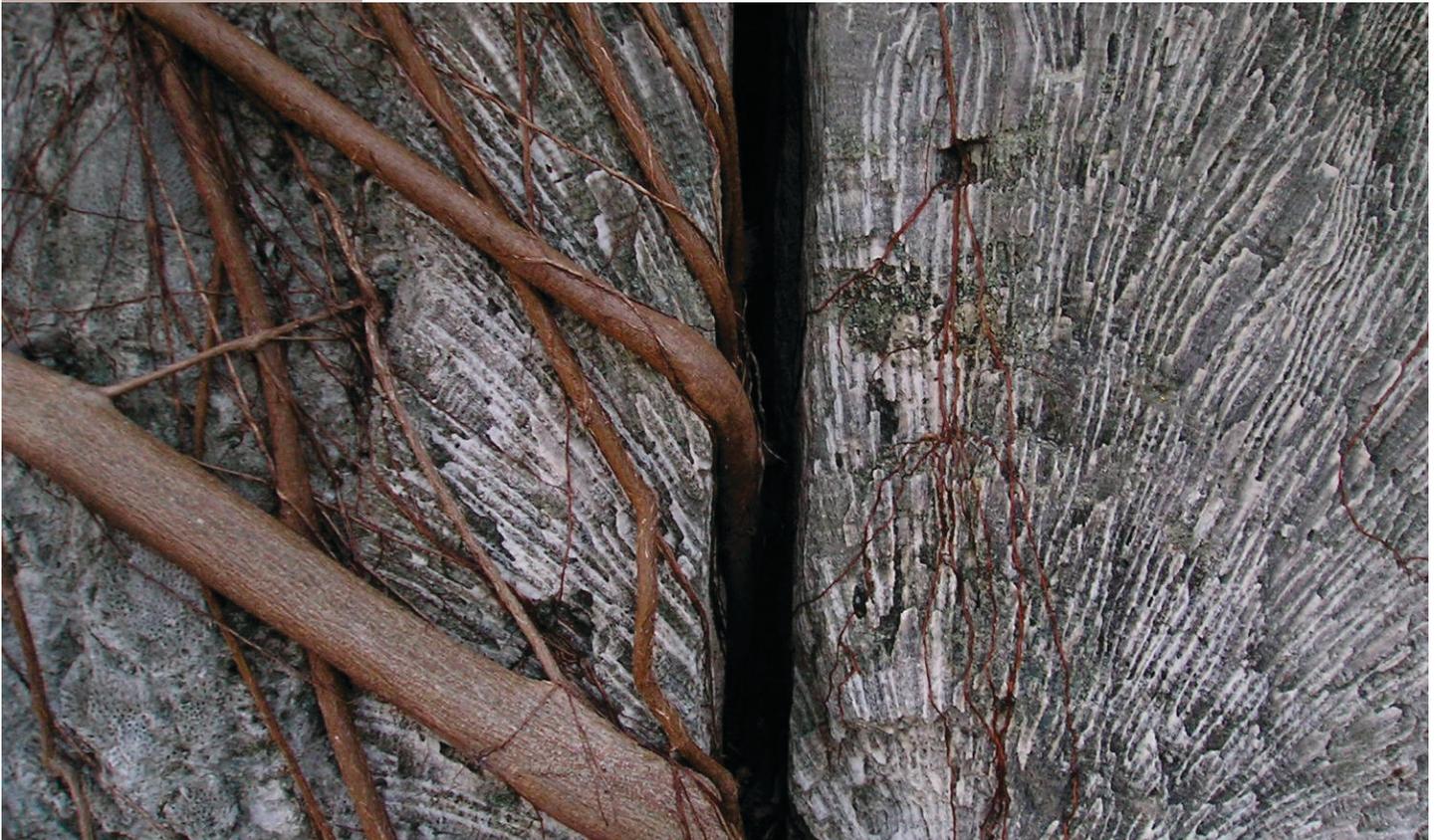


Frontiers in Exploration  
of the

# Critical Zone Critical Zone



# Frontiers in Exploration of the Critical Zone

## An NSF-Sponsored Workshop

University of Delaware

Newark, Delaware

Monday October 24 - Wednesday October 26, 2005

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### Frontispiece caption:

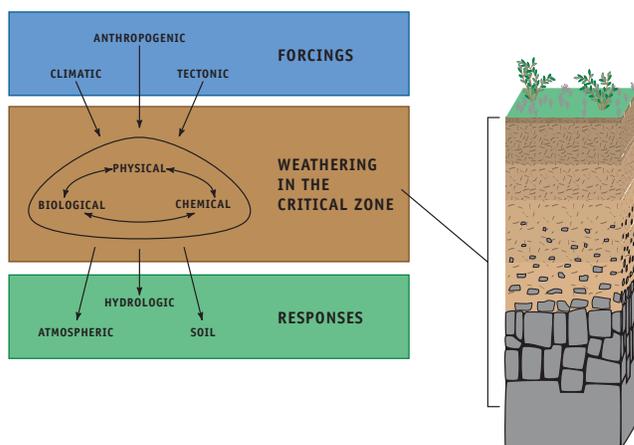
The Critical Zone encompasses Earth's outermost surface defined from the vegetation canopy to the zone of groundwater. This zone, the interface between Earth materials and the biotic world, modulates the transfer of nutrients into terrestrial lifeforms. In this photograph, a tree root anchored onto the Key Largo Limestone, an exposed reef with fossilized hermatypic corals, is shown. The limestone is overlain by thin soil in the Windley Key Fossil Reef Geological State Park, forcing plants to anchor themselves directly to the bedrock for stability and nutrients. To understand processes in such settings, scientists from multiple disciplines must unravel similarly complex inter-relationships within the hydro-, litho-, and biosphere. Photograph by Heather Buss, Penn State.

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## Executive Summary

The surface of the Earth is rapidly changing, largely in response to anthropogenic perturbation. How will such change unfold, and how will it affect humankind? The Critical Zone is defined as the external terrestrial layer extending from the outer limits of vegetation down to and including the zone of groundwater. This zone sustains most terrestrial life on the planet. Despite its importance for life, scientific approaches and funding paradigms have not promoted and emphasized integrated research agendas to investigate the coupling between physical, biological, geological, and chemical processes in the Critical Zone.



A national initiative is needed that incorporates a systems approach to investigation of Critical Zone processes across a broad array of sciences: geology, soil science, biology, ecology, geochemistry, geomorphology, and hydrology. Only with such an approach will we be able to answer the following question:

*How do the physical, chemical, and biological components of Earth's weathering engine transform mineral and organic matter to nourish and sustain ecosystems, regulate the migration and fate of toxins, sculpt terrestrial landscapes, and control the exchange of greenhouse gases and dust with the global atmosphere?*

This initiative will enable prediction of complex feedbacks among processes in the Critical Zone, including changes in fluxes driven by climatic, tectonic, and anthropogenic forcing over a wide range of temporal and spatial scales. Of particularly pressing importance is the need to understand how the Critical Zone is being transformed by rapid anthropogenic change.

This effort will require a network of observatories and people to quantify responses of the Critical Zone to environmental change. The Critical Zone Exploration Network will include short-term deployments of instrumentation at field sites along environmental gradients as well as long-term sites that will be instrumented hierarchically and intensively. Importantly, sites will be chosen by peer review to answer fundamental questions requiring the entire network. By choosing sites with important questions in mind, the Critical Zone Exploration Network will thus tackle questions of great societal and global importance by uniting a multi-disciplinary and diverse community of scientists and their students.

*Figure 1. The coupled chemical, physical, and biological processes that define Earth's weathering engine are driven by climatic, anthropogenic, and tectonic forcing that can be investigated at all scales. The characteristic rates and extents of weathering are recorded in the concentrations of atmospheric gases and aerosols in hydrologic responses, and in soil chemistry, and can be inferred from historical data and from the geologic record (ANDERSON ET AL., 2002). Reproduced with permission from the American Geophysical Union.*

### Introduction: What is the Critical Zone?

At the Earth's surface, a complex suite of chemical, biological and physical processes combine to create an engine that transforms bedrock and biomass into soil (Figure 1). Earth's weathering engine provides nutrients to nourish ecosystems and human society, controls water runoff and infiltration, mediates the release and transport of toxins to the biosphere, and creates conduits for the water that erodes bedrock. The weathering engine also affects the sequestration and release of greenhouse gases that impact climate change, and generates aerosols and dust that provide nutrients to the land and ocean. All of these processes occur within the Critical Zone, defined by the National Research Council's Committee on Basic Research Opportunities in the Earth Sciences (2001) as the external surface of the Earth extending from the outer limits of vegetation down to and including the zone of groundwater. At present, humankind is radically changing the Critical Zone by altering the magnitudes of both the reservoirs and fluxes in ways that we do not understand and cannot predict (Table 1).

Table 1. Some Changes in the Critical Zone

Over the past 3 centuries, 30-50% of global land surface and more than 50% of freshwater has been used by humans <sup>1</sup>

Croplands and pastures now rival forest cover as the major biome on Earth <sup>2</sup>

At least 20% of plant species on continents are frequently nonindigenous <sup>3</sup>

Humans have doubled the rate of nitrogen inputs to terrestrial ecosystems <sup>4</sup>

Contaminants have been documented in 80% of representative streams in U.S. <sup>5</sup>

Cropland per person has decreased from 0.5 to 0.35 ha worldwide <sup>6</sup>

Weathering rate increases over the last 50 y related to changes in climate and land use are changing the chemistry of North America's largest river <sup>7</sup>

Current rates of loss of U.S. soil from development of pastureland are about  $400 \text{ m}/10^6 \text{ y}$  <sup>8,9</sup>

Current rates of loss of U.S. soil due to cropland tillage are  $680\text{-}1400 \text{ m}/10^6 \text{ y}$  <sup>8,10,11</sup>

<sup>1</sup>Crutzen (2002); <sup>2</sup>Foley et al., (2005); <sup>3</sup> Vitousek et al. (1997) and references therein; <sup>4</sup> Vitousek et al. (1997); <sup>5</sup> Kolpin et al. (2002); <sup>6</sup>Ramankutty et al. (2002); <sup>7</sup> Raymond and Cole (2003); <sup>8</sup> Wilkinson (2005); <sup>9</sup> U.S.D.A. (1988); <sup>10</sup> Pimentel et al. (1995); <sup>11</sup> Pimentel and Skidmore (2004)

Despite the fundamental importance of the Critical Zone, our knowledge of its central component – soil, the complex biomaterial that promotes the growth of terrestrial organisms – is remarkably limited. This limitation in knowledge persists because scientific approaches and funding paradigms have tended to emphasize reductionist approaches

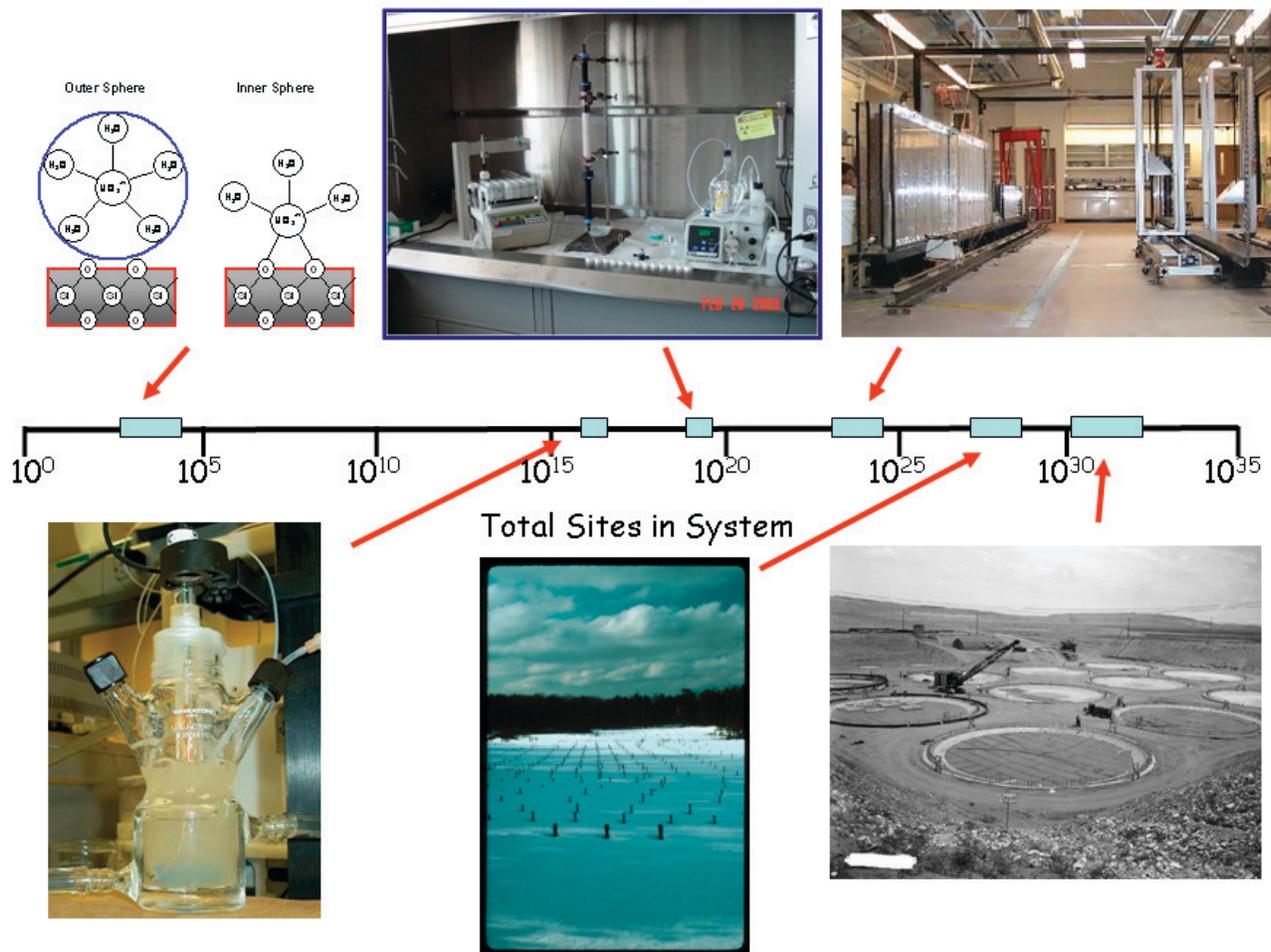


Figure 2. Processes in the Critical Zone that occur at the nano-scale control observations at the soil-profile scale. Similarly, processes occurring at the soil-profile scale control fluxes observed in watersheds and processes occurring over the entire globe. To make predictions needed at regional and global scales for societal decision-making requires models that span almost thirty orders of magnitude in numbers of reactive sites. This vast range of scale is difficult to incorporate into models and into training paradigms for environmental scientists, but if the challenge of crossing scales is incorporated into an initiative for Critical Zone exploration, then advances will be made. Figure courtesy of B. Honeyman, Colorado School of Mines.

