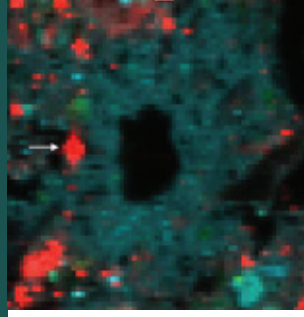

Soil Biogeochemical Processes within the Critical Zone

Jon Chorover,[1] Ruben Kretzschmar,[2] Ferran Garcia-Pichel,[3] and Donald L. Sparks[4]

Many processes that affect soil and water quality occur at the water-wetted interface of weathering products such as clays, oxides, and organic matter. Especially near the sunlit surface of the Critical Zone, these interfaces associate with plant roots and soil organisms to form porous, aggregated structures. Soil aggregates and intervening pore networks give rise to a patchwork of interconnected microenvironments. The ensuing steep geochemical gradients affect weathering processes, fuel the activities of microbes, and drive interfacial reactions that retain and transform rock- or ecosystem-derived chemicals and anthropogenic pollutants.

KEYWORDS: soil particles, natural organic matter, sorption processes, biogeochemical weathering

BIOGEOCHEMICAL INTERFACES AND CRITICAL ZONE FUNCTION

Traditionally, the various aspects of the Critical Zone have been studied by scientists in distinct and often isolated disciplines. Vegetation, for example, has been the domain of biologists; soils, the terrain of soil scientists; groundwater, the focus of hydrogeologists; and the underlying sediment or bedrock, a geologist's realm. While separate studies of these various compartments are essential, it is now clear that this approach cannot be used to predict the overall behavior of the Critical Zone (CZ). In fact, the functional, emergent properties of such a complex system are the result not only of its various parts, but also of the interactions among them.

Vegetation, soils, and landforms are integral parts of the CZ, an open system that exchanges matter and energy with the atmosphere, lithosphere, and hydrosphere. Over time, the exchange processes alter the internal composition of the CZ, and this can be observed at scales ranging from weathering particles through soil profiles to watersheds (FIG. 1). As water passes through the CZ pore network, it makes contact with a diversity of exposed solid surfaces, each of which affects the transfer of solutes into and out of solution. Locally, such *heterogeneous reactions* drive the evolution of particle surfaces and their biogeochemical reactivity, whereas integrated over the contributing areas in a watershed, they control stream and groundwater quality.

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In this paper, we emphasize the importance of soil *biogeochemical interfaces* to internal CZ function and focus on their effect on environmental pollutants. Reactions that occur at the boundary between multicomponent solid, liquid, and gas phases in weathering systems are indeed critical to the capacity of the Earth's surface to sustain water and soil quality. Removal of pollutants, sustainable provision of clean water, and support of productive ecosystems are all inextricably linked to the diversity and reactivity of natural interfaces formed by interaction of biota and water with lithogenic materials in the CZ.

FORMATIVE ROLE OF BIOTA

Plants and autotrophic microorganisms that colonize the sunlit surface of the CZ play a central role in the formation of these interfaces by transforming radiant energy to chemical form. Photosynthate becomes the primary source of carbon and energy for a complex food web of chemoheterotrophic organisms that oxidize it to CO_2 and H_2O or to partially oxidized organic matter. Organic products also create a geochemical environment that promotes subsurface mineral transformation, alters particle surface chemistry, and influences the mobility of redox-active elements including Fe, Mn, As, U, N, and S (Chadwick and Chorover 2001).

The surface soil is a CZ hot spot of metabolic and geochemical activity. It contains the highest number of roots and their fungal associations (mycorrhiza), the greatest microbial biomass, and the largest pool of natural organic matter (NOM). Plant root–microbe associations take up water and nutrients from the soil solution and release protons and organic exudates (e.g. low–molecular weight organic acids, siderophores, polysaccharides, biosurfactants). Some of these form strong complexes with mineral-derived cations, thereby enhancing mineral dissolution and releasing nutrients (Landeweert et al. 2001). Others adsorb to mineral surfaces or nucleating precipitates where they influence interfacial processes such as crystal growth, ion adsorption, and aggregate formation. Decomposition of NOM by organisms releases CO_2 and essential nutrient elements (e.g. N, P, S), forms biomolecular fragments, and leads to the formation of dissolved organic matter (DOM) and humic substances. In addition to their effects on soil acidity and ligand concentration, biota may promote weathering of primary (lithogenic) minerals by depleting pore water of rock-derived nutrient elements. For example, potassium uptake by plants can increase mica weathering rates in soils. The details of these processes are a poorly resolved and challenging area of research, partly because of

