Elements

An International Magazine of Mineralogy, Geochemistry, and Petrology

Rock and Mineral Coatings:
Records of Climate Change, Pollution, and Life

MICHAEL SCHINDLER and RONALD I. DORN, Guest Editors

Rock and Mineral Coatings:
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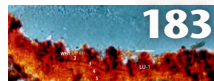Ronald I. Dorn, William C. Mahaney, and David H. Krinsley

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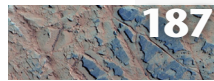**177 Marine Ferromanganese Encrustations: Archives of Changing Oceans**
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DEPARTMENTS

Coatings on Rocks and Minerals:
The Interface Between the Lithosphere and the Biosphere, Hydrosphere, and Atmosphere

Michael Schindler[1] and Ronald I. Dorn[2]

Coatings occur along interfaces between rocks and minerals and their environment. Coatings result from the wide variety of reactions and/or processes that occur at the interface between the lithosphere and the biosphere, hydrosphere, and atmosphere. Such coatings are biochemically, mineralogically and isotopically complex and have the potential to record changes in their immediate environment. The transition between a coating and its underlying host is abrupt and defined by a sharp interface at the nanoscale. Articles in this issue highlight new and exciting research in the field of coatings, focussing on coatings formed in deserts, soils, sediments, oceans, and on rocks from Mars.

KEYWORDS: coatings, weathering rind, biofilm, ferromanganese crust, Mars, rock-inhabiting fungi

INTRODUCTION

Coatings, in the sense of one substance covering another, define the surfaces of many rocks and minerals. They occur on rocks exposed to the atmosphere, biosphere, and hydrosphere and they cover mineral grains in soils, sediments, and anthropogenic features such as mine tailings and mine waste piles.

The occurrence of coatings on rocks and minerals was first described scientifically over two centuries ago by Alexander von Humboldt in his *Personal Narrative of Travels to the Equinoctial Regions of the New Continent During the Years 1799–1804* (von Humboldt 1814), where von Humboldt correctly deduced that the dark covering on rocks in the Orinoco River (which flows in Venezuela and Columbia) was a Mn-rich accretion (FIGS. 1A, 1B). Since then, our knowledge about coatings on rocks and minerals have increased steadily to the point where coatings on rocks and minerals are now studied to understand past and present geobiological, geomorphological, (astro-)biological, pedological, archaeological, and environmental processes (see articles in this issue).

Coatings form in various geological, bioclimatic, and anthropogenic environments. For example, black rock-coatings composed of Fe–Mn oxides and clay minerals (termed "rock varnish") (FIG. 1) occur on different types of rock substrates in the arid environments of Antarctica, Arizona (USA) and Peru (Dorn 2013), whereas black Fe–Mn-oxide coatings also form on submarine rock surfaces (Koschinsky and Hein 2017 this issue) and can accumulate for far longer than any known terrestrial coating because erosion of the underlying rock material is much slower than in terrestrial settings. Terrestrial and submarine rock coatings represent mainly accretions derived from external constituents, but marine Fe–Mn crusts involve precipitation from sea water, while terrestrial rock coating formation varies greatly depending on the type of coating. Black coatings may also accrete on stone surfaces in air-polluted cities where the interaction between building stones and exposed rocks with sulfuric acid and/or nitric acid may result in the formation of coatings composed of amorphous silica, sulfates, and particulate matter (FIG. 2) (Smith and Prikryl 2007; Mantha et al. 2012).

Coatings on rocks and minerals are studied on the kilometer- (FIG. 3A), meter- (FIG. 3B), micrometer (FIG. 3C) and nanometer-scale (FIG. 3D). For example, the distribution of coatings on the surface of the Earth and on other terrestrial planets can be mapped using remote-sensing techniques (e.g. Malcolm et al. 2015). Details on their mineral, chemical, and isotope compositions can be analysed, for example, with bulk analytical tools such as X-ray diffraction, inductively coupled plasma mass spectrometry (ICP–MS) and conventional stable isotope techniques. Site-specific information on the nano- to micrometer scale can be gained through the combination of focused ion beam transmission- and transmission electron microscopy (e.g. FIG. 1C), scanning electron microscopy (FIG. 1B, 2B), synchrotron spectroscopy techniques, laser-ablation ICP–MS (FIG. 2C) and secondary ion mass spectroscopy.

In this issue of *Elements*, we present an overview of research on different types of coatings with respect to their formation on aerially exposed rocks, the role of bacteria and fungi during their formation, their ability to sequester contaminants and to preserve records of past and recent environmental processes, and on their potential role in understanding past biogeochemical processes on other terrestrial planets.

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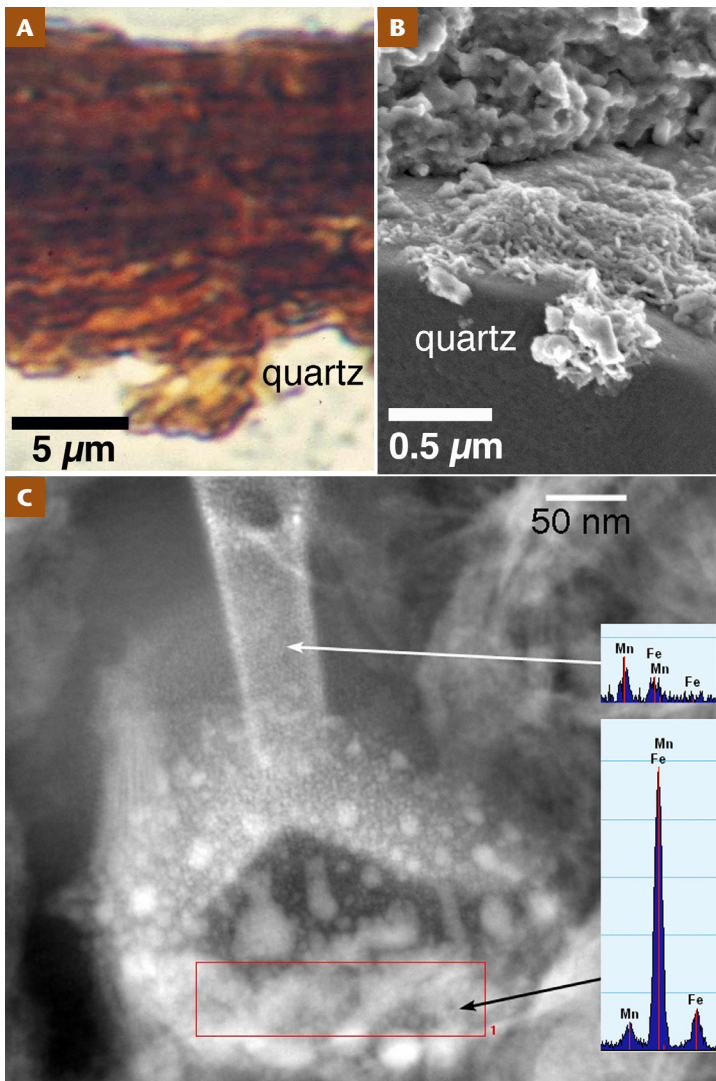   E-mail: ronald.dorn@asu.edu

COATINGS AND WEATHERING LAYERS: FORMATION, PROPERTIES AND ENVIRONMENTAL INDICATORS

There is no clear definition for the term *coating* in the Earth sciences. Dorn et al. (2017 this issue) distinguish between weathering rinds and coatings. These authors define *weathering rinds* as a product of chemical weathering and *coatings* as a product material deposition from the surroundings, i.e. the constituents of a coating originate exclusively from the surroundings (FIG. 1A). Mantha et al. (2012) and Schindler and Singer (2017 this issue) consider coatings as heterogeneous surface layers that can contain constituents from the underlying rock or mineral and from the surroundings (FIGS. 2A, 2B).

The distinction between the weathering rinds of rocks formed through chemical weathering and coatings formed by deposition from the exterior allows Dorn et al. (2017 this issue) to depict the dynamic transition between weathering processes occurring on the surface of the underlying rock and the infilling of newly formed pore spaces by rock-coating components. These authors show, however, that this case-hardening process eventually leads to the detachment of the rock coatings and, thus, to the loss of features such as rock art, the surfaces of stone monuments, and the facing stones of buildings.

Schindler and Singer (2017 this issue) emphasize that mineral surface coatings in soils are complex entities of nano-size abiotic- and biotic-formed mineral assemblages that contain constituents both from the underlying mineral and from the mineral's surroundings. The authors show that, regardless of the origin of the coating constituents, nano-size pores within coatings allow sequestration of contaminants and the preservation of past and recent environmental processes in soils and sediments.

Gadd (2017 this issue) discusses the role of fungi and lichens as rock coatings and also as major geobiological agents altering Earth's surface. The author focuses on the role of fungi during bioweathering, fungi's ability to adapt to adverse environments, their organic carbon-based metabolism and their symbiotic relationships with other organisms, such as lichens. The author shows that the excretion of geo-active metabolites – such as organic, carbonic, and oxalic acids – is of fundamental importance in many environmental mineral transformation processes.

FIGURE 1 Rock coatings from natural and anthropogenic environments explored at different scales. (**A**) Optical thin section image of a Mn-rich coating from the Orinoco River (South America) that was discussed by von Humboldt (1814). The optical image reveals the presence of laminations. (**B**) Secondary electron image of the coating shown in 1A illustrating how the Mn-rich coating gradually spreads onto smooth quartz surfaces. (**C**) Focused ion beam preparation revealing the presence of budding bacteria that are able to concentrate Fe (in the cocci structure) and both Mn and Fe in the bacteria bud (Krinsley et al. 2017).

FIGURE 2 Anthropogenic processes can result in the formation of rock coatings. (**A**) Photograph of black coatings formed on granite in Sudbury, Ontario (Canada) through the interaction of the siliceous rock with sulfuric acid. Sulfuric acid and particulate matter were emitted during years of smelting activities, causing rain water to reach pH values as low as pH ~3. (**B**) Scanning electron microscope image of the black coating shown in 2A. Weathering of exposed rocks in the Sudbury area resulted in the formation of amorphous silica layers which trapped and encapsulated the emitted sulfate aerosols and metal(loid)-rich particulate matter (which yielded to the black colour of the coating). The coatings are composed of multiple layers, which include layers composed of mainly amorphous silica (darker parts) and those containing metal(loid)-bearing sulfates and particulate matter embedded in an amorphous silica matrix (thin bright layer). (**C**) The compositional changes across the coating and thus multiple layers can be recognized using laser ablation ICP–MS line scans. Data shown for the traverse from "1" to "2" as shown in 1B (modified from Mantha et al. 2012).

Whitley et al. (2017 this issue) present the use of microlaminations in rock varnish as both a tool to analyse paleoclimatic changes and also as a chronometric tool, a technique that allows the dating of commonly non-dateable stone artefacts and art, such as petroglyphs. Dating surface artefacts and petroglyphs provides valuable insight about the peopling of the Americas and the age and changing environmental adaptation of the prehistoric inhabitants of the hemisphere.

Koschinsky and Hein (2017 this issue) emphasize that iron–manganese oxyhydroxide coatings (Fe–Mn coatings) on submarine rock surfaces and on sediment represent vast archives of changing ocean conditions, including variations in climate, ocean currents, geological activity, erosion processes on land, and even anthropogenic impacts. These authors illustrate that slow-growing Fe–Mn coatings in deep oceans provide proxies of paleoceanographic changes over the time periods of hundreds of thousands to tens of millions of years. In contrast, fast-growing coatings in shallow waters on continental margins can record anthropogenic environmental impacts.

Marnocha (2017 this issue) explores the potential implications of rock coatings on Mars. Micro-environments in rock coatings can sometimes provide habitats for microbial life because such coatings contain sufficient inorganic nutrients as "microbe food" and can shield microbes from harmful radiation. This author suggests that rock coatings are able to preserve petrified biosignatures and that new technology in future Mars rover expeditions may provide valuable information about the potential occurrence of these signatures in rock coatings on Mars.

The reader can find below a glossary with the most important technical terms used in the articles of this issue of *Elements*.

OUTLOOK

Deciphering environmental records in coatings on rocks and minerals is a burgeoning field in the Earth sciences. The application of relatively new analytical tools and approaches in mineralogy (e.g. focussed ion beam/transmission electron microscopy) and (bio-)geochemistry (e.g. metal stable-isotope analyse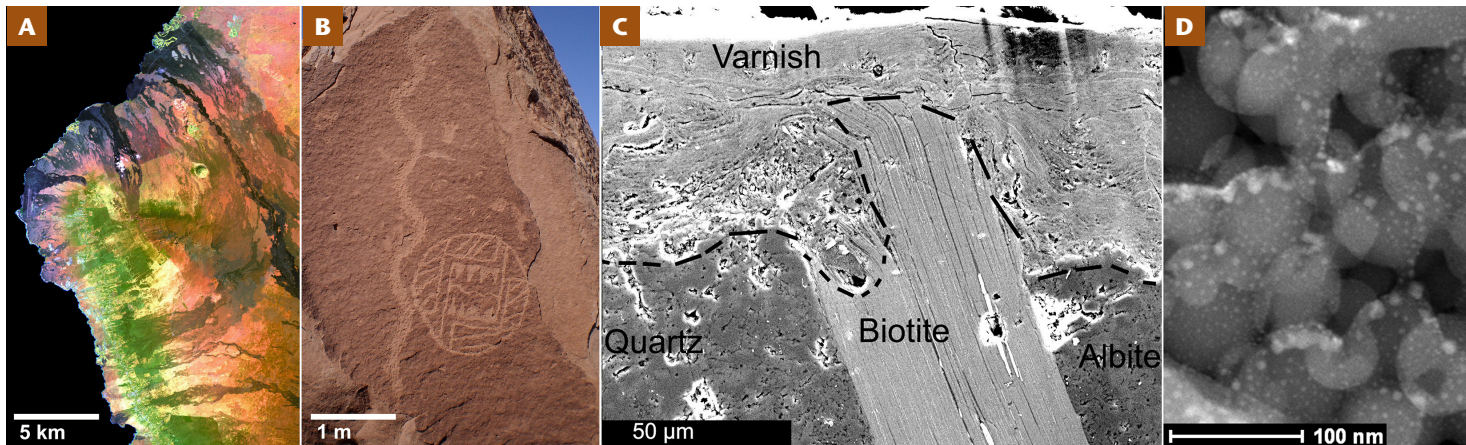s) will assist in the deciphering of past and present environmental processes as recorded by soil and rock coatings. This information will help us to better understand the formation of coatings in the presence and absence of micro-organisms; the ability of coatings to sequester toxins in soils, rivers, lakes and oceans; and how coatings record past environmental changes. And all this may, one day, be done on the surfaces of other planets.

ACKNOWLEDGMENTS

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GLOSSARY

Important technical terms used in the articles of the June 2017 (v13n3) issue of *Elements*.

Adsorption	The binding of an ion or small molecule to a surface at an isolated site as a 2-D surface complex. There is little to no interaction between adsorbed species
Biodeterioration	The deterioration of organic and inorganic substances mediated by living organisms and their products.
Case hardening	Process of surface hardening the outer surface of a rock
Equifinality	The same end state can be reached by many potential processes in an open system
Focused ion beam (FIB) technology	Technology to lift out electron-transparent micrometer-size sections using Pt-glue and Ga-ions
Fungus (plural = Fungi)	A member of the kingdom Fungi, a group of eukaryotic organisms distinct from plants and animals, that predominantly exhibit a filamentous branching growth form.
Geomycology	The roles of fungi in processes relevant to geology.
Heterogeneous precipitation	A 3-D growth mechanism of a species on a surface. This mechanism differs from adsorption in that the retained species directly interact with each other on the surface and can even have the solid structure grow away from the original substrate
Homogeneous precipitation	The formation of a 3D structure without the association of a substrate (sorbent) material. This process occurs in solution directly and leads to discrete particles.
Hydrogenetic/ hydrogenesis	Precipitation of metals from cold ambient seawater; all ferromanganese crusts, and some nodules, form solely by this process.
Hypha (plural = hyphae)	The typical unit of form in filamentous fungi, being tube-like and exhibiting apical (= tip) growth, and with the capacity to branch and create a filamentous network (mycelium).
Induration	Hardening of the outer surface of a rock face by different biotic or chemical agents
Intragranular or extragranular spaces	Within or outside of pore spaces between grains, precipitates or crystals in a coating
Low-index element	Element that becomes enriched during chemical alteration processes due to its low mobility
Lichen	A fungal growth form consisting of a mutualistic relationship between a fungus (yeast) and a photosynthetic organism (such as an alga or a cyanobacterium).
Magnetosome	Magnetite crystal in prokaryotic (magnetotactic) bacteria
Metabolite	A chemical substance produced by an organism during metabolism. Fungal metabolites involved in rock and mineral transformations include CO_2 and organic acids.
Microaerophilic	Aerobic environment with oxygen at lower concentration than in the atmosphere
Microcolonial fungi (MCF)	A group of rock-inhabiting fungi exhibiting unicellular yeast-like and microcolonial growth, and occurring as small black melanized colonies on colonized substrates.
Mycelium	The overall hyphal network of a fungus.
Nanofossil biostratigraphy	The use of changes in discoaster (an extent genus of star-shaped algae) and coccolith assemblages in ferromanganese crust layers to age date the crusts by comparison with the known Cenozoic/Cretaceous evolutionary changes in nanofossil assemblages.
Paleomagnetic stratigraphy	The use of remnant magnetization in the ferromanganese crust and nodule layers to determine stratigraphic intervals of normal and reverse polarities.
Pore	A *space* within a mineral/rock/coating that is unoccupied by solid material
Rhizine	A lichen's anchoring structure, composed of fungal hyphae.
Rock varnish (synonymous with desert varnish)	Composed of clay minerals, Mn and Fe hydroxides, and minor and trace elements; color is typically black from the Mn, but can be more orange when Fe is in greater abundance.
Sorption	Partitioning of ions from solution onto or near a mineral surface; can include adsorption and precipitation
Spalling	The detachment of rock pieces of varying sizes from a bare rock face
Thallus	The vegetative body of an organism, a term typically applied to mosses, liverworts, seaweeds and lichens.
Turgor pressure	The internal hydrostatic pressure within a cell that maintains rigidity and can also be a determinant of hyphal penetration of a solid substrate.
Weathering rind	The outer layer of a pebble, boulder, or other rock fragment that has formed as a result of chemical weathering.
Yeast	A fungus that exists predominantly in a unicellular form, reproducing by budding or fission. Many yeasts can also produce filamentous hyphae.

Mineral Surface Coatings: Environmental Records at the Nanoscale

Michael Schindler[1] and David M. Singer[2]

Past and present (a)biotic soil processes can be preserved by mineral surface coatings, which can sequester contaminants in soils and sediments. The coatings can contain complex assemblages of nanometer-size minerals and organic components. The formation, composition, and morphology of these complex mineral assemblages depend on, and hence reflect, the mineralogical and chemical composition of the substrate they develop on and the environmental factors in the surrounding soils and sediments. Mineral surface coatings typically contain complex and variable porosities, many with regions of limited fluid flow. Low-flow conditions, combined with different nanometer-size phases in the interior of mineral surface coatings, allow coatings to sequester contaminant-bearing solutes, complexes, and nanoparticles.

KEYWORDS: soils, geochemical records, contaminants, sorption, transport, microaerophilic conditions

Many chemical and mineralogical transformations in soils and sediments occur on the surface of colloids, mineral grains, and organic material. These soil constituents are often coated with secondary phases that form patchy to continuous mineral surface coatings at the nano- to micrometer scale. These coatings are not only part of the critical zone, the skin of our planet, they also share many of its attributes. Coatings can be a complex mixture of water, organic matter, and minerals, and chemical reactions proceed both abiotically and through catalysis by micro-organisms. Minerals in the upper part of mineral surface coatings re-equilibrate with percolating fluids in soils and sediments to create environmental gradients between early and later-formed mineral assemblages. As a result, there is no representative naturally occurring mineral surface coating.

Coatings can occur in different environmental, mineralogical, and chemical settings. For example, goethite can coat nanoparticles of crandallite $[CaAl_3(PO_4)_2(OH)_5(H_2O)]$ in surficial soils (FIG. 1A); Fe-oxide-bearing nanocrystalline Al-silicate can coat sand grains in aquifers (FIG. 1B); Fe-hydroxide can coat Fe-sulfide grains in acidic soils (FIG. 1C); and anglesite $[PbSO_4]$ can coat organic material from Pb-contaminated soils (FIG. 1D). There are as yet no systematic studies on the abundance and composition of mineral surface coatings with depth or soil horizon. However, studies of surficial, highly weathered soils in

Canada indicate that ~2/3 of all silt- to sand-size grains are coated with visible (micrometer-thick) material (Schindler et al. 2016).

Mineral surface coatings form through the influx of constituents from the dissolving underlying mineral and from fluids originating in the surrounding soils and sediments; constituent proportions in the coatings vary with the solubility and reactivity of the mineral and with the chemical and mineralogical environment. Mineral surface coatings that result from the weathering of primary aluminosilicate grains common in soils and sediments typically produce a thin, hydrous, patchy, natural coating of amorphous and crystalline secondary aluminosilicates that can range up to 10 nm in thickness. (Nugent et al. 1998; Zhu et al. 2006). These coatings often form from coupled dissolution–precipitation reactions at the interface between the mineral surface and the coating (Putnis and Ruiz-Aguda 2013) where the dissolution of the silicate results in the release of all incorporated elements and in the reprecipitation of a surface layer enriched in one of the major elements. Crystalline secondary phases, such as clays (e.g. kaolinite, smectite) on the surface of silicate minerals (Banfield and Eggleton 1990) and Fe-hydroxides on the surface of Fe-sulfide minerals (Huminicki and Rimstidt 2009), can form porous layers that are tens of micrometers in thickness. These thicker coatings do not commonly constitute a diffusion barrier for external solutions and, thus, do not prevent further weathering of the underlying mineral grain. Inclusion of external species, typically dominated by insoluble Fe(III), Al, and Mn(IV) oxy-hydroxides, may result in the formation of mineralogically complex surface coatings whose formation only partially depends on the underlying composition of primary and/or secondary phases. These coatings often contain confined pore spaces with adsorbed species, nanoparticles, and assemblages of nano-size minerals which are not in equilibrium with other constituents in the coatings or with pore solutions in the surrounding soils.