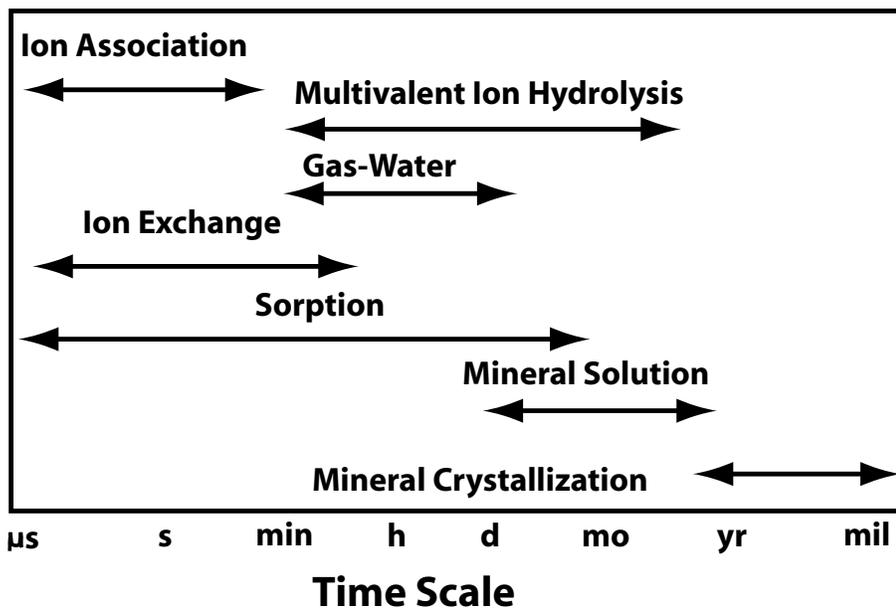


Figure 3. Like spatial scales, the timescales of water-rock interaction span over many orders of magnitude. To understand the Critical Zone will require multi-disciplinary scientists working over this vast scale of time. Figure from AMACHER (1991). Reproduced with permission from Elsevier.

and have not emphasized integrated interdisciplinary research agendas. In addition, understanding the Critical Zone requires knowledge of an extremely heterogeneous system across a vast range of spatial (Figure 2) and temporal scales (Figure 3). No national or international initiative has promoted a systems approach to investigation of weathering science and soil ecosystems across the broad array of requisite fields including geology, soil science, biology, ecology, and hydrology. Here, we discuss the intellectual excitement that surrounds Critical Zone science and we articulate the need for an initiative to answer the following first-order question:

*How do the physical, chemical, and biological components of Earth's weathering engine transform mineral and organic matter to nourish and sustain ecosystems, regulate the migration and fate of toxics, sculpt terrestrial landscapes, and control the exchange of greenhouse gases and dust with the global atmosphere?*

Only with such an effort will we be able to predict how weathering and biological processes in the Critical Zone respond to climatic, tectonic, and anthropogenic forcing over time and space (Figure 1). In November 2005, a group of 150 scientists met at the University of Delaware to discuss such an initiative, the Critical Zone Exploration Network (CZEN).

The fundamental question driving CZEN lies at the center of a host of societal issues. We now realize that almost half of the land surface on Earth has been transformed by human activity (VITOUSEK ET AL., 1997), including vast and sometimes deleterious transformations of soils that affect our ability to feed the human populace (e.g., STOCKING, 2003; SANCHEZ AND SWAMINATHAN, 2005). The range in native soils, critical for understanding the functioning of ecosystems, is being severely reduced (Figure 4) as urbanization, agriculture, forestry, and mining change the global landscape. Scientists and policymakers alike seek to quantify release of dust and trace gases to the atmosphere to model ongoing climate change and the effects of dust on human health. In order to safeguard drinking water, we seek to investigate how mineral-water interactions impact the quality of surface and ground waters (Figure 5). We seek to predict how toxic elements such as arsenic and chromium are released into natural aquifers and how toxics introduced by humans are mobilized in the environment. Understanding and predicting responses to such global and regional change is necessary as we seek to mitigate anthropogenic impacts on the Earth (Figure 6).

#### **Four Critical Zone Questions**

The Critical Zone manifests an extraordinary diversity of soils and ecosystems ranging from the tropics to the poles, from deserts to wetlands, and from rock-bound uplands to delta sediments. As a constantly changing open system, the Critical Zone represents the equilibration of rocks and minerals, commonly formed at high-temperatures and pressures deep in the Earth, to ambient surface conditions. Equilibration occurs across a range of time scales as bedrock is continually exposed by

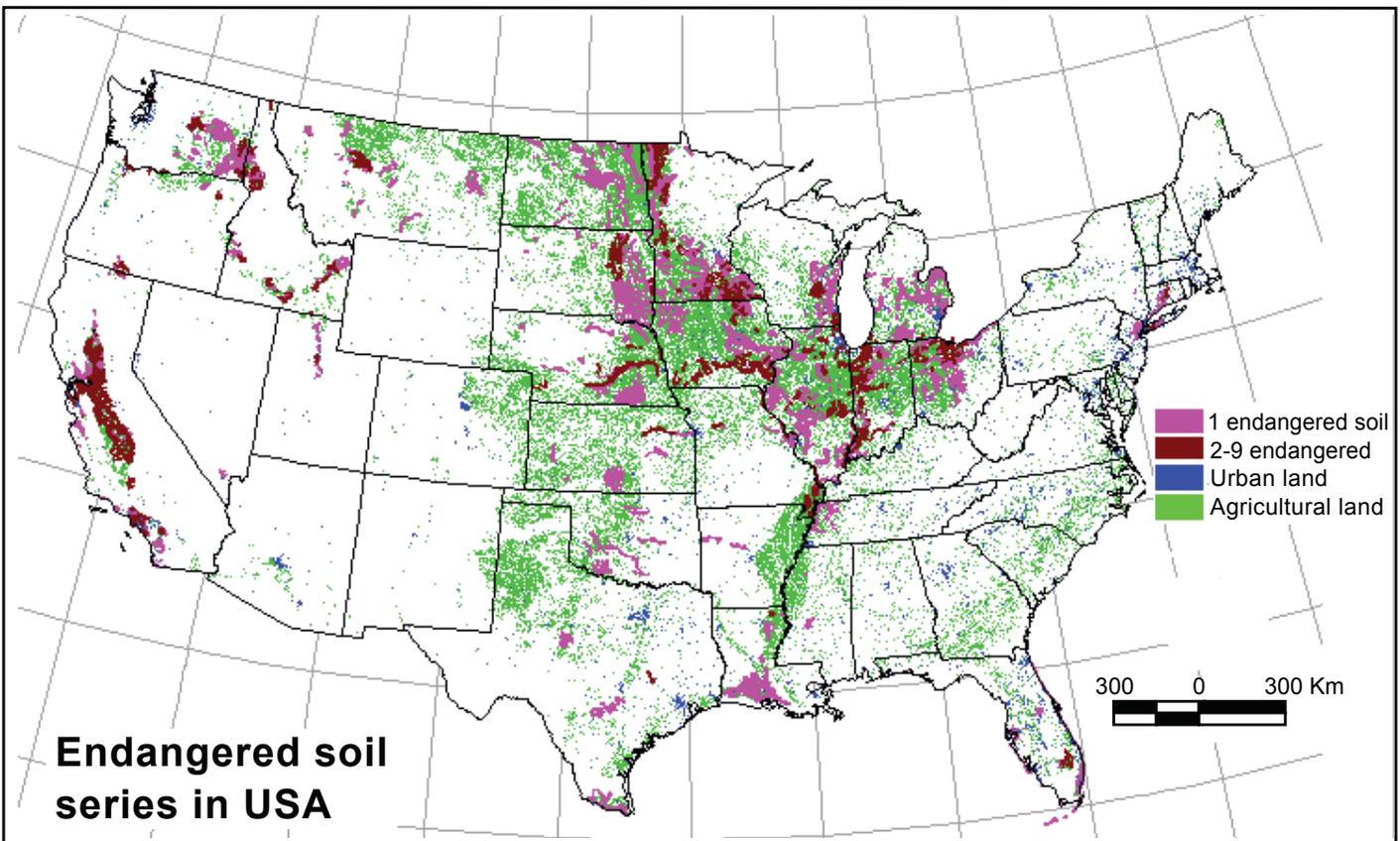
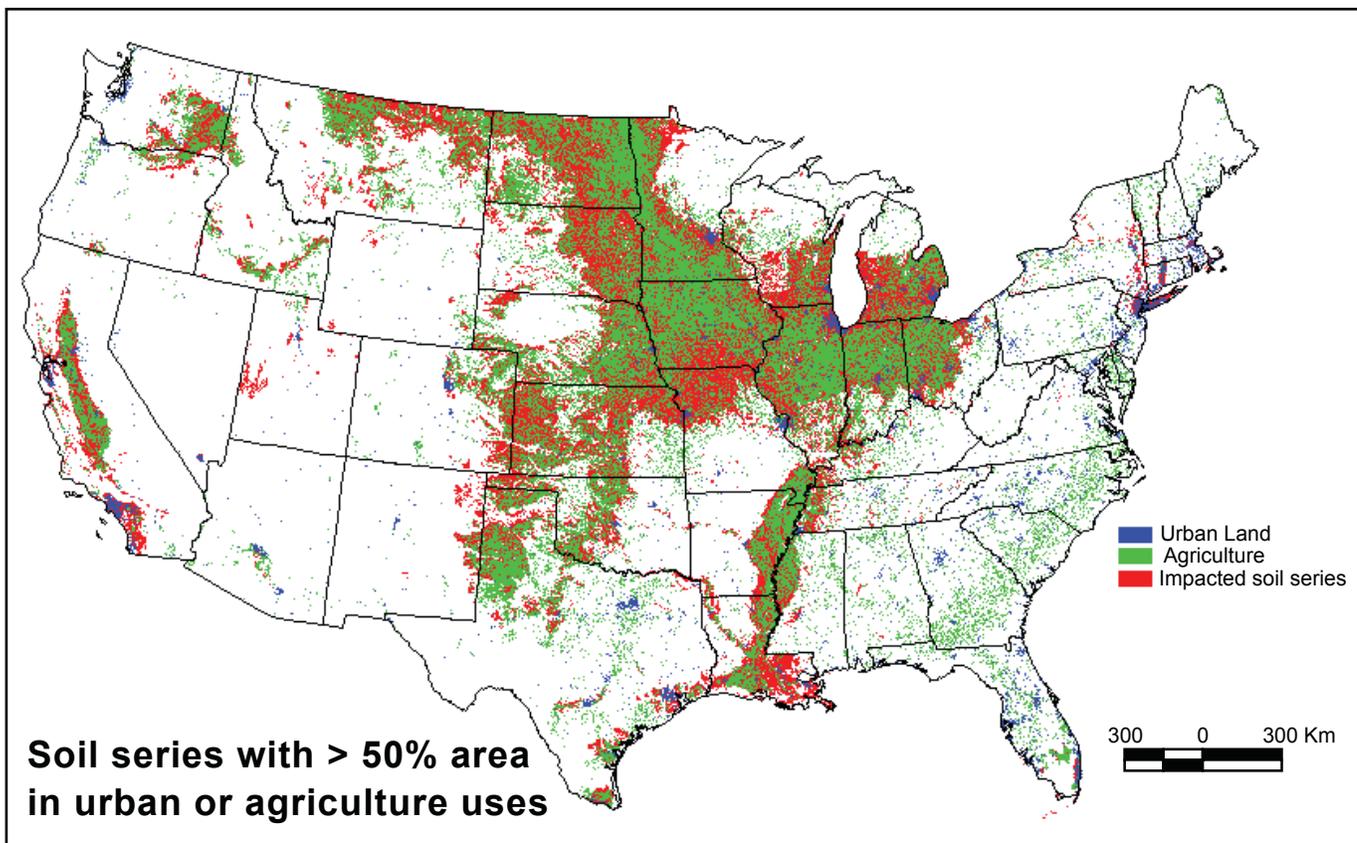


Figure 4. Top: Map showing the distribution of agriculture (green) and urban lands (blue) in the USA, and the distribution of soil types (series) that have lost 50% or more of their original area to combined human uses. Bottom: Map showing the geographical distribution of endangered soil types (series) in the USA. Endangered soils are those that naturally have a distribution of 10,000 ha or less which have lost 50% or more of their area to combined human disturbances. Figure after AMUNDSON ET AL. (2003). Reproduced with permission from Elsevier.