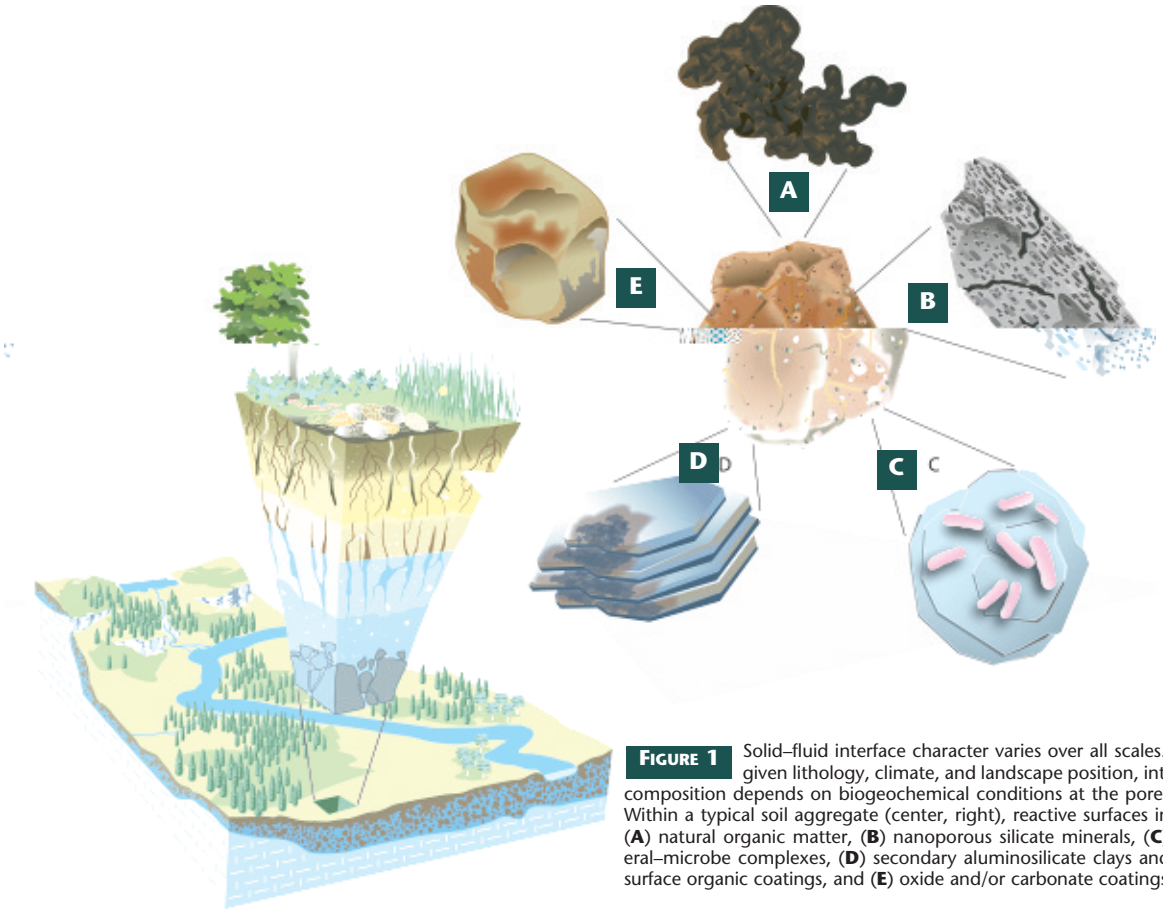

FIGURE 1 Solid–fluid interface character varies over all scales. For a given lithology, climate, and landscape position, interface composition depends on biogeochemical conditions at the pore scale. Within a typical soil aggregate (center, right), reactive surfaces include (**A**) natural organic matter, (**B**) nanoporous silicate minerals, (**C**) mineral–microbe complexes, (**D**) secondary aluminosilicate clays and their surface organic coatings, and (**E**) oxide and/or carbonate coatings.

difficulties involved in probing the rhizosphere, the microscale environment immediately surrounding root tissue. It is clear, however, that the root zone often exhibits steep, micrometer- to millimeter-scale gradients in pH, dissolved ligand and nutrient concentrations, and microbial activity (Hinsinger et al. 2006).