BUILDING COMPLEX ASSEMBLAGES OF NANO-SIZE MINERALS

The formation of complex mineral assemblages in surface coatings (FIG. 2) is often the result of various chemical, physical, and biological processes, such as abiotic- and biotic-controlled dissolution–precipitation reactions, encapsulation of minerals and bacteria through silicification, and the aggregation of nanoparticles to larger

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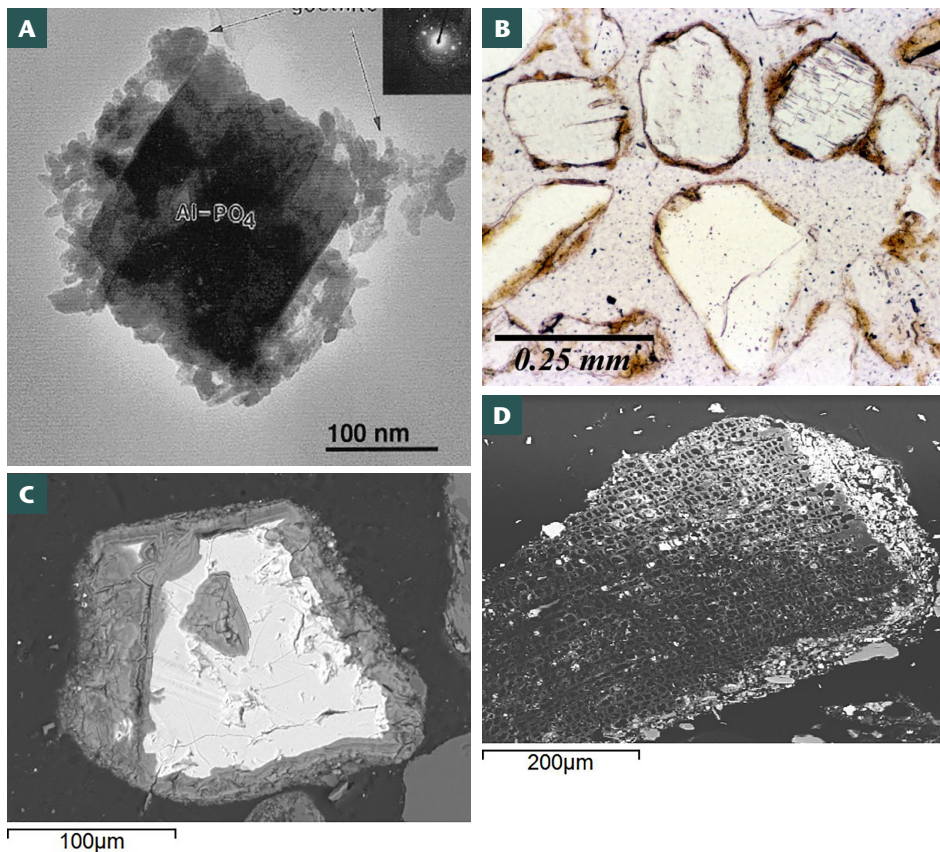   E-mail: dsinger4@kent.edu

FIGURE 1 (**A**) Transmission electron microscope image of goethite coating nanoparticles of crandallite [$CaAl_3(PO_4)_2(OH)_5(H_2O)$] in surficial soils. USED WITH PERMISSION OF THE NATIONAL ACADEMY OF SCIENCES USA FROM BERTSCH AND SEAMAN (1999). (**B**) Optical image of Fe-oxide-bearing nanocrystalline Al-silicate coatings (brown) on sand grains from an aquifer. IMAGE BY R. L. PENN. (**C**) Backscatter scanning electron microscope (SEM) image of Fe-hydroxide coatings on a chalcopyrite grain from acidic soils in Sudbury, Ontario (Canada). (**D**) Backscatter SEM image of a coating containing anglesite ($PbSO_4$) on organic material in Pb-contaminated soils at Trail, British Columbia (Canada). IMAGES FOR C AND D BY M. SCHINDLER.

particles and crystals [so called "crystallization through particle attachment" (De Yoreo et al. 2015)]. For example, recent nanometer-scale characterizations of coatings on sand grains (FIG. 1B) have shown the occurrence of crystalline Fe-oxide fragments in an amorphous/nanocrystalline matrix enriched in Si and Al relative to Fe (Penn et al. 2001). Mineral assemblages of even higher complexity can form in coatings when biogeochemical conditions in soils and sediments change dramatically over time (Schindler and Hochella 2015, 2016). For example, coatings formed in surficial soils that have been impacted by acidification and subsequent remediation can contain different generations of mineral assemblages:

- A first generation of clay minerals formed during the weathering of the underlying mineral at near neutral pH condition and, thus, prior to the acidification of the soils.

- Locally formed crystals of Fe-oxides (labelled "1" in FIG. 2C), precipitates of Fe-oxy-salt minerals and bands of amorphous silica ("2" in FIG. 2C) and aggregates of Ti- and Zr-oxide nanoparticles, all formed during soil acidification.

- Petrified magnetotactic bacteria and preserved magnetosomes (see below), indicators of microbial activity and biotic-controlled dissolution reactions in the coatings ("3" in FIG. 2C).

- A second generation of clay minerals within pore spaces ("4" in FIG. 2C) and on the surface of earlier-formed minerals that had formed during and after remediation of the soils.

These observations indicate that micrometer-thick coatings can preserve past and present environmental changes in local soils and sediments and that these changes can be deciphered through the study of nanometer-size mineral assemblages within these coatings.

COATINGS AS CONTAMINANT SCAVENGERS

Mineral surfaces in soils and sediments can directly affect water quality because these surfaces are able to scavenge contaminants such as metal-bearing complexes and nanoparticles, oxy-anions (phosphates and nitrates), organic matter and microorganisms (Chorover et al. 2007; Schindler et al. 2016). As such, the type and abundance of mineral surface coatings in soils and aquifers have a tremendous effect on the overall ability of the bulk material to sequester contaminants because mineral surface coatings can increase their surface area and modify their surface charges (Bertsch and Seaman 1999).

Scavenging and sequestration of contaminant-bearing complexes and nanoparticles by a mineral surface coating is principally controlled by two factors:

- The occurrence of a porous matrix with spatial domains of limited flow potential (Singer et al. 2013; Zachara et al. 2016). These domains can exist as intra-aggregate and intragranular spaces, and over a wide range of spatial scales. In particular, pore spaces in the nanometer and sub-micron size domain may account for a large volume of reactive surface sites, despite accounting for only a small fraction of the total pore volume. With respect to contaminant transport, the fluids in these regimes are relatively immobile, and solute transport may be dominated by diffusion between extragranular and intragranular pore space, driven by concentration gradients. Furthermore, limited flow regimes can also hinder equilibration between phases of different generations and between such phases and current pore solutions in the surrounding soils and sediments (Wang et al. 2003; Singer et al. 2013).

- Different generations and types of assemblages of nano-size phases in the interior of mineral surface coatings. These phases generate various types, abundances, and distributions of reactive surface sites and surface charges, which, in turn, control diffusion, adsorption and speciation of solutes and colloids (Singer et al. 2013; Schindler and Hochella 2015, 2016; Schindler et al. 2015, 2016).
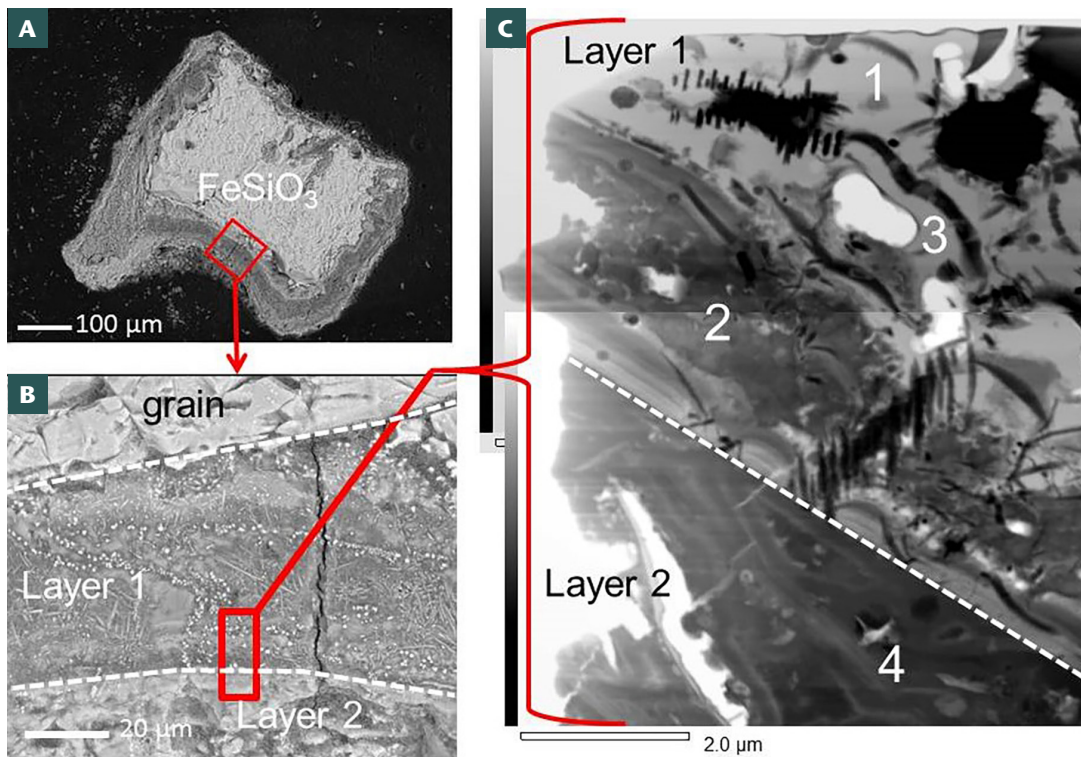
FIGURE 2 (**A**) Backscatter scanning electron microscope (SEM) image of mineral surface coating with multiple layers on an Fe-silicate mineral with a composition close to ferrosilite (FeSiO$_3$). The area depicted in 2B is indicated with a square. (**B**) Higher-magnification SEM image of the square section indicated in 2A showing two distinct interfaces between the underlying grain (dashed lines) and two layers: Layer 1 and Layer 2. The location of a section lifted out with the focused ion beam technology is indicated with a rectangle. (**C**) Scanning transmission electron microscope image of the rectangular section depicted in 2B. The location of Layer 1 and Layer 2 and their interface (dashed line) are shown. The four numbers indicate examples of the major constituents: (1) locally formed crystals of magnetite and goethite; (2) precipitates of Fe-oxysalt minerals (jarosite) encapsulated in bands of amorphous silica; (3) petrified magnetotactic bacteria and magnetosomes (see also FIG. 5); (4) Fe-hydroxide matrix with pockets of encapsulated clay minerals (illite and clinochlore) and ternary Cu-phosphate adsorption complexes.

UNDERSTANDING SOLUTE TRANSPORT THROUGH COMPLEX POROSITY

Solute reactions and transport within mineral coatings occur in a physical environment with inherently complex porosity. Pore-scale simulations have revealed the importance of coupled mass transport and chemical reactions in both intragranular and intergranular domains: these can influence metal-complexation rates in sediments, both spatially and temporally (Liu et al. 2013). Further, these pore-scale simulations also reveal that the rate of coupled diffusion and molecular surface complexation reactions in the intragranular porous domains were slower than either individual process alone. A critical component of building predictive models of contaminant transport is, therefore, to determine the specific controls on metal sorption and diffusion in porous material. Using model materials can aid in these studies.

Porous materials are broadly classified according to IUPAC nomenclature as microporous (<2 nm), mesoporous (2–50 nm), and macroporous (>50 nm) (Rouquerol et al. 1994). Synthetic porous materials are ideal models for studying naturally occurring porous earth materials under variable conditions because they can be tailored to have a simpli-

fied pore geometry, a well-constrained pore-size distribution, and reproducible surface properties (Selvam et al. 2001). Mesoporous materials represent a pore-size regime that can account for a significant fraction of the reactive surface area of porous earth materials and mineral surface coatings (Sammartino et al. 2003). Porous silica is an important constituent in these settings, both as quartz and amorphous silica gels, playing an important role in surface environments by attenuating contaminant transport by sorption and precipitation reactions (Chen and Hayes 1999; Ford et al. 2001). These materials are also relevant to metal transport phenomena in the weathering and degradation of glass and other amorphous materials used in nuclear waste forms (Greaves et al. 1989). Mesoporous silica is, therefore, a useful and relevant model for these materials, while allowing for a high degree of control over the physical and chemical properties of the sorbent.

A fundamental understanding of solute diffusion into micro- and mesoporous materials remains uncertain. The complex relationship between solute transport and reactivity in these systems is exemplified by the sorption of hexavalent uranium [U(VI)]. Under acidic and oxidizing conditions, U exists as uranyl hydrolysis products, and readily forms aqueous complexes with carbonate (CO$_3$) and calcium (Ca) at circumneutral and alkaline pH values (Singer et al. 2014). All of these U species have significantly different solute properties and sorption behaviors. Uptake of U by porous silica compared to bulk material can result in different sorption reaction products, slower desorption kinetics, enhanced nucleation and precipitation, and the capacity of colloidal transport, all of which are dependent on the pore structure and size, as well as the type and density of terminating functional groups at pore surfaces (Štamberg et al. 2003; Vidya et al. 2004; Wang et al. 2013; Singer et al. 2014). One key finding is that rates of desorption from small pores are not only scale-dependent, but they may be concentration- and speciation-dependent due to polymerization and precipitation (Singer et al. 2014). This latter process can result in a recalcitrant pool of ions that are sequestered in deep internal pore spaces (FIG. 3). This highlights the need of future work aimed at eluci-
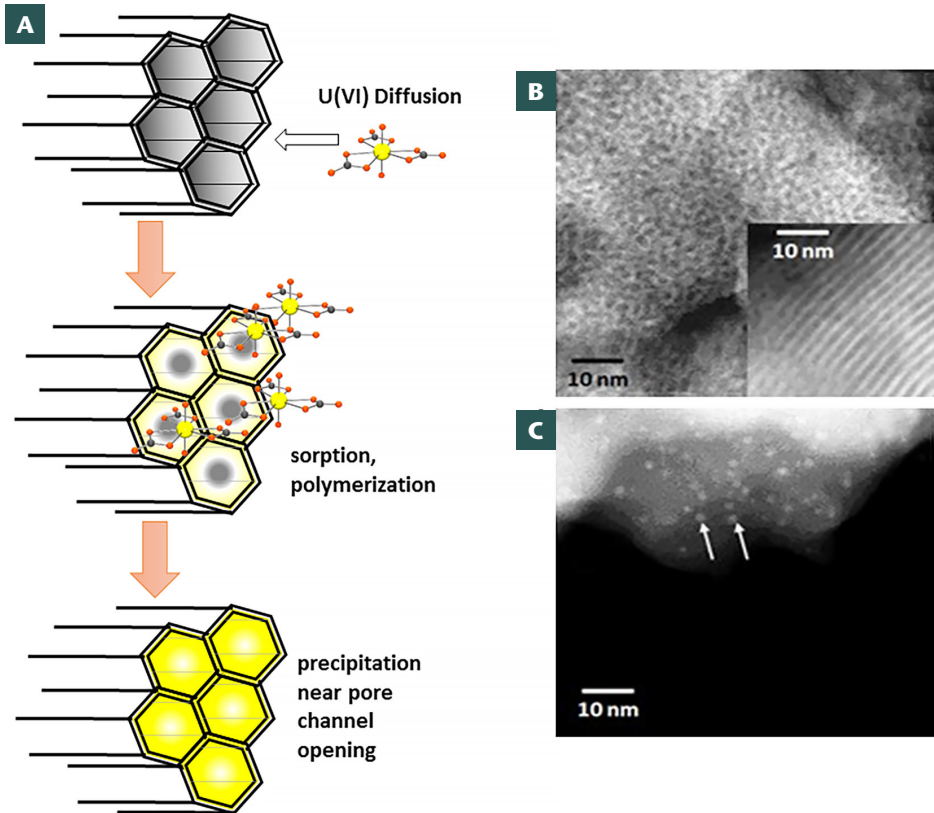
FIGURE 3 (**A**) Schematic of uranium (U) interacting with mesoporous silica. As U diffuses into the pore channels, sorption along the pore walls leads to polymerization and will prevent U from diffusing more deeply into the channels. As the concentration gradient near the channel openings increases, polymerization at these corner sites lead to a precipitation front that moves deeper into the channels along the pore walls through the polymerized surface species. (**B**) Transmission electron microscope image of washed, unreacted mesoporous silica. INSET: cross section of a particle exhibiting the regular channel array structure. (**C**) Mesoporous silica reacted with 10 mM U at pH 4.0 with no carbonate and no calcium present. The white arrows point towards some of the precipitates. MODIFIED WITH PERMISSION OF ELSEVIER FROM SINGER ET AL. (2014).

dating the relationship between coupled geochemical processes occurring in nano-size pore spaces and solute transport in confined pore spaces.

SOLUTE TRANSPORT AND REACTION IN CONFINED PORE SPACES

Pore spaces in mineral surface coatings with limited flow potential often create microaerophilic conditions: aerobic environments with oxygen at lower concentration than in the atmosphere. These conditions can affect the speciation of contaminants in pore spaces and promote the formation of minerals and the activity of bacteria that do not commonly occur in upper soil horizons due to high O_2 fugacity (FIGS. 4 AND 5). In one study aimed at determining the role of nano-size pore spaces on limiting contaminant transport, Singer et al. (2013) examined mineral surface coatings from a well-characterized field site to determine the rate-limiting causes of arsenic (As) sorption and redox processes within mineral coatings (FIG. 4). Sediments were obtained from the US Geological Survey's field research site at Cape Cod (Massachusetts, USA) and these sediments were exposed to synthetically contaminated groundwater solutions. Uptake of As(III) and
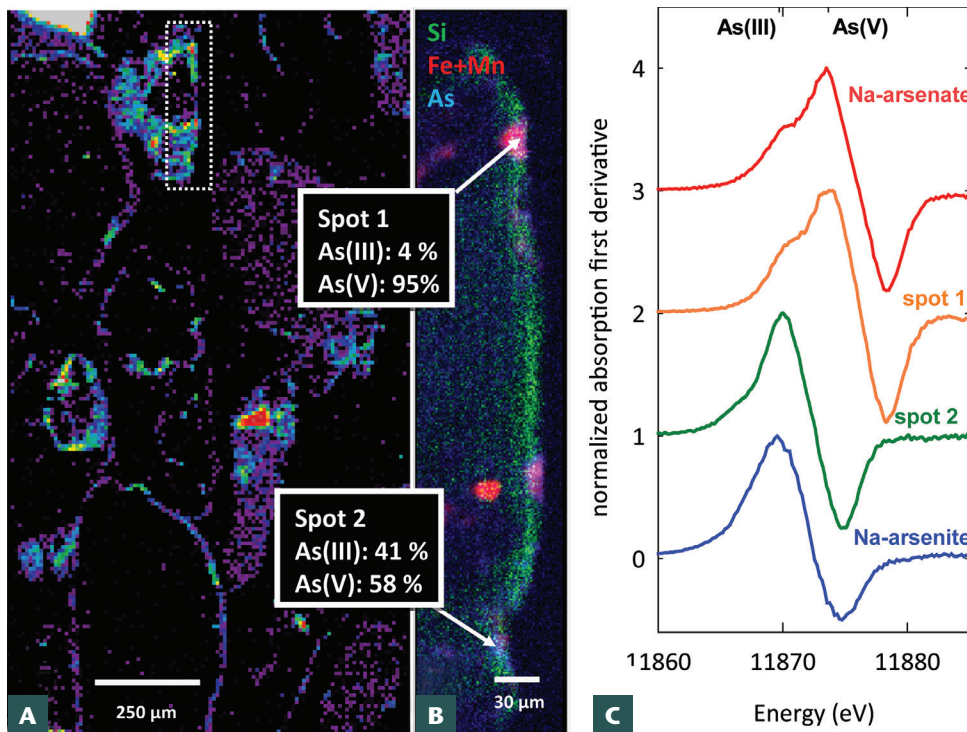
FIGURE 4 (**A**) Fe micro-X-ray fluorescence (micro-XRF) tri-colored map of characteristic coatings on primary quartz grains in a polished thin section. The map shows the distribution of silicon (green), iron plus manganese (red), and arsenic (blue). The white-dashed rectangle indicates the area shown in 4B. (**B**) Fe micro-XRF map of the rectangular section shown in 4A. Arrowed white-framed boxes indicate the amount of remaining As(III) in a Mn-bearing Fe-rich phase (likely nano-size goethite) determined from micro-X-ray absorption near-edge structure (μ–XANES) spectra shown in 4C. The amount of As(III) remaining is related to the extent of available surface area in contact with the exterior of the mineral coating (the blackish area is epoxy and denotes the original grain surface/solution contact). This sample was exposed to As(III) for 30 minutes. (**C**) First derivative As K-edge μ-XANES spectra of the approximate location where the arrows point in 4B. Sodium arsenite and sodium arsenate were used as As(III) and As(V) standards, respectively.
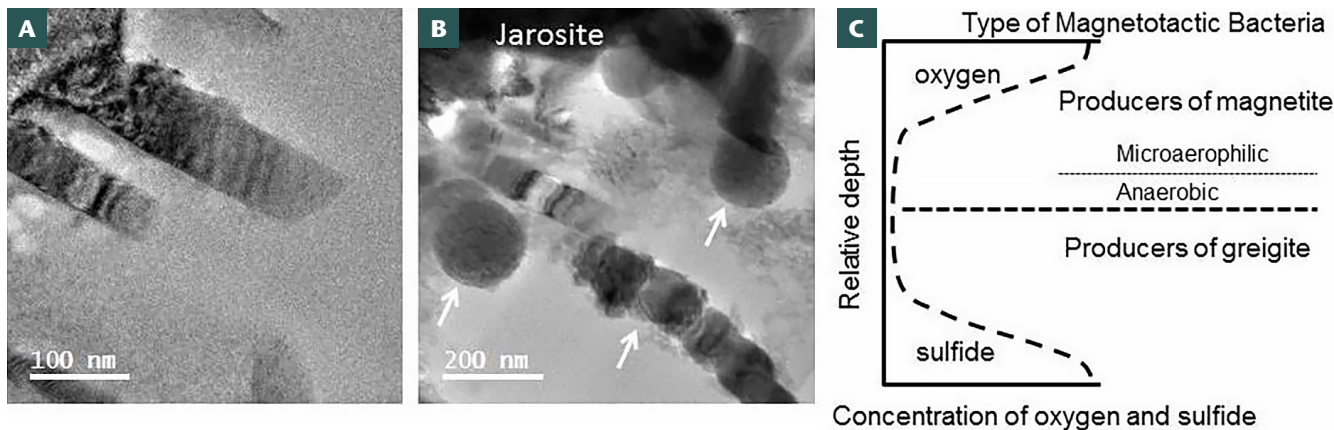
FIGURE 5 Microaerophilic conditions (aerobic environments with oxygen at lower concentration than in the atmosphere) in confined pore spaces in mineral surface coatings within the upper 5 cm of surficial soils can be identified on minerals and bacteria that form under wet and reducing conditions. (**A**) Transmission electron microscope (TEM) image of elongated crystals of green rust. Crystals of green rust commonly form in wet soils under reducing conditions but are observed in mineral surface coatings formed in the upper 5 cm of a soil profile. (**B**) TEM image of magnetosomes (chains of small cubes; indicated with arrow) in proximity to petrified magnetotactic bacteria. Also, spherical parti- cles of magnetite on the surface of jarosite, likely of abiotic origin (indicated with arrow). (**C**) A plot with the concentration of sulfide and oxygen versus depth. Higher concentrations of oxygen occur at shallower levels near the surface and higher concentration of sulfide occur at deeper levels. Note that the depth scale is undefined because it depends on the porosity of the material; it can be on the nanoscale in mineral surface coatings and on the centimeter- to meter-scale in soils. Magnetite-producing bacteria are only active at low concentrations of O_2 and sulfide. After Kopp and Kirschvink (2008).

