3.09 Nanoscale Mineral Decay and Its Importance in Geomorphology

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Glossary

Authigenic phase: The phase resulting from the adsorption of previously dissolved elements in the water column overlying the sampled sediments.

Back-scattered electron (BSE) microscopy: An accelerated electron beam in an electron microscope produces collisions between electrons and atoms, where the largest atoms with the highest atomic number (Z) generate a "brighter" intensity when imaged with a back-scattered detector.

Biotic weathering: Mineral weathering caused by life, including bacteria, fungi, algae, plants, and animals.

Case hardening: The outer shell of a rock that has been hardened (indurated) through the addition of elements such as silica or iron.

Cosmogenic nuclides: Rare nuclides produced by high-energy cosmic ray induced nuclear reactions in the atmosphere (meteoric) or in surface rocks and minerals (in situ-produced). There are stable (e.g., 3He) and radioactive (e.g., 14C, 10Be, 26Al, 36Cl) cosmogenic nuclides and used for a variety of applications in geomorphology.

Etching of minerals: Mineral dissolution is not an even produce; areas of more intense dissolution are seen as pits on the scale of micrometers.

Heavy metal scavenging: Iron and manganese oxides and hydroxides scavenge heavy metals such as zinc, copper, and lead.

High resolution transmission electron microscopy (HRTEM): 2-D spatial imaging if very thin samples able to image mineral lattices with a spatial resolution of greater than 0.08 nm.

Meteoric 10Be: Produced in the Earth’s atmosphere (half-life: 1.39 Ma) that is often utilized as process tracers in Earth’s environment.

Microfractures: Breaks in minerals that can carry capillary water.

Nanoscale: Features between one nanometer (10⁻⁹ m) and 100 nm (10⁻⁷ m) or 0.1 μm.
3.09.1 Introduction to nanoscale mineral and rock decay

Scale is a vitally important concern in the development of geomorphic weathering theory (Finlay et al., 2020; Hall, 2006a, 2006b; Matsuoka et al., 2017a, 2017b; Phillips, 2000; Pope, 2015; Turkington et al., 2005; Viles, 2001). Scale is a key variable in the boundary layer model designed to interpret spatial variability in weathering (Pope et al., 1995). Scale have consumed much thought and research trying to link the largely disparate weathering subfields of controlled laboratory studies and field-based investigations (Ranfield and Barker, 1994; Brantley, 2005; Brantley and Mellott, 2000; Brantley and Velbel, 1993; Casey et al., 1993; Hellmann et al., 2012; Matsuoka et al., 2017b; Meunier et al., 2007; Navarre-Sitchler and Brantley, 2007; Nishiyama and Yokoyama, 2017; Putnis and Ruiz-Agudo, 2013; Swoboda-Colberg and Drever, 1993; Turkington and Paradise, 2005; White, 2005; Yokoyama and Nishiyama, 2017; Zhu et al., 2006).

Thresholds are also an important focus in geomorphic weathering research (Paradise, 1995; Pope et al., 2002). A key scale threshold exists between nanoscale processes and those operating even at the micron-scale. In his 2001 presidential address to the Geochemical Society, Michael Hochella, Jr. emphasized: “nanoscience is based on the premise that materials properties in the bulk do not simply scale into the nanodomain, but property modification, and in some cases entirely different properties, are to be expected… In the nanoscale size range, physical, electrical, magnetic, thermal, kinetic, and other properties can be altered dramatically simply due to the physical dimensions of the material” (Hochella, 2002a, 2002b, p. 738).

Interactions at the micron-scale simply do not reflect molecular dynamics in the nanoscale chemical environment, in part because processes at the nanoscale can undergo substantial changes when exposed to water (Hovelmann et al., 2018; Kalinichev et al., 2007; Putnis, 2019; Wang et al., 2006; Zhang et al., 2003). Putnis and Ruiz-Agudo (2013: 177) explain the basics:

When minerals come into contact with aqueous fluids with which they are out of equilibrium, reactions begin as the new system seeks to establish a new equilibrium (lower energy state). If the aqueous fluid is undersaturated with respect to a mineral, the mineral will dissolve until the fluid becomes saturated with the mineral phase. However, if the fluid becomes supersaturated with any new mineral phase, the latter may precipitate by nucleation and subsequently grow.

Nanoscale is typically defined as examining features between one nanometer (10^{-9} m) and 100 nm (10^{-7} m) or 0.1 microns (Fig. 1). One way to visualize the nanoscale is to look at your hand; the scale jump between the entire Earth and your hand is the same dimensional scale difference as the jump from your hand to a nanoparticle. Nanoscale processes are not included in the "microscale," defined by Pope et al. (1995: 220) as being submillimeter, because a very different realm of weathering processes operate below 0.1 μm. Research on nanoscale weathering is no longer in its infancy, having grown up with progressive improvements in high resolution transmission electron microscopy (HRTEM) since the 1980s. The first of this research tended to focus on the very different water-mineral interaction that occurs in the nanodomain within minerals, in that even microfracture capillary water (Meunier et al., 2007) behaves differently from water held within mineral internal surfaces (Hochella, 2002b). The first two decades in the 21st century has seen a diversification of nanoscale weathering research (Matsuoka et al., 2017a; Mantha et al., 2019; Putnis, 2019), including the beginnings of attention paid to connections between geomorphology and nanoscale processes (Basilie-Doelsch et al., 2015; Finlay et al., 2020; Lybrand et al., 2019; Yokoyama and Nishiyama, 2017).

After introducing nanoscale techniques and issues related to geomorphic interpretation, this article covers case studies in four different areas: interpreting forms of rock decay; nanoscale processes limiting rates of erosion; biological mineral decay at the nanoscale; the importance of nanoscale processes related to dust generation, and some applications of meteoric 10Be. Exactly how the study of nanoscale rock and mineral decay will alter the field of geomorphology is severely limited by the relatively few number of geomorphologists who study these processes. Not enough researchers have carried out at the nanoscale to reach a critical mass of scientists to discuss cohesive theory-building on connections with landform evolution. That is why this review consists of a series of case studies organized around geomorphic themes. Thus, our hope is that a dialogue will develop on how the nanoscale connects to broader theoretical issues in geomorphology. Such an informed dialogue, however, will require that more geomorphologists engage in nanoscale geomorphic research.

Please note that we try to eschew here, as much as possible, the term “weathering” for the reasons explained by Hall et al. (2012) and also in the Dixon and Hall article of this volume. We will use instead the suggested term rock decay. Sometimes, however, the term weathering is simply too enounced at the present time to completely discard and we feel forced to use weathering in certain contexts.

**Splintering** Rock fracturing in a pattern of subparallel fractures that resembles a book that has been thrown in water and then dried.

**Thermal fracturing** Breaking of minerals from the process of heating and cooling, such as the passage of a wildfire over rock surfaces.
3.09.2 Nanoscale techniques and interpretation issues in geomorphology

3.09.2.1 Nanoscale resolution microscopy

The study of earth materials has been enhanced in the past two decades through the use of high-resolution transmission electron microscopy (HRTEM) and other precision techniques. Ongoing technique developments over the past four decades has led to an array of imaging and analysis tools available to examine weathering processes and products (Table 1). Each technique has its advantages and limitations that are reviewed in detail elsewhere (Lee, 2010) with a useful review on strategies to understand bacteria and fungal interactions by Balogh-Brunstad et al. (2020). Mitchell et al. (2021) also offer a useful strategy of bringing many of the methods in Table 1 together called “correlative microscopy” that crosses dimensions (2D-3D) and scales (from nm to cm). This section overviews a few methods that we have used here or could be used in geomorphological studies of nanoscale mineral and rock decay.

