be a source of additional understanding if we can identify tipping points that have been crossed in the past. For example, ancient soils – paleosols – could allow us to identify tipping points that may have been involved before, during, or after the Paleocene–Eocene thermal maximum (PETM). Considered an analog for future global warming, the PETM was characterized by releases of greenhouse gases that drove rapid warming of 5–9 °C that resulted in alteration of terrestrial ecosystems (Wing *et al.*, 2005; Zachos, 2005). Changes in chemical weathering related to such greenhouse episodes may reveal evidence for or against tipping points in the surface Earth system (Thiry, 2000; White *et al.*, 2001).

CONCLUSION

We have advanced 12 hypotheses that can be tested concerning the geobiology of weathering through the use of tools and approaches available today. Interestingly, several of the hypotheses are contradictory: nonetheless, each hypothesis is thought to be defensible by at least one segment of the CZ scientist community. This suggests that even at a very basic level, we do not understand CZ function.

To build understanding, new observatory initiatives are underway to investigate the CZ in a more holistic fashion. For example, in the USA, six CZ Observatories have been funded since 2006. Likewise, in Europe, a group of CZ scientists has been funded as the SoilTrEC International CZO Network with partners in the European Union, China, and USA. This program has explicit links to the CZO program in the USA. Other researchers are similarly designing

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or extending observatory networks in other countries around the world.

However, observatories alone cannot test the hypotheses in this paper. Quantitative models are being developed to understand observatory data and these models are needed to test the hypotheses (e.g. Parton *et al.*, 1987; Tucker & Slingerland, 1994; Iverson & Prasad, 1998; Goddéris *et al.*, 2006; Yoo *et al.*, 2007; Steefel, 2008; Banwart *et al.*, 2009). Discrepancies between models and observations will drive improvements in our understanding of many of the important phenomena. Only with such efforts will models yield accurate 'Earthcasts' that project how the three forcing factors – tectonism, climate, anthropogenic activity – individually and together cause the CZ to change.

Of these three forcings, anthropogenic activity could be the most important driver of CZ change into the immediate future. In other words, the largest impact of biology on weathering today may be that of humans. In turn, this impact impairs the ecosystem services and soil health that human society relies upon. Unlike the other two forcings, however, the direction of anthropogenic activity can sometimes be reversed by learning and behavioral change. In this regard, the CZ is a powerful integrating concept for both scientists and the public alike because it fosters comprehension of the interconnectedness of water, land, air, and biota. It is perhaps reassuring therefore that in November 2009, a Google Scholar search generated 303 000 unduplicated hits of web-pages dedicated to educating the public about foundational concepts in CZ science. However, the increasing use of web-delivered education for the public (Hill & Hannafin, 2001) is actually a symptom of another trend that is cause for concern. In industrialized societies, children increasingly spend less time outside but more time online (Sallis *et al.*, 2000; Norman *et al.*, 2006). Without experiential learning, the dialog between natural scientists and stakeholders is limited and people increasingly experience a disconnect from the natural environment (Fischer, 2004; Rogers, 2006). Thus, just as humans have attained the status of a geological force (Vitousek *et al.*, 1997; Wilkinson, 2005), they ironically are disconnecting from their natural environs. Given all of these trends, the observatories and models needed by scientists to understand the CZ must also be designed to engage the public in the puzzle of how to live sustainably during the Anthropocene.

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