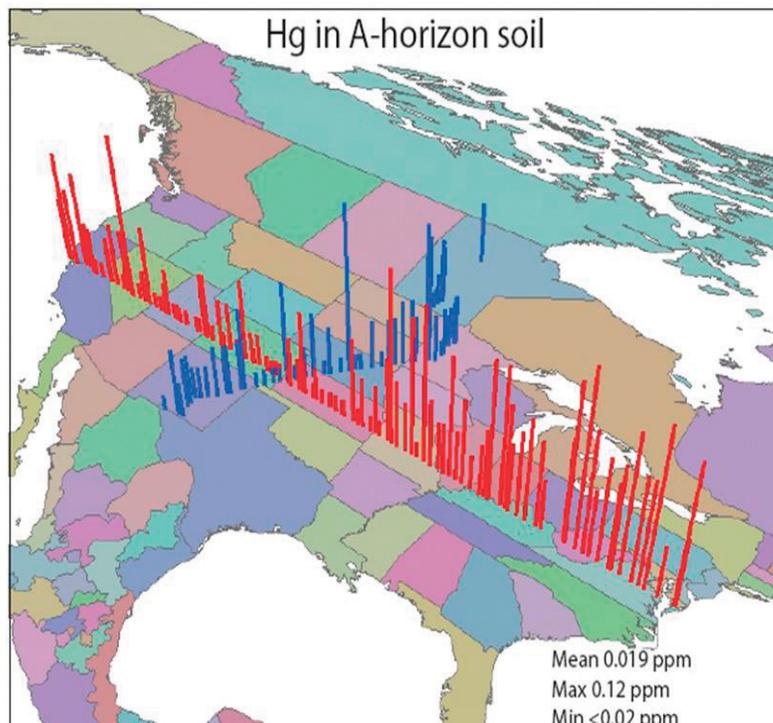
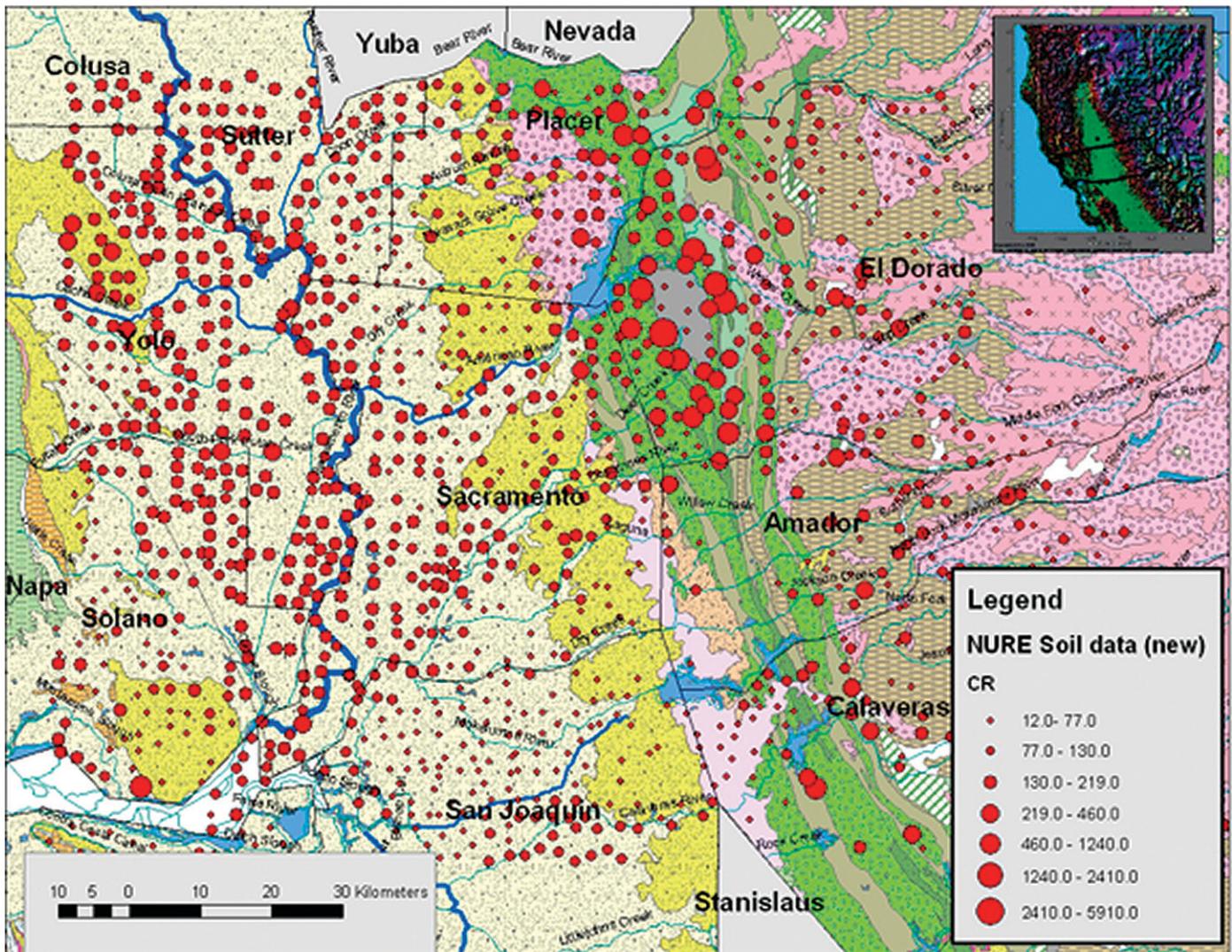
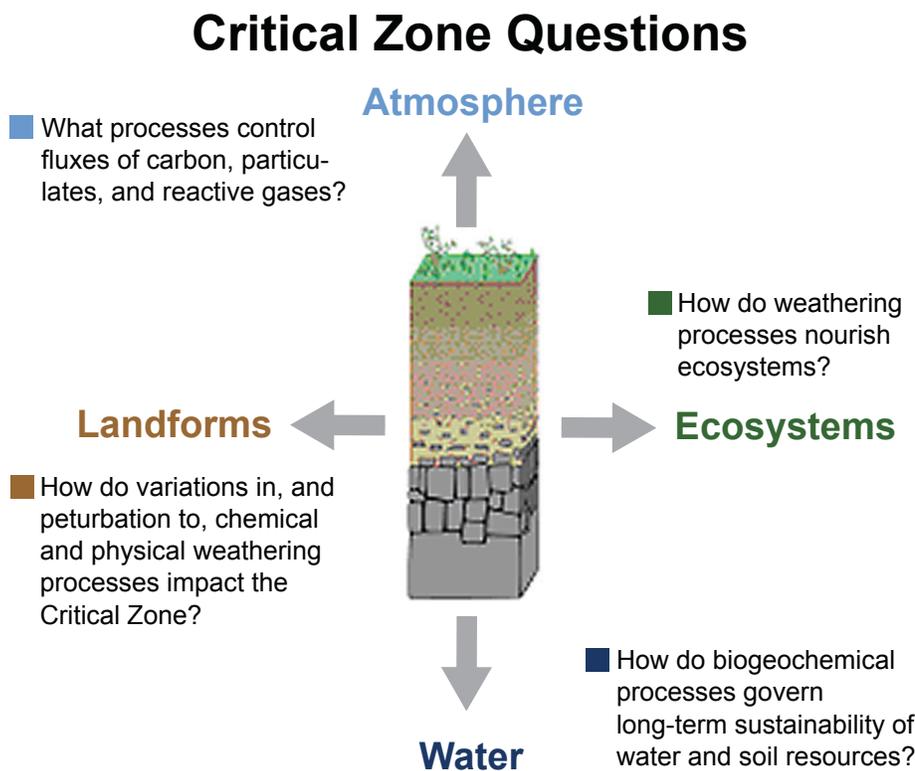


Figure 5. Top: Map showing the Cr concentration in the upper 30 cm of soils in CA. The sampling transect crosses the NV border to the Pacific Ocean (see inset). The base map documents the geology of CA at a 1:750,000 scale. Red dots are sized proportionally to Cr content (in ppm). Extremely high Cr concentrations >1000 ppm occur in rocks in the foothills of the Sierra Nevada. Bottom: Map showing Hg concentration in A-horizon soils along two North American transects. Higher Hg content in eastern soils likely results from both natural and anthropogenic factors including organic content and industrial activities in the densely populated eastern US. (Figures from SMITH ET AL., 2005).

physical erosion and tectonic forcing (Figure 1). The energy inherent to this disequilibrium is harvested by Earth's biota at the same time that biotic processes also create and maintain disequilibrium. In the past, the complexity of these processes produced landscape-scale variability of soils that were controlled principally by climate, exposure age, lithology, topographic position, and biota. In addition, today, anthropogenic factors are changing the surface of the Earth at rates that may never have been experienced on Earth heretofore (Figure 7; see also WILKINSON, 2005). The investigation of these "state factors" in soils has long been a guiding principle for investigation.

The influence of these individual factors on soil formation has been documented in soil sequences in which other variables are relatively constant or of less importance. For example, rock types respond differently to equivalent environmental forcings because of variation in silicate mineral content and grain size. For a given lithology, the rate

Figure 6. The Critical Zone impacts the atmosphere, biosphere, hydrosphere, and lithosphere through the complex interplay of biological, geological, chemical, and physical processes. We seek to address questions related to how the Critical Zone cleanses and purifies surface and ground waters, nourishes ecosystems, sculpts landscapes and controls the exchange of trace gases and dust with the atmosphere. Frontiers in investigations of the Critical Zone addressing these areas are described in this report as Questions 1 through 4.



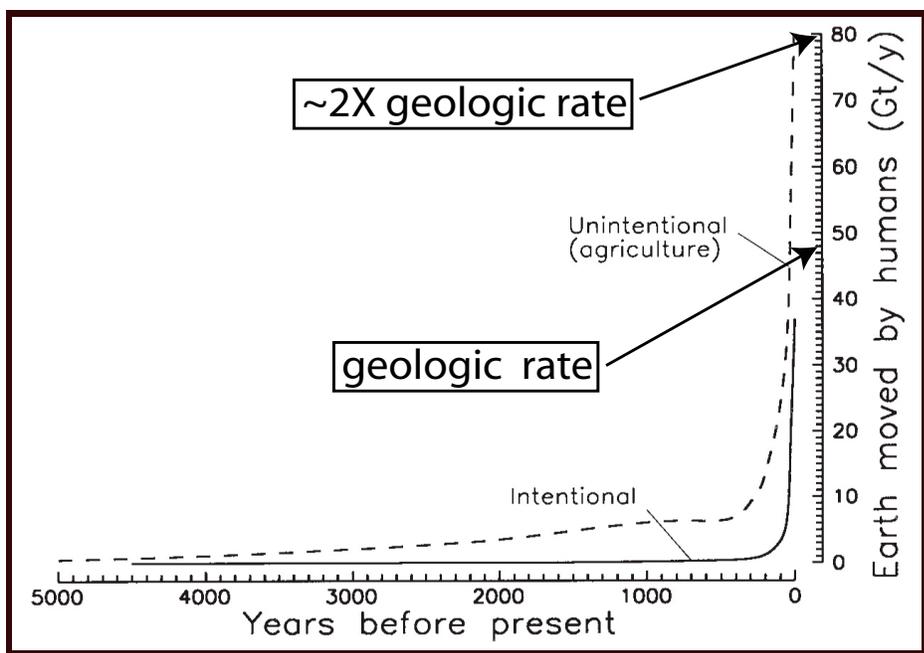
of formation of the regolith increases with increasing rate of flushing with freshwater, whereas the nature of secondary mineral formation depends on fluid residence times, the extent of solution phase supersaturation, and the kinetics of nucleating phases. We have learned a great deal about biogeochemical reactions for individual components of these heterogeneous systems, but only now are we prepared to integrate these processes in the context of the Critical Zone as an open system and to elucidate the complexity of their interactions, thresholds, and feedbacks.

What has emerged from these individual studies is the recognition that the interaction among these key variables gives rise to key life-sustain-

ing processes in the Critical Zone. For example, the use of advanced analytical techniques, including those employing synchrotron facilities, have led to our understanding that biogeochemical processes at mineral surfaces are tightly coupled to fluid flow and the associated transfer of reactive species (HOCELLA, 2002). As another example, the isolation of state variables in models that do not incorporate coupling precludes the prediction of complex system behavior (CHADWICK AND CHOROVER, 2001).

The Critical Zone Exploration Network presents four driving questions that incorporate the coupled behavior of process dynamics among the state variables. Each of these questions addresses a major societal concern related to global changes in the atmosphere, biosphere, hydrosphere, and surficial lithosphere (Figure 6). Most importantly, each question is interrelated and will only be answered through interdisciplinary collaborations and the opportunity to study environmental conditions worldwide. These questions are described below.

Figure 7. Estimate of the total amount of earth moved annually by humans as a function of time. Curves (from HOOKE, 2000) were calculated from earth movement per capita multiplied by population. Humans now move about 10 times more sediment as all natural processes combined. Reproduced with permission from the Geological Society of America.