The basic idea behind most high-resolution microscopy is to thin a sample enough so that electrons can pass through the sample upon irradiation with a 80–300 kV electron beam. Given the nature of the material and the particular techniques...
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Table 1 Overview of nanoscale microscopy techniques useful in rock decay research.

<table>
<thead>
<tr>
<th>Technique (and acronym)</th>
<th>Information obtained</th>
<th>Spatial resolution</th>
<th>Limitations</th>
</tr>
</thead>
<tbody>
<tr>
<td>Coupled dual-beam focused ion beam electron microscopy (FIB-EM)</td>
<td>Used to create and image cross-sections in situ, widely used to extract sections for TEM analysis. Real-time imaging in SEM mode during ion milling.</td>
<td>( \approx 1 \text{ nm} )</td>
<td>Maximum sample and scan size, requires vacuum, Ga ion implantation</td>
</tr>
<tr>
<td>High resolution transmission electron microscopy (HRTEM)</td>
<td>2-D spatial imaging, lattice imaging</td>
<td>( \approx 0.08 \text{ nm} )</td>
<td>Small area, sample preparation challenges, sample thickness (&lt; 50 \text{ nm} ); Detection limit varies, ( \approx 0.2 \text{ Wt.%} ).</td>
</tr>
<tr>
<td>Energy dispersive X-ray analysis (EDX)</td>
<td>Elemental composition, X-ray mapping of elements</td>
<td>( &gt; 1 \text{ nm} ) (HRTEM); ( &gt; 20 \text{ nm} ) (SEM)</td>
<td>Difficult for light element detection; best results with light elements, requires high vacuum and thin specimens</td>
</tr>
<tr>
<td>Energy-filtered TEM (EFTEM)</td>
<td>Mapping of elements detectable from EELS spectrum</td>
<td>( &lt; 1 \text{ nm} )</td>
<td></td>
</tr>
<tr>
<td>Scanning Transmission Electron Microscopy (STEM)</td>
<td>2-D special imaging, high contrast</td>
<td>( &lt; 1 \text{ nm} )</td>
<td>Requires vacuum, thin specimen</td>
</tr>
<tr>
<td>Scanning electron microscopy (SEM) with back-scattered electron detector (BSE)</td>
<td>Average atomic number (Z) revealed through contrast in grayscale image</td>
<td>( &gt; 5 \text{ nm} )</td>
<td>Generally requires vacuum (dry samples), sample size dependent on chamber size</td>
</tr>
<tr>
<td>Scanning electron microscopy (SEM) with secondary electrons (SE)</td>
<td>2-D spatial imaging</td>
<td>( &gt; 1 \text{ nm} )</td>
<td>Requires vacuum, sample size dependent on chamber size</td>
</tr>
<tr>
<td>Atomic Force Microscopy (AFM or FM)</td>
<td>3-D surface microtopography</td>
<td>( &lt; 1 \text{ nm} ) in Z, (&lt; 10 \text{ nm} ) X,Y</td>
<td>Maximum scanning area of about ( 150 \times 150 \mu\text{m} ); flat samples ideal</td>
</tr>
<tr>
<td>Secondary ion mass spectroscopy (SIMS)</td>
<td>Elemental and isotopic composition</td>
<td>( 50 \text{ nm} ) with NanoSIMS</td>
<td>Requires vacuum, damages analysis region</td>
</tr>
</tbody>
</table>

used the thickness for high-resolution imaging can vary from \( \approx 10 \) to \( 50 \text{ nm} \). Today most high-resolution TEM specimens are prepared using a coupled dual-beam focused ion beam electron microscopy (FIB-EM). The FIB-EM can site specifically ion mill and deposit metals; coupled with a micromanipulator the FIB-EM can extract features/regions on the order of \( 10-30 \mu\text{m} \) wide and carry out nanoscale tomography (Schiffbauer and Xiao, 2009). Once extracted and mounted to a TEM grid in situ the FIB-EM is used to thin the extracted region until it becomes electron transparent and usable in the TEM (often referred to as a lamella) (Brown and Lee, 2007). FIB-EM prepared samples have many advantages, such as allowing investigators to see the context of a lamella in BSE, SE, STEM, and EDX modes prior to breaking vacuum and moving the specimen to a TEM for higher resolution analysis. Other techniques used to prepare samples for TEM include mechanical crushing of minerals, which can generate edges that are sufficiently electron transparent and ultramicrotoming, which can prepare electron transparent slices of material using a diamond knife. Tripod polishing and precision ion polishing (PIPS) are also useful for obtaining electron transparent areas from bulk specimens for TEM analysis.

The reader who has not yet utilized modern scanning/transmission electron microscopes (TEM/STEM) should be aware of the need for understanding careful sample preparation and technical details. For example, imaging starts with placement of the TEM grid into a sample holder and insertion of the holder through an airlock, into a high vacuum electron column. HRTEMs use much higher electron beam voltages (typically from 80 to 300 kV) than SEMs used by a lot of weathering researchers. The high voltage, coupled with a thin sample, decreases interaction volume and allows EDX measurements to be made with spot sizes of \( < 10 \text{ nm} \), in contrast to typical SEM interaction volumes on the order of \( \approx 1 \mu\text{m} \) at 15 kV with thicker/bulk samples. Higher voltage has disadvantages that can become advantages; for example, we illustrate how beam damage on thin samples, leaving behind a series of holes or grid patterns (e.g., Lee, 2010: 10) can be used in nanoscale mapping of mineral decay. In general, the high spatial resolution of STEM and the ability to utilize atomic number (Z) contrast makes it a particularly powerful tool in weathering studies (Brown and Lee, 2007).

Nanoscale studies generate a variety of different types of imagery, formed by filtering scattered electrons. Bright-field images are generated from a direct beam that contains unscattered and low-angle forward scattered electrons. Dark-field images, in contrast, are generated only from forward-scattered electrons. The thickness, atomic number and Bragg diffraction (in crystalline material) will control the angle of scattering and the intensity of scattering—all creating the HRTEM image. Since mineralogy is often important in weathering, electron diffraction patterns record the angular distribution of electrons where minerals can be identified by the spacing of spots using selected-area electron diffraction (SED), precession electron diffraction (PED), or convergent-beam electron diffraction (CBED). It is also possible to generate images of specific elements at the subnanoscale using energy-filtered TEM imaging that takes a specific region of an EELS spectrum to form an image.

Compositional analysis is typically carried out by energy dispersive X-ray spectroscopy (EDX) for higher atomic number elements, and electron energy loss spectroscopy (EELS) for lighter elements. EELS measures energy lost through ionization of sample atoms, separating electrons according to the energy they have lost. EELS can measure elemental abundance and also determine valence states at spatial resolutions less than one nanometer.
### 3.09.2.2 Linking scales through digital image processing

An increasingly important weathering literature focuses on explaining offsets between field-based quantification of weathering and laboratory studies of weathering rates (Banfield and Barker, 1994; Brantley, 2005; Brantley and Mellott, 2000; Brantley and Velbel, 1993; Casey et al., 1993; Hellmann et al., 2012; Matsuoka et al., 2017b; Meunier et al., 2007; Navarre-Stitchler and Brantley, 2007; Nishiyama and Yokoyama, 2017; Putnis and Ruiz-Agudo, 2013; Swoboda-Colberg and Drever, 1993; Turkington and Paradise, 2005; White, 2005; Yokoyama and Nishiyama, 2017; Zhu et al., 2006). Brantley (2005, p. 108) concisely summarized some key issues:

> ... extrapolating from one scale to another (scaling up) is often not quantitatively successful. For example, quantitative extrapolation of laboratory rates to field systems remains difficult, and we now recognize that multiple factors contribute to this discrepancy... Of particular importance is the reactive surface area of dissolving minerals: this term must be investigated and understood more thoroughly. In addition, laboratory rates are generally measured far from equilibrium, whereas natural weathering often occurs closer to equilibrium where dissolution is slower. The scaling-up problem inherent in the laboratory-field discrepancy may well be solved through increased understanding developed as we bridge scales of analysis from the nano to global scale...