As(V) into the (pre-existing) coatings was studied with a combination of high-resolution transmission electron microscopy and synchrotron techniques to assess concentration gradients and reactive processes, including electron transfer reactions. Arsenic was primarily associated with micron- to submicron aggregates of Mn-bearing nano-size goethite. Oxidation of As(III) by goethite was spatially limited to the exterior of the mineral coatings where goethite grains had exposed surface area. Little to no oxidation of As(III) to As(V) occurred deeper in the coating (Fig. 4). This work showed that microaerophilic conditions in the interior of mineral surface coatings can prevent oxidation of redox-sensitive elements and that mineral surface coatings are potentially both sinks and sources of contaminants (depending on the history of a contaminated site) and may need to be included explicitly in reactive transport models.

Minerals formed under microaerophilic conditions in mineral surface coatings have been identified by Schindler and Hochella (2015). For example, single crystals of fougèrite {[$Fe^{2+}_{6(1-x)}Fe^{3+}_{6x}O_{12}H_{14-6x}CO_3$]($H_2O$)$_3$}, which is also known as green rust, can occur in nano-size pore spaces of coatings from the upper 5 cm of surficial soils (Fig. 5A), despite fougèrite most commonly being formed in wet soils under reducing conditions. Similarly, petrified magnetotactic bacteria occur in proximity to earlier-formed jarosite [$KFe^{3+}_3(OH)_6(SO_4)_2$] in the same mineral surface coatings, despite such bacteria being commonly active under reducing to microaerophilic conditions (Kopp and Kirschvink 2008) (Figs. 2, 5B, 5C).

The above findings may be relevant for identifying and understanding potential storage places for carbon in surficial soils. The carbon budget of soils is controlled by the stability of natural organic material, which is commonly stabilized against microbial degradation in two ways: first, by adsorption on clay minerals and poorly crystalline Al and Fe oxides; second, by enclosure into micrometer-size pore spaces (Brantley et al. 2007; Chorover et al. 2007). On the basis of the observations made by Schindler and Hochella (2015), pore spaces in mineral surface coatings should be able to prevent the degradation of encapsulated carbon species, making such pore spaces potential locations for the long-term storage of carbon species in surficial soil horizons.

A NEW DIMENSION IN EARTH SCIENCES

Mineral surface coatings are structurally and compositionally complex and heterogeneous. They must be probed across a range of scales in order to determine their roles in the sequestration of carbon and in controlling contaminant transport in soils and aquifers. Chemical, mineralogical and biological processes within pore spaces of mineral surface coatings are an underexplored domain in understanding earth processes at the nanoscale. Future nano-mineralogical and geochemical studies of synthetic porous media , soils, and sediments will most likely discover many unexpected features in terms of adsorption, attachment and formation of contaminant-bearing aqueous species, colloids and mineral assemblages.

ACKNOWLEDGMENTS

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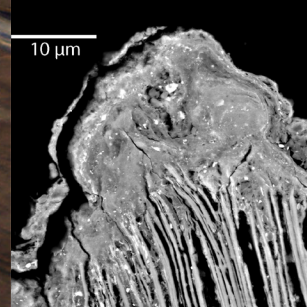
Backscatter electron image of Mn–Fe–Si case hardening biotite. Sample is from Tibet. Scale bar = 10 μm

Case Hardening: Turning Weathering Rinds into Protective Shells

Ronald I. Dorn[1], William C. Mahaney[2], and David H. Krinsley[3]

Case hardening is the process by which the outer shell of an exposed rock surface hardens due to near-surface diagenesis. Rock coatings and weathering rinds are distinct phenomena: rock coatings accrete on surfaces; weathering rinds derive from mineral dissolution and mechanical fracturing of the outer millimeters of a rock to create porosity. Ongoing reaction with rain, dew, or melted snow results in the downward migration of rock-coating components into weathering-rind pores. Initially, pore infilling protects the outer surface of the rock from flaking. As case hardening progresses, however, ongoing mineral dissolution underneath the case-hardened zone eventually leads to detachment. This sudden loss can destroy rock art, the surfaces of stone monuments, and facing stones of buildings.

KEYWORDS: rock coating, weathering rinds, case hardening, diagenesis

INTRODUCTION

Geochemical case hardening is the formation of a hard protective "shell" on the surfaces of rocks, and the process can dramatically change the appearance of Earth's landforms. The discontinuous spalling, or detachment, of these protective shells from the rock surface facilitates the formation of features such as limestone towers (Mitchell et al. 2003), pedestal rocks, tafoni (multiple small cave-like erosional features on rock surfaces) (Migoń and Goudie 2003), and a variety of other erosional forms (Conca and Rossman 1982). Case hardening alters historic buildings, including the pyramids of Egypt (Emery 1960), as well as prehistoric rock art (Whitley 2001). Planetary geologists have invoked case hardening to explain differential rock decay observed on Mars (Thomas et al. 2005).

THE ROLE OF WEATHERING RINDS

Weathering[4] rinds (Oguchi 2013) are ubiquitous terrestrial features that contain potential archives of information about rates of mineral alteration (Brady et al. 1999) and paleoenvironments (Mahaney et al. 2012). Mineral alteration is an important part of rind development (Navarre-Sitchler et al. 2011; Oguchi 2013). Rinds are formed as rock minerals are dissolved or mechanically fractured and transported away from the rock surface, leaving behind a porous layer. Trapped moisture derived from rain, dew, or snow increases rind porosity through mineral dissolution, after which a threshold is reached and the rind detaches from the less-decayed rock.
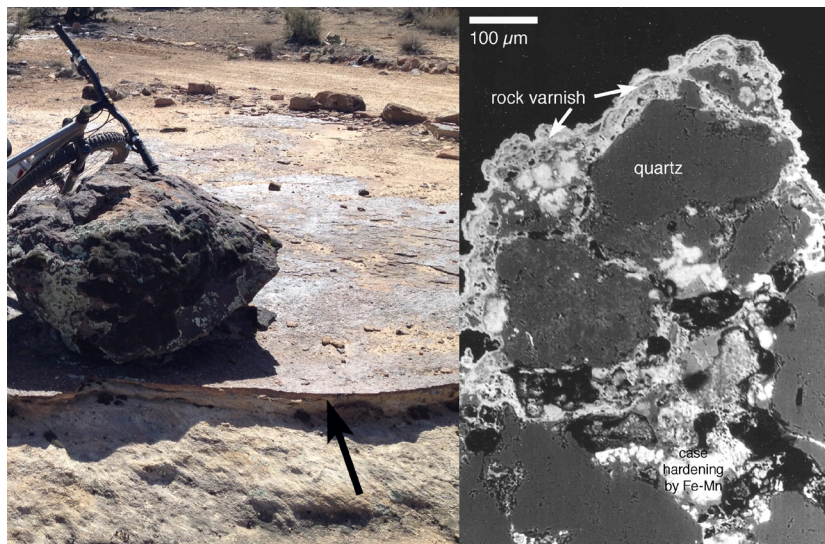
FIGURE 1 (**LEFT**) A case-hardened surface of sandstone (identified by the black arrow) at Gooseberry Mesa, Utah (USA). (**RIGHT**) Back scattered electron image of two hardening agents that indurate the sandstone surface: (1) an outer coating of rock varnish; (2) Mn–Fe, mobilized from the varnish, has infilled former pores in the weathering rind and now forms the cement binding quartz grains together.

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4 The general term 'weathering' is best expunged from Earth science for reasons elaborated elsewhere (Hall et al. 2012). Thus, the term 'rock decay' is used as a synonym for 'weathering' in this paper. But we are forced to use the general term 'weathering rind' because there is no better alternative at present.

Porosity in the outer few millimeters of a rock surface is a precondition for spalling of rinds (Gordon and Dorn 2005) and rindlets (Behrens et al. 2015) and for the development of case hardening. FIGURE 1 exemplifies the dual importance of porosity: (1) pores generate a weakness that can lead to surface detachment; (2) pores provide spaces that can be infilled by secondary minerals (e.g. Fe or Mn oxides, clays, silica) that then act to strengthen and protect the outer surface of the rock.

CASE HARDENING OF ROCK SURFACES

The outer surfaces of rocks can be hardened by "indurating agents"—the Fe or Mn oxides, clays, and silica minerals mentioned above. Although some believe that the source of the indurating agents are elements leached from the underlying rock and subsequently reprecipitated, there is very little evidence that indurating agents have an internal origin. Rather, externally derived abiotic and biotic materials (e.g. accreted rock coatings) increase the resistance to detachment in the outer few millimeters of a rock surface (Dorn et al. 2012).

A rock coating alone can sometimes produce case hardening to strengthen the outer surface of a rock. This is particularly true for organisms that grow on rock surfaces—such as fungi (see Gadd 2017 this issue) and lichens (Mottershead and Lucas 2000)—that form what are known as litho-biont rock coatings (Viles and Goudie 2004). Inorganic rock coatings can also case-harden surfaces (Dorn 1998). However, the hardening effect of a rock coating alone is minimal compared to when the constituents of the rock coating migrate downward into the porous weathering rind.
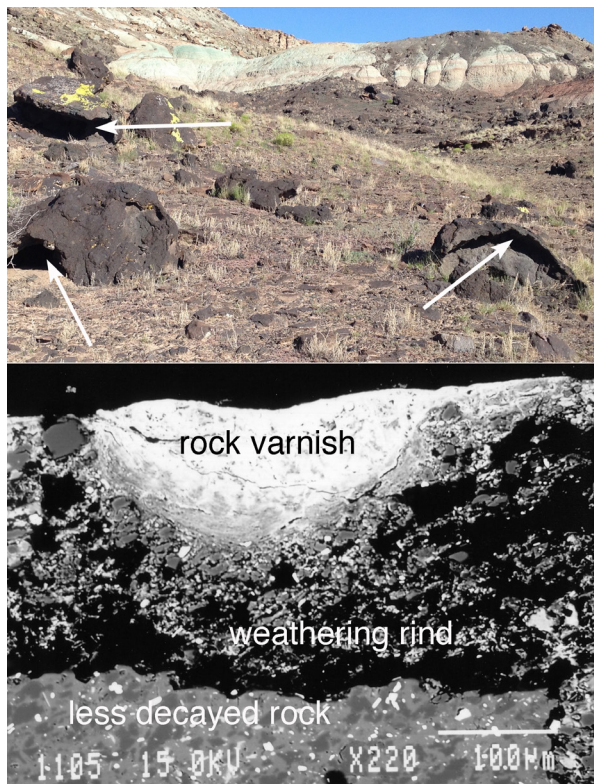
FIGURE 2 (UPPER) Hollowed out sandstone blocks (1 m diameter) from the Cedar Mountain Formation, Moab, Utah (USA). These blocks experience both case hardening of the outer shell and core softening (white arrows) of the block interior. (LOWER) Backscatter electron (BSE) image of the Mn–Fe-rich rock varnish that is responsible for case hardening the sandstone blocks. Spalling occurs along the base of the weathering rind where porosity (dark open spaces) is greatest.

Over time, rock coatings accrete on surfaces and, at the same time, mineral dissolution and mechanical fracturing of the outer millimeters of a rock creates porosity in the weathering rind. Ongoing precipitation of the coating results in the downward migration of rock-coating components into weathering-rind pores. At first, pore infilling protects the outer surface of the rock from flaking. As case hardening progresses, however, ongoing mineral dissolution underneath the case-hardened zone eventually leads to detachment (FIG. 2) and the sudden loss of features such as rock art, the surfaces of stone monuments, and the facing stones of buildings.

INFUSION OF WEATHERING-RIND PORES WITH THE PRODUCTS OF ROCK-COATING DIAGENESIS – EXAMPLES

Rock Varnish

Although rock coatings represent accretions that typically thicken over time, they also undergo diagenetic alteration. Rock varnish formation (a Mn-rich rock coating that forms in all environments) requires nanoscale diagenesis to mobilize Mn and Fe from bacterial casts into clay minerals (Dorn 1998; Krinsley et al. 2009). Some of the dissolution products of rock coatings mobilize downward and reprecipitate in weathering-rind pore spaces (FIG. 3).
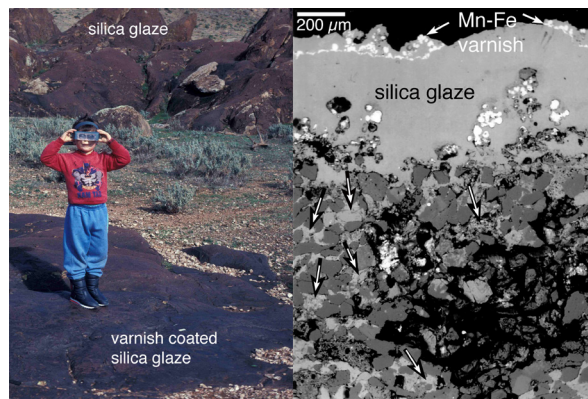
FIGURE 3 (LEFT) Silicified dolomite at Wharton Hills in South Australia covered by a 0.5 mm coating of dusky brown-colored silica glaze. The silica glaze itself is coated by a patchy Mn–Fe varnish that turns the rock surface black. (RIGHT) Backscatter electron image of the Wharton Hills rock coatings shows that dissolution–reprecipitation processes have operated in the pore spaces of the weathering rinds (black arrows with thin white center).

Petroglyphs

Whoopup Canyon in western Wyoming (USA) illustrates case hardening via the infusion of rock-coating materials into the underlying weathering rind (FIG. 4). Whoopup Canyon hosts a world-class petroglyph site, where the rock art experiences ongoing flaking (FIG. 4A), after which weathering-rind porosity increased to the point when detachment took place (FIG. 4B). The prehistoric peoples of Wyoming were able to create the engravings because there was a mixture of rock-coating materials that had been remobilized into the underlying weathering rind to case harden its surface (FIG. 4B).

Silica Glaze

Perhaps the most common agent of case hardening is silica glaze. Soluble aluminum–silicon (Al–Si) complexes $[Al(OSi(OH)_3)^{2+}]$ dissolve from the silica glaze and infiltrate down into pores in the weathering rind. The transition
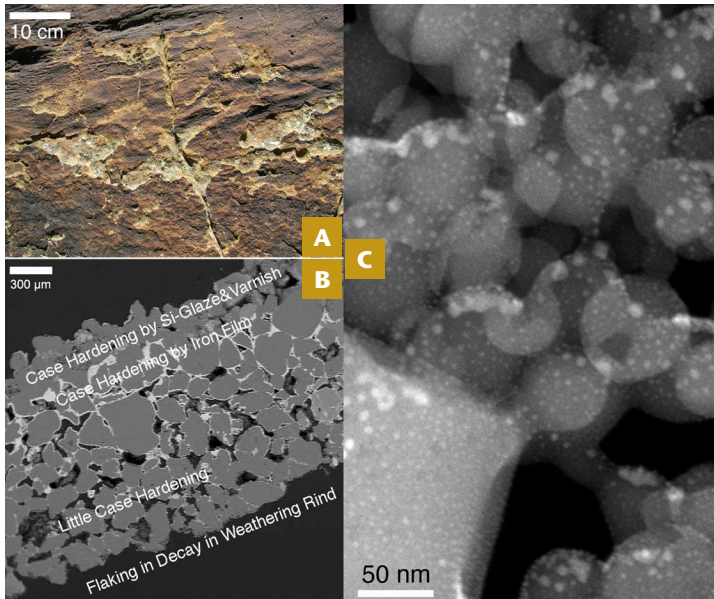
FIGURE 4 (**A**) Petroglyphs in Whoopup Canyon, Wyoming (USA) are case hardened by a mix of different materials that includes silica glaze, rock varnish, and iron films. Underneath this case-hardened surface, dissolution of the rind continues until the petroglyph experiences detachment. (**B**) Backscatter electron image of the case-hardened surface. This detachment surface derives from one of the flaked-off surfaces in 4A. (**C**) High-resolution transmission electron microscope image of silica glaze spherules deposited in a weathering-rind pore. Sample is from Tibet.
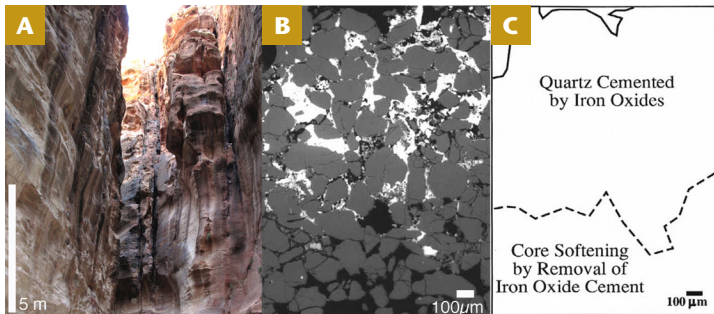
FIGURE 5 (**A**) Dark streaks on the sandstone at Petra (Jordan) formed, at least partially, of iron oxides. (**B**) A backscatter electron image shows that iron oxides (white) have been reprecipitated into the weathering rind, infilling pore spaces and indurating the rock face. (**C**) Map of the structural zones in the rind shown in 5B. Core softening of the weathering rind beneath the iron oxide cement is an important part of rock-face spalling.

between complete and partial wetting on silica surfaces occurs at about 20–70 nm for liquid droplets. Upon crossing this transition, a metastable wetting film is ruptured, initiating the formation of silica glaze through spheroid deposition (Dorn 1998). This explains the size of the silica spherules (Fig. 4C) being deposited in weathering rinds, as discovered through high resolution transmission electron microscopy analysis of a sample from the Ashikule Basin in Tibet (Langworthy et al. 2010).

Dark Streaks on Cliffs

Water streaks on cliff faces have to be one of the most photographed contexts involving case hardening. It is often difficult to discern the reason for these dark streaks in the field. Although these dark streaks are often attributed to rock varnish (sometimes termed "desert varnish"), fungi, lichens, oxalate, iron films, organics embedded in silica

FIGURE 6 (**A**) Surficial dark streaks (indicated by arrow) that impregnate the sandstone of Sedona, Arizona (USA) consist of heavy metals (mostly Fe and Mn) that have been mobilized from rock varnish. (**B**) A second outcrop of sandstone from Sedona, Arizona (USA), showing similar dark streaks to 6A. (**C**) Backscatter electron (BSE) image of a sample collected from the arrowed location in 6A. (**D**) Map explaining the structural and compositional features of the BSE image shown in 6C. The Mn and Fe have replaced the former silica cement of the sandstone and, thus, case hardening the outer surface of the cliff.

glaze also produce streaks of similar dark appearance. Case hardening as a result for iron oxide development can also be a cause of streaks (Fig. 5), or streaks can result from a mixture of manganese and iron oxides (Fig. 6).

Pedestal Rocks

As exemplified in Figures 1–6, case hardening displays a considerable range in thickness, from tens to hundreds of micrometers. However, case hardening does not have to be particularly thick to indurate a rock surface, as illustrated by the granite rocks of the MacDowell Mountains of Arizona (USA) (Fig. 7). The cap of the pedestal rock is coated with a < 10 μm layer of rock varnish (Fig. 7B), but it is not the varnish that creates the cap. The top of this pedestal has been indurated where biotite splitting has been slowed. Biotite hydration and oxidation is a common cause of the grussification of this granite, as illustrated by the splitting seen in Figure 7B. However, the top surface has partially stabilized where the remobilized constituents of the varnish (Fig. 7B) reprecipitated within the splitting biotite (arrow in Fig. 7B). This case hardening is not continuous, nor is it thick; however, the effect produces the observed cap to this "mushroom rock".
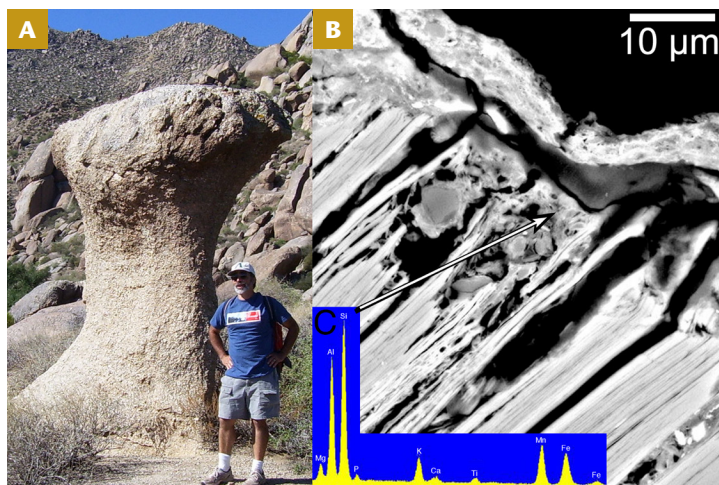
Figure 7 (**A**) Pedestal rocks commonly occur in granitic rock types. Example here is from the McDowell Mountains of Arizona (USA). The rough sides of this pedestal display a texture typical of grussification, here caused by the splitting of biotite minerals due to hydration and iron oxidation (**B**) Backscatter electron image of biotite splitting from the granite shown in 7A. Rock varnish forms on the surface of the pedestal and is then remobilized and precipitated into the biotite fractures (arrow in B). (**C**) Energy dispersive spot analysis reveals the composition of this material in the biotite fractures shown in 7B is similar to the overlying varnish: a mixture of Al and Si from clay minerals and Mn–Fe oxides.

CONCLUSION AND THE IMPORTANCE OF SCALE

Case hardening on Earth requires that two different types of processes operate in tandem: decay of the outer rim of the host rock, which opens up pore spaces, and the remobilization of rock-coating constituents that then infills these pores. Though the processes generating extraterrestrial forms are not known at the present time, case hardening forms certainly appear to exist on Mars and other non-terrestrial planetary bodies (Fig. 8).

The literature on case hardening (Table 1) ascribes induration to a wide variety of agents that operate on different rock types in vastly different environmental settings. Because
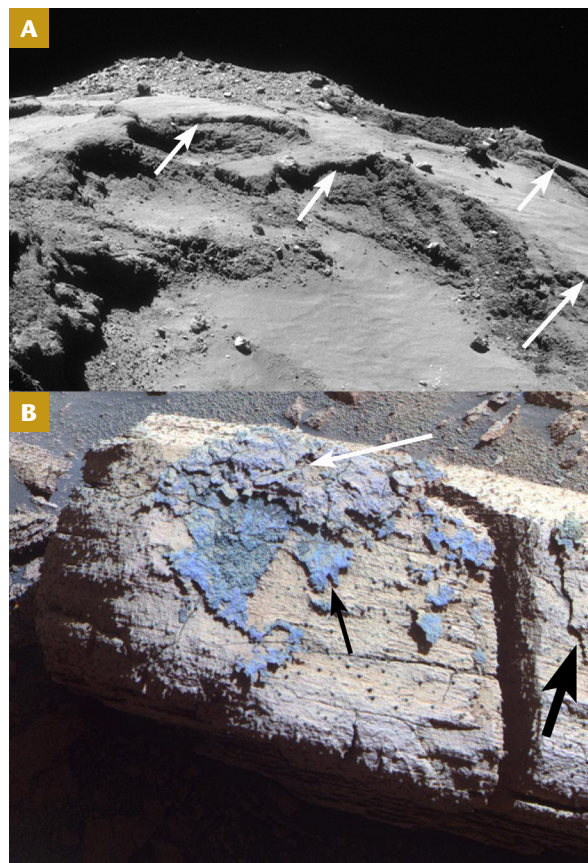
Figure 8 Examples of extraterrestrial case hardening. (**A**) Image of the surface of comet 67P/Churyumov–Gerasimenko (view is ~900 m across). While dust appears to generate smooth surfaces, unknown agents have created induration features, as evidenced by eroded edges of the crust (arrowed). Image from NASA's *Rosetta* spacecraft. (**B**) False color image of a boulder about 25 cm wide, nicknamed Chocolate Hills, on the edge of Concepción Crater on Mars. The thin black arrow identifies a section of case hardening where the coating could be related to impact melt. In addition, two other types of surfaces also display case hardening (white arrow and thick black arrow) with the cause(s) of the indurations unknown. Image by NASA's *Opportunity* rover.

of this, case hardening is sometimes offered as support for the notion of *equifinality*—that the same end state can be reached by many potential processes in an open system (Phillips 1997; Turkington and Paradise 2005). Consider, for example, the coated and case-hardened rock surfaces in Figures 2 and 3 that are visually similar in the field, but yet very different processes led to the accumulation of silica (Fig. 3) and rock varnish (Fig. 2) at the different sites. While dark streaks on the sandstone of Sedona (Arizona) and Petra (Jordan) (Figs. 5 and 6) appear similar in the field, case-hardening processes led to the accumulation of both manganese and iron at Sedona, but just iron at Petra. While case hardening and rock coating processes occur at nanometer and micrometer scales on Earth, they produce a broadly similar range of surface features that suggest a convergence of similar surface forms seen at the scale of meters on a rock face.