**Question 1: How are the rates of physical and chemical weathering perturbed by environmental forcing?** The chemical instability of Earth material drives the production of regolith and dissolved loads that either remain in residual material or are transported away from the weathering regime (e.g. RAYMOND AND COLE, 2003). While these components of weathering have been described for more than a century, details of the mechanisms and rates of chemical and physical weathering, the manner by which they are coupled in Critical Zone formation, and the response of weathering to environmental changes related to biologic, climate and anthropogenic forcing, are still poorly understood. The coupling of chemical and physical weathering ultimately is responsible for the development of the landscapes upon which we live. Furthermore, biological sustainability depends upon the rates of mineral nutrient release from chemical weathering. Release of elements is sometimes accompanied by mobilization of toxic minerals or elements such as selenium, arsenic, aluminum, chromium, and mercury (Figure 5). Chemical weathering

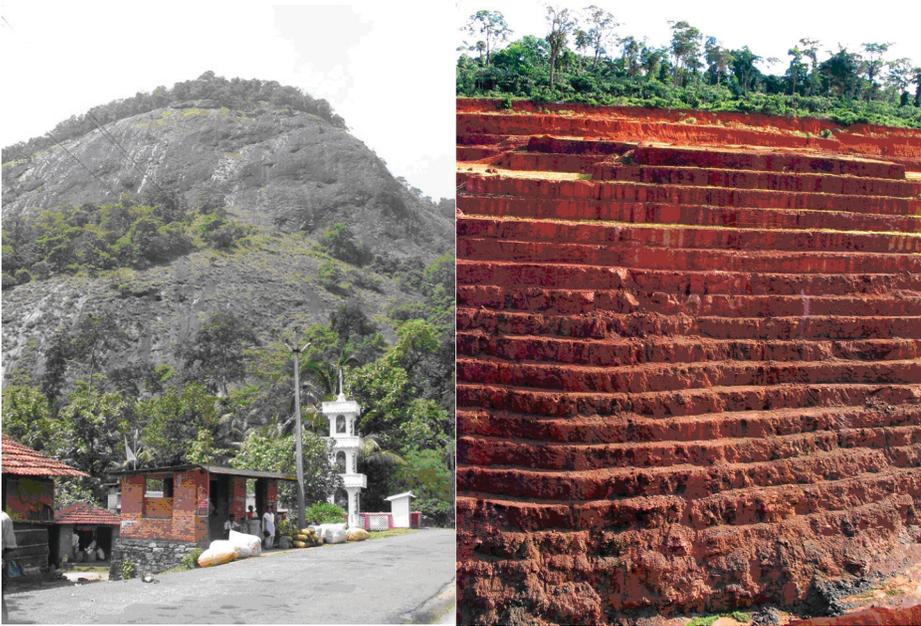


Figure 8. A 70 million year old weathering profile in Carajas, Brazil (right) contrasts with unweathered rock slopes in southern India (left). Erosion processes and ecosystem function in these environments both control and reflect processes of weathering front propagation. How humanity develops sustainable livelihood on such contrasting soils and landscapes is a very pressing question. Brazil photo by Bill Dietrich, Univ. of California, Berkeley; India photo by Suzanne P. Anderson, Univ. of Colorado, Boulder.

also neutralizes acidity over the long term (uptake of carbon dioxide and production of alkalinity) as well as the short term (mitigation of anthropogenically-produced acid rain). We require quantitative understanding of weathering processes in the Critical Zone that we do not yet possess.

A number of specific questions relating to weathering in Critical Zone development need to be addressed within Question 1:

- *What controls the thickness of the Critical Zone?* The depth of the weathered profile, varying from zero at sites where fresh rock extends to the surface to sites with residual soil thicknesses of 100s of meters (Figure 8), represents a balance between the rates of physical erosion and rates of conversion of bedrock to soil. We still have a very poor understanding of the mechanisms and rates by which soil is produced from bedrock. How do we determine if an individual soil thickness represents a steady state or whether the soil has been continuously accreting or degrading over time? What feedbacks exist between regolith thickness, erosion, and chemical weathering? Is the current thickness of the Critical Zone sustainable under future climatic and anthropogenic forcing?

- *What controls the vertical structure and heterogeneity of the Critical Zone?* Shallow soils and soil structures have been extensively characterized and classified by soil scientists. In contrast, the structure of deep soil horizons down to unweathered bedrock is generally poorly documented. Can we develop a unified approach to characterize the environmental conditions and mechanisms that produce differences in soil types and individual horizons over the full weathering or soil profile?

- *What controls the rate of chemical and physical weathering?* Weathering rates of silicate minerals measured in the laboratory are orders of magnitude faster than those measured in the field. In addi-

tion, weathering rates appear to decrease with increasing regolith age. What are the processes controlling retardation of chemical weathering? How is solid-fluid surface area generated in the Critical Zone and what controls its variation in reactivity? In what CZ regimes is chemical weathering limited by interfacial kinetics versus solute transport processes? What are the roles of organic and inorganic ligands in controlling metal solubility and transport? What controls redox cycling of reactive metals and organic compounds? How do physical weathering rates impact chemical weathering, and vice versa?

- *How is weathering linked to hydrology in the Critical Zone?*

Both sediment and solute fluxes correlate directly with the magnitude of precipitation and hydrologic flushing. Chemical weathering can therefore be limited by permeability. In turn, permeability can be increased by weathering due to dissolution of minerals, or decreased due to clay formation. What controls the relative rates of these processes, and how does this coupling evolve over time and space to produce soil structure?

- *How is weathering linked to biology in the Critical Zone?*

Quantitative approaches are needed to understand how vegetation both suppresses and enhances physical erosion in hillslope environments through soil stabilization and bioturbation, respectively. How important is the acceleration of chemical weathering by plants due to increasing soil acidity and complexing organic ligands associated with root or microbial respiration and growth? Is nutrient cycling by vegetation open or closed to inputs from chemical weathering, and how is this affected by depth and weathering intensity of the CZ? How efficient are biota in extracting mineral nutrients?

- *What weathering thresholds produce irreversible changes in the Critical Zone?* Time and climate sequence studies demonstrate that the CZ commonly exhibits trends in composition and structure that evolve non-linearly, suggesting that irreversible processes occur that limit responses to environmental variability. For example, weathering may lead to collapse or to cementation of the soil. These features fundamentally alter the movement of water and gases within the CZ. How can we characterize and model such threshold effects?

*Research Agenda.* The research questions related to Question 1 are interdisciplinary and require the application of an array of existing techniques and tools, in addition to the development of new approaches from a number of scientific disciplines. To answer these complex questions, an organized integrated approach to specific sites is required. It will be necessary to 1) develop tools to access and characterize the CZ from the surface down into bedrock; 2) apply geophysical methods to profile regolith depths, densities and structures; 3) characterize hydrologic flow paths, fluid potentials, and hydraulic conductivities; 4) measure exposure ages and the rates of chemical and physical processes; 5) develop tools to study biophysical and biochemical processes in the CZ and particularly in bedrock; and 6) develop isotopic techniques to trace nutrient cycling and to distinguish between lithogenic versus biogenic sources.

**Question 2: How do important biogeochemical processes occurring at Critical Zone interfaces govern long-term sustainability of soil and water resources?** The Critical Zone is a living membrane that transforms the composition of the fluids that traverse it. It acts as an open thermodynamic system, subjected to a continuous exchange of matter and energy. As a result, the Critical Zone is in a persistent state of disequilibrium. The energy made available by disequilibrium drives transformative biogeochemical reactions which are catalyzed by diverse microbial populations. Spatial heterogeneity is extreme in the Critical Zone and nanofilms and nanoparticles play a disproportionately large role in controlling biogeochemical processes (Figure 9). The complex interactions among physical, chemical and biological processes result in a life-sustaining capacity for cleansing water and soil. Investigations of such processes have shown that the whole system may deviate significantly from predictions based upon the sum of the parts, where each interface is studied in isolation or *ex situ*. Furthermore, non-linear behavior derives from the fact that Critical Zone biogeochemistry is subjected to biotic-abiotic feedbacks that are not predictable from disciplinary perspectives.

The societal need to sustain water and soil resources gives rise to fundamental and applied questions that drive future research in Critical Zone biogeochemistry, as described on the next pages.

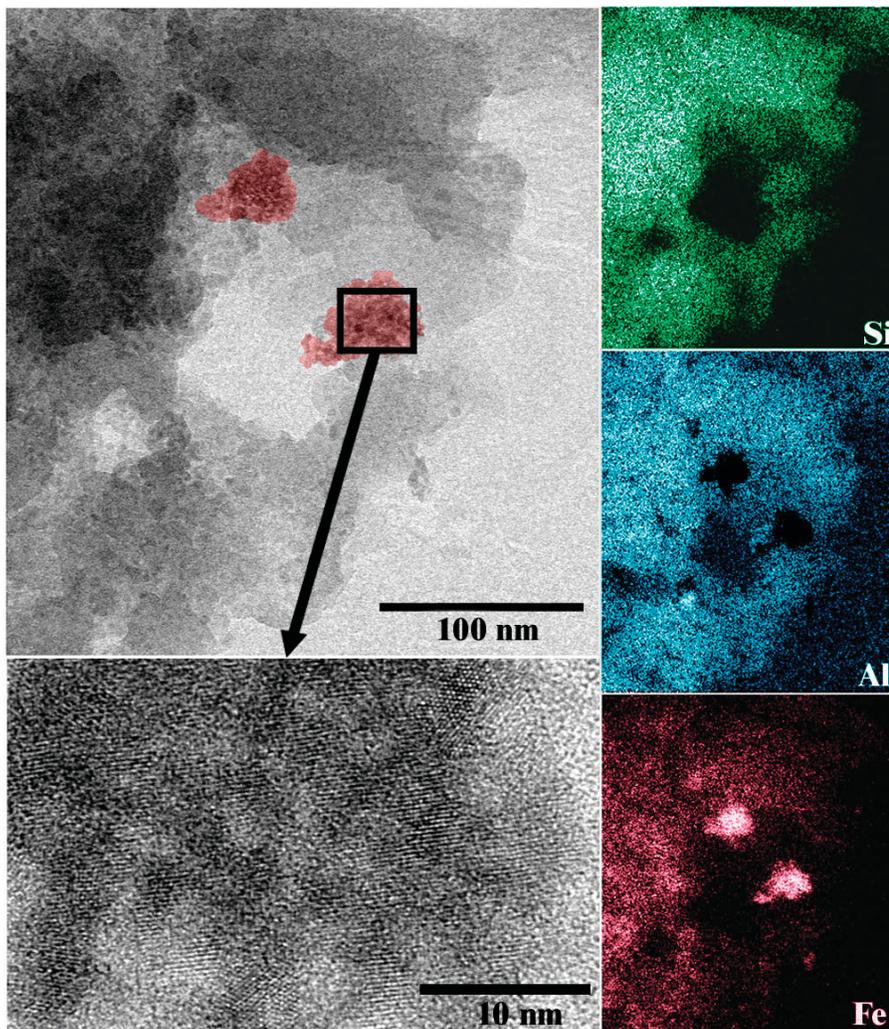


Figure 9. Compilation of transmission electron microscopy (TEM) images from iron oxide-coated sands, Oyster Bay, VA (PENN ET AL., 2001). Iron oxide-coated sands are commonly assumed to consist primarily of iron oxides and oxyhydroxides; however, here these nanophase materials are predominantly Si- and Al-rich materials of variable crystallinity with interspersed smectite and agglomerates of goethite nanoparticles. The upper left-hand image shows a zero-loss TEM image of typical coating material, with Fe "hot-spots" in red. At right, brighter areas correspond to areas containing higher levels of the specified element. The lower left image is a high-resolution image of one of the two iron "hot spots," and lattice fringes demonstrate that this object is an agglomerate of 3-5 nm goethite nanoparticles that exhibit substantial preferred orientation. Although the iron oxide agglomerates constitute a small mass fraction (~0.1 wt %) of the sediment, they dominate reactive surface area and control chemical reactivity.

- *How do we characterize the spatial and temporal heterogeneity of the Critical Zone, and how does heterogeneity impact Critical Zone function?* Especially in comparison to the atmosphere and oceans, the Critical Zone is extremely heterogeneous in space and time. For example, over small distances, the concentration of oxygen can vary over orders of magnitude in a soil and can vary with time due to climatic and biotic -- including anthropogenic-- forcings. Such variations result in changing micro-scale niches for microorganisms and chemical reactions. How do these biogeochemical niches and their associated gradients interact in space and time to affect water and soil quality?
  - *What is the nature of biotic-abiotic feedbacks in biogeochemical reactions subjected to open system fluid flow?* Recent studies highlight the role of organisms in affecting mineral formation and dissolution. Conversely, the availability of mineral and dissolved substrate can control microbial activity. However, much of our mechanistic understanding of these processes derives from highly simplified chemostat systems. How can we deduce biotic-abiotic interactions in heterogeneous natural systems where the molecules, microbes and minerals of interest may be present at trace levels, and where the physical fluid transport properties of the medium are extremely complex?
    - *What are the essential components of a predictive model of the Critical Zone?* We know little about how the Critical Zone recovers from human-induced physical erosion (e.g., topsoil loss) or chemical contamination (e.g., mining activity or solvent release). To move forward on this difficult task requires the establishment of an interdisciplinary dialogue regarding the essential components needed for such a model. How can we integrate these components to predict (i) response to perturbation, (ii) recovery from degradation, and (iii) resiliency?
      - *How can we quantify the “ecosystem services” of the Critical Zone to educate policy-makers?* Disturbance of riparian zones, wetlands, and other essential ecosystems diminishes the capability for natural water purification. How can we quantify such ecosystem services that sustain water quality? Given the pre-eminence of economic drivers in land use decision-making, how can we educate scientists and economists to enable effective decision-making and policy?
        - *What fundamental knowledge can facilitate the engineering of the Critical Zone so that essential Critical Zone resources are preserved on a sustainable basis?* As natural systems are transformed through land use change, engineered systems including constructed wetlands and restored ecosystems will be increasingly needed to serve a growing population. Given the rapid pace of environmental change, how can Critical Zone engineering be integrated with fundamental science so that advances in understanding can be translated directly into engineered solutions? For example, what processes lead to salinization and desertification of soils and how extensive is this problem globally?