Meunier et al. (2007: 432) explicitly advocates that the missing link in bridging scales rests at the scale of hand specimens:

> As weathering is a multi-scale phenomenon, theoretically any model needs to integrate the solid-fluid exchanges from the atomic interactions at the very surface of primary and secondary minerals (nanometer), to the rock sample (decimeter) and finally to the watershed (kilometer)... The extensive use of high-resolution transmission electron microscopy (HRTEM), atomic force microscopy (AFM) and spectroscopy have significantly improved our knowledge of fluid-mineral reactions and their related interactions. Conversely, the large-scale studies based on isotope mass balance methods provide denudation rates for provinces or continents. Surprisingly, it is at the hand-specimen scale where efforts should now be directed.

One strategy that could help bridge the discrepancy at the hand sample level is *in situ* quantitative analysis of mineral dissolution (Dorn, 1995) using digital image processing (e.g., Fig. 2). This direct measurement of mineral dissolution has led to an understanding of field relationships on the temperature dependence of weathering (Dorn and Brady, 1995), and understanding of the effects of rainfall and temperature on mineral weathering (Brady et al., 1999), long-term rates of glass dissolution (Gordon and Brady, 2002), and the role of lichens and rock coatings on field mineral weathering rates (Gordon and Dorn, 2005a, 2005b).
Although digital image processing of BSE imagery has only been used to analyze 
field weathering that has taken place over $10^1$ to $10^5$ years and at the micron scale, there is no reason why laboratory samples or nanoscale samples could not be similarly analyzed. For example, the subnanometer conduits that carry aqueous fluids (Banfield and Barker, 1994) or the nanoscale etch pits could be prepared for digital image processing to quantify nanoscale porosity (Fig. 2).

Previous research on digital image processing to quantify weathering focused on the micron scale, typically measuring $10^5$ square microns of mineral cross sections imaged with BSE per field site. New advances in electron microscopy increased the resolution of back-scatter images. It is now possible to analyze mineral dissolution at the nanoscale with BSE (e.g., Fig. 3). “Scaling-up” (cf. Brantley, 2005: 108) and then “scaling-down” becomes a task of taking lower resolution BSE and higher resolution BSE images using STEM at different scales and measuring in situ dissolution. Measurement of field and laboratory weathered samples alike at different scales, thus, enables the integration of data to the hand sample level—as advocated by Meunier et al. (2007).

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### 3.09.2.3 Crossing the nanoscale to micron-scale threshold

There is a danger involved in extrapolating nanoscale weathering observations to smaller scales (larger areas). Misunderstanding of the threshold between processes operating at the micron-to-meterscale versus the nanoscale environment can lead to confusion and misinterpretation. An example comes from the rock varnish literature where nanoscale instability was simply assumed to invalidate (Garvie et al., 2008, 2009) observations at the micron scale of over 10,000 microlamination sequences (e.g., Fig. 4) recording paleo-climatic fluctuations (Liu, 2003, 2010; Liu and Broecker, 2000, 2007, 2008a, 2008b; Liu et al., 2000; Zhou et al., 2000). In summary, Garvie et al. (2008, 2009) analyzed only three samples with HRTEM at the nanoscale, finding evidence for nanoscale instability of manganese oxides. Garvie et al. (2008, 2009) made the mistake of simply assuming that nanoscale instability meant that micron-scale paleo-climatic interpretations of over a decade rock varnish research by T. Liu and colleagues must be invalid. That is an invalid assumption.

The issue here is not a problem with the basic observation of nanoscale instability. Prior to Garvie et al. (2008, 2009), others noted that nanoscale instability of Mn-oxides is the key to explaining how rock varnish forms (Dorn, 1998, 2007; Krinsley, 1998; McKeown and Post, 2001; Potter, 1979). In the polygenetic model of varnish formation, micron-scale microbial processes fix Mn and Fe oxides (Fig. 5), followed by nanoscale instability that moves Mn and Fe oxides between bacterial casts and clay minerals. Ongoing shuffling of Mn-Fe oxides reoccurs at the nanoscale to cement clays and Mn-Fe oxides to rock surfaces and to previous layers of varnish (Dorn, 2007; Krinsley, 1998; Krinsley et al., 2017).
While nanoscale instability is a key to varnish formation, it does not invalidate micron-scale processes—as Garvie et al. (2008, 2009) naively assumed. As Krinsley (1998, p. 721) explained: “at the spatial scale of microns... some varnish appears quite stable with distinct layering patterns... At the spatial scale of nanometers as viewed with HRTEM, varnish appears to be in an open system... This is analogous to automobiles moving in a crowded parking lot, with oxides moving around until they find a suitable parking space in clay minerals.” Cars moving in a parking lot does not imply that the parking lot itself is unstable.

The broader issue here is that the geochemistry newly formed mineral material at the nanoscale involves a great number of unknown issues. Every investigator who has explored, for example, varnish at the nanoscale agrees that Mn and Fe oxide instability is common (Dorn, 1998, 2007; Krinsley, 1998; Krinsley et al., 1990, 1995, 2017; Macholdt et al., 2015; McKeown and Post, 2001; Garvie et al., 2008, 2009), but HRTEM nanoscale observations do nothing to invalidate the extensively replicated-scale stratigraphy (Liu, 2003, 2010; Liu and Broecker, 2000, 2007, 2008a, 2008b; Liu et al., 2000; Zhou et al., 2000). This example highlights just one of the dangers of extrapolating nanoscale observations to even micron-scale phenomena.
3.09.3 Applying nanoscale strategies to rock decay forms

This section presents different areas of research in geomorphology where attention to the nanoscale has either yielded or has the potential to yield new insights.

3.09.3.1 Case hardening

Case hardening of the outermost shell of a rock involves the migration of rock coating constituents into pore spaces in the weathering rind of minerals (Fig. 6A) and the outer rim of a rock (Conca and Rossman, 1982; Dorn, 2009; Dorn et al., 2012, 2017; Gordon and Dorn, 2005a). At first, it might seem counterintuitive to think that both dissolution and precipitation of new mineral matter can occur together, but both processes do operate in tandem at the nanoscale (e.g., Emmanuel, 2014). The dissolution of a variety of different rock coatings that have formed on top of a weathering rind produces case hardening; this section focuses on two of the most common remobilized rock coatings: silica glaze and rock varnish.

Fig. 5  Nanoscale instability of manganese and iron is key to the formation of rock varnish. (A) Budding bacteria hyphae form (Krinsley et al., 2017) emerging from a cocci-form. The EDS spectra measured in the box consists mostly of artifacts associated with mounting and preparation of the sample. However, annotation of the EDS spectra with a larger font identifies the composition of the hyphae form as mostly Mn and Fe, with some Si and Ca. Notice that the granules of Mn-Fe mobilize from bacterial sheath fragments, are transported a few nanometers, and then are fixed into mixed-layered illite-montmorillonite clays. These nanometer-scale Mn-oxides can be remobilized and refixed over and over again in a shifting nanoscale mineral structure (McKeown and Post, 2001: 712). However, this nanoscale remobilization does not erase the varnish lamination layers observed at the micron scale (Fig. 4).