ACKNOWLEDGMENTS

TABLE 1	CASE-HARDENING STUDIES CONSISTENT WITH EQUIFINALITY		

Rock Type	Location	Case-Hardening Agents	Reference
Andesite	Yalour Islands, Antarctica	calcium phosphate	Arocena and Hall (2003)
Basalt	Hawai'i, USA	silica glaze	Gordon and Dorn (2005)
Dolerite	Antarctica	iron, silica	Conca and Astor (1987)
Granite	Alaska, USA	calcite	Yoshikawa et al. (2006)
Gypsum	Spain	lichen	Mottershead and Lucas (2000)
Lahar	California, USA	hydrous silica, ankerite	Arnold (1962)
Sandstone	Antarctica	silica glaze	Weed and Norton (1991)
Sandstone	Arizona, USA	heavy metal skins	Dorn (1995)
Sandstone buildings	United Kingdom	iron	McAlister et al. (2003)
Sandstone	Italy	iron oxide, calcite, quartz	McBride and Picard (2004)
Sandstone	Nevada, USA	kaolinite, calcite	Conca and Rossman (1982)
Trachyandesite	Tibet	silica glaze, rock varnish	Krinsley et al. (2009)

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Fungi, Rocks, and Minerals

Geoffrey M. Gadd[1]

Fungi are ubiquitous inhabitants of rock and mineral surfaces and are significant geoactive agents. Capable of numerous transformations of metals and minerals, fungi can prosper in the most adverse of environments, their activities underpinned by growth form and metabolism. Free-living filamentous species, microcolonial fungi and lichens can significantly change a rock's surficial structure and appearance, ranging from discolouration and staining to biodeterioration and the formation of new biogenic minerals and rock coatings. The presence and activity of fungi should be considered in any study of rock and mineral transformations that seeks to understand the biotic and abiotic processes that underpin geochemical change in the biosphere.

KEYWORDS: critical zone, biomineralization, bioweathering, geomycology, rock coating

INTRODUCTION

Fungi are significant geoactive agents and are particularly important in the critical zone. Fungi are microorganisms capable of numerous transformations of metals and minerals and can, therefore, significantly alter the surface structure and chemistry of rocks and their constituent minerals. "Metal transformation" here refers to the direct and indirect roles of fungi in altering metal speciation and mobility. Rock and mineral alteration processes are important in rock bioweathering because they contribute to the formation and development of mineral soil and global biogeochemical cycles for constituent elements, including element availability for living organisms (Sterflinger 2000; Burford et al. 2003; Gadd 2007).

The study of the roles of fungi in geologically relevant processes is termed geomycology, which is an important part of the more general area of geomicrobiology (Gadd 2007, 2010). Because the vast majority of organisms and cellular structures are microscopic, fungi are studied using techniques commonly employed in microbiology. Bioweathering, soil formation, metal and mineral transformations, and element cycling are the most obvious phenomena mediated by fungi. The additional significance of fungi as major decomposers of organic material in the biosphere underlines their crucial role in the cycling of all elements associated with organic matter. Living organisms can host most of the stable elements, and the release of these elements can result in further interaction with environmental components, including mineral precipitation. The characteristic utilization of organic substrates by fungi for growth and metabolism underpins their capacity for mediating geochemical change.

The kingdom Fungi is extraordinarily diverse, with some estimates reaching several million species. While mushrooms, brackets, puff balls and lichens may be obvious macroscopic forms, most fungi are microscopic, ranging from unicellular yeasts to those with a branching filamentous lifestyle exhibited by the vast majority. Even mushrooms and toadstools arise from such a filamentous network (called the mycelium) that may occupy a large volume of the substrate. The filaments are called hyphae and these grow from the tip forward (apical growth).

Fungi are eukaryotic organisms, i.e. their cells contain membrane-bound organelles and clearly defined nuclei, making them distinct from bacteria and archaea (prokaryotes). Their lack of chlorophyll, as well as certain structural, growth and metabolic characteristics, separates them from plants and animals, though it is animals that are their closest evolutionary relatives. The most significant environmental roles of fungi are as decomposers of organic material and as animal and plant pathogens and symbionts. But there is a growing awareness among scientists that fungi are also significant geoactive agents. However, the demarcation between fungal and bacteriological research and the wider range of prokaryotic metabolic diversity has ensured that the geoactive significance of fungi has been largely unappreciated in consideration of biosphere processes. A recent collection of geomicrobiology reviews completely excluded fungi, even to the extent of defining "microbes" as being only bacteria and archaea (Druschel and Kappler 2015).

The ecological success and geoactive properties of fungi are underpinned by their growth habit and metabolism and their ability to form symbiotic relationships with other organisms, e.g. lichens and mycorrhizas. The vast majority exhibit a filamentous, branching mode of growth and have a range of sensory mechanisms that enables them to explore their environment, locate nutrients and avoid stress. Additional physiological and morphological responses can also be involved in survival, such as the production of black melanized cell forms that are resistant to thermal fluctuations, desiccation and ultraviolet irradiation (Gorbushina 2007).

Lichens are a fungal growth form, consisting of a symbiotic partnership between a fungus and a photosynthetic organism – either an alga or a cyanobacterium, but sometimes both. It is now known they can also contain a yeast as another fungal partner. Lichens are pioneer

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colonizers of rocks and are the initiators of bioweathering biofilms that are involved in the early stages of mineral soil formation. Symbiotic root-associated mycorrhizal fungi (outside the scope of this article) are associated with the majority of plant species and are responsible for major mineral transformations and redistributions of essential metals and phosphate in the soil (Gadd 2007). Fungi are chemoorganotrophs, which means that they use carbon-containing organic compounds for growth and energy generation, and they excrete extracellular metabolites, such as organic acids, which are key to their interactions with rocks and minerals. Concrete, rock and mineral substrates used in buildings, monuments, statues, gravestones and other constructions of cultural heritage are also subject to fungal colonization and transformation (Gadd 2017). In such locations, fungi are often the most visible and destructive of the colonizing microbiota.

FUNGI ON ROCK SURFACES

Free-living and symbiotic fungi are ubiquitous and are often the dominant inhabitants of rock and mineral surfaces and outer layers. Fungi may, in fact, be the most significant organisms in nature that can biodeteriorate rocks and minerals (Warscheid and Braams 2000).

A capacity for morphological and physiological adaptation ensures that fungi are found even in the most hostile of environments—such as deserts, polar regions, and polluted environments—where, among other stresses, they may be subject to extremes of temperature, solar irradiation, and water availability. While most fungi are aerobic, it is now known that they have a significant presence in locations not usually regarded as prime fungal habitats, e.g. deep aquatic sediments, hydrothermal vents, and the igneous oceanic crust, where they may exist in symbiosis with prokaryotes (Iversson et al. 2016).

Although a variety of nutrients may be available on rock surfaces (e.g. airborne dust particles, industrial and domestic emissions and pollutants, and exudates from microbes, insects and animals), many fungi can grow in the presence of very limited amounts of nutrient. Diverse fungal communities are found, and there may even be some mineralogical control on the structure and diversity of rock-inhabiting populations. Colonization and metabolic activity can be affected by rock porosity and geochemical heterogeneities, which may provide specific nutrients and essential metals. For example, fungi that preferentially colonize a pegmatitic granite may have done so in response to the elemental constituents of the individual mineral components (Gleeson et al. 2005). This suggests that the organisms are selectively bioweathering minerals to release essential elements (e.g. potassium). Such effects of the rock substrate on fungal community composition may not be so obvious in rocks of lower heterogeneity (e.g. sandstone).

Lichens

Lichens are probably the most obvious fungal inhabitants of rock surfaces (Fig. 1). They are, therefore, intimately associated with elements that, besides O, account for over 99.9% of crustal rocks (i.e. Na, Mg, Al, Si, P, K, Ca, Ti, Mn, Fe). The nature of the rock can influence lichen communities, and this may be particularly evident on metalliferous substrates (Purvis and Pawlik-Skowronska 2008). Lichens exert physico-chemical changes on a rock substrate and interact with other rock-inhabiting microorganisms. The photosynthetic symbiotic partner of the lichen provides carbon for the fungus, while, if present, nitrogen-fixing cyanobacteria enrich the nitrogen status of the symbiosis

FIGURE 1 Rock surface completely covered with multiple lichen species in Wester Ross (Scotland). Scale bar ~3 cm. IMAGE BY G.M. GADD.

and microenvironment, enhancing further biofilm development by free-living organisms.

The surface area of the terrestrial lithosphere colonized by lichens is colossal. Many lichens form an intimate association with outer rock layers, something that dramatically alters the rock's appearance and weathering rates. In contrast to bioweathering, the concept of "bioprotection" is the ability of lichens, and other biologically initiated rock crusts, to stabilize rock surfaces and protect against further erosion. Lichens also entrap airborne mineral particles and pollutants (de los Rios et al. 2002). Many thousands of lichen species are known as rock inhabitants, although relatively little is known about their geochemical activities, and they are quite unappreciated in geobiology, despite the fact that the lichen-rock system provides a fundamental paradigm model for microbial interactions with rock and mineral substrates (Banfield et al. 1999). As a result of lichen bioweathering, many rock-forming minerals exhibit extensive surface alteration, biodeterioration and chemical transformation (Chen et al. 2000).

Lichens that live on rocks are known as "saxicolous" lichens, and include all the distinct morphological forms that occur in lichens (crustose, foliose, and fruticose) (Chen et al. 2000; de los Rios et al. 2002). Crustose lichens form a crust on or beneath the rock and are tightly attached across their entire lower surface, becoming fully integrated within the stone substrate (Fig. 2). Foliose (leaf-like) and fruticose (bush-like) lichens attach to rock surfaces by only a proportion of their underside (de los Rios et al. 2002). The areas of attachment of lichens to rocks are where significant geochemical transformations occur, and where free-living cyanobacteria, bacteria, algae and fungi can also be involved in altering a rock substrate (de los Rios et al. 2002; Gadd 2017). Some lichens (especially crustose species) are epilithic (surface dwellers) and/or endolithic (interior dwellers), with cryptoendoliths occupying structural cavities, chasmoendoliths inhabiting fissures and cracks, and euendolithic forms capable of active rock penetration (Wierzchos et al. 2012). These terms are also used for other rock-inhabiting microorganisms, although there are many overlaps, even for a given species. Colonization of the rock interior may provide protection from environmental extremes, an example being the lichen-dominated cryptoendolithic communities that are widespread in Antarctic deserts. Such endolithic microhabitats may include lichenized and non-lichenized fungal hyphae (Wierzchos et al. 2012).
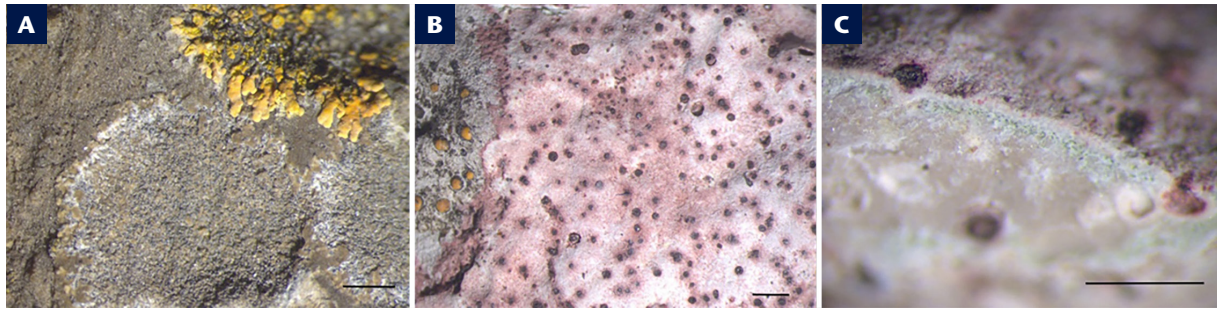
FIGURE 2 Crustose lichens on calcareous rock showing dissolution and integration with the rock. (**A**) *Caloplaca erodens* Hafeliner can dissolve a rock surface, turning it mealy and depressed. The grey particles belong to the lichen structure. The yellow colony in the top-right is a different species. (**B**) *Verrucaria maura* Obermayer 11298 becomes tightly integrated with the rock surface, forming a lithocortex. The black spots are apical parts of perithecia (reproductive structures containing fungal spores). When perithecia decay, they leave distinct pits in the rock surface. (**C**) The lithocortex formed by *V. maura* which develops from bioweathered rock material. The small dark dots are the algal symbiont occurring as single cells or clusters of cells. Scale bars all 1.0 mm. IMAGES COURTESY OF MARTIN GRUBE (KARL-FRANZENS-UNIVERSITÄT, GRAZ, AUSTRIA).

Microcolonial fungi

As well as free-living fungi, many of which may be of soil origin, there are a particular group of fungi that inhabit rocks known as the microcolonial fungi (FIG. 3). These do not exhibit the hyphal mode of growth but produce unicellular yeast-like and microcolonial growth, occurring as small black melanized colonies. This results in dark brown to black discolouration on colonized surfaces (Marvasi et al. 2012). This growth habit confers a high degree of resistance to environmental stresses and these organisms are considered the most persistent inhabitants of exposed rock surfaces. Filamentous hyphae may develop from these colonies and penetrate further (several mm to cm distances) into the rock through fissures and cracks, as well as by intracrystalline penetration. The interactions of microcolonial fungi with the rock substrate can lead to a variety of surface coatings or varnishes through the accumulation of metals and minerals in cell walls and extracellular materials (Gorbushina 2007).

Microcolonial fungi can cause "micropitting" in rocks, which leads to cavities that can contain the fungal colonies. The mechanism used by microcolonial fungi to produce these micropits appears to be by mechanical destruction through intracellular turgor (= hydrostatic) pressure and extracellular polysaccharide production rather than by the acid dissolution mechanism used by many other types of fungi (Marvasi et al. 2012). Microcolonial fungi may also form casual mutualistic associations with algae in rock crevices in order to obtain carbon from their photosynthetic partner (Gorbushina 2007).

The biodiversity of microcolonial fungi is large and severely underestimated: only a relatively small number of species have been fully characterized. Nevertheless, several hundred strains have been documented, and numerous novel genera have been discovered.

MECHANISMS OF INTERACTION WITH ROCKS AND MINERALS

Fungal colonization can result in physical and biochemical effects on rocks, these effects being influenced by the rock's chemistry and mineralogy. The presence of weatherable minerals, such as feldspars, may increase susceptibility to attack (Warscheid and Braams 2000). Transformation mechanisms involve physical and biochemical processes. These processes are not mutually exclusive: rather, they are generally interlinked.

Physical mechanisms include penetration by the hyphae along points of weakness, or by direct tunnelling or boring, especially in a weakened or porous substrate (Jongmans et al. 1997; Hoppert et al. 2004). Weakening of a mineral lattice can also occur through wetting and drying cycles and subsequent expansion or contraction of the biomass. Lichens can cause mechanical damage, such as disaggregation and exfoliation. This can occur by penetration of their anchoring structures, e.g. rhizines in foliose lichens, between grains and cleavage planes, and through expansion/contraction of the thallus (= vegetative body) on wetting/drying cycles (Chen et al. 2000). Separated rock and mineral grains can be incorporated into the thallus, as well as secondary mineral products (de los Rios et al. 2002) (FIG. 4). These effects, in addition to removal of the lichen itself by animals and the weather, can lead to visible damage to a rock in just a few years (Gadd et al. 2014).
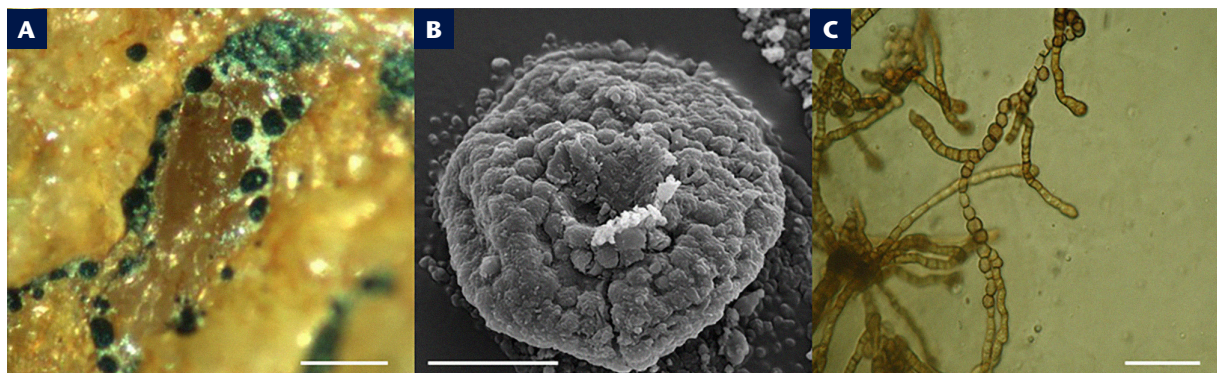
FIGURE 3 Colony appearance, structure and cell form in microcolonial fungi (MCF). (**A**) Pinhead-size MCF colonies on rocks from the central Namib desert (southwest Africa). Scale bar 150 µm. (**B**) Scanning electron microscope image of a typical fungal microcolony consisting of yeast-like melanized cells. Scale bar 30 µm. (**C**) Light microscope image of typical MCF cell form in culture. Scale bar 50 µm. IMAGES COURTESY OF ANNA GORBUSHINA (FREIE UNIVERSITÄT BERLIN, BERLIN, GERMANY).
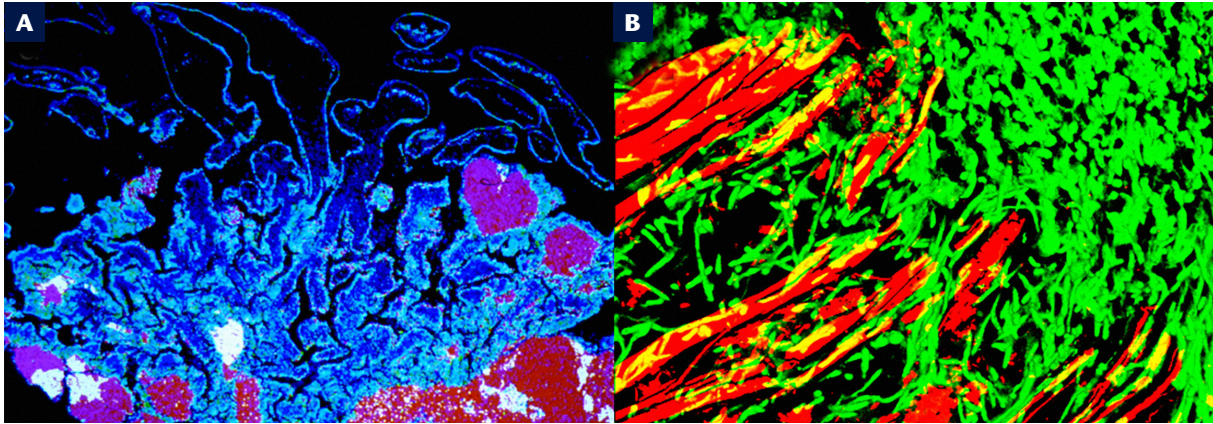
FIGURE 4 Transverse sections of lichen interacting with a granitic rock and a mica. (**A**) Artificially coloured scanning electron microscope (in back-scattered electron mode) image of the lichen thallus and granite interface. The blue is the lichen thallus, the fragments in red and pink are feldspar, and white is quartz. Scale bar 0.5 mm. (**B**) Superimposition of two images: one from the contact zone between the lichen fungal partner (mycobiont) and the mica obtained using scanning electron microscopy in back-scattered electron mode, the other being the same sample observed with confocal laser scanning microscopy. Red indicates the mica and oxalates; green (and yellow) corresponds to the mycobiont. Scale bar 40 μm. IMAGES COURTESY OF CARMEN ASCASO AND JACEK WIERZCHOS (MNCN, CSIC, MADRID, SPAIN).

Other physical effects are caused by a lichen's cell turgor pressure, its exopolysaccharide production, and lichen-induced secondary mineral formation. Secondary mineral formation through reaction of lichen-excreted organic acid anions with cations from the rock can result in "efflorescence", causing blistering, scaling, granular disintegration, and flaking (or "spalling") of the rock's outer layers. This is often considered to be a major mechanism of rock decay (Ranalli et al. 2009).

Biochemical weathering of rock and mineral substrates occurs through excretion of H^+, CO_2, organic acids, siderophores, and other metabolites, and this produces pitting, etching or dissolution (Banfield et al. 1999; Gadd 2010). Some organic metabolites effect dissolution by metal complexation and removal of these complexes from the mineral in a mobile form. Siderophores are Fe(III)-binding compounds excreted by organisms, but siderophores can also interact at lower affinity with other metals. Biogenic organic acids are very effective at mineral dissolution and are one of the most damaging agents of rock and mineral substrates, clearly underlining the importance of fungi in biochemical weathering (Gadd 2007). Of the suite of organic acids produced by fungi, oxalate is of major significance because of its ability to form metal complexes, resulting in mineral dissolution, and to cause physical damage by forming secondary metal oxalates that can expand in pores and fissures (Gadd et al. 2014). Citric and gluconic acid are other significant fungal metabolites. Oxalic acid is probably the most significant bioweathering agent produced by lichens, although lichens also produce a plethora of other compounds, termed 'lichen acids' (mainly polyphenolic compounds), which cause damage at the stone/lichen interface (Adamo and Violante 2000). In some extreme cases, and depending on the rock substrate, up to 50% of certain lichen thalli may comprise metal oxalates, which are the main secondary crystalline products of lichen bioweathering (Purvis and Pawlik-Skowronska 2008).