The infusion of NOM into deeper subsoil has several implications. First, because of gas diffusion limitations, biologically active porous media can have CO_2 partial pressures that are greater than those of the atmosphere by a hundredfold (or more). As a result, pore water is enriched in carbonic acid, which increases proton attack on primary minerals and promotes formation of high-surface-area and surface-reactive secondary (pedogenic) minerals. Second, these organic constituents strongly influence mineral transformation pathways and rates, the speciation and mobility of metals and organic pollutants, and the sequestration of atmosphere-derived carbon into mineral–organic complexes and aggregates. Third, because of its consumption during metabolism as a preferred electron acceptor for respiration, the O_2 partial pressure of the gas phase may be decreased in biologically active subsurface environments. This occurs even in near-surface biological soil crusts in desert environments (FIG. 2). As a result, in anoxic systems, heterotrophic oxidation of NOM is typically coupled to alternative electron acceptors such as NO_3^-, Mn(IV), Fe(III), SO_4^{2-}, and organic carbon (Hunter et al. 1998).

FORMATION AND DISTRIBUTION OF MINERAL–ORGANIC INTERFACES

Interfaces between liquid, gas, and solid (including microorganism surfaces) are of fundamental importance for almost all biogeochemical processes along the water transport pathway through the CZ. Hence, their impact on nutrient cycling and pollutant fate is profound. Accurate characterization of soil and sediment interface activity poses unique challenges and is not achievable by measuring bulk solid composition alone. In particular, discontinuous thin films of organic and inorganic material often coat mineral surfaces (FIG. 1). Although present at trace levels, these "surface modifiers" can significantly alter interfacial chemistry relative to that of the underlying solids and thereby control solute partitioning and colloidal behavior (Bertsch and Seaman 1999).

Particle surface properties change through interaction with meteoric water and the solutes it accumulates along its flow path. Leaching through the root and unsaturated zones (FIG. 1) drives incongruent weathering of primary to secondary minerals. This promotes formation of clay-sized layer silicates ("clay minerals") and various oxides and hydroxides of Fe, Al, and Mn, including those that may "armor" primary mineral surfaces (FIG. 3). Because of their high specific surface area (10–800 $m^2\ g^{-1}$), these phases can dominate the solid–water interface, even where their mass fraction is low. Their high surface charge and reactive surface functional groups make them effective sequestering agents for metals, metalloids, and radionuclides. For example, oxyhydroxide colloids serve as "hot spots" for the sequestration of toxic transition metals (Manceau et al. 2003).

Formation of secondary clays in the vadose zone also affects the behavior of NOM, and vice versa. Poorly crystalline Al and Fe oxides stabilize NOM against microbial degradation and increase soil capacity for storing otherwise-labile carbon (Mikutta et al. 2006). Surface-stabilized organic matter, in turn, alters the interfacial behavior of associated mineral particles, creating hydrodynamically rough and chemically heterogeneous surfaces in contact with the pore water (Kretzschmar et al. 1999). These heterogeneous mineral–

organic associations not only retard the advective–diffusive transport and deposition of solutes and colloidal particles, they also provide a diversity of surfaces for nucleation and growth of neoformed precipitates. While the environmental significance of mineral–organic association is apparent, the molecular-scale controls are not well understood. Unraveling the nature of NOM–mineral bonding and how these complexes are incorporated into higher-order aggregated structures poses a unique challenge to biogeochemists. A multifaceted approach is required that integrates field work, modeling, and laboratory experiments with advanced high-resolution spectroscopic techniques that are now increasingly accessible to geoscientists.