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The first nanoscale investigation of silica glaze formation revealed that silica precipitates in the form of spheroids with diameters between 20 and 70 nm (Langworthy et al., 2010) as seen in Fig. 6B. EDX analyses by Langworthy et al. (2010) indicate that these spheroids are composed of just Si and O. Spheroid diameter is particularly significant for interpreting the behavior of water at the nanoscale. There is a transition between complete and partial wetting on silica surfaces between 20 and 70 nm (Churaev, 2003; Zorin et al., 1992). This is the size range of the observed spheroids. Dom (1998) originally suggested that crossing this transition ruptures the metastable wetting film (Zorin et al., 1992) resulting in silica precipitation—a hypothesis that is consistent with the presence of these spheroids (Langworthy et al., 2010).

Silica is an important case-hardening agent (Conca and Rossman, 1982; Dom, 2004; Dom et al., 2012; Gordon and Dom, 2005a; Mottershead and Pye, 1994; Washburn, 1969; Wilhelmy, 1964; Robinson and Williams, 1992; Tratebas et al., 2004). Silica fills in voids in the weathering rind by growing new spheroids into pore spaces, since droplets “do not cling to a surface immediately after formation, but move somewhat before they attach to the [pre-existing] solid” (Koopal et al., 1999, p. 24). Thus, nanoscale silica instability explains silica-impregnation and subsequent case hardening of weathering rinds (Fig. 6).

While silica glaze is the most dominant case hardening agent, all rock coatings undergo dissolution and reprecipitation of the mobilized constituents into the underlying weathering rind. Fig. 7 illustrates an example where rock varnish forms on a surface with abundant microcolonial fungi that dissolves varnish; thus, varnish is always growing and dissolving. The mobilized constituents reprecipitate inside the pore spaces of the weathering rind—much in the same way as silica glaze (Fig. 7B).

Rock coatings can also stabilize flaking rock surfaces by themselves, as exemplified in Fig. 8. The granitic clasts on many pediments and alluvial-fan surfaces in warm deserts undergo exfoliation (flaking) due to instability of the underlying weathering rind. It is common to see patches of rock surfaces darkened by the accumulation of rock varnish (Fig. 8). The BSE image in Fig. 8 reveals that rock varnish stabilized such patches—at least temporarily. This sort of flaking and case hardening can occur in multiple cycles, where varnish reforms over a flaked surface that in turn hardens the underlying weathering rind.

3.09.3.2 Tafoni

Tafoni (Paradise, 2013) can enlarge by a variety of processes that can involve internal moisture (Mol and Viles, 2012), temperature fluctuations (Hall and André, 2006), precipitation of carbonate and dissolution of primary mineral grains (Campbell, 1999), sea salts (Mottershead and Pye, 1994), and other rock-weakening processes. The location of rock detachment, however, has rarely been examined at the nanoscale.

Figs. 9 and 10 provide both micron-scale and nanoscale views of detachment of material inside a tafone in breccia (originally debris flows) and granodiorite, respectively. BSE imagery at the micron scale shows that several processes happen in tandem: dissolution increasing porosity, and mineral alteration and then physical separation are both occurring in the matrix of old debris flows (Figs. 9C and 10B). Nanoscale imagery of the detachment of individual grains of debris-flow matrix (Fig. 9D) and biotite (Fig. 10C) suggest that detachment is a gradual process starting with a few nanometers of separation that then grows along a grain boundary and widens.

3.09.3.3 Arctic & alpine settings

Thermal stresses (Hall, 1999, 2006b; Hall and André, 2001, 2003; Hall and Thorn, 2011) and frost cracking (or frost wedging) (Van Vliet-Lanoë and Fox, 2018; Walder and Hallet, 1986) greatly influence cold climate geomorphic systems. The visual dominance of bare rock in alpine, arctic and Antarctic landscapes led to the paradigm that “physical weathering” dominates cold climates as...

Nanoscale observations in cold climate settings ranging from Antarctica, to Greenland and the Tibetan Plateau fully support prior research highlighting the importance of chemical decay of rock and minerals (Dorn and Krinsley, 2019; Smith and Horgan, 2021). For example, quartz is generally thought to be highly resistant to chemical reactions, especially in a cold and dry setting like the Tibetan Plateau, a perspective that is not supported by nanoscale observations. A free quartz sample from the Akesu volcanic field, for example, shows nanoscale roughness from dissolution (Fig. 11C), and this roughness plays an important role in the adhesion of dust (Fig. 11A). Dorn and Krinsley (2019) also found nanoscale evidence of iron mobility, manganese mobility, as well as magnetite and plagioclase dissolution.

3.09.3.4 Splintering and nanoscale etching

Etching is a term used at almost all scales in geomorphology (Fig. 1), from etch plains that are erosion surfaces (Campbell and Twidale, 1991; Twidale, 2002), to etching that generates karst weathering forms in sandstone (Young, 1988; Young and Young, 1992), to etching of minerals in soils used as a relative dating method (Locke, 1979, 1986), to nanoscale etch pits generated by bacteria and analyzed by atomic force microscopy (Buss et al., 2007). In the context of mineral weathering, however, analyses of etch pit morphologies are traditionally carried out with secondary electrons and sometimes back-scattered electrons (Hall and Michaud, 1988; Lee and Parsons, 1995; White, 2005; Song et al., 2010), although they are sometimes studied at both the micrometer and nanometer scale (Brandt et al., 2003; Buss et al., 2007; Hochella and Banfield, 1995; Lee et al., 2007). As one would expect, isolated etch pits can be seen at the nanometer scale that “are typically only a few nanometers in depth and therefore not visible with SEM” (Brandt et al., 2003: 1457). Higher resolution nanoscale research reveals that the nanotexture of minerals, produced by defects dislocation densities and patterns, play a key role in how minerals decay (Banfield and Barker, 1994; Brown and Lee, 2007; Hochella and Banfield, 1995; Lee et al., 2007).

Studies of mineral etching at the nanoscale have raised a critically important conundrum with respect of clay mineral production by chemical weathering. Decades of thought about mineral weathering generated a paradigm that feldspar chemical weathering always leads to clay mineral production, as supported by some of the first nanoscale weathering studies of feldspars (Banfield and Egggeleton, 1990). More recent research, however, reveals that water to rock ratios in the weathering environment may be
a key determinant in whether or not clay mineral alteration products are found at the nanometer scale (Lee et al., 2007). In other words, clay minerals do not always occur next to feldspar minerals; the nanoscale weathering environment is an important player, especially via capillary scale and nanoscale water.

The scale jump connection between mineral nanoetching and much larger forms has not been considered in the literature, according to our understanding. However, we believe that making such a linkage is possible and propose here a speculative connection between nanoetching and the weathering form termed "splintering" (Dom et al., 2008; Fitzner and Heinrichs, 2004; Fitzner et al., 1997; Stoppato and Bini, 2003). Splintering is where all different types of rocks, from basalt to sandstone to schist to granite, have the appearance of pages of a book that has been wetted and then dried (Fig. 12).