Biomineralization is the biologically mediated formation of minerals, and this process forms a core component of bioweathering of rocks and minerals. Fungal biomineralization can result from the oxidation or reduction of a metal species (which leads to altered solubility of that species) and to fungal metabolite excretion (e.g. oxalate). For example, soluble Mn(II) can be oxidized by many microbes, including fungi, and this results in the formation of the black Mn oxides that are a common component of rock varnish. Other metabolites include respiratory CO_2, which can lead to carbonate precipitation. The release of metals from rocks in mobile forms from abiotic weathering or biologically mediated mechanisms can, therefore, result in a variety of secondary mineral precipitates that include carbonates, phosphates, oxides and oxalates (Gadd 2010; Gadd et al. 2014). Such biomineral formations may contribute to physical disruption, staining and discolouration, and rock coating development (Gadd 2007, 2017; Gorbushina 2007; Fomina et al. 2010).

Fungal tunnels within soil minerals have been explained as a result of dissolution and "burrowing" within the soil mineral (Jongmans et al. 1997). Tunnels may also result after fungal exploration of pre-existing cracks, fissures, and pores in weatherable minerals and from the formation of a secondary mineral matrix of the same or different chemical composition as the substrate, e.g. secondary $CaCO_3$ or an oxalate (Fomina et al. 2010). The formation of a secondary mineral matrix can result in the fissures and cracks becoming cemented with mycogenic minerals. After the death and degradation of the original fungal hyphae, tunnels of similar dimensions to hyphae are left within the minerals.

SPECIFIC EXAMPLES OF FUNGAL ROCK AND MINERAL TRANSFORMATIONS

Fungi are involved in many environmental mineral transformations, and the roles of plant-root symbiotic fungi in releasing phosphate and other nutrients from minerals is a major determinant of plant productivity. Many other transformations affect the structure and stability of rocks and minerals, leading to mineral dissolution and biodeterioration, as well as the formation of new minerals, crusts and coatings. It is likely that many more novel and exciting mycogenic biominerals await discovery.

Carbonates

Carbonates can be broken down by fungi, usually as a result of acid formation (Adamo and Violante 2000). Fungal attack of carbonate substrates (e.g. limestone) can result in diagenesis of these substrates to secondary minerals that include dolomite [$CaMg(CO_3)_2$], glushinskite ($MgC_2O_4 \cdot 2H_2O$), weddellite ($CaC_2O_4 \cdot 2H_2O$), and whewellite ($CaC_2O_4 \cdot H_2O$) (Burford et al. 2003). Many lichens can dissolve calcite in limestone and dolomite through oxalate
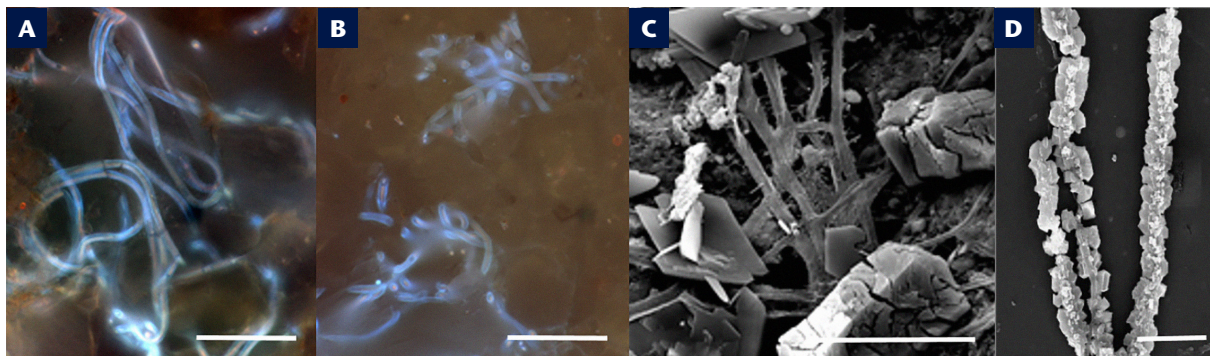
FIGURE 5 Fungal growth and biomineralization in limestone and dolomite. (**A**) Fluorescence microscope image of fungal hyphae (blue) growing between mineral grains in dolomite from Mount Nemo (Ontario, Canada). Scale bar 50 μm. (**B**) Fluorescence microscope image of hyphae (blue) growing in dolomite from Kelso (Ontario, Canada). Scale bar 50 μm. (**C**) Scanning electron microscope (SEM) image of in situ mineral precipitation (calcite and/or calcium oxalate) on fungal hyphae in Kelso limestone. (**D**) SEM image of calcite and calcium oxalate on hyphae of a *Serpula* species after growth in a limestone-amended microcosm. Scale bar 20 μm. Images Euan Burford and G.M. Gadd, unpublished and adapted from Burford et al. (2003, 2006).

production, subsequent precipitation of calcium oxalate occuring at the lichen–rock interface.

In contrast to dissolution, many microbes (such as cyanobacteria, bacteria and algae) mediate carbonate formation, and a significant proportion of insoluble carbonate at the Earth's surface is biotic in origin. Certain fungi can deposit calcium carbonate extracellularly (Burford et al. 2006; Li et al. 2015; Savkovic et al. 2016), although this is more clearly demonstrated in the laboratory than in the environment (Bindschedler et al. 2016). For example, a mixture of calcite $(CaCO_3)$ and calcium oxalate was precipitated on hyphae when selected species were grown in simulated limestone microcosms (Burford et al. 2006) (FIG. 5). In experiments by Li et al. (2015), fungi from calcareous soil precipitated calcite, strontianite $(SrCO_3)$, vaterite in different forms $[CaCO_3, (Ca_xSr_{1-x})CO_3]$ and olekminskite $[Sr(Sr,Ca)(CO_3)_2]$. However, despite the frequent presence of $CaCO_3$ in fungal-containing biofilms and crusts (FIG. 5), in situ direct demonstration of the role of fungi in carbonate formation is scarce. The formation of needle-fibre calcite has long been attributed to fungal activity in calcareous environments, although physico-chemical processes are also plausible (Bindschedler et al. 2016).

Oxalates

Calcium oxalate is the most common environmental form of oxalate (Gadd et al. 2014). Calcium oxalate is produced by many free-living and symbiotic fungi, being formed by the precipitation of soluble calcium with fungal-excreted oxalate (Adamo and Violante 2000). Fungi can also produce many other metal oxalates when they interact with minerals that contain metals, including Ca, Cd, Co, Cu, Mg, Mn, Sr, Zn, Ni and Pb (Gadd 2007; Gadd et al. 2014). Some secondary crystalline metal oxalates that have been associated with lichens include glushinskite (hydrated magnesium oxalate) on serpentinite and manganese ore, and moolooite (hydrated copper oxalate) on copper-containing rocks (Chen et al. 2000; Purvis and Pawlik-Skowronska 2008). In many arid and semi-arid regions, calcareous soils and near-surface limestones (calcretes), biomineralized fungal filaments occur secondarily cemented with calcite and calcium oxalate. Calcium oxalate can also be degraded to calcium carbonate, which may cement pre-existing limestones (Bindschedler et al. 2016). Many limestone and marble monuments develop orange-brown patinas, called *scialbatura*, on their surfaces. These mainly consist of calcium oxalate and calcium carbonate, and their formation by free-living fungi and lichens may provide surface protection (Savkovic et al. 2016).

Oxides

Several fungi can promote Mn(II) oxidation to black $Mn(IV)O_2$. In many cases, fungal oxidation is effected through production of hydroxycarboxylic acid metabolites such as citrate, lactate, malate, or gluconate. Fungal MnO_x material has a todorokite-like tunnel structure, which contrasts with other reported bacterial MnO_x materials which have layered birnessite-type structures. Some fungi can oxidize Mn(II) and Fe(II) in metal-bearing minerals such as siderite $(FeCO_3)$ and rhodochrosite $(MnCO_3)$ and precipitate them as oxides. Manganese and iron oxides are major components (20%–30%) along with clay (~60%) and various trace elements in the brown-to-black veneers known as desert varnish or rock varnish (Gorbushina 2007). Conversely, manganese-reducing microbes may mobilize oxidized or fixed manganese. Most fungi that reduce Mn(IV) oxides do so through the production of metabolites that can act as reductants, such as oxalate, which results in the formation of lindbergite (Mn oxalate dihydrate) (Wei et al. 2012).

Phosphates

Fungi can liberate orthophosphate from insoluble inorganic phosphates in rocks and minerals by producing acids or chelators (e.g. gluconate, citrate, oxalate, and lactate) which complex the metal and result in dissociation. Liberated phosphate can then be used as a nutrient by the fungi, or another organism, or can reprecipitate with other mobile metal species and so form metal phosphates. Fungal solubilization of rock phosphate results in reprecipitation of calcium oxalate, while fungal dissolution of pyromorphite $[Pb_5(PO_4)_3Cl]$ results in lead oxalate formation (Sayer et al. 1999). Many fungi are also capable of uranium oxide solubilization and can form secondary uranium phosphate minerals of the meta-autunite group: uramphite and/or chernikovite (Fomina et al. 2007). Fungi may also liberate orthophosphate from sources of organic phosphate in organic matter by means of phosphatase enzymes, the liberated phosphate then reprecipitates with other reactive metals. Several common soil fungi and yeasts can induce lead bioprecipitation as highly insoluble pyromorphite during growth on organic phosphates (Liang et al. 2016).

Silicates

Many lichens and free-living fungi play a role in silicate dissolution and therefore contribute to the genesis of clay minerals and to soil and sediment formation (Banfield et al. 1999; Adamo and Violante 2000). Etching may be observed on silicate surfaces after fungal colonization.

In Antarctic sandstone, cryptoendolithic lichens caused a reduction in cohesion between individual sandstone grains, which resulted in surface flaking (Chen et al. 2000). Silicate dissolution may release important nutrients that otherwise would remain bound (e.g. P, K and Fe). In lichen weathering of silicates, fungal extracellular polysaccharides can become mixed with calcium, potassium, iron, clay minerals and nanocrystalline aluminous iron oxyhydroxides. Biotite-group minerals $[K(Mg,Fe(II))_3AlSi_3O_{10}(OH,F)_2]$ can be penetrated along cleavage planes by fungal hyphae, partially converting biotite to vermiculite $[(Mg,Fe(II),Al)_3(Al,Si)_4O_{10}(OH)_2 \cdot 4H_2O]$. Depending on the species and the mineral substrate, clay minerals associated with lichen weathering also include kaolinite, halloysite, goethite $[FeO(OH)]$, illite, allophane and imogolite, with halloysite, kaolinite and vermiculite being the most common (Chen et al. 2000).

CONCLUSIONS

Fungi are critically important biotic agents of geochemical change, especially in the critical zone at the interface between the atmosphere, hydrosphere, biosphere, and lithosphere, and fungi can exist as rock coatings. They effect many metal and mineral transformations in rock substrates through their branching, filamentous mode of growth, their ability to morphologically adapt to adverse environments, their organic carbon-based metabolism that excretes a range of geoactive metabolites, and their symbi-otic relationships with other organisms (e.g. lichens and mycorrhizas). Such biotic processes can occur faster than purely abiotic changes. The full range of their activities and their proper significance in the environment, as well as their relationships with other geoactive microorganisms that inhabit rocks and minerals, requires further detailed study. Geomycology has an important role to play at the interface between biology and geology. There is a need for both biologists and geologists to broaden their intellectual scope and to initiate more interdisciplinary research and collaboration to achieve a fuller understanding of the roles that these remarkable organisms play in shaping our planet.

In brief, fungi rock!

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Marine Ferromanganese Encrustations: Archives of Changing Oceans

Andrea Koschinsky[1] and James R. Hein[2]

Marine iron–manganese oxide coatings occur in many shallow and deep-water areas of the global ocean and can form in three ways: 1) Fe–Mn crusts can precipitate from seawater onto rocks on seamounts; 2) Fe–Mn nodules can form on the sediment surface around a nucleus by diagenetic processes in sediment pore water; 3) encrustations can precipitate from hydrothermal fluids. These oxide coatings have been growing for thousands to tens of millions of years. They represent a vast archive of how oceans have changed, including variations of climate, ocean currents, geological activity, erosion processes on land, and even anthropogenic impact. A growing toolbox of age-dating methods and element and isotopic signatures are being used to exploit these archives.

INTRODUCTION AND OCCURRENCE OF MARINE Fe–Mn COATINGS

Seventy-one percent of the Earth's surface is covered by ocean, and vast areas of the global seafloor, including the deep-sea and shallower or near-coastal areas, are covered with iron–manganese oxide coatings. These oxides encrust the rocky surface of seamounts, forming so-called ferromanganese (Fe–Mn) crusts, or accrete around small solid nuclei, such as rock fragments or fish teeth, forming Fe–Mn nodules (FIG. 1). Due to their special physicochemical properties and slow growth rates, these crusts accumulate large quantities of trace metals from their environment (TABLE 1), including economically interesting elements such as Co, Ni, Cu, Mo and the rare-earth elements plus yttrium (REY) (Hein et al. 2000). As a consequence, Fe–Mn nodules and crusts have been intensively discussed as potential ore deposits for high-tech metals required for new and emerging technologies (Hein et al. 2013). Nearly 40 years ago, when scientific research on these marine encrustations was emerging (e.g. Bischoff and Piper 1979; Halbach et al. 1988), it was evident that these nano-structured layered materials also recorded changing environmental conditions during their growth and could provide exciting proxies for local, regional, and global changes in the oceans over millions of years.

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So-called hydrogenetic Fe–Mn crusts (FIG. 2) are composed of Mn oxides and Fe oxyhydroxides (Mn/Fe ratios mostly around 1–2) that precipitate from seawater and that are found throughout the world's ocean basins in water depths between 400–7,000 m on the flanks and summits of seamounts, ridges, and sediment-free plateaus (FIG. 1) (Hein et al. 2000). The most extensive and thickest crust occurrences are from the Pacific, which has the oldest oceanic crust and more seamounts than the Atlantic and Indian Oceans. Crusts have even been discovered in the polar regions, though these are much less studied. The low-crystallinity Fe–Mn oxide phases that form the crusts have large surface areas and are efficient sorbents for a wide variety of trace metals, which are scavenged from seawater and enriched within the oxide phases. These deep-water crusts grow incredibly slowly (a few millimetres per million years, mm/My). Crusts that are as thick as 25 cm have been found to 'house' archives up to 70 million years old.

Iron–manganese nodules (also referred to as 'manganese nodules') (FIG. 3) grow on the surface of abyssal plain sediments (FIGS. 1, 3) in water depths of 4,000–6,500 m where they cover vast areas of seafloor. For example, the Clarion–Clipperton Zone (CCZ) nodule field in the northeast equatorial Pacific covers about 5.9×10^6 km². Nodules often have a hydrogenetic component, reflecting the composition of and processes within the oceanic water column. However, in many areas, Mn nodules partly (e.g. CCZ nodules) (TABLE 1) or even largely (e.g. Peru Basin nodules) (TABLE 1) form by redox cycling of Mn, Fe, and associated metals during diagenetic processes in the sediment that are driven by microbial degradation of organic matter. In these types of nodules, the oxide phases and associated trace metals precipitate wholly or in part from the pore fluid. Their growth rates are of the order of a few mm/My (purely hydrogenetic) up to 250 mm/My (purely diagenetic), and ages of nodules with a diameter up to about 20 cm range up to ~12 My old.

Hydrogenetic Fe–Mn crusts form in ambient ocean waters, and these waters provide the only significant metal source. However, in areas of hydrothermal activity, such as mid-ocean ridges and island arc systems, another source of metals for Fe–Mn oxide coatings is hydrothermal fluids. These fluids are usually extremely rich in Fe or Mn, though not rich in many other metals. While a major portion of the metals precipitates in the form of sulfide or sulfate minerals, away from the vent source and after a significant
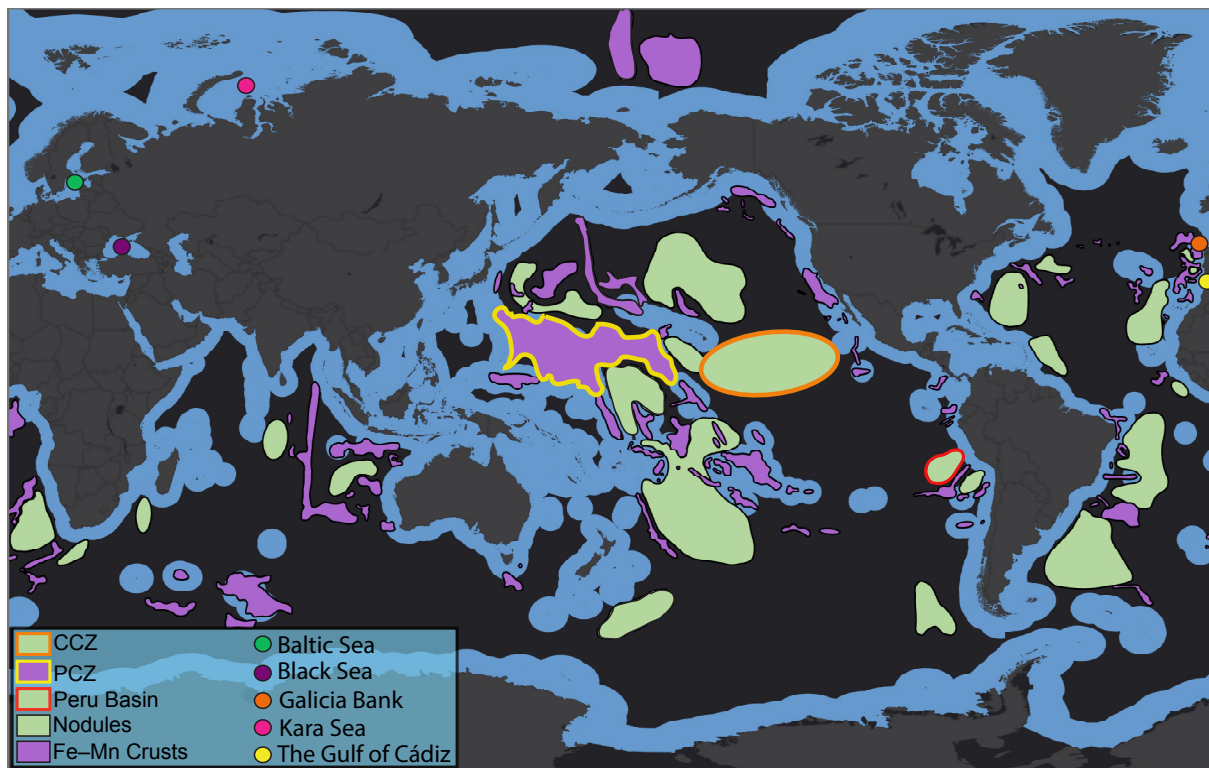
FIGURE 1 Global distribution of Fe–Mn coatings from both deep-ocean and shallow-water settings; blue is ocean areas within the 200-nautical-mile Exclusive Economic Zone of coastal nations, and black is oceanic areas beyond national jurisdictions. CCZ = Clarion–Clipperton Zone; PCZ = Prime Crust Zone. MODIFIED FROM HEIN ET AL. (2013).

degree of mixing with cold oxygenated (oxic) seawater, Fe and Mn dissolved in the hydrothermal plumes oxidize, scavenge other metals from ambient seawater, and settle in the form of hydrothermal or mixed hydrogenetic–hydrothermal encrustations. These 'mixed origin' rock coatings grow much faster (up to 125,000 mm/My) than crusts and nodules, and they archive information in their growth layers on the type and intensity of the source

hydrothermal activity (e.g. Usui and Nishimura 1992; Hein et al. 2008).

While most Fe–Mn crust and nodule occurrences are found in the deep ocean where sedimentation rates are low, and so allow for largely undisturbed precipitation over millions of years, shallow-water crusts and nodules exist in a number of places throughout the global ocean

TABLE 1 SELECTED ELEMENT COMPOSITIONS OF CRUSTS AND NODULES FROM AREAS OF THE GLOBAL OCEAN[a]

	Arctic Ocean		Atlantic Ocean		Indian Ocean		Prime Crust Zone[b]		South Pacific		CCZ[b] Nodules		Peru Basin Nodules[c]	Indian Ocean Nodules	
	Mean	N	Mean	N	Mean	N	Mean	N	Mean	N	Mean	N	Mean	Mean	N
(wt%)Fe	19.8	85	20.9	43	22.1	33	16.8	368	18.1	286	6.16	66	6.12	7.14	1,135
Mn	7.66	85	14.5	43	16.9	33	22.8	368	21.7	321	28.4	66	34.2	24.4	1,135
Si	11.1	85	5.21	43	6.78	33	4.04	309	4.75	255	6.55	12	4.82	10.0	36
(ppm)Co	1,501	87	3,608	43	2,956	33	6,655	368	6,167	321	2,098	66	475	1,111	1,124
Cu	646	83	861	43	1,114	33	982	368	1,082	321	10,714	66	5,988	10,406	1,124
Mo	209	83	409	43	416	33	463	334	418	67	590	66	547	600	38
Ni	2,310	83	2,581	43	2,396	33	4,216	368	4,643	321	13,002	66	13,008	11,010	1,124
Pb	238	87	1,238	43	1,366	33	1,636	332	1,057	113	338	66	121	731	38
Y	194	86	181	43	190	33	222	300	177	49	96	66	69	108	38
Zn	347	87	614	43	516	33	669	331	698	181	1,366	66	1,845	1,207	692
Ce	854	86	1,392	42	1,605	31	1,311	89	818	75	284	66	110	486	24
Nd	168	86	243	42	285	31	255	89	184	67	140	66	63	146	50

[a]Table modified from Hein et al. (2013) and Hein and Koschinsky (2014) and references therein. [b]Prime Crust Zone contains ~7.5 × 10^9 dry tons of crusts including 1.7 × 10^9 tons of Mn and 89 × 10^6 tons of Co + Ni + Cu in place metal; CCZ = Clarion–Clipperton Zone, which contains ~21 × 10^9 dry tons of nodules including 5.2 × 10^9 tons of Mn and 544 × 10^6 tons of Co + Ni + Cu in place metal (Hein et al. 2013); [c]Peru Basin data for a diagenetic nodule standard prepared by the Bundesanstalt für Geowissenschaften und Rohstoffe (BGR) (Germany) of a large, but unknown, number of nodules
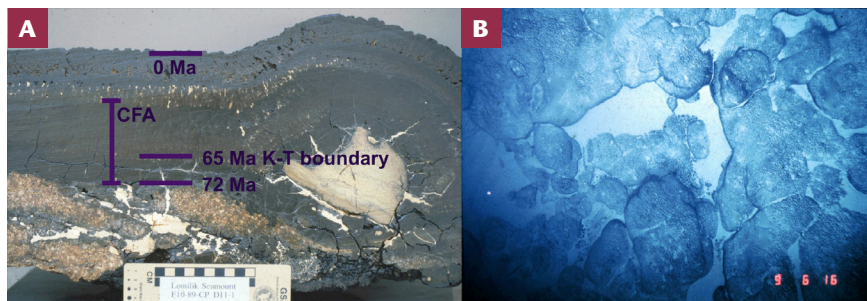
FIGURE 2 (**A**) Multilayered 18 cm thick Fe–Mn crust from the Pacific Ocean showing age profile and the section phosphatized by carbonate fluorapatite (CFA). (**B**) Photo of an Fe–Mn crust on the seafloor at Horizon Guyot, central Pacific. Area is ~3 m × 3 m. PHOTO CREDIT: USGS

(FIG. 1). These encrustations grow rapidly (in the range of 1,000–10,000 mm/My), have low concentrations of associated metals, and have much younger ages.