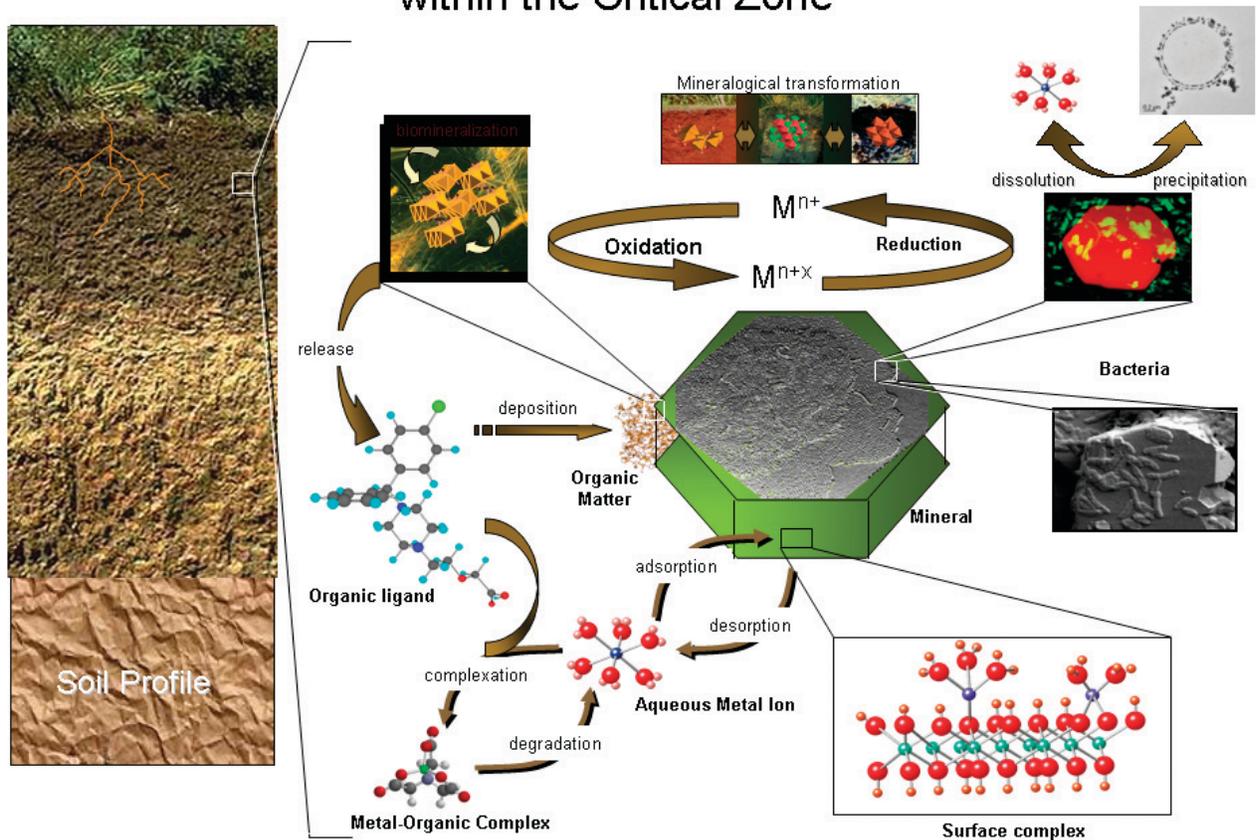
*Research agenda.* The principal obstacle to progress on these questions is the notable absence of established and well equipped interdisciplinary research programs. The requisite interdisciplinary approach includes the need to not only interface surface chemistry with

microbiology at the molecular to particle scale, but also to develop a conceptual framework for describing material mixing and transport in porous media from the scale of molecules and microbes to hillslopes and catchments and entire regions. The Critical Zone Exploration Network provides a well-constrained context for extracting mechanistic controls on the behavior of biogeochemical systems. A major challenge for instrumentation of the Critical Zone is well within our reach: sensors and probes must be developed and deployed to report on biogeochemical reaction paths in complex field situations.

**Question 3: How do processes in the Critical Zone nourish ecosystems and how do they respond to changes in external forcing?** The Critical Zone hosts oxidation–reduction reactions and acid–base reactions that are tightly linked and that drive chemical transfers among biological and geological components (Figure 10). Atmospherically-derived C and N are reduced by biological processes and synthesized into biomass. In turn, organic decomposition oxidizes plant and animal material releasing N and other nutrients, organic acids, and CO<sub>2</sub> that dissolves to produce carbonic acid. Respiration produces excess acidity that is neutralized by reacting with aluminosilicate minerals. Mineral decomposition in the face of acid attack releases Ca, K, P and trace elements that are required for plant and microbial growth. Weathering also produces clays with imperfectly neutralized crystal structures leading to charged surfaces that can retain nutrients. Water mediates these chemical reactions directly, but also acts as a transport agent moving soluble elements

Figure 10. Sustaining water resources requires sustaining soils as living filters. The biogeochemical processes that control the long-term sustainability of soil and water resources operate at molecular to nano-scales and exhibit increasing complexity at larger spatial scales because of environmental heterogeneity. New theoretical and spectroscopic techniques are expanding our ability to predict chemical reactions across scales. (Figure courtesy of Scott Fendorf, Stanford Univ.).

### Intergraded Processes Controlling Elemental Cycling within the Critical Zone



down a natural chromatographic column (Figure 11). Changes in hydrologic leaching, driven by climate, vegetation, and permeability; modify the rate of nutrient availability and create significant feedbacks among the biogeochemical reactions within the Critical Zone, (Figure 12). A number of specific questions relating to nutrient availability in the Critical Zone need to be addressed within Question 3:

- *How will the Critical Zone respond to climate change?* Critical Zone changes driven by climate include changes in temperature, rainfall and altered plant productivity under enhanced atmospheric CO<sub>2</sub> levels. In particular, how will water availability and plant production affect carbon input to and storage within the CZ (Figure 13)? How will weathering fluxes of nutrient elements, microbial release of organically bound nutrients, and storage and cycling of bioactive elements be affected by climate change? What microbiota live in the Critical Zone and how will this be affected by climate change?

- *How is human modification of landscapes influencing mineral aerosol generation and the cycling of bioactive elements?* The Critical Zone is an open chemical system that responds to nutrient inputs from external sources and in turn can become impoverished through losses. What are the present balances among internal release and external inputs of nutrients from mineral and marine aerosol sources? How do existing ecosystems respond to changes in these input balances? What are the global variations in these responses given varying mineralogy and bulk chemistry within the CZ? How do changes in overland water flow affect the balances between physical erosion and chemical weathering, and impact ecosystem productivity and nutrient biocycling?

- *How do Critical Zone processes respond to changes in the composition of the plant and soil biotic communities?* Biogeochemical cycling within the Critical Zone is strongly impacted by rapid invasions of new species as well as slower ecosystem responses to global change. With climate change, vegetation will respond to and affect water availability. How will ecosystem changes, driven by climate change, feed back on nutrient availability? How will direct and severe human intervention through land cover change affect that balance within biogeochemical cycles?

- *Is it more likely that Critical Zone processes approach and exceed thresholds in response to acute extreme events or in response to slow chronic changes in forcing functions?* Chemical reactions governing nutrient availability can be subject to gradual change or dramatic thresholds in response to forcing functions. What are the internal CZ properties that buffer response to forcing functions and what causes these buffers to shift at threshold points? How does the CZ respond to rapid changes in forcing functions such as extreme rainfall events that lead to far greater than usual hydrologic leaching?

*Research agenda.* Research to solve these questions needs to include the following: 1) selection of a series of model landscapes to isolate the variables under consideration, 2) budgeting of water and nutrient fluxes in long-term soil experiments and whole catchments, 3) use of chemical and isotopic tracers to differentiate between lithogenic and

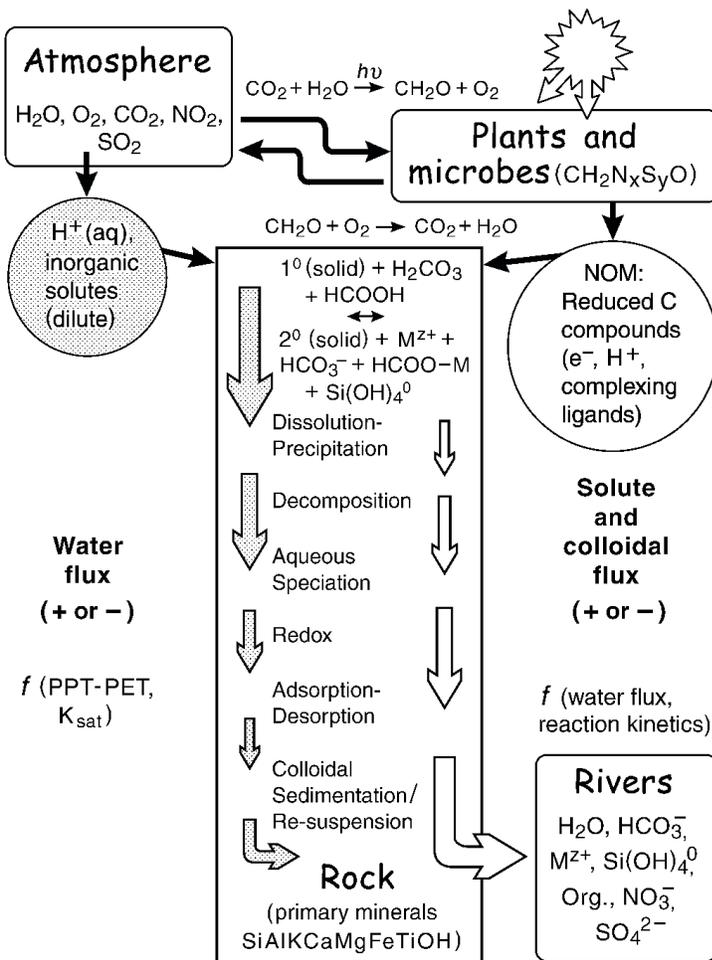


Figure 11. The Critical Zone is characterized by active mixing of living and dead organic matter, water, gas and rock. Energy is provided by photosynthesis and gravity (mediated by water). Water facilitates chemical reactions and transports reactants and products through the Critical Zone. Mineral weathering acts as a sink for atmospherically and biospherically derived acids; the reaction products either accumulate within the Critical Zone as secondary precipitates, are utilized by biota, or are leached in aquatic systems. Reduced carbon compounds also complex, reduce, and leach otherwise sparingly mobile cations. Chemical reaction rates are controlled both by the intensity of extrinsic climatic factors and by intrinsic thermodynamic and kinetic properties that are themselves being continually modified. (After CHADWICK AND CHOROVER, 2001). Reproduced with permission from Elsevier.

biogenic sources and nutrient sources and sinks, and 4) use of explicit scaling models that link soil-scale and watershed-scale processes and allow reasonable prediction of regional-scale impacts associated with exceeding thresholds and/or human disturbance. One successful approach is to substitute space for time to analyze change in a series of soils and watersheds that are embedded in landscapes of different ages. Such a series of sites would allow input/output and tracer studies to be conducted on CZ systems with very different balances between weathering and atmospheric contribution of nutrients. Chemical and isotopic tracers will be used to document storage, evolution and loss of mineral and organic compounds as well as the fate of dissolved ions. For example, the use of  $^{13}\text{C}$  and  $^{14}\text{C}$  (for analyses of the sources and fates of carbon), the use of  $^{137}\text{Cs}$ ,  $^{210}\text{Pb}$ , and  $^{10}\text{Be}$  (for quantifying erosion and soil production over short to long time scales), the use of  $^{87}\text{Sr}/^{86}\text{Sr}$ ,  $^{44}\text{Ca}/^{40}\text{Ca}$ ,  $\text{Sr}/\text{Ca}$ ,  $^{15}\text{N}$ , and rare earth elements (for identifying nutrient sources and fates), and the use of  $^{18}\text{O}$ ,  $^{30}\text{Si}/^{28}\text{Si}$ , and  $\text{Ge}/\text{Si}$  (for identification of mineral weathering and plant cycling sources of nutrients in stream water) can elucidate a wide range of ecosystem-relevant Critical Zone processes. Interpolation statistics and numerical and simulation modeling will provide appropriate synthesis and scaling tools.