In the case of a foliated metamorphic rock, where grains are aligned, the weathering form of splintering is likely a consequence of differential weathering of more susceptible minerals at the micrometer to millimeter scale. Splintering simply reflects the millimeter to centimeter expression of micron-scale processes (Fig. 13). However, splintering is a ubiquitous weathering form in virtually all rock types, even those with no obvious alignment of minerals. Explaining how this takes place at the hand-sample scale has not been a topic of focus in the geomorphic weathering literature.

Our hypothesis that relates splintering forms (Fig. 12) to the nanoscale alignment of etching is that subparallel alignment of mineral etching at the nanoscale can lead to alignment of capillary water conduits at the micrometer and then millimeter scales. These capillary water conduits appear to be key agents for the propagation of mineral weathering (Meunier et al., 2007).

Evidence in support of this hypothesis is presented in Fig. 14, a case study of a silicified dolomite from South Australia, where the alignment of splintering at the hand sample scale corresponds with dissolution of microfractures carrying capillary water at the micron scale, and then also with alignment of connected weathered pores at the nanoscale. Nanoscale alignments appear to enable
propagation of capillary water-bearing fractures in subparallel alignments that in turn generated the splintering weathering form seen at the hand sample scale. By way of analogy, this conceptual model is similar to the way a parallel drainage pattern develops through taking advantage of fracture patterns.

3.09.4 Nanoscale processes as a limiting factor in erosion

Geomorphologists have long been aware of the importance of rock decay in limiting rates of erosion. G.K. Gilbert introduced the notion of a “weathering-limited” landscape (Gilbert, 1877) bare-rock landforms. Gilbert’s concept differs from a more popular and more recent derivative of a detachment-limited condition (Ahnert, 1976). Gilbert (1877: 105) explained that “in regions of small rainfall, surface degradation is usually limited by the slow rate of disintegration; while in regions of great rainfall, it is limited by the rate of transportation.” Rather than trying to measure Gilbert’s (1877: 105) “rate of disintegration,” geomorphologists tended toward measuring “detachment-limited” systems (Howard, 1994). Howard (1994: 2261–2262) noted that the rate of transport of weathered materials is “limited by the ability of the flow to entrain or erode regolith (residual soils or colluvium) or bedrock, giving ‘detachment-limited conditions.’” Thus, detachment-limited systems can be analyzed through sediment transport measurements over short timescales (Howard, 1994), while cosmogenic nuclides measure bedrock detachment rates over longer timespans (Seong et al., 2016a).

The first part of this section focuses on the importance of nanoscale processes in controlling Gilbert’s weathering-limited processes of disintegration operating in warm deserts, while the second part of this section explores an example of how nanoscale processes influence Ahnert’s detachment-limited erosion in the context of pediment and strath erosion in granitic materials of the Sonoran Desert, Arizona, USA.

3.09.4.1 G.K. Gilbert’s weathering-limited landscapes

Fractures found in Earth’s rocks originate through rock-forming processes and tectonic deformation (Ehlen, 2002; Engelder, 1987; Eyles et al., 1997; Hobbs, 1967; Molnar et al., 2007; Schultz, 2000; St Clair et al., 2015; Twidale and Bourne, 1978). These fractures, or joints, influence geomorphic processes and forms across different scales (Scheidegger, 2001; Scott and Wohl, 2018). Although

Fig. 9 Tafone enlargement through nanoscale detachment at Papago Park, Phoenix, USA. Image (A) illustrates a pediment and inselberg complex composed of breccia that originated as debris flows, where the arrow points to the sampled tafone. (B) Sampling location at the rear of the tafone. (C) Micron-scale BSE image showing how the silty-clay matrix of the debris-flow breccia separates and allows detachment, where the small D indicates the location of the HRTEM image. (D) HRTEM image showing particles in the matrix of the debris-flow breccia that are separating from one another. This separation is just a few nanometers at first, but grows until a fracture can be seen at the micron scale.
fracture widening and lengthening can occur by a variety of erosive processes (Scott and Wohl, 2018). Rock decay by physical and chemical processes plays a key role in fracture propagation—often leading to rock detachment. Three general types of rock-decay processes physically wedge open fractures through frost cracking (or frost wedging) (Walder and Hallet, 1986), roots and their associated fungi (Bramley et al., 2017; Gadd, 2007; Merrill, 1906), and dirt cracking (Ollier, 1965). Dirt-cracking fines found inside rock fissures are not skeletal or embryonic soils (Certini et al., 2002; Darmody et al., 2008) or fills found in situ decayed rock (Frazier and Graham, 2000; Thoma et al., 1992). While the first two fracture-wedging processes are generally well known and generally taught in introductory courses, dirt cracking is rarely taught. Originally proposed in Australia as an insolation-related process (Ollier, 1965), experimental evidence and electron microscope studies revealed that the widening of fractures due to dirt cracking in warm deserts relates to two complementary processes (Dorn, 2011): first, calcrete precipitation wedges open fractures wide enough so that desert dust can begin to accumulate; second, wetting and drying of the desert dust then widens fractures to the point where spalling occurs (Dorn, 2011; Ollier, 1965). Dirt cracking leaves behind a visible signature, because the dust inside fractures promotes the development of an iron film on the walls of the fracture, while the laminar calcrete often leaves behind a whitish coating (Fig. 15).

The ubiquitous dust in warm deserts (Bullard and Livingston, 2009; Goudie, 1978) and laminar calcrete (Chitale, 1986; Coudé-Gaussen et al., 1984; Koning and Mansell, 2017; Shtober-Zisu et al., 2018; Villa et al., 1995) moves deeper into fractures, and dirt cracking eventually leads to erosion of bedrock desert landforms at rates ranging from 0.17% to 1.12% of a surface spalled every
thousand years (Dorn, 2018); thus, the dirt-cracking process alone is able to completely resurface desert bedrock landforms such as bornhardts in 165–600 ka, cliff faces composed of basalt and other resistant rocks in 139–417 ka, and slick rock in ~100 ka (Dorn, 2018).

Dirt cracking can be studied at a variety of spatial scales. At the field scale, areas of detachment can be mapped and quantified (Dorn, 2018). At the micron scale, the processes of dust infiltration and laminar calcrite precipitation can be analyzed through

Fig. 11 Altered quartz on the surface of a lava flow, Akesu volcanic field, Tibetan Plateau. (A) A dust particle adheres to the quartz surface that maintains a roughness from nanoscale dissolution. Note the bumpy appearance of the quartz. The dust particle has adhered to the surface long enough to accumulate a titanium-iron-rich film. (B) EDX analysis of the iron-rich film that is composed of mostly Si and Al, but with major amounts of Ti and Fe. (C) The very surface of the quartz has a microtopography that appears to be dissolution grooves.

Fig. 12 The weathering form of splintering seen at a hand specimen scale (left, where the flower width is 2 cm) and where the talus boulder is 2 m tall (right). Left image is of a hornfels at Black Canyon, Arizona; right image is of sandstone at Bryce National Park, Utah.
back-scattered electron microscopy and energy dispersive X-ray spectrometry (Fig. 16). However, it is at the nanoscale where the fissure wedging can be best observed (Fig. 17).

Quantitatively, dirt cracking is the single most important physical weathering process yet known in warm deserts (Dorn, 2018). This statement is true, in part, because no other physical weathering process has yet been measured in terms of its influence in resurfacing weathering-limited bedrock landforms. Ultimately, however, the rate of dirt cracking is limited by the rate of nanoscale processes widening fissures to the point of detachment.