That NOM itself remains poorly characterized, despite its contribution to interfacial processes in the upper CZ, is a serious problem. However, novel approaches, particularly those combining computational methods with spectro- and microscopic techniques, such as soft-ionization mass spectrometry, multidimensional nuclear magnetic resonance (NMR) methods and soft X-ray spectromicroscopy, are providing new insight (Hedges et al. 2000). NOM is a complex mixture of intact and partly degraded biopolymers (proteins, carbohydrates, aliphatic biopolymers, lignin) and their fragments, aggregated into labile supramolecular structures through hydrogen bonding, cation bridging, and hydrophobic interaction. This suggests that the intrinsic characteristics of NOM and humic substances are the sum of the characters of their constituent biomolecular fragments, bound cations, and the higher-order aggregates that these form (Sutton and Sposito 2005). The amphiphilic properties of NOM are probably fundamental to the formation of mineral–organic complexes, but the structures of these complexes remain unresolved.

Particularly in the root zone, primary mineral–organic complexes are thought to form *microaggregates* that then assemble into *macroaggregates* (Six et al. 2000). Because mineral–surface interaction and aggregate occlusion can potentially inhibit enzymatic degradation of NOM, accurate characterization is a key to predicting organic carbon stabilization in soils. Spatially resolved near-edge X-ray absorption fine structure (NEXAFS) and attenuated total reflectance infrared absorption spectroscopic methods are proving useful for understanding these nano- to microscale structures (Solomon et al. 2005).

The saturated zone is often less altered than the root and vadose zones, especially in calcareous terrains, because groundwater is less acidic and longer residence times allow closer approach to equilibrium with soil minerals. Also, weathering reactions needing an electron acceptor may be suppressed by lack of O_2 (e.g. oxidative weathering of biotite and other Fe(II)-containing minerals). However, even in aquifer sediments, primary mineral surfaces can become coated with (hydr)oxide precipitates, dramatically altering surface reactivity. For example, Coston et al. (1995) showed that thin Al- and Fe-oxyhydroxide coatings (Fig. 3A) dominate the adsorption of Pb^{2+} and Zn^{2+} in Cape Cod aquifer sands. Despite their presence at trace levels, such thin coatings often control the behavior of important species.

The CZ exhibits heterogeneity in its physical character as well. A wide variety of pore sizes (Fig. 1) leads to a wide distribution of water flow velocities. Pores are not randomly disseminated; their network depends on the process leading to their formation, which, in turn, depends on location within the CZ. Small (nm to µm) pores within mineral particles, black carbon (char), or particle aggregates can form by chemical weathering, fire, abiotic aggregation, and root–microbe–soil interactions. In the latter case, the "granular" structure of surface soil, compared to the "blocky" structure of the subsurface, results directly from activity of plant roots, the influx of NOM, and associated microbial activity (Feeney et al. 2006).

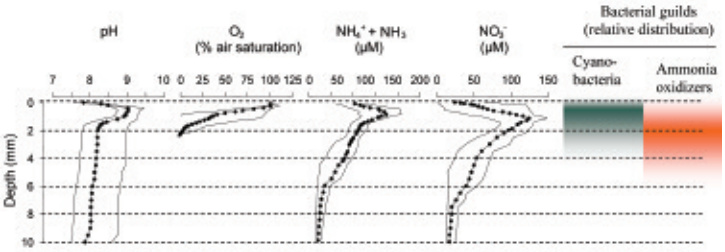

Figure 2 Chemical gradients in an active (wet) biological soil crust. Microelectrodes reveal microbial metabolic activity. Photoautotrophic cyanobacteria close to the surface consume CO_2, driving pH up and creating an internal O_2 supply, which is quickly respired by heterotrophs leading to anoxia 2–3 mm below surface. Leakage of cellular NH_3 produced by cyanobacteria during N_2 fixation creates a thin layer with both free NH_3 and O_2, which provides a habitat for chemolithoautotrophic ammonia-oxidizing bacteria. These provide nitrate through metabolism. These microscale processes provide the mechanistic basis for the fertilizing role of soil crust communities in arid lands at landscape scale (Garcia-Pichel et al. 2003).