**Question 4: What processes in the Critical Zone control biosphere-atmosphere exchanges of atmospherically important gases and particulates?** Plants are the transducers that provide the energy for microbial metabolism through root exudation, cell sloughing, and root

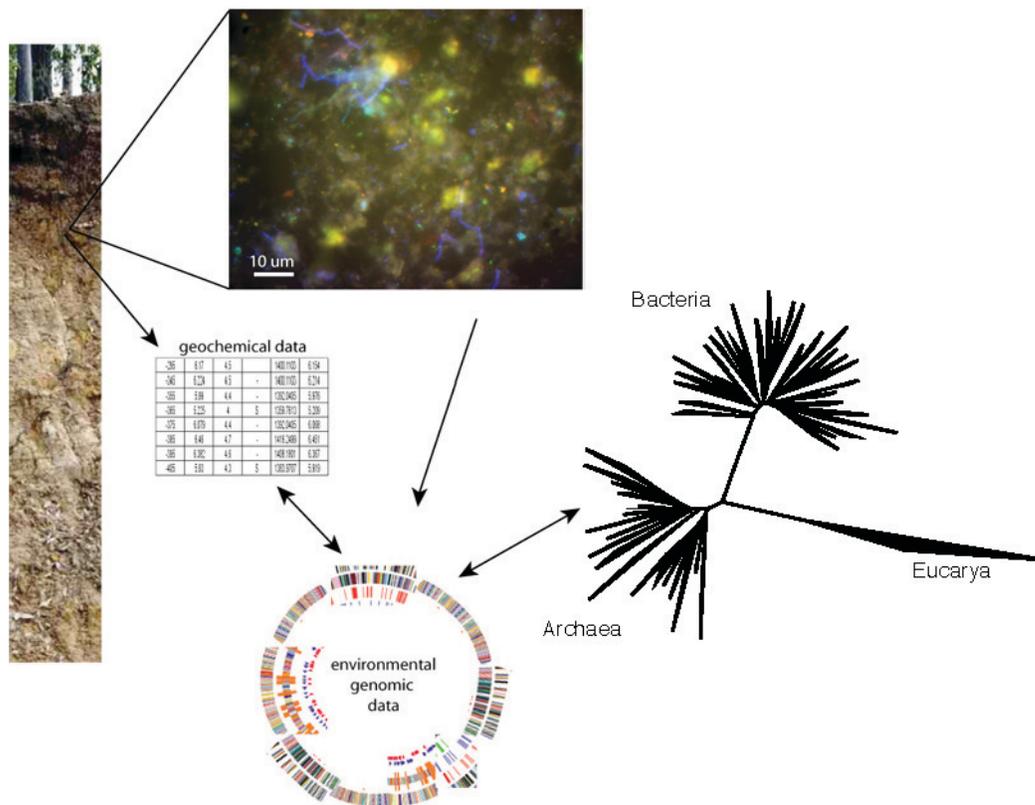
and mycorrhizal turnover. Changes in Earth's atmosphere, such as increasing atmospheric CO<sub>2</sub> and N deposition, modify plant net primary productivity and plant C allocation directly. This in turn, initiates a series of biochemical changes in dead leaves and fine roots, a response which moves through the rhizosphere to structure soil food webs and control rates of nutrient cycling. In addition, all of these biological processes interact with solid earth materials in the Critical Zone to mediate atmospheric changes in trace gases over longer time periods. Fine root physiology, tissue biochemistry, and fine root growth and mortality play pivotal functions controlling the flux of C back to the atmosphere over short timescales. Understanding how plant processes, microbial dynamics, and water and solid reservoirs in the Critical Zone respond to changes in Earth's atmosphere is important to the understanding of feedbacks and the prediction of atmospheric chemistry over short and long time periods.

- *How is root respiration controlled by whole-plant carbon allocation?* The efflux of CO<sub>2</sub> from the Critical Zone to the atmosphere is one of the largest fluxes of C in most terrestrial ecosystems. Often, plant root respiration is the dominant component of total soil respiration: because changes in Earth's atmosphere directly alter plant physiology, it is important to improve our understanding of how plant processes control the concentration and flux of CO<sub>2</sub> in the Critical Zone.

- *How can we improve our understanding of rates of fine root turnover and soil respiration?* Fine root turnover, the flux of carbon and nutrients from plants into soil per unit area per unit time, is a major component of terrestrial ecosystem carbon and nutrient cycling. Fine root production has been estimated to account for up to 33% of global annual net primary productivity. How can we measure the pool of carbon and nutrients in fine roots, and quantify the rate of turnover in this reservoir? How can we measure and predict rates of soil respiration?

- *How is plant respiration related to microbial respiration in the Critical Zone over space and time?* On various times steps ranging from minutes to 1000's of years, plants ultimately provide the substrate for the majority of microbial respiration in terrestrial environments. However, we lack the ability to partition the components of soil CO<sub>2</sub> efflux into its plant and microbial components, and we need a better understanding of the mechanisms that control plant and microbial respiration so that we can predict and model how ecosystems will respond to climate change. Can we establish the link between the biochemistry of plant litter inputs to soil and the metabolic response of soil organisms? Can we develop a mechanistic understanding of the controls on C transformation in the soil and the flux of C back to the atmosphere?

- *How do we model element cycling in mycorrhizae?* It is widely recognized that mycorrhizae are a significant component of the biogeochemical cycles that control mineral weathering and nutrient availability in the Critical Zone. How can we account for the importance of mycorrhizae in mass balance estimates of biogeochemical cycles? How can we accurately and consistently predict the role mycorrhizae play in controlling C transformations, soil CO<sub>2</sub> efflux back to the atmosphere, and mineral weathering rates?



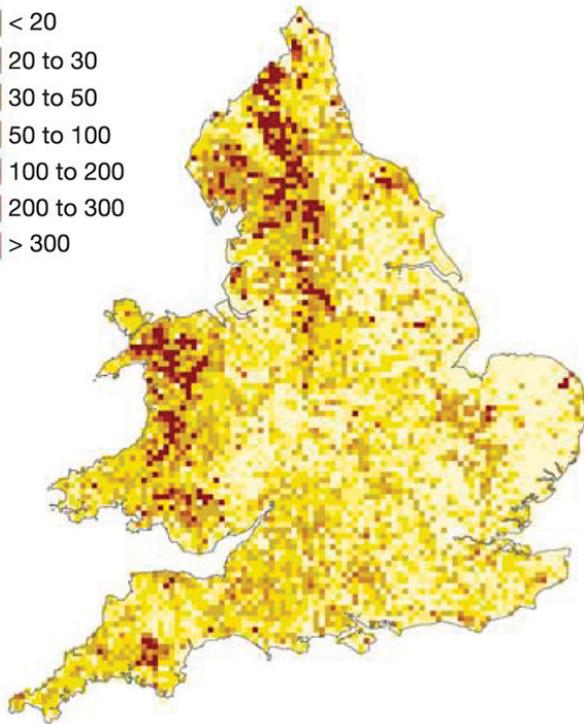
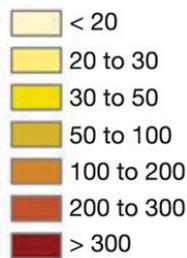
- *How do changes in the atmosphere cascade through plants and microorganisms to control soil carbon storage and mineral weathering rates over short and long timescales?* Recent studies have demonstrated that changes in the concentration of CO<sub>2</sub> and O<sub>3</sub> in the atmosphere can directly alter C storage in soil (Figures 13, 14). However, our understanding of how changes in plant physiology and productivity cascade into the Critical Zone to alter C transformations and mineral weathering is notably deficient. Because plants respond directly to changes in resource availability, strong linkages must exist between plant productivity and carbon cycling in the Critical Zone. These linkages need to be carefully studied because the soil is such a large and potentially labile pool of global carbon. How will the pool of soil organic carbon be affected by climate change (Figure 15)? How will climate change affect carbon drawdown from the atmosphere due to mineral weathering?

- *How do variable chemical and physical properties manifested in the diversity of microbial habitats at all scales impact fluxes of gases and particulates between the Critical Zone and the atmosphere?* Physical and chemical properties of soils and ecosystems vary over a variety of scales from nanometers to kilometers. This physicochemical variability is manifested in variability of habitats for micro- and macrofauna. How can we characterize and interpret the physicochemical and biological variability at all scales in the Critical Zone to predict how the Zone controls atmospheric properties (Figure 12)?

- *How do inputs of dust (mineral aerosols) to the Critical Zone impact important soil properties and function and how do changes in the Critical Zone impact the flux and chemistry of*

Figure 12. Soil microbiota mediate transformations of organic and inorganic molecules that drive pollutant degradation, weathering reactions, soil-atmosphere gas exchange, nutrient availability, and other important services provided by the Critical Zone. New, cost-efficient DNA sequencing technologies make it possible to retrieve environmental genomic data that directly reflect the relative abundances of functional and taxonomic marker genes in microbial communities. Genetic data can then be compared with geochemical data to reveal the microbial underpinnings of Critical Zone processes across targeted spatial and temporal gradients. (Figure courtesy of Jenn Macalady, Penn State).

**a** Original  $C_{org}$  ( $g\ kg^{-1}$ )



**b** Rate of change ( $g\ kg^{-1}\ yr^{-1}$ )

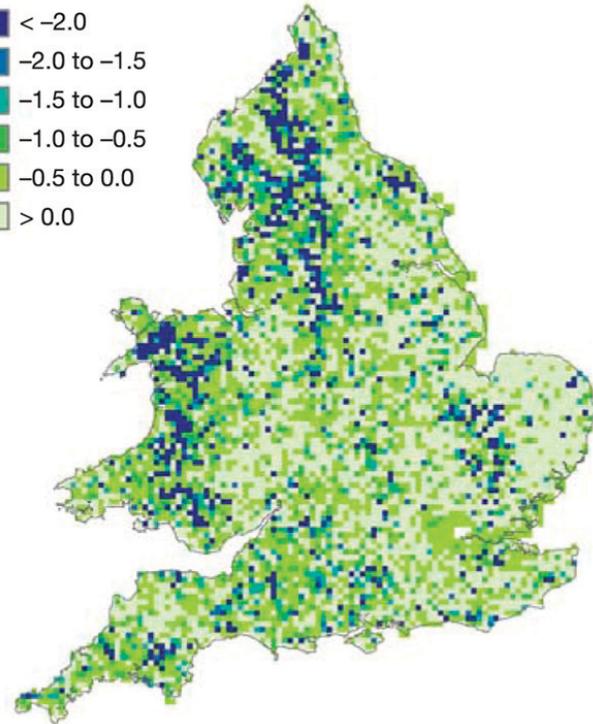
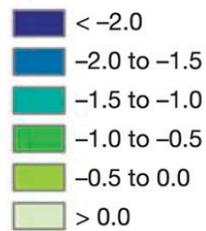


Figure 13. Changes in soil organic carbon as measured in soil surveys in England and Wales from 1978-2003. a) Carbon contents measured in original sampling in 1978. b) Rates of change of soil organic carbon as calculated from successive samplings. Where sites were not resampled, soil organic carbon was calculated from a model equation. Changes in soil organic carbon were negative in all but 8% of the sites. Such repeated measurements of soil change are critical for understanding how humanity is transforming the Critical Zone. Figure from BELLAMY ET AL. (2005). Reproduced with permission from Nature.

dust particulates to the atmosphere? Older landscapes can still support vegetation despite significant nutrient losses through weathering over time. In many cases, inputs from dust may provide a significant flux of nutrients. How much dust is input to soils? How can we model such inputs to predict nutrient fluxes? What chemical, physical, and biological processes control dust output from soil?

- How do human-induced perturbations impact atmospheric fluxes from the Critical Zone? What is the carrying capacity of the Critical Zone and how can this zone be maintained as a sustainable resource? How is human health affected by the physicochemical and biological properties of the Critical Zone? How will climate change impact vegetation, dust availability, and trace gas emissions from soils globally?

*Research Agenda.* The questions represented in Question 4 must be answered with real-time measurements that allow the identification of mechanisms that control biosphere-atmosphere exchanges of atmospherically important gases and particulates. Significant effort will be needed to understand and delineate the spatial heterogeneity of microbial, chemical, physical, and geological variables. To move forward in terms of regional and global understanding, we need conceptual and numerical models that allow scaling from short times and small scales up to geological and global scales. New technologies will be necessary to measure chemical, physical, and biological change at the microscale within the Critical Zone. Finally, new tools for cyber-collaboration and sharing of research databases among multiple disciplines will be necessary so that cross-discipline collaborations can proceed.

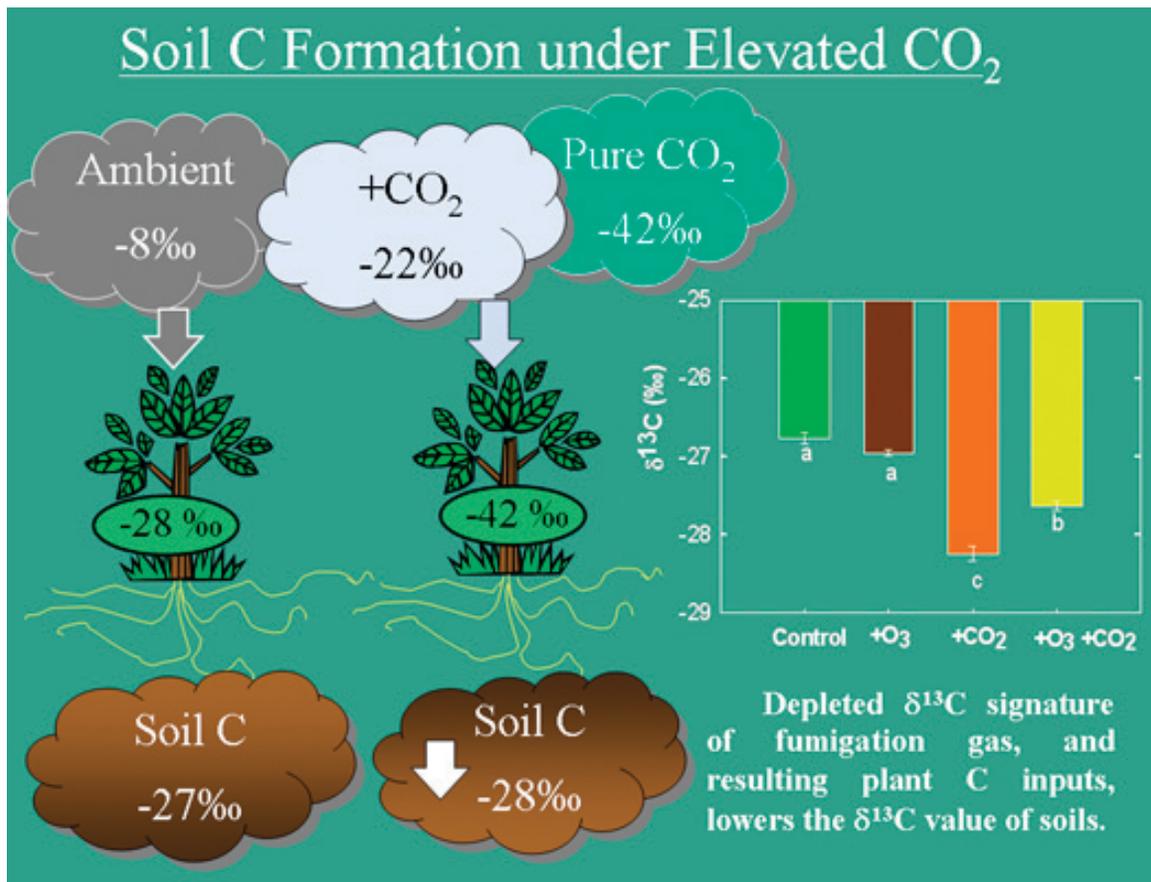


Figure 14. Manipulation experiments allow analysis of biogeochemical response to change in environmental variables. The <sup>13</sup>C signature of CO<sub>2</sub>, plant biomass, and soil organic matter in the Aspen Free-Air Carbon Dioxide Enrichment (FACE) experiment in Rhinelander, Wisconsin (USA) is documented here. Two of the experimental treatments, elevated atmospheric CO<sub>2</sub> and the interaction treatment (elevated CO<sub>2</sub> + O<sub>3</sub>), are fumigated with highly depleted <sup>13</sup>CO<sub>2</sub> (-42‰). In these two treatments, it is possible to partition soil organic matter into a pool of C that existed before the experiment began (“old C”) and a pool of “new C”, fixed by photosynthesis since the initiation of the experiment. Notice that after 5 years of exposure, soil organic matter in the elevated CO<sub>2</sub> treatment contains more new C than soil organic matter in the interaction treatment. The dynamics of organic matter in the Critical Zone is tightly coupled with the activity of plants that root in the zone (adapted from LOYA ET AL., 2003).