3.09.4.2 Detachment-limited pediment & strath erosion

Larson and co-workers studied processes and rates of granitic landform development in the Sonoran Desert (Larson and Dorn, 2014; Larson et al., 2014, 2016; Seong et al., 2016b). A key-limiting factor in rates of erosion of granitic pediments (e.g., Fig. 18) and granitic straths is the detachment of grus (granitic minerals) from bedrock.

For pediments adjusting to base level changes (e.g., Fig. 18), erosion requires that the granitic bedrock be in a sufficient state of decay to enable detachment (Larson et al., 2016). Using the BSE technique discussed in Section 3.09.2, Larson et al. (2016) used the ratio of porosity in the incising channel to the porosity in bank materials as a proxy for erodability of bedrock. Banks that have less porosity are more resistant to erosion than channel floors and produce narrow incising washes (e.g., Mine Pediment in Fig. 18). In contrast, more decayed banks allow channels to widen and plane the pediment (e.g., Bush Pediment in Fig. 18). Fig. 19 illustrates the nature of granitic decay that leads to grussification and enables pediment erosion.

Concomitantly, analyses of ephemeral granitic drainages at South Mountain, Phoenix, USA, indicates that strath widening also requires mineral decay. Micron and nanoscale electron microscopy reveals that grussification of granitic bedrock in straths of even small washes occurs primarily through abiotic biotite oxidation and also biotic processes associated with mycorrhizal fungi and roots of plants growing along wash banks (Fig. 20). Ultimately, rates of strath widening are limited by long-term rates of decay of granitic minerals to the point where physical detachment can occur.

3.09.5 Nanoscale biological mineral decay

3.09.5.1 Ants as agents of carbon dioxide sequestration

Rising levels of atmospheric CO₂ and other greenhouse gases have been a major focus of interest in the late 20th and 21st centuries. Under natural conditions and over geological timescales, dissolution of calcium and magnesium silicates have played a major role in the sequestration of carbon dioxide through the precipitation of limestone and dolomite (Brady, 1991). Abiotic dissolution of Ca-Mg-silicates is much slower than dissolution influenced by biological agents; the biotic enhancement of weathering (BEW) has promoted global habitability (Schwartzman, 2002, 2017; Schwartzman and Volk, 1989) by accelerating rates of CO₂ sequestration. A quarter-century of monitoring samples extracted every 5 years from ant colonies reveals that ants may be the single most powerful
Fig. 14. The weathering form of splintering of a silicified dolomite, South Australia (A—hand sample scale), appears to correspond with the development of aligned micron-scale fractures that carry capillary water (B—micron scale BSE image), and in turn with the alignment of nanoscale pores that are connected (C—nanoscale HRTEM image) and could be responsible for fostering the growth of micron-scale fractures. Lines indicate locations of sample collection for analysis at progressively finer scales.

Fig. 15. This fissure once hosted eolian dust and some weathered rock fragments that were washed away prior to photography. The innermost side of the opened fissure is coated with laminar calcrete. The outer few centimeters are coated by a ring of black rock varnish. The remainder of the fracture side is covered by orange iron film.
agent of natural carbon sequestration; Ca-Mg-silicates placed in colonies of different ant species dissolved at rates 50x–300x controls, much faster than Ca-Mg-silicates placed in termite colonies or even root mats (Dorn, 2014).

Schmeckle et al. (2021) investigated a possible mechanism by which ant colonies greatly enhance BEW. They took an aqueous solution derived from crushed California harvester ants (*Pogonomyrmex californicus*) and used atomic force microscopy (AFM) to measure dissolution directly. The whole ant extracts (WAE) greatly accelerated rates of Ca-feldspar dissolution, supporting the assertion that ants can act directly as BEW agents (Schmeckle et al., 2021). They observed visible effects (e.g., Fig. 21) just 6 h after WAE was placed on polished surfaces of plagioclase feldspar samples.

![Fracture enlargement by dirt cracking](image)

Fig. 16 Fracture enlargement by dirt cracking. The “V” in the middle of the diagram is an idealized rock fracture where the different samples were collected to analyze dirt cracking. Ubiquitous fractures in warm deserts, such as this sample collected from Papago Park, Phoenix, USA, display a general sequence illustrated by micrographs taken at different depths. An idealized fracture contextualizes the depths at which the images were acquired. In this case, the fissure length was 5 mm. To preserve in situ relationships, the fissure was first filled with epoxy in the field prior to mechanical sampling. The scale in each micrograph is 100 μm in length. Top Position in Fissure: the fissure opens its widest at the intersection of the fissure and the inside of a tafone. Black epoxy indicates an abundance of void space, but some infilled debris eroded from the rock along sidewalls mixes with dust. Second Position in Fissure: silicate-dominated dust and rock debris (according to EDS spectra) fill in fractures a millimeter underneath the opening. Third Position in Fissure: as the fissure penetrates more into the host rock, carbonate, rock material from the side walls, and dust intermix. Deepest within the fissure: carbonate (calcium and magnesium carbonate, according to EDS Spectra), carbonate fills almost the entire fracture. Ongoing mobilization and reprecipitation appears to be the process by which fractures deepen.
A newly recognized form of calcium carbonate, hydrated crystalline calcium carbonate, is a product of biomineralization (Zou et al., 2019). When a plagioclase (Ca-silicate) grain was examined from the *Pogonomyrmex* ant nest, Palo Duro, West Texas from the 25-year study (Dorn, 2014), the texture of calcium carbonate had the same appearance as the hydrated crystalline calcium carbonate identified by Zou et al. (2019) (Fig. 22).

Further nanoscale evidence for the importance of ants in promoting the dissolution of Ca-silicates comes from a study of a polished cross-section of Hawaiian basalt placed in the same *Pogonomyrmex* ant nest, Palo Duro, West Texas (Dorn, 2014). A polished cross-section was removed from the field after 10 years and examined for changes. Ground control points (epoxy dots)
helped relocate different spots on the cross-section. Fig. 23 exemplifies the sorts of plagioclase etching that occurred in the ant colony after just 10 years. The pitting process appears to involve both dissolution of plagioclase and alteration to clay minerals. Gentle washing of the cross-section dislodged most of the alteration products, but some clays can be seen at nanoscale resolutions (Fig. 23C).

3.09.5.2 Biological processes and the fallacy of Goldich’s weathering sequence

The generally accepted view is that mineral weathering proceeds along the reverse of Bowen’s reaction series that explains mineral crystallization. The weathering sequence published by Goldich (1938) is the opposite of Bowen’s sequence. It starts with the weathering of olivine, since olivine formed at the hottest temperatures, and ends with quartz being one of the most stable minerals because it formed last at the coolest temperatures. Research on biotic mineral and rock decay over the past several decades continues to reveal its importance at Earth’s surface by such agents as fungi (Gadd, 2007, 2017; Li et al., 2016; Wild et al., 2021), and also far below as microorganisms are found at great depth in Earth (Reith, 2011). Biological processes, and not thermodynamics, may explain why Goldich’s weathering sequence is valid in some conditions and locations.

An unstated but critical assumption in Goldich’s thermodynamic interpretation was discovered through field-based research using BSE to study the surfaces of lava flows of Hualalai, Hawaii. This research revealed that olivine does not weather first (Wasklewicz, 1994; Wasklewicz et al., 1993; ), as predicted by the Goldich weathering sequence (Goldich, 1938). The field sites where olivine weathered last, not first, had a paucity of organic acids—being located in the rainshadow of both Mauna Loa and Hualalai. Olivine was much less weathered than plagioclase and clinopyroxenes in those lava flow surfaces devoid of acid-producing lichens and fungi and distant from vegetation. In contrast, olivine weathered much faster at lava flow surfaces that hosted acid-producing organisms. Nanoscale research may hold the key to explain the apparent contradiction between Goldich’s (1938) sequence and the observations from the rainshadow of Hawaii.