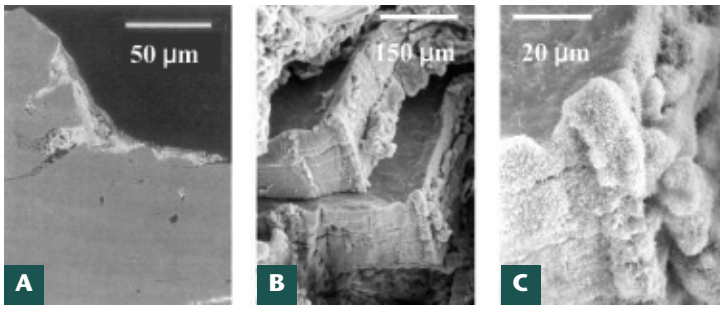

Figure 3 Incongruent dissolution and accretion on interfaces. (**A**) Backscatter electron image of surface coatings of polycrystalline Fe and Al oxyhydroxide on quartz from Cape Cod aquifer sand (Coston et al. 1995); (**B**) weathering of primary biotite grains and formation of secondary halloysite in a granitic gneiss saprolite and (**C**) close-up of (B) showing tubular halloysite on edge surfaces of the weathering biotite (Kretzschmar et al. 1997).

Large (mm to cm) pores arise from roots, soil fauna, and frost-heaving. In some soils, where clays predominate, shrinking and swelling produce large cracks. At depth, large pores can result from rock fractures and zones of preferential weathering. The connectivity and length of large pores affect water flow and control the amount of interface contacted by solutions traversing the CZ (Jarvis 2007). Water and solutes travel faster through macroporous soils than through a homogeneous medium with the same total porosity. While this diminishes the extent of interfacial contact and reaction with the soil matrix, it can enrich macropore surfaces with sorbing pollutants. Similarly, enhanced delivery of nutrients or metabolic substrates for bacteria may promote preferential growth on large pore walls. In extreme cases, such as the disposal of organic waste, enhancement of bacterial growth can lead to pore clogging and decreased hydraulic conductivity.

Superimposed on the particle- to pedon-scale distribution of CZ interfaces is the landscape-scale variability resulting from hydrologic partitioning through geomorphically variable terrain (Fig. 1). Landform structure forces migrating water through particular geochemical environments. One example is the movement of rain through oxic conditions on uplands, where Fe(III) oxyhydroxides might form, to an

organic-rich zone at lower elevations where reducing conditions may predominate, promoting dissolution of Fe(II). Geomorphic structure feeds back to affect the nature of interfaces formed at different locations in the landscape. "Hot spots" of biological activity may favor local N depletion through denitrification under anoxia or enhance local accumulation of trace components such as As, Se, and U (Gonzalez et al. 2006).

INTERFACIAL PROCESSES AFFECTING POLLUTANT FATE

The diversity of dissolved species and solid surfaces and the catalytic activity of organisms in the CZ provide capacity for transport, retention (i.e. sorption), and chemical transformation of solutes that affect water quality. Of particular interest to human and ecosystem health are metals, metalloids, and organic pollutants. Whereas some pollutants may pass through the CZ largely unimpeded (e.g. some polar organic compounds and weakly sorbing oxyanions), others are retained. Unraveling the reasons for these different behaviors necessitates combining macroscopic studies of contaminant uptake and release with molecular observations of the contaminant bonding environment. Such studies will help to elucidate aqueous complexation, sorption, and chemical transformation reactions that control the behavior of pollutants in the CZ.

Sorption in Heterogeneous Weathering Systems

Sorption is among the most important processes controlling the fate, mobility, and bioavailability of molecules in the CZ. Sorption is dynamic over timescales ranging from the rapid water–ligand exchange on dissolved species ($<10^{-9}$ s) to slow changes in sorbent structure resulting from weathering ($>10^{3}$ s). When natural or xenobiotic compounds meet an assemblage of natural particles, an interplay of environmental factors, such as sorptive species, pH, ionic strength, surface loading, and contact time, determines the sorption product. The distinction between interfacial (adsorption) complexes that are (1) outer-sphere or (2) inner-sphere provides a molecular-level perspective on solute mobility in the weathering environment. In outer-sphere adsorption, water molecule(s) occur between the surface and the solute, resulting in a relatively weak bond that can be reversed, for example, by increased concentration of competing species. In inner-sphere adsorption, a species is directly attached to the substrate. With no water displacing the adsorbate, immobilization is stronger.