The research agenda to address these questions should include: (1) a new generation of studies using <sup>13</sup>C and <sup>14</sup>C to understand the fundamental linkages between plant physiology and Critical Zone processes; (2) development of a new generation of sensors and approaches to better measure Critical Zone processes; (3) design of experiments to understand how changes in Earth’s atmosphere provide feedback to control mineral weathering; and (4) a new generation of intensive methods comparison studies to understand the most productive ways to study processes in the Critical Zone.

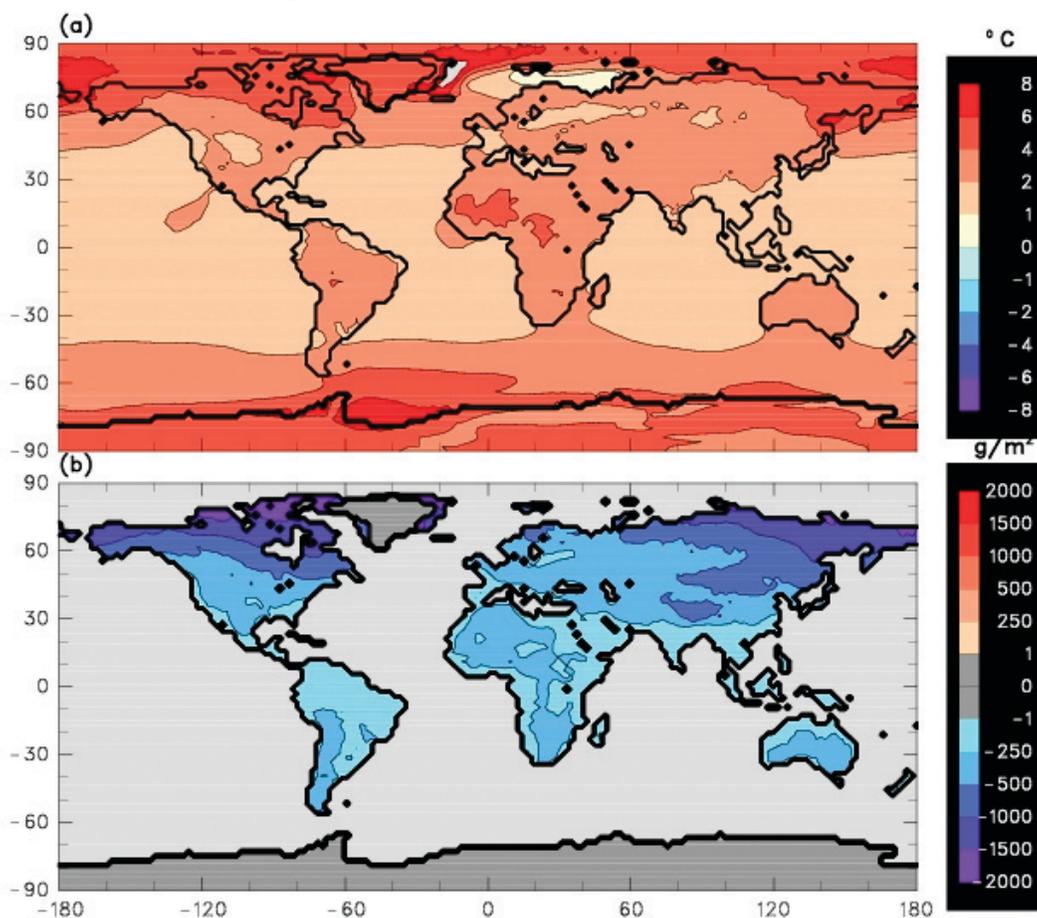
## CZEN: The Research Strategy

Figure 15. Global Climate Model (GCM)-based estimates of changes in soil organic carbon content as a function of greenhouse gas-induced global warming. Upper panel displays the modeled change in surface temperatures as determined using GENESIS version 2 GCM simulations, determined by subtracting modern temperatures from the results of a present-day  $\text{CO}_2$  simulation. Lower panel shows corresponding change in soil organic carbon (SOC,  $\text{g}/\text{m}^2$ ), using parameterization in Schimel et al.(1994) based on the Century model averaged over many cases. Averaged over land, SOC losses from warming could account for an appreciable increase in atmospheric  $\text{CO}_2$  content. At present, we lack models to predict changes in soil parameters such as soil organic carbon with confidence. (Modeling and figure courtesy of Dave Pollard, Penn State).

Research that characterizes the Critical Zone and its response to climatic, tectonic, and anthropogenic forcing (Figure 1) is now conducted by a diverse group of disciplinary scientists including geochemists, geomorphologists, hydrologists, microbiologists, soil scientists, and ecologists. Development of a concerted programmatic initiative of linked research and educational activities, the Critical Zone Exploration Network, will promote a systems framework to deconvolute these complex interactions. CZEN will thus be a network of sites, people, ideas, data, and tools, all aimed to use the environmental gradients on Earth as natural experiments (Figure 16). The CZEN network will facilitate investigation of biological, physical, and chemical coupling by deliberate integration of new tools in the physical, chemical and biological sciences. The network will be dedicated to predicting how the Critical Zone will change due to long and short timescale perturbations of the Earth.

*CZEN: A network of sites.* We propose to construct a network of field-based research sites where the critical factors are both isolated and then integrated within a multi-dimensional matrix (climate, time, biota, topography, parent material, disturbance, etc.). A key feature of this network is that it is a deployable network of short-duration studies at carefully chosen sites.

The sites will be chosen by peer review from new or previously investigated sites based upon their ability to advance and integrate an-



swers to the driving questions (Figure 6, Table 2). We envision each site will be supported for ~ 5 year increments, and the possibility of renewal will be assessed against the value of new sites. Sites at the interstices or nodes of the network will be targeted for longer term funding schemes. Such longer term sites will be instrumented more intensively, will employ hierarchically nested approaches, and will involve large diverse communities of students and scientists. All sites will become foci for multi-disciplinary teams of researchers.

What is different about this deployment from the current approach of studying the Critical Zone? Two factors are paramount. First, network sites will be chosen by peer review, but with the entire network of sites in mind and the overarching driving questions articulated. Thus, research will be targeted and systematic. Second, to secure CZEN funding, investigators will agree to share their data within an agreed upon timeframe and will promote site access to all researchers. Thus, the research community that benefits from these sites will be diverse and multi-disciplinary.

A demonstration phase of CZEN construction began with a critical review of 23 sites presented at the University of Delaware, October 24-26, 2005 (see Table 3). The review led to a ranking of the proposed sites, from which 8 were selected for seed funding as demonstration sites. These seed sites will be early examples of how CZEN will evolve; no commitment has been made to the longevity of CZEN's support for these individual sites.

*CZEN: A network of tools.* Each CZEN site will be characterized using a suite of instrumentation to enable systematic analyses (Table 4). The most heavily instrumented sites located at interstices or nodes of the CZEN legs (e.g., green sites on Figure 16) will contain hierarchically nested instrumentation. The range of investigation will extend from the atmosphere through the vegetative cover, soil, and into the deep regolith. The program will utilize existing sites, instrumentation, and data resources developed by NSF and other scientific programs if doing so will meet CZEN criteria.

Less-instrumented sites designed for shorter duration studies (blue sites on Figure 16) will complement the heavily instrumented sites. The blue sites will target specific questions such as the impact of exposure age on nutrient cycling, or the role of rainfall seasonality on clay formation and hence the electrochemical properties of the Critical Zone. At all sites, a standard set of physical, chemical and biological parameters over a range of depths will be measured. By standardizing data and sample collection for these sites, CZEN will promote inter-comparison of Critical Zone processes across a variety of lithologies, ecosystems, climate zones, and landscape positions.

CZEN will provide support for field tools, equipment and other project components that might be unavailable through individual efforts. Equipment will be generally recycled from project to project and new

techniques will be promoted. It will be an innovation platform where the participants can agree on tool needs and collectively design prototypes. CZEN will facilitate contracting with local providers for services that require large equipment or may fund such instrumentation for all.

Site-specific scientific questions will drive the development of new tools in Critical Zone science. For example, cosmogenic isotopes allow dating of exposure surfaces, new molecular biological techniques allow the investigation of geobiological phenomena, new nanoscale

Table 2. Attributes to be Considered in Site Selection for CZEN

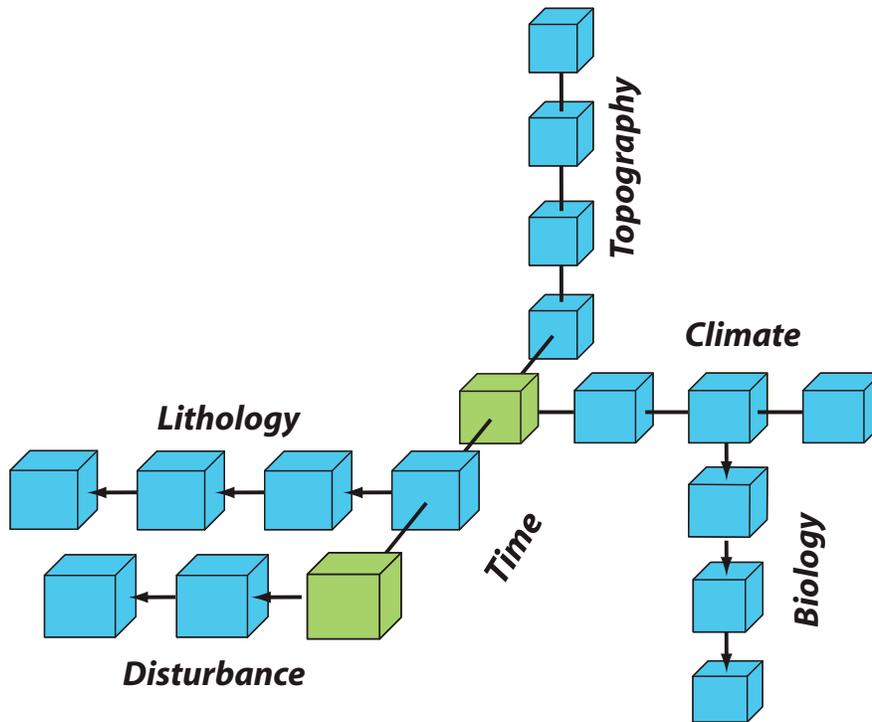
Parent lithology	Chemical, mineralogical, and physical properties
Topography	Slope, aspect, uplift and erosion rates
Climate	Temperature, precipitation, seasonality
Hydrology	Drainage characteristics, saturated versus unsaturated
Biota	Abundance, diversity, and distribution of biota
Time	Exposure age, rock age, time evolution
Logistical considerations	Ease of accessibility, availability of prior data
Quality of site	Pristine or disturbed characteristics, suitability for upscaling, suitability for lab-scale modeling/experimentation
Isolation of variables	Site allows observational testing of one isolated variable
Outreach potential	Opportunities to encourage education

spectroscopies allow investigation of the chemistry of mineral-soil-water-biota interfaces, new hybrid mass spectrometry systems allow investigation of metal-ligand complexes, and the fractionation of isotopes and other tracers can document biological cycling, age of grain formation, and rates of dissolution near equilibrium. Furthermore, geomorphological models have advanced to the point that new ideas concerning weathering can be tested. Similarly, reactive transport codes are now available to allow investigation of multicomponent multiphase systems. A key feature of CZEN is the promotion of these techniques for a diverse cadre of researchers for use across all the environmental gradients. *It is envisioned that CZEN funding will provide salary for instrumentation or analytical specialists who will disseminate the utilization of important techniques.*

*CZEN: A network of data and samples.* Data and samples from these sites will be incorporated into a CZEN database and will be made available to any CZEN scientist after an agreed-upon embargo period. *At present, no such agreed upon embargo period is employed within Critical Zone science and the establishment of such an agreement is a key feature of CZEN.*

To enable inter-comparison of Critical Zone data as it emerges, CZEN will provide coordinated cyberinfrastructure for scientific networking, data management infrastructure, and sample storage systems. Data and samples will be accessible to all scientists, allowing new and emerging methodologies to be tested on well-characterized samples as projects unfold.