Marine Fe–Mn oxide coatings considered here, as well as micronodules and grain coatings in abyssal sediments, are considered to be the most important players in the geochemical balance of the oceans. They are a major sink of metals entering the ocean from terrestrial input, submarine weathering, and hydrothermal discharge. This keeps the levels of dissolved and bioavailable metals in the ocean low, in the range of nanomolar or picomolar concentrations. The important role of Fe–Mn encrustations for the depletion of many trace metals in seawater is impressively demonstrated in the distribution patterns of REY, which in seawater show a pronounced negative Ce anomaly, while hydrogenetic crusts have a large positive Ce anomaly produced by Ce acquired from seawater. Such specific accumulations of certain elements can also be used to discriminate between the different types of Fe–Mn oxide encrustations: hydrogenetic, diagenetic, or hydrothermal (Bau et al. 2014).
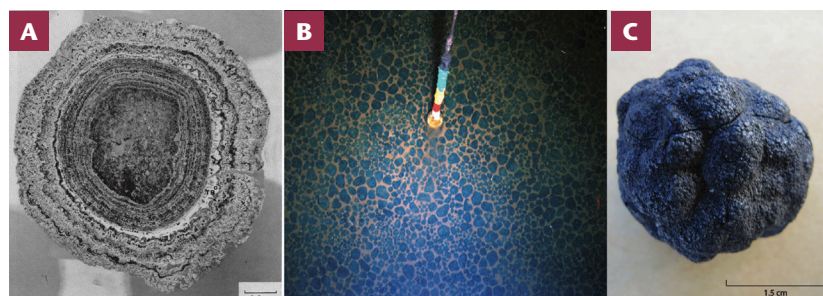

FIGURE 3 (**A**) Cross section of nodule showing fine laminations. FROM SOREM AND FEWKES (1979). (**B**) Nodules on the seafloor near the Cook Islands. Area is ~4 m × 4 m area. PHOTO CREDIT: JAMSTEC. (**C**) Typical black nodule from the Clarion–Clipperton Zone (see FIG. 1).

THE FORMATION OF MARINE Fe–Mn ENCRUSTATIONS: CHEMICAL OR BIOLOGICAL SIGNATURES?

Inorganic Precipitation Model

The generally accepted model for the formation of hydrogenetic Fe–Mn nodules and crusts is based on inorganic chemical sorption and precipitation processes in the oceanic water column (FIG. 4). These sorption and precipitation processes are seen as a prerequisite for a straightforward interpretation of crust composition with respect to environmental conditions during formation of individual growth layers. Manganese and Fe oxide colloids in oxic seawater are characterized by high specific surface areas (mean 325 m^2 g^{-1}) and opposite surface charges (Mn oxide is strongly negatively charged, Fe oxyhydroxide is slightly positively charged), making them excellent scavengers for both cationic (e.g. Cu^{2+}, Ni^{2+}) and anionic (e.g. AsO_4^{3-}) metal species (Koschinsky and Hein 2003; Hein and Koschinsky 2014). Uncharged species (e.g. $Ti(OH)_4$) form covalent bonds with functional groups of the low-charged Fe oxyhydroxide surface. Some redox-sensitive elements, such as Co, Ce, Te, and possibly Pt, are enriched during incorporation on the crust via surface oxidation processes with Mn oxide. These processes allow for the acquisition of high concentrations of many elements that vary on a regional scale and by deposit type (TABLE 1). This genetic model allows for an interpretation of the crust composition with respect to water masses that originate from different areas, to climatic conditions that will influence element input, to environmental conditions, and to redox conditions impacting the accumulation of redox-sensitive elements.

Diagenetic nodules, in contrast, do not provide a direct record of seawater composition but reflect processes in the surface sediment related to productivity and carbon fluxes. Diagenesis may take place under oxic or suboxic conditions, which has an impact on the type of Mn-oxide minerals that form the Fe–Mn nodules.

Potential Impact of Biological Processes

Although evidence for rich microbial life in and on marine Fe–Mn oxide coatings has been increasing, how these biota contribute to mineral formation and whether these processes are metabolically controlled remain poorly understood. Certain species of bacteria and fungi are known to accelerate the oxidation rate of Mn^{2+}; hence, Mn oxides in natural environments could largely be of biogenic origin (Tebo et al. 2004), with implications for the incorporation of trace metals. While this appears to be a reasonable argument for freshwater and shallow-water marine systems with high productivity, it remains an open question whether this is also applicable for slow-growing deep-ocean Fe–Mn oxide encrustations.

Without doubt, bacteria live in and on Fe–Mn nodules and crusts, including Mn oxidizers and reducers, but there are also bacteria that are unrelated to Mn redox cycling (Ehrlich 2001). Within nodules, free-living and biofilm-forming bacteria provide the matrix for Mn-oxide deposition, and coccolithophores in crusts have been suggested as bio-seeds for Mn-oxide precipitation (Wang and Müller 2009). In more recent studies using molecular 16S rRNA gene techniques (the part of the DNA commonly used for bacteria and archea taxonomy), nodule-specific Mn(IV) reducers and Mn(II) oxidizers identified in nodules were not found in the surrounding sediment: this could be viewed as an argument for a biologically driven closed Mn cycle inside the nodule that may be relevant to their formation (e.g. Blöthe et al. 2015). A shift in dominant bacterial metabolism from metal oxidation on the exterior of nodules to metal-oxide reduction in the inner part of nodules has been suggested to explain the different micro-
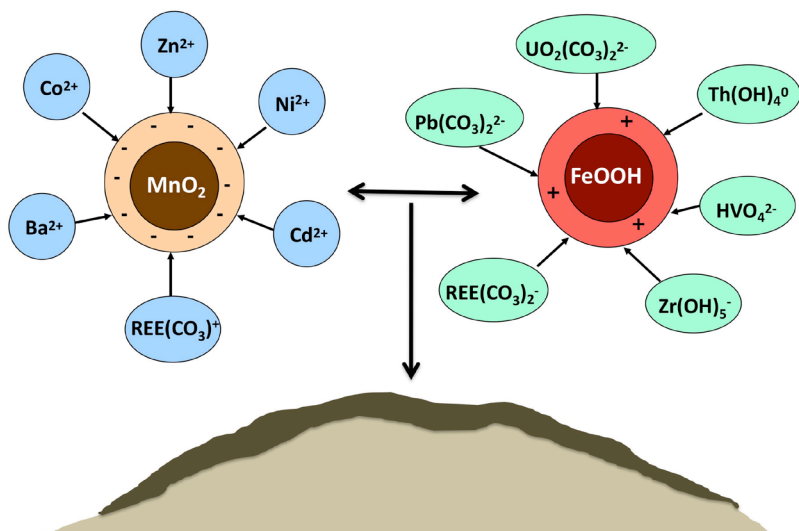
FIGURE 4 Simplified electrochemical model for the sorption of example trace metal species in seawater on the charged surfaces of colloidal or particulate Mn oxide and Fe oxyhydroxide. Coulombic interaction is followed by the formation of chemical bonds and integration of the adsorbed metals in the oxide mineral structures, forming ferromanganese encrustations or nodules. Note that some elements, such as the rare-earth elements (REEs), occur in several dissolved forms in seawater and can sorb onto both Mn and Fe phases.

bial communities (Tully and Heidelberg 2013). A recent study found mineral structures characteristic of biogenic oxides in a nodule and suggested Marine Group 1 (MG1) chemoautotroph Thaumarachareota as a potential Mn oxidizer because they use multi-copper oxidase, which would be supported by the high contents of Cu in deepwater nodules (Shiraishi et al. 2016). A 16S rRNA gene analysis confirmed that the microbial communities of a Fe–Mn crust were unique when compared with sediment and seawater communities: a feature comparable to nodules (Nitahara et al. 2011).

While the bacterial communities might benefit from the redox processes involved in the formation of the nodule and crust matrix, and may participate in certain redox processes within them, there is no evidence so far that these redox processes have a significant and potentially overprinting effect on the inorganic chemical precipitation as discussed above.

PALEOCEANOGRAPHIC RECORDS IN MARINE Fe–Mn OXIDE COATINGS

Slow-growing, thick Fe–Mn crusts in the deep ocean have recorded in their stratigraphic layers variable metal fluxes over tens of millions of years. In contrast, fast-growing crusts from near-coastal areas are known to accumulate metals of anthropogenic origin. For a full exploitation of these archives, age-dating methods covering a wide range of time frames are needed, and, in addition, various proxies representing different kinds of changes will be useful.

Deep-Ocean Fe–Mn Oxide Crust Records

Various physical and compositional characteristics of crusts can provide paleoceanographic information. For example, the older part of thick Fe–Mn crusts can be phosphatized millions of years before the younger part of the crust had precipitated. Phosphatization of crusts occurred several times during the Paleogene through middle Miocene. Those geochemical changes mark times of reduced

dissolved oxygen in seawater, the phosphatization occurring under suboxic conditions. It must be taken into account that the impregnation of primary Fe–Mn crusts with carbonate fluorapatite under suboxic conditions may have modified the primary element signatures: mobilization and loss or re-organization of certain elements have been identified in phosphatized crusts compared to non-phosphatized layers (Koschinsky et al. 1997). However, for immobile and particle-reactive elements (e.g. Pb, Nd, Hf, U, and Os), consistent profiles of their isotopes indicate that they were not affected by post-depositional diagenetic processes such as phosphatization (e.g. Lee et al. 1999). Another indicator of environmental change recorded in crusts is the internal structure of the layers, which include columnar, botryoidal, laminated, mottled, and massive structures (FIG. 2). Each change in structure indicates a change in bottom-water flow and, hence, the amount of incorporated detrital grains.

Iron–manganese crusts record the paleoceanographic/paleoclimatic conditions that occurred over the past 70+ My. The duration of the record depends on the thickness and growth rate of the crust. The temporal resolution of age measurements is course and ranges from a few 100 ky to ~2 My. The key to using crusts as archives is developing an age model for the crusts being studied. For this, isotopes play a key role. The most used and reliable dating technique is $^{10}Be/^{9}Be$ ratios (maximum ages ~12 My) and $^{187}Os/^{186}Os$ ratios (maximum ages ~80 My) for longer records. The upper few millimeters of crusts can be dated using ^{230}Th (maximum ages ~300 ky), and the newly applied ^{129}I (maximum ages ~80 My) dating method. Another commonly applied dating technique uses an empirical equation, the so-called cobalt chronometer. The most-used equation is that of Manheim and Lane-Bostwick (1988): growth rate = $0.68/(Co^n)^{1.67}$, where Co^n = Co × (50/Fe + Mn), and Co, Fe, and Mn are in wt%. The age is calculated using the growth rate and the crust thickness.

Oxide crusts occur throughout the global ocean and at a wide-range of water depths (FIG. 1), thus, they are ideal archives to trace different water masses and identify regional and global changes. Regional changes can be traced using elements with oceanic residence times that are less than the mixing time of the global ocean. Elements with residence times greater than the mixing time (~1,000 years) will record global events.

Temporal changes in metal isotopes of Fe–Mn crusts have been used in many studies to reconstruct past circulation patterns of the global ocean (FIG. 5) (e.g. von Blanckenburg et al. 1996). The number of tools in the isotope toolbox grows every year and now contains a dozen elements with commonly used isotopes, with another dozen that have just begun to be applied to paleoceanography. Three sets of isotopes are used: radiogenic isotopes (e.g. $^{206,207,208}Pb/^{204}Pb$), cosmogenic isotopes (e.g. $^{10}Be/^{9}Be$), and metal stable isotopes (e.g. $^{56}Fe/^{54}Fe$) (Anbar and Rouxel 2007). Metal stable isotope ratios are fractionated between their dissolved form and that contained in the Fe–Mn crusts during sorption, organic and inorganic complexation, and oxidation–reduction at the oxide surface, all of which depend on the molecular coordination environment (e.g. Wasylenki et al. 2011; Little et al. 2014). Dissolved organic-complexed Cu, for example, will have a different isotopic ratio after sorption on crusts than sorption of Cu in its ionic form. These metal isotope ratios also change in seawater with time. Stable isotopes of Mo in seawater, for example, depend on the ratio of anoxic to

oxic sediment. The isotopic ratios disclose changes in these global sedimentary properties when measured through the temporal archive of the Fe–Mn crusts.

Besides changes in radiogenic isotopes along the flow path of deep-ocean water (Fig. 5), water masses at different water depths have characteristic isotopic signatures. An excellent example of using isotopes to decipher changes in circulation patterns is the temporal changes in Nd and Pb isotopes in crusts from the SW and equatorial Pacific. The trends of Nd and Pb isotopes are similar for the Paleogene record, diverge in the Oligocene–middle Miocene record, and then converge again from the middle Miocene to the present (van de Flierdt et al. 2004). These changes support a common source dominated by the end-member isotopic composition of the equatorial circulation deep water mass, with little contribution from Antarctic Bottom Water (AABW) to the Pacific during the Paleogene. During the Oligocene–middle Miocene period, intensification of the Antarctic Circumpolar Current, and weak circulation in general, weakened water-mass exchange; therefore, the Nd and Pb isotope systems produced distinct isotopic signatures for the SW and the equatorial Pacific sites. Pacific circulation became more vigorous in the middle Miocene to the present as the result of the development and export of AABW, which was promoted by growth of the East Antarctic Ice Sheet (van de Flierdt et al. 2004). These changes in circulation patterns were intensified by the opening and closing of gateways to the flow of oceanic currents, e.g. opening of the Tasmanian gateway (between Australia and Antarctica) and the Drake passage (between South America and Antarctica) during the earlier and part of the middle periods, and closure of the Indonesian gateway (between Australia and Asia) during the middle period.

An interesting example of global changes in seawater composition related to tectonic events can be found in crust records from the Atlantic and Pacific Oceans. A drop in the middle Miocene (15–12 Ma) $^{187}Os/^{188}Os$ curve for the crusts marks a global change in seawater composition. Mass-balance calculations indicate that the magnitude of this excursion requires the input of unradiogenic Os, which can be explained by the eruption of the middle to late Miocene Columbia River Basalt Group (flood basalts, part of a large igneous province in the western US) combined with the concurrent bolide impact that created the Nördlinger Ries crater in Germany (Klemm et al. 2008).

Shallow-Water and Continental Margin Fe–Mn Oxide Encrustations

While shallow-water continental margin Fe–Mn concretions have been reported from several places, the best-studied sites are in the Baltic Sea (Glasby et al. 1997). The Baltic Sea is a marginal sea having limited water exchange with the North Sea and a strong seasonal difference in water column conditions. In summer, the well-stratified water column often causes anoxic conditions, which prohibits Mn–Fe oxide precipitation, whereas in winter the deep water is re-oxygenated and Mn, Fe, and trace metals that had accumulated in the bottom water will precipitate around available nuclei, such as pebbles. Such encrustations are found at water depths between 20 m and 100 m. Growth rates are orders of magnitude faster than for deep-water crusts (up to 20 mm/ky, calculated from $^{226}Ra_{excess}/Ba$), giving them maximum ages of several thousand years, which coincides with the time when the present Baltic Sea formed. Concentrations of REEs and isotopes of Sr, Os and Nd have been used to study post-glacial weathering and erosion, as well as the impact of the Little Ice Age (LIA), which affected life during the Middle Ages (roughly, between the 5th and 15th centuries), and on the input of elements into the Baltic Sea (e.g. Bock et al. 2005). For example, Nd isotopes can track LIA climate changes that may have been related to shifts in atmospheric circulation triggered by the North Atlantic Oscillation. An anthropogenic impact on Nd isotopes during the LIA has also been discussed, because there was a decrease in agricultural activity during the LIA that might have lessened soil erosion. Later anthropogenic signatures can be related to a significant increase in Zn concentrations in layers formed after ~1870, which coincides with an enhanced rise in anthropogenic metal emissions due to energy production and transportation (Hlawatsch et al. 2002). However, possibly, post-accretion transformation of the primary precipitates (e.g. during anoxic periods) may weaken the potential of such shallow-water rock coatings for monitoring metal inputs to the system.

An interesting example for paleoceanographic records in deeper continental margin Fe–Mn encrustations is nodules and crusts from the Cadiz Contourite Channel (in the Gulf of Cadiz, off southwest Spain) linked to contourites (850–1,000 m) under the influence of the Mediterranean Outflow Water (MOW). Diagenetic Fe–Mn carbonate

$^{\varepsilon}Nd = -13$
$^{\varepsilon}Hf = 1.6$
$^{206}Pb/^{204}Pb = 19.1$
$^{10}Be/^{9}Be = 0.4 \times 10^{-7}$

$^{\varepsilon}Nd = -3$
$^{\varepsilon}Hf = 3.6$
$^{206}Pb/^{204}Pb = 18.7$
$^{10}Be/^{9}Be = 1.1 \times 10^{-7}$

$^{\varepsilon}Nd = -8$
$^{\varepsilon}Hf = 1.7$
$^{206}Pb/^{204}Pb = 18.8$
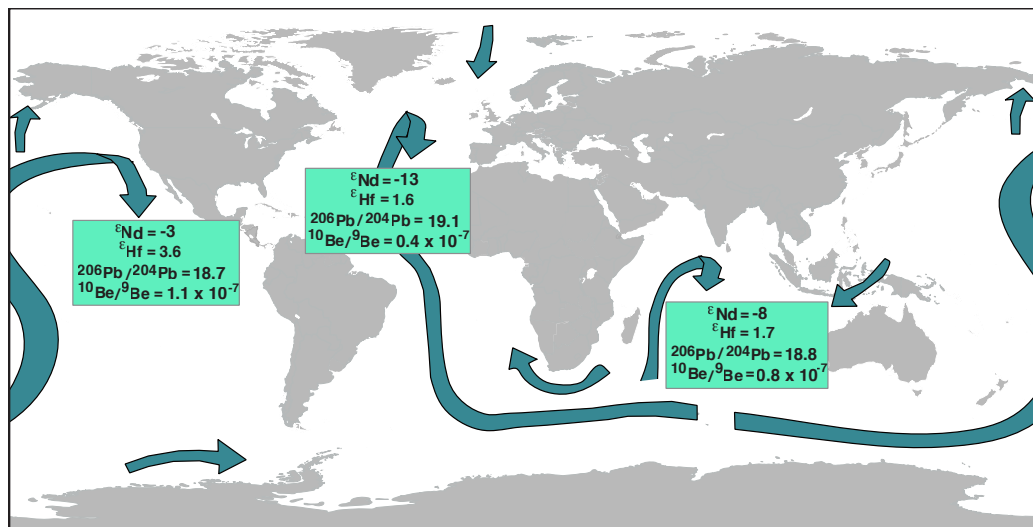$^{10}Be/^{9}Be = 0.8 \times 10^{-7}$

FIGURE 5 General global deep-ocean circulation and the evolution of isotopic signatures with distance from the production of deep water in the North Atlantic. Elements shown have residence times less than, or near to, the mixing time of the global ocean.

nodules formed in the Cadiz Contourite Channel under reducing conditions and in the vicinity of ancient hydrocarbon seeps were exposed to oxidizing conditions during intense bottom currents of the MOW during glacial periods (González et al. 2012).

CONCLUSIONS

Deep-ocean Fe–Mn oxide encrustations are excellent proxies for paleoceanographic changes in the time frame of hundreds of thousands to tens of millions of years. Biological signatures do not appear to be important proxies and do not obscure or modify the inorganic isotopic proxies. Organic complexation of some metals in seawater, especially Cu, will affect stable isotopic ratios when sorbed on Fe–Mn crusts. Shallow-water Fe–Mn oxide rock coatings may be more strongly influenced by post-depositional diagenetic and oceanographic processes but can still house records of changing environmental conditions on timescales of hundreds to thousands of years, including anthropogenic modifications of climate and element fluxes.

Care should be taken to preserve the temporal archives on the seafloor in key areas. These provide a comprehensive history book of our changing oceans. This idea is gaining ground through the establishment of protected areas, such as marine national monuments and reserves, and should be extended to include Marine Geoparks.

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Climate Change, Rock Coatings, and the Archaeological Record

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Rock varnish commonly occurs in arid environments. It can coat not only rock surfaces but also any exposed prehistoric stone artifacts and rock art. Thin sections of varnish coatings reveal microlaminations that reflect major changes between wet versus dry paleoclimates. These microlaminations can be used to assign minimum ages to the underlying rock surface, providing dates for otherwise undateable stone artifacts and rock art. This dating approach has provided important information about the peopling of the Americas (North and South America), including how and when the native American populations adapted to changing climatic conditions.

KEYWORDS: archaeology, artifacts, geochronology, paleoclimate, petroglyphs, rock coatings

INTRODUCTION

For over a century, archaeological dating has partly relied on geological chronologies tied to paleoclimatic changes. More than simply dating archaeological remains, these chronologies have allowed investigations of human adaptation to changing environments. The resulting findings explain processes such as population expansion and social system collapses. The use of rock-coating geochronologies is especially important in arid lands research because they allow us to date surface archaeological remains, including stone tools, petroglyphs (rock engravings) and rock alignments (geoglyphs). These latter artifacts are found outside of buried stratigraphic contexts and, thus, have always been difficult to relate to the stratigraphic archaeological record, even though they constitute a significant proportion of that total record. Although a variety of kinds of rock coatings have been dated using a growing number of different techniques (e.g. Dorn 1998), our emphasis here is on rock dating using the varnish microlamination (VML) technique, and its implications for climatic changes and cultural processes.

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ROCK VARNISH AND VARNISH MICROLAMINATION (VML) DATING

Rock (or "desert") varnish is a dark, paper-thin rock coating consisting to approximately two-thirds of clay minerals cemented to underlying rock by about one-fifth manganese, iron oxyhydroxides and other minerals (Dorn 1998). Rock varnish is not a "patina" or geochemical crust derived from the host surface; rather, it is largely derived from windblown fines (e.g. Fleisher et al. 1999). Rock varnish is internally layered due to a microdepositional process resulting from climatic changes (e.g. Liu 1994). Although different kinds of rock varnish exist, each with their different geochemical properties (Dorn 1998), our discussion only involves the subaerial type of varnish that is typically found on open boulders, cliff faces, and rock outcrops.

Dark rock-varnish coatings provide particularly good canvases for creating petroglyphs that, themselves, are found on open, exposed rock surfaces. Designs can be made by chipping or cutting through the thin surficial rock coating, exposing lighter-colored original rock underneath. With time, a new varnish layer begins to develop within the clean, engraved-out area of a motif (FIG. 1). This new layer provides a minimum age for the creation of the art. Similarly, rock varnish forms on the flaked surfaces of stone tools discarded on stable landforms. Varnish begins to grow within a few hundred years in southwestern North America, as revealed by direct observations of faced stone (Dorn and Whitley 1984) and measurements of lead contamination in varnishes formed during the 20th century (Dorn et al. 2012). Although varnish accretion in some microenvironments can exceed 10 micrometers per thousand years (10 µm/ky) (Liu and Broecker 2008), it is more typical that varnish accretes on the order of 1–3 µm/ky. Because varnish development is influenced by microenvironmental context, there is no necessary direct correlation between varnish thickness and age from one location to the next (Liu and Broecker 2000).