Spectroscopic studies show that minimally hydrolyzing Group II cations, such as Sr^{2+}, Mg^{2+}, Ca^{2+}, and Ba^{2+}, are weakly adsorbed as outer-sphere complexes, while the hydrolyzing, divalent, first-row transition metals, Mn^{2+}, Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, and Zn^{2+}, and heavy metal cations, such as Cd^{2+}, Hg^{2+}, and Pb^{2+}, form stronger, inner-sphere surface complexes. Strong acid anions, such as NO_3^-, Cl^-, and ClO_4^-, are thought to form outer-sphere complexes on positively charged surfaces, although spectroscopic confirmation is challenging. Sulfate and selenate are sorbed as both outer- and inner-sphere complexes, depending on environmental conditions, whereas most weak acid oxyanions, such as molybdate, arsenate, arsenite, chromate, selenite, phosphate, and silicate, sorb as inner-sphere complexes on clay edges and oxide surfaces via ligand exchange (Sparks 2005). Organic pollutant sorptivity depends on the polarity and functional group character of the compound and substrate. For polar compounds, surface interactions include ionic and/or covalent and hydrogen bonding. For non-polar compounds, van der Waals and hydrophobic interaction dominate. NOM is the most important sorbent for hydrophobic organic contaminants (HOC), where hydrophobic domains constitute important sorption sites (Semple et al. 2003).

Prolonged sorbate–sorbent contact in the CZ can result in diminished bioavailability. Macroscopic observations of this "aging effect" are attributed to numerous molecular-scale mechanisms, including pore and surface diffusion to sorption sites and long-term changes in bonded sorbate–sorbent structure. For example, ^{13}C nuclear magnetic resonance spectroscopy has demonstrated that partial degradation of organic contaminants, catalyzed either by enzymes or mineral surfaces, can produce reactive intermediates forming covalent bonds with NOM (Dec and Bollag 1997).

Bioavailability of inorganic contaminants can slowly decrease during weathering, favoring formation of nanoparticle aggregates, polymeric complexes, or low-solubility precipitates. When inorganic contaminants coprecipitate with major lithogenic elements, such as Si, Al, and Fe, their bioavailability depends on mineral transformation rate and the solubility of the newly formed secondary mineral. For example, for high metal loading and pH > 7, sorbed Co^{2+}, Ni^{2+}, and Zn^{2+} cations are incorporated into mixed (e.g. Al-bearing) hydroxide surface precipitates of layered double hydroxides (LDH). Using synchrotron-based micro-XAFS and micro-X-ray fluorescence spectroscopy, McNear et al. (2007) showed that Ni-LDH was prominent in smelter-contaminated soils (Fig. 4). Over the long term, these phases may transform to stable phyllosilicates, with metal sequestered in a less mobile and bioavailable form. DOM also plays a role in pollutant sorption and mobility. It has polar (e.g. carboxyl, hydroxyl) functional groups that form stable complexes with metals, potentially increasing their mobility, and it has non-polar (e.g. aromatic, aliphatic) groups that can solubilize hydrophobic organic pollutants and enhance their uptake into groundwater.

Biogeochemical Gradients and Chemical Transformation Reactions

DOM is a carbon and energy source for heterotrophic microorganisms that drive biogeochemical reactions. Where oxygen is minimal, alternative electron acceptors for respiration can lead to valence state change in elements such as As, Cr, and U, influencing their mobility. This feature can be used for bioremediation (Valls and de Lorenzo 2002). For example, dissimilatory reduction of U(VI) and Cr(VI) to U(IV) and Cr(III) can remove both from solution, diminishing bioavailability. In contrast, As is mobilized under anoxic conditions. Substrate Fe(III)-hydroxides are reductively dissolved, releasing adsorbed As, and As(V) is reduced to As(III). A tragic example comes from West Bengal and Bangladesh, where high levels of dissolved As(III) in anoxic shallow groundwater are causing severe mass poisoning of the rural population (Charlet and Polya 2006).

The CZ has enormous capacity for chemical transformation of pollutants. Steep geochemical gradients develop because of spatial and temporal heterogeneity. Factors include inhibited groundwater mixing and periodic precipitation events. The result is a patchwork of distinct zones with local microbial associations and geochemical environments varying from the regional scale (10^{1}–10^{3} m) to the scale of particle aggregates (10^{-3}–10^{-6} m). At the particle scale, the genetic structure of microbial communities differs between the exterior and interior of soil aggregates as well as between variably sized aggregates and bulk soil. Indeed, destruction of aggregate structure through land use diminishes microbial diversity and patchiness, which has implications for pollutant transformation. For example, Tokunaga et al. (2003) demonstrated that reduction of