# Critical Zone Exploration Network



The organizing principles of a CZEN data and sample archive will be based on uniform accessibility to CZEN scientists, accountability, continuity, reliability, timeliness, and standard formats. A database manager will develop archive formats and data submission protocols, and will maintain the distributed database and the physical facility for sample archiving.

Cyberinfrastructure will provide high-performance computing and data storage capabilities to allow such computationally intensive activities as genomic analysis, theoretical chemical modelling, and reactive transport modelling.

*CZEN: A network of people and ideas.* The inherent multi-disciplinarity of Critical Zone science demands scientists working together across disciplines. This integration of scientists can happen if CZEN promotes such efforts through a variety of community-building approaches. Therefore, key features of CZEN will be the organization of a network of universities guided by a Steering Committee to promote CZEN and the establishment of a synthesis center to facilitate this network of universities and the network of sites. CZEN meetings or workshops will promote advances and will introduce models to interpret Critical Zone systems. Such workshops will promote the active integration of field and laboratory efforts as well as cross-site comparisons.

Another key feature of the CZEN idea is that outreach and education efforts will be integral to the formative stages. Faculty members from predominantly undergraduate institutions and minority-serving colleges and universities, and K-12 teachers will be

Figure 16. The Critical Zone Exploration Network will consist of a network of Critical Zone observatories that span environmental variables including (but not limited to) those shown here. Sites will be instrumented for investigation of important properties in the Critical Zone. Some sites (e.g. those shown here in green) will be instrumented more intensively and maintained for longer time periods. Others will be investigated for shorter durations (sites in blue). The key to forward progress with respect to understanding the Critical Zone is the study of observations that can test the effects of important variables across environmental gradients. Of particular importance is the collection and analysis of both genomic and geochemical data for interpretation of how biology varies across environmental gradients.

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Table 3. Proposed CZEN sites

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Shale Hills, PA  
Panola Mountain, GA  
Rio Icacos/Luquillo Mtns. Puerto Rico  
Illinois River basin, IL  
Saguaro NP, AZ  
Merced River, CA  
Bonanza Creek, AK  
Hawaii  
Harvard Forest, NH  
Conesus Lake watershed, NY  
Urban building stones, NYC  
Pine Barrens, NJ  
Bousson Forest, PA  
Coweeta Hydrology Lab, NC  
Calhoun Soil Experiment, SC  
Sand dunes, southern GA  
Northeastern AL  
Iowa  
Gunnison Gorge NCA, western CO  
Nevada test site, NV

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International Proposed Sites

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Fu Shan, Taiwan  
Bhetagad watershed, India  
Sikfokut, Hungary  
Siemianice, Poland  
Czech Republic  
Strasbourg, France  
Grenoble, France  
Svalbard, Norway  
Goteborg, Sweden  
Nottingham, England  
Basse-Terre, Guadeloupe  
Southwest Iceland

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invited to all planning conferences. CZEN will promote science literacy, access to fieldbased research coupled to experiential learning, and interdisciplinary research opportunities to as wide a range of constituencies as possible, with particular emphasis on underrepresented groups. CZEN sites will provide the opportunity for undergraduates to work side by side with graduate students and postdoctoral scientists on a fascinating array of interdisciplinary research projects.

Another key feature of CZEN will be an annual student fellowship competition to fund students to work at multiple CZEN sites or to enable laboratory investigations driven by field observations. These CZEN fellows will “cross-pollinate” sites so that techniques and models will be widely utilized, and will promote a future generation of multi-disciplinary scientists.

*Linkages to other efforts.* CZEN is a model for an observatory network driven to answer questions related to processes in the Critical Zone. These questions demand knowledge of the interface between Earth materials and the biotic world. Linkages among other observatory initiatives in the U.S. including CUAHSI (the Consortium of Universities for the Advancement of Hydrologic Sciences, Inc.), CLEANER (the Collaborative Large-scale Engineering Analysis Network for Environmental Research), LTER (Long Term Ecological Research), and NEON (National Ecological Observatory Network) are being explored.

Because of the global nature of Critical Zone science, international collaborations will be integral to addressing the four driving questions (Figure 6). Such efforts have begun: numerous international scientists have participated in Critical Zone meetings and international sites for CZEN have been proposed (see Table 3) Thus far, much of this international outreach campaign has been facilitated by logistical and partial financial support from the World Universities Network (WUN).

Table 4. Examples of Proposed Activities and Instruments for Sites in CZEN

Stream measurements	<ul style="list-style-type: none"> <li>Continuous stage recorders</li> <li>Automated water samplers</li> <li>Sediment collectors</li> <li>Satellite linkups (stream gauge + weather station)</li> </ul>
Climate/weather measurements	<ul style="list-style-type: none"> <li>Precipitation gauges</li> <li>Temperature gauges</li> <li>Humidity sensors</li> <li>Wind sensors</li> <li>Wet- and dry-fall collectors</li> <li>Radiometers</li> <li>Soil moisture detectors</li> <li>Thermistors for soil temperature</li> </ul>
Water, gas, soil measurements	<ul style="list-style-type: none"> <li>Unsaturated zone monitoring nests</li> <li>Suction water samplers</li> <li>Tensiometers</li> <li>Thermocouple psychrometers</li> <li>Time domain reflectometry</li> <li>Gas samplers and flux chambers</li> <li>Portable gas chromatographs</li> <li>Ground water monitoring wells</li> <li>Piezometers</li> <li>Recording pressure transducers</li> <li>Sampling pumps</li> <li>Drilling equipment</li> <li>Soil Sampling</li> </ul>
Biological measurements	<ul style="list-style-type: none"> <li>Electrochemical analyzers for water chemistry</li> <li>Rhizotrons, mini-rhizotrons, stereo microscopy</li> <li>Deployable units for molecular biological analysis</li> </ul>

### Conclusions

Earth's terrestrial organisms, including humans, depend on the Critical Zone for survival. The rates of change of air, water, solid Earth materials, and biota must be understood as humans drive environmental change on the planet. We have outlined the significant unanswered questions but more importantly, we have outlined a program that will provide answers related to the Critical Zone and how it will change in response to human perturbation. Overall, the CZEN research philosophy attempts to leverage multi-agency resources to solve some of the most scientifically challenging questions relevant to human society. The CZEN model has been crafted to respond to inherent multi-disciplinary scientific and educational needs required by these questions. The proposed initiative outlined here will provide initial solutions to the driving questions while educating the next generation of scientists to expand this knowledge for stewardship of our environment.

## References

- Amacher, M. (1991) Methods of obtaining and analyzing kinetic data. pp. 19-59. In D.L. Sparks and D.L. Suarez (editors) Rates of Soil Chemical Processes. Soil Science Society of America Special Publication Number 27, Soil Science Society of America, Madison, Wisconsin.
- Amundson, R., Guo, Y., and Gong, P. (2003) Soil diversity and land use in the United States. *Ecosystems*. 6:470-482. doi: 10.1007/s10021-002-0160-2.
- Anderson, S.P., Blum, J., Brantley, S.L., Chadwick, O., Chorover, J., Derry, L.A., Drever, J.I., Hering, J.G., Kirchner, J.W., Kump, L.R., Richter, D., White, A.F., (2004). Proposed initiative would study earth's weathering engine. *EOS Transactions, American Geophysical Union*, 85:28, 265-269.
- Bellamy, P.H., Loveland, P.J., Bradley, R.I., Lark, R., Murray, K., Guy, J.D. (2005) Carbon losses from all soils across England and Wales 1978-2003, *Nature*, 437 (7056):245-248.
- Chadwick, O.A., Chorover, J. (2001) The chemistry of pedogenic thresholds, *Geoderma*, 100 (3-4):321-353.
- Crutzen, P.J. (2002) Geology of mankind, *Nature*, 415:23.
- Foley, J.A., DeFries, R., Asner, G.P., Barford, C., Bonan, G. (2005) Global consequences of land use, *Science* 309:570-574.
- Hochella M.F., Jr. (2002) There's plenty of room at the bottom: Nanoscience in geochemistry, *Geochimica et Cosmochimica Acta*, 66:735-743
- Hooke, R. L. (2000) On the history of humans as geomorphic agents, *Geology*, 28 (9): 843-846.
- Kolpin, D., et al. (2002) Pharmaceuticals, hormones, and other organic wastewater contaminants in streams 1999-2000: A national reconnaissance, *Environ. Sci. Technol.* 36:1202-1211.
- Loya, W.M., Pregitzer, K.S., Karberg, N.J., King, J.S., Giardina, C.P., (2003) Reduction of soil carbon formation by tropospheric ozone under increased carbon dioxide levels, *Nature*, 425 :705-707.
- National Research Council Committee on Basic Research Opportunities in the Earth Sciences, (2001) Basic Research Opportunities in the Earth Sciences, Washington, DC: National Academies Press.
- Pimentel, D., Harvey, C., Resosudarmo, K., Sinclair, K., Kurz, D., McNair, M., Crist, S., Shpritz, L., Fitton, L., Saffouri, R., Blair, R. (1995) Environmental and economic costs of soil erosion and conservation benefits, *Science*, 267:1117-1123.
- Pimentel, D., Skidmore, E.L. (2004) Rates of soil erosion--Discussion, *Science* 286:1477.
- Ramankutty, N., Foley, J.A. Olejniczak, N.J. (2002) People on the land: Changes in global population and croplands during the 20th century, *Ambio*, 31:251-257.
- Raymond, P., and Cole, J. (2003) Increase in the export of alkalinity from North America's largest river, *Science*, 301:88-90.
- Renewable Natural Resources Foundation (2006) Environmental impacts of emerging contaminants, *Renewable Resources Journal*, 24 (1):1-36.
- Sanchez, P., and Swaminathan, M. (2005) Cutting world hunger in half, *Science*, 307: 357-359.
- Schimel, D.S., Braswell, B.H., Holland, E.A., McKeown, R., Ojima, D.S., Painter, T.H., Parton, W.J., and Townsend, A.R. (1994) Climatic, edaphic, and biotic controls over storage and turnover of carbon in soils. *Global Biogeochem. Cycles*, 8:279-293.
- Smith, D., Goldhaber, M., Rentz, A., Garrett, R., and Salina, J. (2005) Continental-scale Pilot Studies for Soil Geochemical Survey of North America, USGS factsheet, 4 p.
- Stocking, M. (2003) Tropical soils and food security: The next 50 years, *Science*, 302: 1356-1359.
- U.S.D.A., (1988) The second RCA appraisal: Soil, water, and related resources on nonfederal land in the United States: Analysis of conditions and trends, USDA Soil Conservation Service, Washington D.C., 54 pp.
- Vitousek, P. M., Mooney H. A., Lubchenco J., and Melillo J. M., (1997) Human domination of Earth's ecosystems, *Science*, 277:494-499.
- Vitousek, P.M., Aber, J.D., Horwath, R.W., Likens, G.E., Matson, P.A., Schindler, D.W., Schlesinger, W.H., Tilman, D.G. (1997) Human alteration of the global nitrogen cycle: sources and consequences, *Ecological Applications*, 7(3):737-750.
- Wilkinson, B., (2005) Humans as geologic agents: A deep-time perspective, *Geology*, 33 (3):161-164.

**INVITED SPEAKERS for NSF Sponsored Workshop  
“Frontiers in Exploration of the Critical Zone”  
University of Delaware – Newark, Delaware, October 24-26, 2005**

Bill Dietrich, UC Berkeley	Jennifer Harden, USGS
David Furbish, Vanderbilt Univ.	Claudia Mora, Univ. of Tennessee
Tim Drever, Univ. of Wyoming	Ron Amundson, UC Berkeley
Mike Hochella, VA Tech	Joel Blum, Univ. of Michigan
Michelle Walvoord, USGS	Scot Martin, Harvard
Scott Fendorf, Stanford	Eric Davidson, Woods Hole
Allan Stone, Johns Hopkins	Kurt Pregitzer, Michigan Technological University
George Luther III, University of Delaware	Martin Schoonen, Stony Brook University

**Participants of the NSF Workshop**

Bruce Allison	David Furbish	Jennifer McIntosh	Brian Stewart
Ron Amundson	Ferran Garcia-Pichel	David McNear	Alan Stone
Suzanne Anderson	Karl Glasener	Frits Meijboom	Dan Strawn
Scott Andres	Marty Goldhaber	Doug Miller	David Sylvia
Richard April	Art Goldstein	Joel Moore	M. Ali Tabatabai
John Baham	Richard Grauch	Claudia Mora	Ryan Tappero
Steve Banwart	Earl Greene	Simon Mudd	Robert Taylor
Enriqueta Barrera	Mingxin Guo	Mark Noll	Brian Teppen
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Will Bleam	Jennifer Harden	Erin O'Reilly	Ben Turner
Joel Blum	Gerald Hendricks	Laurie Osher	Bill Ullman
Alex Blum	Paul Hendrix	Sanjai Parikh	Paul Verburg
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Oliver Chadwick	James Kubicki	Allan Reed	Baoshan Xing
Jon Chorover	Praveen Kumar	Rich Reeder	Kyungsoo Yoo
Robert Cook	Andrew Kurtz	Martha Relyea	Michael Young
David Crowley	Maria Labreveau	Chuck Rice	
Eric Davidson	Brandon Lafferty	Dan Richter	
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Jim Dyer	Kirsty Lloyd	Amy Shoher	
Mike Ellis	Festo Lugolobi	James Sickman	
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Mary Firestone	Scot Martin	Donald Sparks	
Katherine Freeman	Chris Matocha	Sharath Srinvasiah	
Jeff Fuhrmann	Dave McCarren	Kristin Staats	



**CRITICAL ZONE EXPLORATION  
NETWORK**

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