Thin sections of rock varnish usually reveal continuous orange microlayers interbedded with black layers. These microlayers, or microlaminations, represent manganese-poor and manganese-rich layers, respectively (Perry and Adams 1978). These microlaminations can occur over wide regions and correlate with major paleoenvironmental regimes—alternating dry periods (orange layers) and wet periods (black layers) (Liu 1994). These microscopic layers

FIGURE 1 Petroglyphs on basalt from the Coso Range, Mojave Desert (California, USA). The human figures exemplify the revarnishing process that begins after a motif has been engraved through a natural rock varnish coating into the lighter-colored underlying basalt. There is no perfect correlation between varnish darkness and age of a motif (once the engraved-out area of a motif has been revarnished). Still, the more recently created, very light-colored, motif in the center of the photograph lacks significant varnish growth and is probably less than a few hundred years old. The other motifs reflect different, but greater, degrees of revarnishing and age. Rock face is ~3 m high. PHOTO: DS WHITLEY.

Varnish microlamination dating has been combined with cation-ratio varnish dating (Dorn 1990), and other techniques and evidence, to develop a petroglyph chronology in the Mojave Desert (Whitley 2013) (FIG. 3). Cation-ratio dating is based on cation exchange processes in rock varnish. Through capillary action, these processes leach out mobile trace elements (notably potassium and calcium) more rapidly than less mobile trace elements (particularly titanium). The rate of chemical change can be calibrated regionally using independently dated control surfaces, such as varnish-covered basalt flows. An electron microprobe is typically used to measure the chemical constituents of a varnish sample.

Using multiple blind-test VML dating efforts by two different analysts, combined with the cation-ratio technique, a total of 66 petroglyphs have now been dated. The most conservative interpretation of the results indicates that these petroglyphs were made earlier than 11,100 years BP; good evidence suggests that the art may be >12,600 years old, with two as-yet unverified dates extending back to ~14,500 years BP. The plausibility of these early ages is enhanced

act as regional microstratigraphic signatures that can be chronologically calibrated using independent methods of surface dating, such as by cosmogenic nuclides. In order to date the surface of archaeological remains, one must remove a small flake, or thin core, of rock from the humanly created surface that has a varnish coating (such as the pecked-out area of a petroglyph or the flaking scar from a stone tool). This sample is then prepared as a thin section, and its layering correlated with an existing calibration.
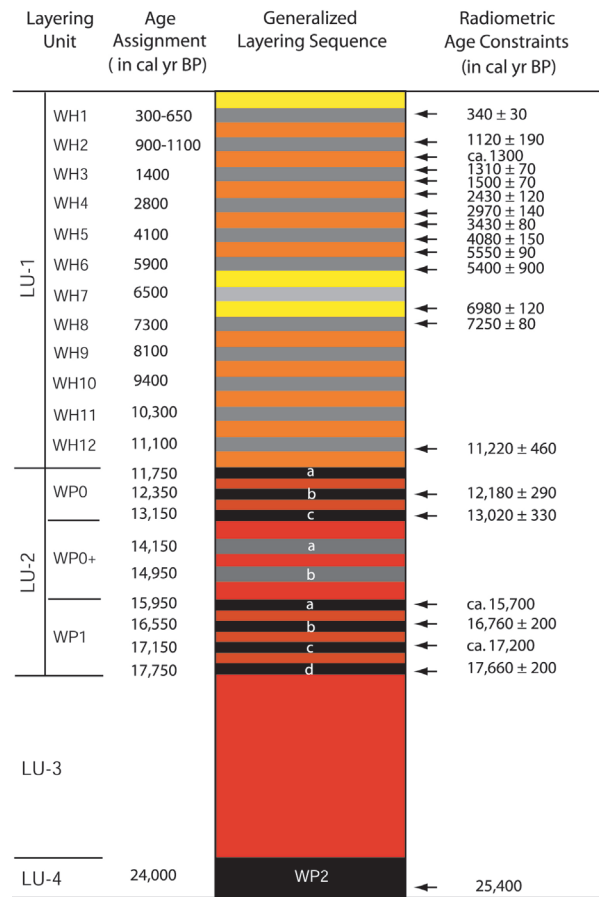
VARNISH MICROLAMINATION DATING IN NORTH AMERICA

Varnish microlamination (VML) dating has been applied to petroglyphs, surface artifacts, rock cairns, and geoglyphs in the Mojave Desert (California, USA), to help address the question of the initial peopling of the Americas (e.g. Cerveny et al. 2006; Whitley 2013). This research is based on a calibration developed for this region by Liu (1994). Although Liu's VML calibration extends back to 140,000 years, the Late Pleistocene and Holocene segments of the calibration are relevant for archaeological purposes in the Americas (FIG. 2) because humans only arrived in the Americas ~15,000–20,000 years before present (BP).

For the Holocene, 12 wet-event dark layers and 13 dry-event light layers have been defined, with 9 wet/dark and 9 dry/light layers for the Late Pleistocene, dating from ~12,000–18,000 years BP. Although the intervals between wet events vary, they average roughly 1,000 years in duration for the Holocene and about 700 years for the Late Pleistocene. The distinctive dark layers in the microstratigraphy of varnish are produced by wet events recorded in other proxy records of climatic change that correlate with millennia-scale cooling in the North Atlantic and Greenland.

Layering Unit	Layering Sub-unit	Age Assignment (in cal yr BP)	Generalized Layering Sequence	Radiometric Age Constraints (in cal yr BP)
LU-1	WH1	300–650		340 ± 30
	WH2	900–1100		1120 ± 190; ca. 1300
	WH3	1400		1310 ± 70; 1500 ± 70
	WH4	2800		2430 ± 120; 2970 ± 140; 3430 ± 80
	WH5	4100		4080 ± 150; 5550 ± 90; 5400 ± 900
	WH6	5900		
	WH7	6500		
	WH8	7300		6980 ± 120; 7250 ± 80
	WH9	8100		
	WH10	9400		
	WH11	10,300		
	WH12	11,100		11,220 ± 460
LU-2	WP0	11,750	a	
		12,350	b	12,180 ± 290
		13,150	c	13,020 ± 330
	WP0+	14,150	a	
		14,950	b	
	WP1	15,950	a	ca. 15,700
		16,550	b	16,760 ± 200
		17,150	c	ca. 17,200
		17,750	d	17,660 ± 200
LU-3				
LU-4		24,000	WP2	25,400

(This graph is not drawn to scale)

FIGURE 2 A generalized varnish microlamination (VML) sequence for the western USA. Wet events appear as dark (black and gray) layers in the varnish layering sequence. WP = wet Pleistocene event; WH = wet Holocene event; LU = layering unit of groups of microlaminations. The wet Holocene events include the Little Ice Age (WH1) and they are not as pronounced in varnish VML as the wet Pleistocene events. The black versus gray color scheme portrays relative concentrations of manganese that darkens the layers. Age assignments are based on independent calibrations where varnish was collected from surfaces dated by an independent means (radiocarbon dating or cosmogenic nuclide surface exposure dating). Where rates of varnishing are particularly rapid, submillennial microlaminations are sometimes seen as very thin black bands, and these are given the designation a, b, c, and so forth in the figure. DIAGRAM BY T. LIU.
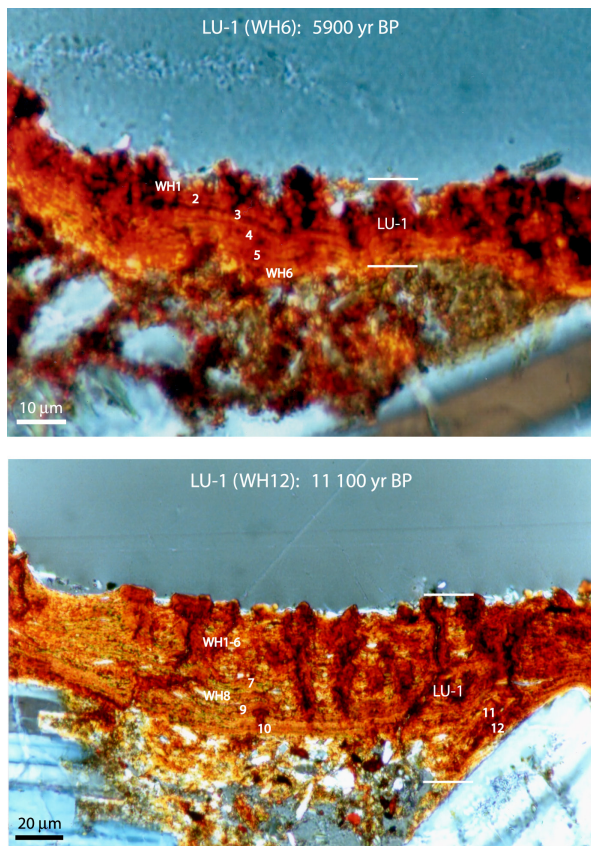
LU-1 (WH6): 5900 yr BP

WH1
2
3
4
5
WH6
LU-1
10 μm

LU-1 (WH12): 11 100 yr BP

WH1-6
7
WH8
9
10
LU-1
11
12
20 μm

FIGURE 3 Varnish thin-sections taken from petroglyphs in the Coso Range, Mojave Desert (California, USA). For symbols and numbers, see FIGURE 2. (**A**) Microlaminations provide a minimum limiting petroglyph age of 5,900 years BP. (**B**) Minimum varnish petroglyph age here is 11,100 years BP. The vertical black "columns" in the upper parts of the orange layers in both images do not contain paleoclimatic information. Rather, they form as a result of postdepositional diagenesis (Krinsley et al. 2013). PHOTOS: T. LIU.

(though not proven) by the facts that the dated art occurs in a region containing numerous examples of artifacts and sites dated, by other means, to between 10,000–12,000 years BP. In addition, VML has been used to date a projectile point (a large spear point) and a human-created rock cairn to >11,000 years BP (Cerveny et al. 2006).

The early Mojave Desert petroglyph ages are matched by roughly equivalent ages on different kinds and styles of North and South American rock art. This similarity indicates that the early production of this art was widespread across both continents. The variability in this art indicates that, by at least 11,000 years BP, diverse regional cultures had developed across the Americas, each with their own styles of art and, presumably, unique sets of cultural traditions, beliefs, and practices. This conclusion contradicts the traditional view of the earliest prehistory in the Americas, which posited one, or just a few, monolithic cultures with a single adaptive strategy, inhabiting the entire region. This view resulted from an analytical over-emphasis on stone toolkits to the near exclusion of other kinds of archaeological evidence.

It is significant to note that late Holocene petroglyphs can provide a vehicle to better understand the paleoclimatology of a desert region. Fast-accreting varnishes can be spotted as millimeter-sized black dots in recent engravings, and fast-accreting varnishes can record millennial- and century-scale climatic events. FIGURE 4 presents a thin section of a geometric petroglyph with a cation-ratio age of ~580 years

(Dorn and Whitley 1984). In a reevaluation of the age, a VML analysis indicated that varnish started to form on the engraved surface near the start of the Little Ice Age, ~650 calendar years before present. For fast-accumulating varnishes, three black layers at the base of the varnish in FIGURE 4 represent the wet intervals of the Little Ice Age (WH1a, WH1b, WH1c; WH = "wet event in Holocene") (Liu and Broecker 2007). Measurements of lead contamination in varnishes formed during the 20th century occur in the upper micrometer of the varnish—identified by electron microprobe measurements of lead as spiking well above background levels (<0.03% PbO) (Dorn et al. 2012).
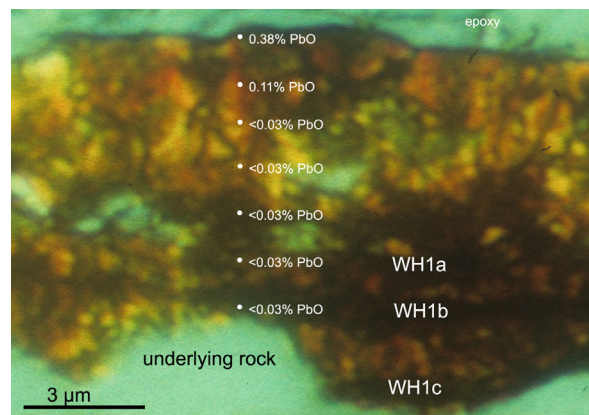

epoxy
• 0.38% PbO
• 0.11% PbO
• <0.03% PbO
• <0.03% PbO
• <0.03% PbO
• <0.03% PbO
• <0.03% PbO
WH1a
WH1b
underlying rock
WH1c
3 μm

FIGURE 4 Ultrathin section showing varnish microlamination pattern taken from a curvilinear abstract petroglyph from the Coso Range, Mojave Desert (California, USA) with a cation-ratio age of ~580 years old. The presence of all three century-scale wet Holocene (WH) events (WH1a, WH1b, WH1c) during the Little Ice Age indicates that this varnish started to form about ~650 years ago. The spike in the PbO measurement in the top micrometer of the varnish reflects 20th century industrial contamination.

VARNISH MICROLAMINATION DATING IN SOUTH AMERICA

The deserts of South America are likewise ideal for applying rock-varnish dating techniques. These arid landscapes are dotted with thousands of open-air surface sites covered by stone artifacts that have been exposed to the elements for hundreds, and even thousands, of years. The region also contains geoglyphs (earth-figures) and petroglyphs, both of which were part of the long-term construction of cultural and spiritual landscapes. Initial South American varnish studies were carried out in Nazca (southern Peru) (Clarkson and Dorn 1995) and Guatacondo (northern Chile) (Clarkson et al. 2001) on geoglyphs and on the rocks of two subterranean irrigation systems (known as *puquios*). More recently, Ugalde et al. (2015) found evidence of rock varnish on exposed lithic artifacts from northern Chile. Though the rock varnishes mentioned in these studies have not yet been dated, these studies illustrate the great potential for future VML applications in western South America.

Varnish microlamination dating has been applied to surface lithic artifacts (FIG. 5) in the Amaicha del Valle, Tucumán (northwestern Argentina) (Baied and Somonte 2012; Somonte and Baied 2013). Natural rock surfaces and stone tool flaking scars in this region were examined to derive minimum surface exposure ages. Natural rock surfaces in this area were dated to ~7,300–6,500 years BP, providing an estimate for the maximum age of the local landforms. The flaking and creation of the first stone artifacts occurred ~6,500–5,900 years BP. Importantly, the Amaicha del Valle region is currently an arid upland basin (experiencing ~200
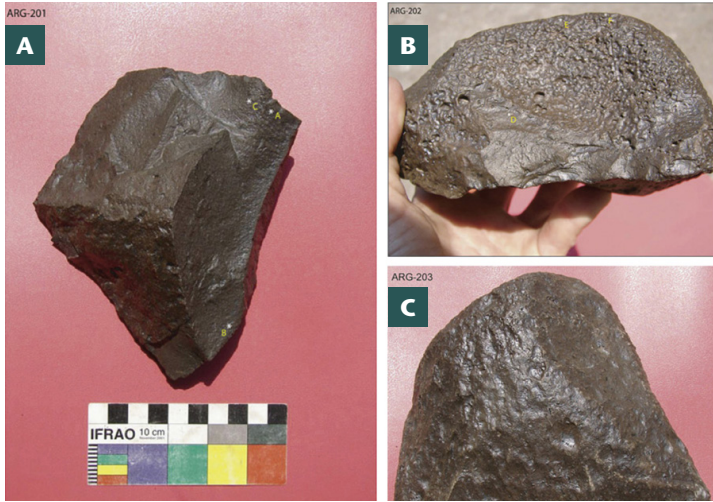
FIGURE 5 Varnish microlamination (VML) dated surfaces of artifact/rock specimens from Amaicha del Valle (Argentina). (**A**) and (**B**) VML surfaces on stone tools. (**C**) VML surface on a natural cobble. IMAGES BY C.A. BAEIED AND C. SOMONTE.

mm, or 8 inches, of rain per year, at about 2,000 meters, or 6,560 feet, above mean sea level). The Amaicha del Valle VML studies illustrate the paleoclimatic, and thus paleo-ecological, change that has occurred in this area, including 12 wet periods during the Holocene (last ~12,000 years). Baied and Somonte (2012) and Somonte and Baied (2013) correlated the human occupation of the basin to these wet phases, allowing them to identify the occupational dynamics of the region and the functionality of the sites. In this sense, VML contributed to an understanding not just of the chronology but also the prehistoric paleoecological adaptation that occurred in this region.

SUMMARY AND OUTLOOK

Archaeology, as a science, is constrained to studying physical remnants of the past. Archaeology previously was limited to the evidence provided by sites, monuments and artifacts. But today, technological and analytical improvements have increasingly allowed archaeologists to obtain additional information from the natural and cultural traces associated with material remains. These include phenomena that, literally, may not be visible to the naked eye. Rock coatings formed over cultural remains constitute one of these kinds of trace phenomena. The geochronological and paleoclimatic data provided by rock varnish microlamination dating provides long-sought, but previously unobtainable, data on exposed surface artifacts and petroglyphs. Although research using this technique for archaeological materials is still in its infancy, it has already demonstrated its value to central problems, such as the peopling of the Americas. Future applications hold great promise not only for dating but also for paleoclimatic reconstructions and for interpretating past paleoecological adaptations.

ACKNOWLEDGMENTS

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Rock Coatings and the Potential for Life on Mars

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Rock coatings observed on the surface of Mars since the Viking landers of the mid-1970s continue to generate considerable interest in the field of astrobiology. Terrestrial rock coatings are associated with diverse microbial life, raising the question as to whether martian rock coatings might also be partly of biogenic origin. Rock coating formation can be mediated by microbes, which in turn are shielded from harmful radiation and can obtain nutrients from the coating. In addition, coatings may be indicative of life and can preserve its signatures. Pragmatically, rock coatings are surface environments accessible by Mars rovers. This article focuses on the habitability, preservation capability, and practicality of rock coatings as astrobiological targets on Mars.

KEYWORDS: astrobiology, biosignatures, Mars, biominerals, endoliths, microbe–mineral interactions

INTRODUCTION

In the search for extinct or extant life on Mars, rock coatings are a target of burgeoning interest. Chemically diverse rock coatings on Earth occur in a wide range of environments, and microbes appear to facilitate their formation. NASA's Viking missions of the mid-1970s first detected coatings on the surface of Mars, a finding later replicated by the NASA rovers *Spirit* and *Curiosity* (FIG. 1). These observations help bolster a rich subfield of research exploring the biological influence on rock varnish and other coatings on Earth, and the *bio*geochemical implications of the observed coatings on both planets.

Currently, the field of astrobiology largely focuses on two areas: habitability and biosignatures. Habitability has historically been a human-centric notion—the idea that the temperature, atmospheric composition, and water activity that give us the abundance and diversity of life on Earth today are prerequisites for life on planets outside of our own. However, two key points run contrary to this idea. First, life on Earth arose during the Hadean Eon, an eon whose name alone evokes the type of violent and inhospitable time that it was (Mojzsis et al. 1996). Second, nearly every one of Earth's extreme environments is habitable, largely by microbes. If even the most inhospitable places on Earth, like Antarctica and the Atacama Desert, are homes to life, then we must carefully consider our definition of habitable environments.

Many extraordinary claims of evidence for life elsewhere in our Solar System have been made, and just as many summarily dismissed. "Extraordinary claims require extraordinary evidence" is an apt aphorism in the field of astrobiology. Biosignatures come in many forms, but most are only suggestive. As a result, astrobiologists carry the onus of defining and finding that extraordinary evidence. Will we know life when we see it? So far, n = 1 when it comes to known life in the universe.

Multiple independent missions to Mars have made visual observations of rock coatings on the surface. On Earth, there is substantial evidence for a biological component in the development of terrestrial rock coatings, and, as a result, coatings are an obvious choice for astrobiology research on Earth and in the exploration of Mars.

In this article, rock coatings are discussed as astrobiological targets, focusing on the evidence they give for life, the protection they offer microbes, their ability to preserve signatures of life, and their practicality as a surface target for current and upcoming missions to Mars.

SURVIVING THE SURFACE OF MARS

Present-day Mars is a vastly different place than Earth. Preconceptions about habitable environments might result in the assumption that the surface of Mars must be sterile: at first glance, the nature of Mars' environmental parameters do not appear promising. The thin atmosphere and lack of ozone do little to block incoming radiation, and the atmosphere does not provide any warming through a greenhouse effect, resulting in temperatures of −125 °C near the poles in winter, up to 6 °C in the equatorial regions during a summer day (though this drops rapidly at night). Water, a prerequisite for life on Earth, is in short supply on Mars. Though there is evidence for intermittent flows (Ojha et al. 2015), the brines that comprise these flows would require life to be halophilic, or salt-loving. But these conditions do not necessarily preclude life: microbes on Earth can survive an incredible range of extreme conditions with little more than genetic adaptations (FIG. 2), and those microbes that prefer less extreme conditions are often able to find microenvironments where conditions are more tolerable. In rock coatings, we find both types.

Extremophiles on Earth can survive temperatures as low as −15 °C, pH as low as −0.06, salt concentrations up to 32%, and radiation levels exceeding 30 kGy. Microbes and complex organisms, such as tardigrades (microscopic water-dwelling animals), are able to survive exposure to radiation in near-Earth orbit. Extremophiles can survive one,

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FIGURE 1 Lander and rover imagery of rock coatings on Mars. (**A**) *Viking 1* lander image of martian surface with dark coatings on rocks, highlighted by a front-lighted view. IMAGE: NASA; BARRY DIGREGORIO. (**B**) MER *Spirit* Pancam image of rock varnish on martian dreikanters (Sol 601A, Seq P2567, LST: 13:11:59). From Krinsley et al. (2009); IMAGE: OLIVIER DE GOURSAC NASA/JPL. (**C**) MER *Opportunity* Pancam image of dark rock coatings preserved by case hardening at the Whitewater Lake outcrop at Endeavour Crater (Sol 3074 P2564 L357). IMAGE: NASA/ JPL/CORNELL. (**D**) MSL *Curiosity* Mastcam image of the Murray Butte outcrop, which stands about 5 m above the rover and 25 m east-southeast. Dark coatings are present along vertical joint planes, suggesting that the coating formed inside vertical fractures while in the Mars regolith and were later exposed after spalling (PIA20843). (**E**) Two MSL *Curiosity* Mars Hand Lens Imager (MAHLI) images showing Mn-oxide minerals on a rock surface at Windjana. Right panel contains scale for panel 1E. IMAGE: NASA/JPL-CALTECH/MSSS (PIA18390)

or even multiple extreme conditions, and such organisms can survive in conditions approaching a simulated martian environment (Diaz and Schulze-Makuch 2006; Mickol and Kral 2016). Endolithic environments on Earth, including rock coatings, support living extremophiles.

Nonextremophilic microbes can also thrive in extreme conditions by taking advantage of microenvironments within the larger, less hospitable environment. In rock coatings, the overlying rock or mineral grains can protect cells from incoming radiation. A study of the spore-forming *Bacillus subtilis* and the extremophilic cyanobacterium *Chroococcidiopsis* sp. showed that both types of bacteria could survive otherwise lethal doses of ultraviolet (UV) radiation by having just 1 mm of mineral covering (Cockell et al. 2008). This protective effect is likely to occur in <1 mm thick coatings, though in a diminished capacity. Another way microbes can protect themselves is through the formation of biofilms, which protect cells from UV radiation (Elasri and Miller 1999). In lithic environments, such as rock coatings, microbes can colonize along mineral lineaments, taking advantage of the increased available surface area that may facilitate the biofilm formation. The result is distinct, sometimes geometric, patterns of cells that can be observed on mineral faces and sulfate crusts (Edwards and Rutenberg 2001; Kolo et al. 2009). Preservation of these patterns can result in robust biosignatures (FIG. 3).