Goldich’s (1938) original field sites were located in a humid environment that contained abundant organic acids and organisms. Other workers have confirmed Goldich’s sequence in similar humid environmental settings (Velbel, 1993). A working hypothesis is that Goldich’s weathering sequence could be more a function of biotic weathering environment than the thermodynamics of mineral formation.

An important biotic influence on the sequence of mineral weathering could be microbial weathering. Laboratory research on bacterial weathering at the micron-scale determined that Goldich’s weathering sequence is in accord with the vulnerability of
Fig. 20  Secondary electron images of rock decay along banks fronted by hard-rock straths. The images all show the effects of mycorrhizal fungi (image A) and roots (B). Mineralogy (q = quartz; p = plagioclase) is based on EDX analyses. Most of the effect appears to be the decay of plagioclase grains to the point where they have very little internal cohesion. Image (C) highlights this where the relatively intact quartz contrasts with the thoroughly disintegrated plagioclase. However, quartz also decays, as exhibited by nanoscale dissolution pits in image (D), where the pits are visible because the mycorrhizal fungi were removed. The lines on the quartz surface have the same EDX Si and O signature as the quartz, and thus they could reflect redeposition of silica. Image (E) shows that the process of decay can involve physical force breaking apart minerals, as evidenced by the angular particles (arrows) of quartz found in abundance in physical proximity to the root. Scale bars are in micrometers.

Fig. 21  A comparison of a polished plagioclase surface before application of a whole ant extract (WAE) solution and after application for 6 h. Rq is a measure of surface roughness used in AFM studies, and Schmeckle et al. (2021) found a highly statistically significant difference between the control (WAE 0 h) and just 6 h of WAE. NOTE: the horizontal streaks are an artifact of the AFM analysis.
minerals to bacteria (Song et al., 2010). One possible reason for microbial activity causing the Goldich sequence could be the nutrient needs of microbes (Bennett et al., 2001):

A basic tenet of sediment diagenesis, the “Goldich Weathering Sequence” (Goldich, 1938), states that the most unstable silicate mineral will weather (dissolve) first, with more resistant silicates taking progressively longer to dissolve (from least to most stable). olivine < plagioclase - < albite < anorthoclase < microcline < quartz. The observed weathering sequence of minerals in an anaerobic, microbially controlled system, however, is almost opposite, with olivine stable with respect to microcline, and the relationship between microbial colonization and weathering rate almost perfectly correlated. This suggests that, in some environments, the indigenous microorganisms may significantly alter weathering patterns as they aggressively scavenge limiting nutrients.

Another nanoscale explanation for the discrepancy between Goldich’s sequence and weathering in abiotic contexts (Barker and Banfield, 1996) follows:

Biologically mediated weathering involves a complex dissolution/selective transport/recrystallization mechanism occurring within the acidic extra-cellular gels coating all mineral surfaces. A specialized weathering microenvironment around each mineral grain initially produces minute phyllosilicate crystallites. A rind of clay minerals forms around the dissolving parent phase, eventually culminating in abundant 5–10 μm diameter polymer-bound aggregates of face-to-face oriented clay minerals of homogeneous composition. Physiochemical weathering of ferrohastingsite produces topotactically oriented smectite and goethite. The cleavage-controlled reaction is neither isochemoal nor isovolumetric.

A sub-40-nm scale study of microbial weathering of a Mg-Fe-pyroxene in a meteorite that was exposed to weathering for about 70 years (Benzerara et al., 2005a, 2005b) provides additional insight. Microbial interactions over seven decades led to carbonate precipitation in the form of rod-shaped nanocrystals of calcite and the development of an amorphous Al-rich layer leading to the conclusion that microorganisms create nanoscale weathering environments that dramatically alter weathering. Micron- and nanoscale studies of fungi and bacteria weathering of an exposed granitic pegmatite similarly stress the importance of microbial ecology in subaerial settings (Gleeson et al., 2005, 2006).

One possible way that microorganisms might affect weathering is through interactions with fungal hyphae (Wild et al., 2021). Nanoscale in situ observations of a soil fungus interacting with biotite over 3 months revealed a nanoscale attachment to the mineral. Biomechanical forcing altered interlayer spacings, and microbial processes leached potassium, all leading to the formation of vermiculate and clusters of oxidized iron (Bonneville et al., 2009; Smits et al., 2009).

These clusters of iron oxides are features commonly seen in BSE images of weathering rinds at the micron scale (Pope et al., 1995), as illustrated in Fig. 24. One nanoscale hypothesis for this ubiquitous weathering-rind phenomenon of submicron fragments of iron oxide could be the ubiquitous presence of fungal hyphae.

Linking micrometer and nanoscales at the hand sample level requires more than examination of just a few samples. However, pilot investigations of randomly selected samples do have the potential to suggest future research directions. A sample from the Hawaii BSE study of olivine weathering (Waslčewicz, 1994; Wasłewicz et al., 1993) was reevaluated with HREM. This sample was collected from a Hualalai Volcano basalt flow f5d c.2 (~ 2000 years old) ad was covered with lichens. As in prior research (Bonneville et al., 2009), hypha appear to be able to exert enough pressure to split apart smectite clays in the weathering rind (Fig. 25A).
As in prior research on bacteria weathering (Hiebert and Bennett, 1992), fungal hypha appear to be able to extract particular elements. Instead of potassium extracted from biotite (Bonneville et al., 2009), there is an uptake in calcium (Fig. 25). EDX analyses reveal that there are strings in the imagery in Fig. 25. These linear strings appear to be rich in calcium. The apparent source of the calcium appears to be an olivine grain. The reason for this uptake is uncertain. The calcium might be used in the formation of calcium oxalates produced by many lichen (Sjelland and Thorseth, 2002; Wadsten and Moberg, 1985) and fungi (Smits et al., 2009), or calcium might be used in another microbial process. Regardless of the need, nanoscale fungal weathering of olivine could provide yet one more explanation why Goldich’s weathering sequence depends upon the presence of organisms and is incorrect where there exists minimal contact between minerals and biotic activity.

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3.09.6 Nanoscale processes and dust generation

Silt in the form of dust is ubiquitous on Earth (Bullard and Livingston, 2009; Goudie, 1978). Earth’s moon (Gaier, 2005), Mars (Israel et al., 1997) and likely elsewhere. Weathering interactions within dust and between dust and underlying mineral surfaces are taking on increasing importance in understanding the decay of building stones (McAlister et al., 2006; Sharma and Gupta, 1993; Smith et al., 2007), formation of rock coatings on earth (Dorn, 2009; Krinsley et al., 2009) and Mars (Johnson et al., 2002; Kraft et al., 2004), in understanding historic and prehistoric archaeology (Ganor et al., 2009), and in Quaternary research (Kleber, 1997; Vyalon and Ganor, 1973). Nanoscale research informs on dust production (Hochella, 2002a; Pye, 1987, 1989) and also what happens when dust deposits on rock surfaces as dust films and components of rock coatings.