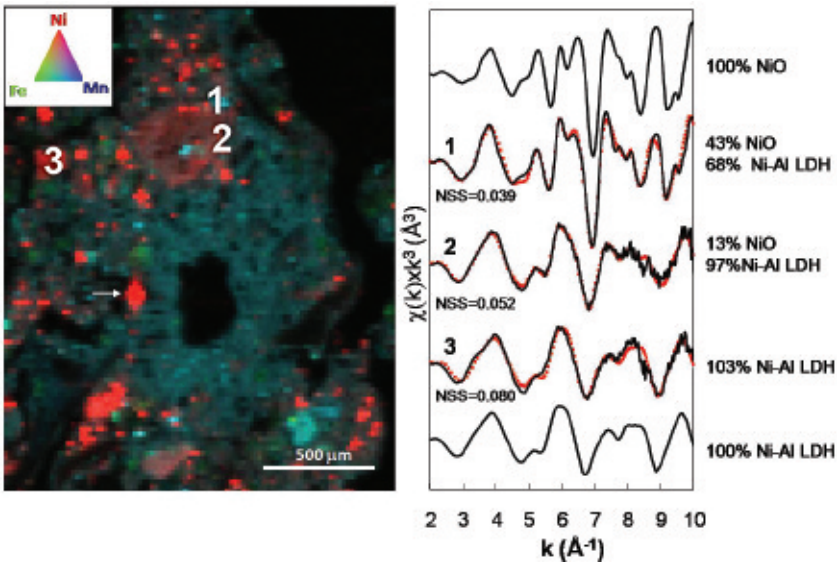

FIGURE 4 Weathering of $NiO_{(s)}$ (at arrow) to form Ni-Al LDH in a smelter-impacted soil: (left) µ-SXRF tricolor map of the Welland loam unlimed soil and (right) µ-XAFS spectra from selected points within the map that show an increasing predominance of Ni-Al LDH relative to $NiO_{(s)}$ resulting from progressive weathering (numbers 1–3). Solid lines represent the k^3 weighted χ-spectra, and the dotted lines are best fits obtained using linear combinations fitting with NiO and Ni-Al LDH references (top and bottom spectra) (McNear et al. 2007).

soluble Cr(IV) to insoluble Cr(III) occurred within the surface layer of soil aggregates where the diffusion of O_2 was limited but where labile NOM concentration was sufficient for rapid microbial respiration. At a slightly larger scale, steep gradients and their biogeochemical consequences have been documented in biological crusts in arid soils (FIG. 2). A final example of a localized environment is the well-known color "mottling," such as where oxidized Fe imparts a red or brown stain and reducing conditions in adjacent zones promote Fe dissolution and soil "gleying" (FIG. 5). The Fe redox systems support the metabolic activity of specific bacteria that profit from these electron and energy transfers.

The spatial distribution of microbially catalyzed redox reactions is also observed at the field scale. One example is the change in redox potential from anoxic to oxic as groundwater moves away from an organic contaminant source. Organic matter decomposition is coupled to terminal electron acceptors of increasing energy yield as stronger oxidants become available (Hunter et al. 1998). Common methods of sediment sampling and analysis often miss these gradients, effectively neglecting important mechanistic information. Hence, the processing of matter and energy in the CZ not only depends on the interacting components (whether biotic or abiotic) but also on their relative location and the transport pathway between them. Future research will have to go beyond mere compilation of compositional and distributional components acting independently of position; rather it will need to focus on understanding the CZ on the basis of integrative "system architecture."

Elucidation of the Microbial Role

Recent reviews have highlighted the role of microbial diversity in contaminant mediation (Lovley 2003). Examples of direct mediation include assimilatory and dissimilatory reduction and detoxification of metals [e.g. Fe(III), Mn(IV), Cu(II), U(VI)] and oxyanions (e.g. NO_3^-, SO_4^{2-} AsO_4^{3-}, CrO_4^{2-}), the oxidative precipitation of metal hydrous oxides, and the biodegradation of organic contaminants. In all cases, organisms derive benefits from the reaction (in terms of energy, nutrition, or decreased toxicity), increasing their chance of survival. These processes are typically efficient and genetically controlled, and thus subject to evolutionary modification. Microbes also affect abiotic reactions indirectly, through local modification of the geochemical environment by extracellular metabolites. Examples include the precipitation of carbonates and dissolution of silicates by proton-consuming metabolic activity such as photosynthesis or dissimilatory sulfate reduction and redox activity of biogenic oxyhydroxides (Tebo al. 2004).