The greatest advantage microbial life has is its small size. In a single bacterial colony, measuring 1–2 mm, there can be $10^7–10^8$ cells. Microscale biofilms in pore spaces, on particles, or as aggregates in rock coatings can create microenvironments that are hospitable for life. Trapped gasses, pools of inorganic electron donors and acceptors, and liquid water can persist in these microenvironments while being absent or inconsistent over larger scales. Mars, particularly the surface, is seemingly uninhabitable—but for microbes to survive, and even thrive, only small environments need to be habitable. Associating with particles and pores in a rock coating can protect microbial life from otherwise lethal conditions only millimeters away. Rock coatings can host an abundance of these microenvironments and are, therefore, a rich target to search for extraterrestrial microbial life.

THE SIGNATURES OF LIFE

The search for and identification of biosignatures in all their forms is a crucial component of the field of astrobiology. When considering biosignatures, it is important to note that there are both *suggestive* and *definitive* biosignatures. Definitive biosignatures include things like biomolecules (e.g. DNA, protein) or the fossilized remains of eukaryotic organisms. However, these are unlikely to be the types of biosignatures we encounter on Mars. Instead, astrobiologists often study suggestive biosignatures:
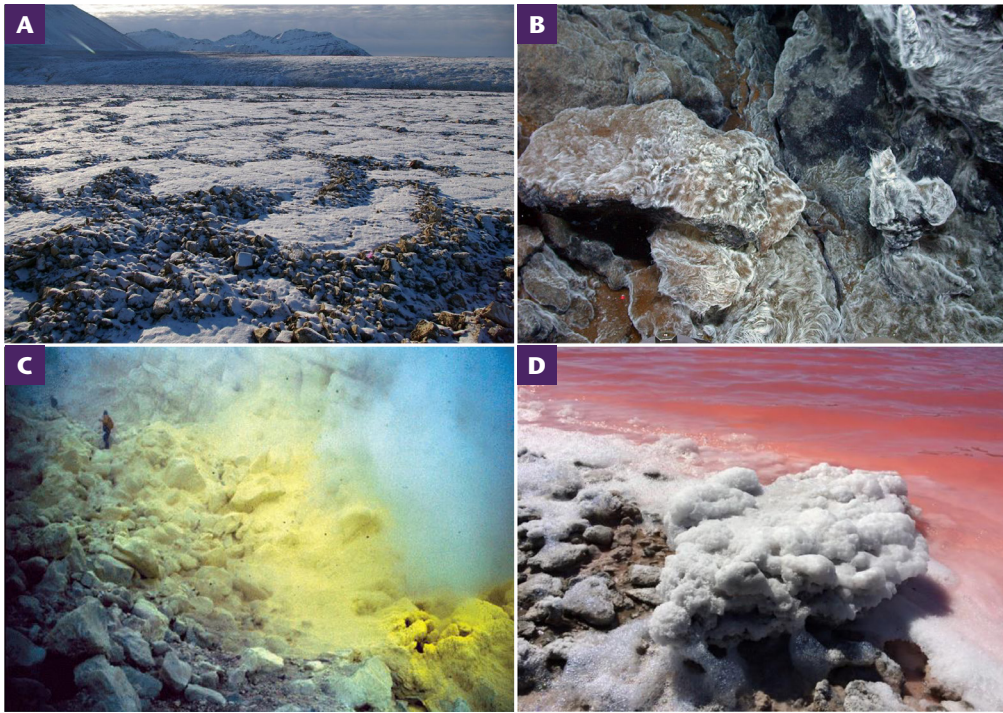
microfossils, biominerals, isotopic fractionation, and metabolic by-products (e.g. methane gas). All these are commonly associated with biological activity on Earth, though many can also form through abiotic processes. Thus, as the name implies, these biosignatures are merely suggestive. And therein lies one of the greatest problems faced by astrobiologists: establishing criteria for evidence of life. Where rock coatings enter the picture is in their ability to preserve biosignatures, be they morphological, mineralogical, or chemical. Biosignatures exposed to the harsh surface of Mars are unlikely to remain stable over geologic timescales. However, for rock coatings, the same protective qualities available for extant life could also serve to protect evidence of past life.

There is a diverse group of microbes that are able to produce minerals through direct and indirect action. The minerals have distinct characteristics that, when biologically produced, can serve as potential biosignatures. For example, magnetotactic bacteria produce magnetite in intracellular, membrane-bound structures called magnetosomes (Blakemore 1975; Bazylinski and Frankel 2004). The magnetite crystals in magnetosomes have unique morphologies, even when compared to other biologically produced magnetite [i.e. via Fe(III) reduction]. The mineral rosickýite is another example. Typically an unstable, high temperature allotrope of elemental sulfur, there appears to be an association between metastable rosickýite, microbes, and organics (Douglas and Yang 2002; Lau et al. 2017). Perhaps most exciting with respect to rock coatings and their astrobiological significance are manganese oxide minerals, such as birnessite and todorokite. These minerals are thought to be the result of bacterial biomineralization and have been found in both terrestrial and marine rock coatings on Earth (McKeown and Post 2001). Other minerals (e.g. iron oxyhydroxide, elemental sulfur minerals) can take on distinct morphologies or textures when produced in association with microbes or organics. Thus, both mineralogy and morphology of these minerals can be useful biosignatures, and rock coatings can preserve these signatures.

Rocks can preserve whole microbial cells or assemblages. Certain microbes have distinct shapes that enable their fossilized forms to be easily identified (e.g. cyanobacteria,
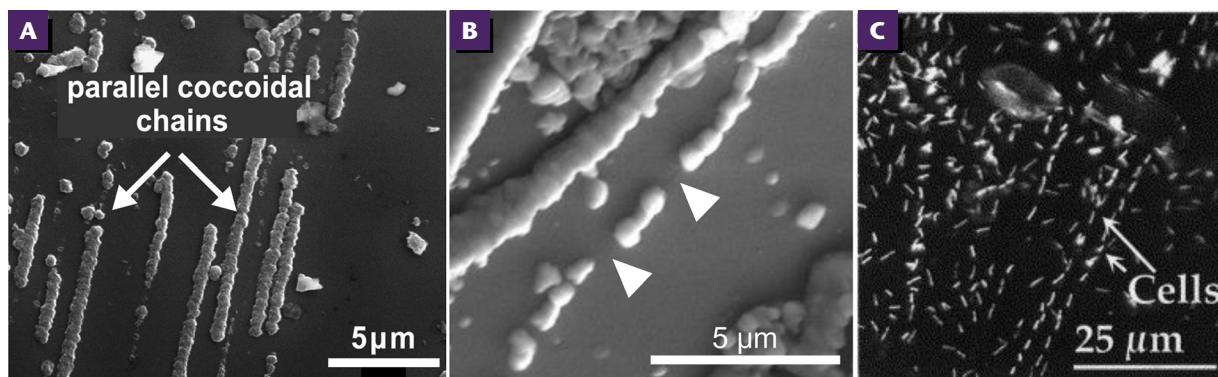

FIGURE 3 Growth of cells along areas of increased surface area, such as mineral lineaments and scratches.
(**A**) Scanning electron micrographs of coccidal chains along a hematite surface. The hematite sample came from remineralized banded iron formation in Zaire. REPRODUCED WITH PERMISSION OF MARY ANN LIEBERT INC. PUBLISHERS FROM KOLO ET AL. (2009)
(**B**) Coccidal chains along a mineral lineament on a sulfate rock coating observed under a scanning electron microscope.
(**C**) Fluorescence micrograph of DAPI-stained cells attached to polishing scratches on a pyrite surface. REPRODUCED WITH PERMISSION OF ELSEVIER FROM EDWARDS AND RUTENBERG (2001)

fungi). While entombment by mineralization is disadvantageous for the microbe, which has limited ways of shedding mineral coatings on the cell surface, it is a distinct advantage for geomicrobiologists if these microbes are entombed and preserved. Microbial cells in various states of mineralization have been observed in rock coatings (Allen et al. 2004; Gorbushina 2007; Krinsley et al. 2009; Northup et al. 2010; Marnocha and Dixon 2013). These forms include rod, cocci, botryoidal features, and more complex filamentous morphologies, some probably eukaryotic. In addition to the morphologies are the inferences that can be made about the state of mineralization of the cell based on whether the cell crosses a crack in the coating or is cracked itself along the same line (Figs. 4A, 4B). Likewise, a trench or bowl in the rock matrix may be interpreted as a location where a cell was mineralized and later weathered away, leaving behind its impression (Figs. 4C, 4D). Combined with spatially resolved chemical information, these features can be used to interpret, on a relative basis, when the coating was inhabited, if it was inhabited continually or by succession, and what the weathering environment might have been like during the coating's development.
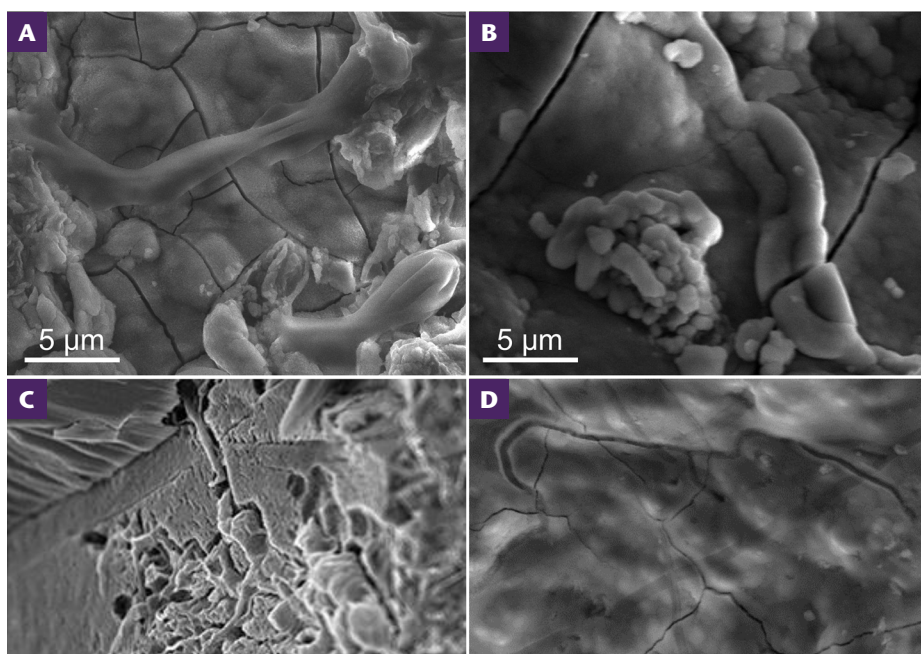
examples of abiotically produced minerals, precipitates, or alteration products that have a convincing microbe-like appearance. Any number of oxidants, radiation sources, or weathering agents can destroy or alter chemical, cellular, and mineral biosignatures. With this in mind, there are several important points to consider when searching for signatures of past or present life on Mars. First, it is important to not only consider the signatures that life produces but also what those signatures might look like over the course of geologic time. Second, as they are largely suggestive, biosignatures in isolation are not sufficient to make claims for life. And third, there is a need for an increased understanding of terrestrial biosignatures, the organisms that produce them, the environments in which they are formed and preserved, and the contexts in which biogenicity can be confirmed.

ROCK COATINGS AS ASTROBIOLOGICAL TARGETS

Rock coatings may be among the best targets for current and near-future missions on Mars. As a surface environment, coatings are both readily identifiable and accessible. With an abundance of Fe, Mn, and clays on Mars, rock varnish is among the best-studied coating types with respect to astrobiological implications for Mars (Murchie et al. 2000; Bishop 2002; Allen et al. 2004; DiGregorio 2005; Krinsley et al. 2009). There are also other coating types that are mineralogically compatible with Mars: Fe-films, silica glazes, and sulfate crusts, for example. The primary minerals in many of these coating types have been observed on Mars both by satellite and by rover; on Earth, these coatings are often, if not always, host to diverse bacterial communities (Northup et al. 2010; Marnocha and Dixon 2014).

Among the instrumentation aboard current rovers on Mars that is best equipped to study rock coatings is ChemCam, a laser-induced breakdown spectrometer (LIBS) aboard the *Curiosity* rover. The instrument fires a laser pulse at material and acquires spectra from the resulting plasma with an imaging camera. The result is the spatially resolved elemental composition of a target rock. ChemCam is an efficient instrument that can access areas otherwise unreachable by the rover's arm, and is able to obtain accurate data up to 7 m away from the rover. The instrument's ability to pulse repeatedly on the same spot is largely used to remove dust layers and regolith coatings; however, the same process can also be used for depth profiling of rocks and rock coatings. The LIBS technique is able to detect manganese layers in terrestrial rock coatings, and similar patterns have been observed on Mars using the ChemCam instrument (Lanza et al. 2015). On Earth, manganese minerals are strongly associated with microbial activity and have been suggested as potential biosignatures. Thus, ChemCam may be able to show evidence for rock coatings and water–rock interactions on Mars, and perhaps, habitable environments and biosignatures in those coatings.

FIGURE 4 Mineralized cells and cell impressions observed using a scanning electron microscope. (**A**) Fungal filament overlying the cracked substrate of an Fe-film rock coating. (**B**) Cells in the same Fe-film as 4A that are cleaved along a substrate crack, suggesting the cell was mineralized at the time of cracking. (**C**) Pitting by a fungal biofilm on marble. Reproduced with permission of John Wiley and Sons from Gorbushina (2007). (**D**) Deep and shallow trenches in an Al-rich rock coating, likely formed by bacterial or fungal filaments that were mineralized, then later eroded away. Modified with permission of Cambridge University Press from Marnocha and Dixon (2013).

Biosignatures encompass a wide range of features, microbial taxa, and lifestyles. But biosignatures must be considered with caution. Life on Mars has been claimed via morphological biosignatures several times in the past, generating considerable controversy in the case of the Antarctic Allan Hills martian meteorite (ALH84001) (McKay et al. 1996; Sears and Kral 1998; Martel et al. 2012). The often indistinct shape of microbes and the diversity in mineral morphologies means the origin of the observed morphology can be misinterpreted: Banfield et al. (2001) provides excellent

The NASA Mars 2020 rover will include an updated and expanded version of the ChemCam instrument called SuperCam. This instrument will add a suite of new spectroscopy instruments to the analytical arsenal: Raman,

time-resolved fluorescence, and both visible and infrared spectroscopy. These will allow the SuperCam to capture molecular data in addition to the elemental data collected by the LIBS component. Raman spectroscopy has been used successfully to identify mineral and organic signatures in endolithic microbial communities (Villar et al. 2005; Vítek et al. 2010). With rock coatings observed by nearly every successful surface mission to Mars since Viking, it will be exciting to see what these new rovers uncover. Until 2020 arrives, advances in high-throughput sequencing, imaging, and spectroscopy techniques and technologies will facilitate the study of terrestrial rock coatings, their microbial communities, and the signatures of life those communities leave behind.

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Meet the Authors
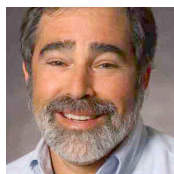
Ronald I. Dorn received a PhD in geography from the University of California at Los Angeles (USA) in 1985, was a faculty member of Texas Tech University (USA) from 1985 to 1988, and has been at Arizona State University (USA) since 1988. It was in graduate school that he started working on the origin and characteristics of manganiferous rock varnish and, since then, his research has expanded to all types of rock coatings, including dust films, heavy-metal skins, iron films, oxalate crusts, and silica glazes and their interface with the underlying decaying rock in the form of case hardening. He studies these deposits from the perspectives of their basic characteristics and origins, their role at the critical zone, and the paleoenvironmental history recorded in their layering patterns.

Geoffrey M. Gadd is a geomicrobiologist whose main research is on geomycology: the role of fungi in processes relevant to geology. He received his PhD in 1978 from University College Cardiff (Wales) and thereafter moved to the University of Dundee (Scotland), where he currently holds the Boyd Baxter Chair of Biology in the School of Life Sciences. His research concentrates on metal–mineral–microbe interactions, especially the processes underlying metal accumulation, detoxification and tolerance, and the mechanisms that alter metal(loid) mobility, including biomineralization. Recent and current geomycology projects include biodeterioration of concrete in the context of nuclear decommissioning; transformations and biomineralization of lead, uranium, cobalt, manganese, selenium and tellurium; microbially induced metal carbonate precipitation; and microbial biomineralization as a route for the production of novel biomineral products.
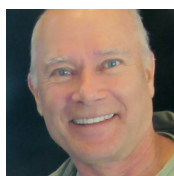
James R. Hein received a PhD from the University of California at Santa Cruz (USA) in 1973 and has been a marine geologist with the U.S. Geological Survey (USGS) since 1974. In 1976, he began working on marine mineral deposits as a member of the Deep Ocean Mining and Environmental Studies (DOMES) team, studying Ni- and Cu-rich ferromanganese nodules from the Clarion–Clipperton Fracture Zone of the Eastern Pacific Ocean. Since then, his research has expanded to include all types of marine mineral deposits throughout the world's oceans, including ferromanganese nodules and crusts, seafloor massive sulfides/sulfates, phosphorite, barite, and potential land-based analogs of these deposits. He studies these deposits from three perspectives: their potential as metal resources, their role in the geochemical balance of the oceans, and the paleoceanographic history recorded in ferromanganese crusts. He has participated in and led many oceanographic research cruises and currently runs the Marine Minerals Program at the USGS.

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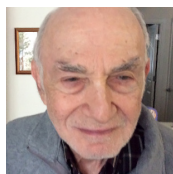
David H. Krinsley is a courtesy professor in Earth sciences at the University of Oregon (USA). He retired from teaching and research at Arizona State University (USA) in 1991, where he headed the Department of Geology for six years. His first and second assignments after his PhD at the University of Chicago (USA) were a postdoc at Columbia University (USA) and an appointment as an instructor at Queens College, CUNY (USA). He initiated the Department of Geology at Queens College and rose through the ranks to become provost. He ran Queens College during the Vietnam riots, and then left to take an appointment as an Overseas Fellow in the Department of Geology at Churchill College, University of Cambridge (UK). His research has involved the surface textures of sand grains, rock varnish, diagenetic processes, and recent meteor impacts in Italy.

William C. Mahaney is emeritus professor of geography at York University (Canada). He is a specialist in glacial geology and geomorphology and President of Quaternary Surveys, a company specializing in Quaternary geology and environmental geomorphology. Professor Mahaney is based in Toronto (Canada) and has undertaken investigations on every continent, his most recent research involving the geology/geomorphology of the Punic invasion route from Spain to Italy during the Hannibalic Wars, the latter resulting in publication of *The Warmaker: A Novel* (2008, iUniverse) and the non-fiction *Hannibal's Odyssey: Environmental Background to the Alpine Invasion of Italia* (2008, Gorgias Press). *Hannibal's Odyssey* provides a scientific analysis of the geological evidence from all major localities/battlefields visited by the Carthaginians during the invasion of Italia and up to the Battle of Cannae (216 BC), where Hannibal showed his true tactical genius.

Cassandra L. Marnocha is an environmental microbiologist with research interests in endoliths, microbe–mineral interactions, and microbial biogeochemical cycling. She received her BS in biology from the University of Wisconsin–Green Bay (USA) (2009) and her PhD in planetary sciences from the University of Arkansas (USA) (2013). During her graduate work, she investigated the bacterial communities of rock coatings from northern Sweden. Following completion of her PhD, she held a postdoctoral position at the University of Delaware (USA) where she studied extracellular biogenic sulfur produced and consumed by microbes. She joined the Department of Biology at Niagara University (USA) in 2016 as an assistant professor. She is currently investigating water–rock–microbe interactions and biogeochemical cycling of acidic freshwater springs.

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Michael Schindler is an environmental mineralogist working on nanoscale processes in soils, tailings, and uranium ore deposits. He received his PhD in mineralogy in 1997 from the University of Frankfurt (Germany) and, until 2004, worked on theoretical crystal chemistry projects at the University in Manitoba (Canada). He then decided to work in the field of environmental mineralogy, specializing in the use of X-ray photoelectron spectroscopy and atomic force microscopy. He is currently an associate professor at Laurentian University (Canada) and a "part time" researcher at the Nano-Earth facility at Virginia Tech (USA), where he uses the combination of focused ion beam technology and transmission electron microscopy to discover new chemical processes operating in the environment.

David M. Singer is an environmental mineralogist and geochemist. He received his BS in geological sciences from the University of Michigan (USA) (2002), his PhD in geological and environmental sciences from Stanford University (USA) (2008), and had a joint post-doctoral position in the Earth and Planetary Sciences Department at University of California, Berkeley (USA) and the Earth Sciences Division of Lawrence Berkeley National Laboratory (USA). In 2012, he joined the Kent State University (USA) faculty as an assistant professor in the Department of Geology. His research involves laboratory and field experiments on the fate and transport of trace metals in the environment, with a focus on water–energy systems. Recent projects include metal speciation and distribution in the Marcellus Shale of eastern North America; transfor-

mations of iron (oxy)hydroxides in acid-mine drainage settings; soil development on coal-mine tailings; and ion sorption and diffusion into natural and synthetic mesoporous materials.

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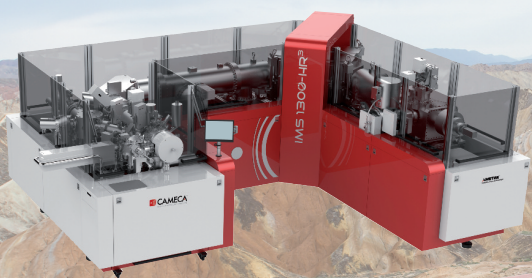
David S. Whitley received his PhD in anthropology, with an emphasis on archaeology, from University of California, Los Angeles (UCLA) (USA) in 1982. He served as Chief Archaeologist at UCLA from 1983 to 1987, taught at the University of the Witwatersrand (South Africa) from 1987 to 1989, and is currently a director at ASM Affiliates, Inc. (Tehachapi, California, USA). His dissertation was the first on North American rock art. His research has focused on the dating, interpretation, and conservation management of rock art. Although the emphasis of his research is western North America, he has also published on southern African and European Upper Paleolithic cave art, and his research has been translated from English into five languages. He is the editor of the *Handbook of Rock Art Research* (2001, Altamira Press) and the *Introduction to Rock Art Research* (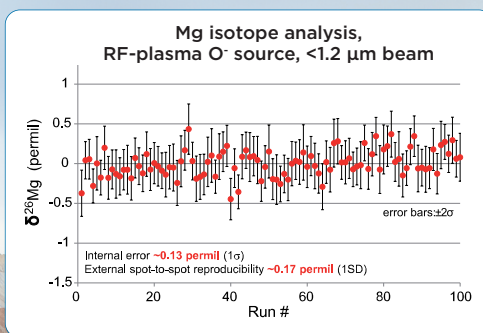2011, Left Coast Press, 2nd edition).