The last two decades have witnessed a revolution in understanding the role of microorganisms in the CZ. This is largely a result of the introduction of molecular genetic techniques, allowing direct detection, thereby avoiding the need for cultivation, which is notoriously biased and slow. Initially, techniques to identify microbes in situ using ribosomal RNA appeared most promising (Pace et al. 1986), and this method is still preferred, in spite of the development of other approaches applied to functionally meaningful genes. Bio-informatic studies of whole genomes and collections of genomes are increasingly being applied to environmental questions. The new field of metagenomics—an attempt to distill functional and structural information from genomic data retrieved from heterogenous, natural CZ samples—is particularly promising because of the potential for defining the functional capacity of extant microorganisms by reading their genetic instructions. However, current accessability is limited by demanding computational and technological

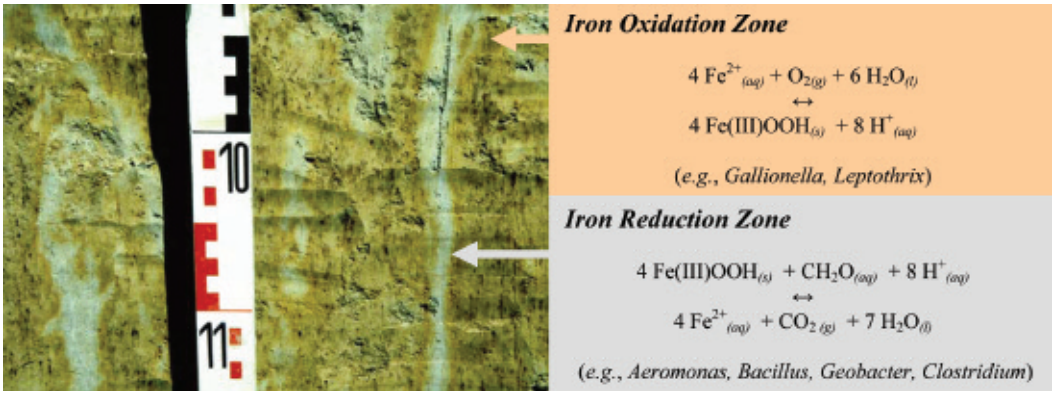

FIGURE 5 A periodically water-logged soil showing the characteristic "redoximorphic" features of iron cycling between oxidized (reddish brown) and reduced (pale, iron-depleted) environments in close proximity to each other. Representative Fe oxidation and reduction reactions are depicted, along with bacterial strains known to catalyze the transformations. A diversity of iron-oxidizing bacteria likely carry out their reactions at circumneutral pH in soil, but their identity is not well documented. Some of them are proteobacteria closely related to *Marinobacter* and *Hyphomomas*, whereas *Gallionella* and *Leptothrix* genera identified in freshwater systems may also be present in soils. Scale numbers in dm

requirements (Riesenfeld et al. 2004). Building molecular sequence databases and assigning functional roles represent the biggest challenges for future applications.

OPPORTUNITIES AND NEEDS FOR TECHNICAL INNOVATION ACROSS SCALES

Understanding the complex processes in the CZ will contribute to sustainable use of soil and water resources. Historically, failure to understand complete systems has produced major environmental problems. Future development of effective contamination remediation will depend on such knowledge. Reaction mechanisms and rates of biogeochemical processes must be defined for model as well as natural CZ materials. Our ability to resolve the composition of natural soils and sediments is advancing rapidly, particularly through advanced analytical techniques based on micro-focused synchrotron radiation. At the same time, the application of molecular genetic and metagenomic techniques will identify the species, metabolic function, and associations responsible for particular biogeochemical processes. Finally, recent advances in geophysical probes now allow high-spatial-resolution measurements, in situ, in field systems. However, these dramatic improvements are not sufficient. Improved biogeochemical understanding also depends on accurate conceptual models for the interaction of the various components in a structured, living soil, with transport pathways controlling matter and energy flux. The enormous growth of computational power during the past two decades will revolutionize modeling capabilities for coupling physical, chemical, and biological processes to produce scaled-up models that can more accurately represent the dynamic nature of the CZ.

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