There is evidence that silt production is a function of inherent weaknesses in minerals such as quartz (Kumar et al., 2006; Moss and Green, 1998; Smalley et al., 2005), as well as external processes such as salt weathering, abrasion, frost weathering (Smalley and Krinsley, 1978; Whalley et al., 1982; Wright et al., 1998), microbial weathering of quartz surfaces (Brehm et al., 2005), and nanoscale interactions between quartz and water (Pope, 1995). The new generation of higher resolution BSE detectors is able to generate nanoscale resolution to illustrate both internal and external modes of quartz silt production (Fig. 26).
The transition between wind-transported dust and dust as an integrated component of rock coatings has seen surprisingly little study. Even though there is a general consensus in the rock coating literature that aeolian dust contributes to the formation of rock varnish, phosphate skins, and silica glaze (Dorn, 1998, 2009; Langworthy et al., 2010; Potter and Rossman, 1977), we do not know of a systematic study of nanoscale alternations of dust in the transition from rock-surface loess to rock coating constituent.

We present here a nanoscale study of the transition from dust to rock coating in the Ashikule Basin, Tibet (Fig. 27). The 4700—4800 m high graben is a dusty, sulfate-rich, high-elevation and high UV flux environment. This field site offers the opportunity to study dust/substrate interactions distant from industrial pollution. The cold, dry, lower-air pressure nature of the field suggests potential for a Mars analog site in part because the substrate is a lava flow, a trachyandesite of Ashishan Volcano in the Akesu Volcanic field (Wei et al., 2003).

While nanoscale mineral etching is of key importance as a process in chemical weathering, etched mineral surfaces could also play a role in the initial stages of the physical attachment of dust particles to mineral surfaces. Dust accretion on mineral surfaces is generally thought to occur from electrostatic or physical forces that hold dust particles together (Bishop et al., 2002; Ganor et al., 2009; Jordan, 1954). Nanoscale mineral etching creates an irregular surface that could play a key role in the initial attraction (Fig. 28).

![Fig. 26](images) Images of quartz weathering observed in a desert pavement near Florence Junction, Arizona. These images show formation of silt-sized quartz fragments that appear to depend on both the existence of a fracture inside the quartz grain (white arrows) and also fragmenting along angles that are not aligned with the fracture (black arrows). For example, the subparallel fracturing seen in the right image likely relates to aligned crystal defects. However, the jigsaw puzzle appearance of quartz fragments on the edge of the fracture (upper left white arrow) in the left image is not easily explained by aligned defects.

Fig. 26 Images of quartz weathering observed in a desert pavement near Florence Junction, Arizona. These images show formation of silt-sized quartz fragments that appear to depend on both the existence of a fracture inside the quartz grain (white arrows) and also fragmenting along angles that are not aligned with the fracture (black arrows). For example, the subparallel fracturing seen in the right image likely relates to aligned crystal defects. However, the jigsaw puzzle appearance of quartz fragments on the edge of the fracture (upper left white arrow) in the left image is not easily explained by aligned defects.

![Fig. 27](images) Ashishan Volcano study site in the Ashikule Basin, Tibet at 35.6988°N, 81.57623°E. The length of Urukele Lake is about 7 km, Ashikule Lake about 5.5 km, and the width of the graben at the location of the Ashishan Volcano is about 22 km. Modified from a raw image designed by William Bowen.
The particular sample selected for a detailed elemental nanoscale analysis is dust that accumulated on top of a rock coating that is a mixture of silica glaze and rock varnish. Silica glaze dominates this rock coating, but pods of rock varnish 2–40 mm across exist and are enveloped by the silica glaze (Krinsley et al., 2009; Langworthy et al., 2010). We selected a form with two oval shapes in the dust on top of the rock coating. This pod-form has a texture suggestive of a biological origin (Fig. 29), in that it has a granular texture similar to microbial hyphae observed elsewhere (Bonneville et al., 2009).

Our nanoscale investigation of grain alternation generated EDX data in a pattern of 300 points in a 10 × 30 matrix, where measurements are taken approximately 1.3 nm apart. Beam damage allows visualization (Lee, 2010) of the clear grid pattern (Fig. 30). The grid serves as ground control points, allowing mapping of digital EDX data with geographic information system (GIS) software and subsequent visualization of nanoscale weathering.

**Fig. 28** Mineral etching creates nanotopographic irregularities on the scale of less than 10 nm, as seen in this HRTEM image of cross-section of a dust particle attracted to the underlying mineral surface of a rock. Nanoscale topographic irregularities likely contributed to the physical attachment of dust to this mineral surface, collected from the Akesu volcanic field, Tibet.

**Fig. 29** HRTEM image of dust particles on top of silica glaze and rock varnish. Many dust particles appear to be clay minerals, while others are fragments of other minerals. We selected a particle with two oval forms that could have a biotic origin (arrow). These oval forms appear to be undergoing post-depositional modification, as indicated by the uneven texture of bright and dark areas that suggest differential movement of elements.

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**Fig. 31** displays a visualization of the 300-point grid of EDX data using a Kriging algorithm to map out elemental patterns. The dominant peaks in the EDX analyses consisted of the inorganic components of silicon and oxygen, and potential organic components of carbon and phosphorus. The highest concentrations of Si and O occur underneath the granular oval; this particle has a parallel structure suggestive of a clay mineral composition that would be consistent with the higher abundance of Si and O. In contrast, the highest concentration of carbon occurs where the oval form displays a gray granular texture that transitions to an area of greater porosity with the lowest carbon concentrations. The area richest in C does appear to correspond with high P concentrations, but some areas of high P do have low concentrations of C. Bonfield et al. (1999; 3407) found potential complex mixtures of clay minerals and complex organic polymers associated with microbial weathering, and this is a possible for the analyzed oval in Figs. 30 and 31.

Visualization of nanoscale spatial geochemistry with EDX grids has been accomplished in mineralogical research (Lee, 2010), but not analyzing rock coatings. Thus, the following interpretation of this single pilot analysis is speculative. Starting with the
assumption that the oval particle had an organic origin, it appears as though Si and O (likely silica) has begun to migrate from the underlying clay inward—a possibility deduced by the gradient of Si and O from the clay at the bottom into the granular particle. The lower levels of C at the top of the grid could reflect the electron transparency of the middle of the oval form; picture sectioning a highly desiccated bacterial cell (or cross-section of a desiccated fungal hypha). The thickest portions would be on the margins,

Fig. 30  EDX data were collected in a grid pattern, where X-rays were generated every 1.3 nm apart. The center right part of the particle appears to be the most porous. The beam damage (seen in upper right inset image) creates a grid on the sample, and thus the precise locations of data are known and can be analyzed using geostatistical methods.

Fig. 31  Nanoscale EDX mapping of a 300-point grid. Each grid point is approximately 1.3 nm apart, and the grid is 10 columns and 30 rows. The visual grid corresponds in size with maps of the four most common elements. Fig. 30 shows the larger context and a HRTEM pre-beam-damaged image of the analyzed area. The Kriging algorithm used to map out elemental patterns presents an intuitive color scale where lowest values are dark green and highest values are brown to pink.
while the center would be thinnest—explaining why the lowest carbon concentrations occur in the middle of a possible desiccated microbial form. The behavior of phosphorus appears to link with a brighter area of the HRTEM image, and this bright area sends stringers toward the upper left. Like Si and O, the spatial pattern of phosphorus suggests nanoscale movement and hence instability. Our interpretation of nanoscale instability is not unique to rock coatings such as rock varnish (Dorn, 1998; Dorn and Krinsley, 1998; Dorn and Krinsley, 2019; Krinsley, 1998; McKeown and Post, 2001) or silica glaze (Dorn, 1998; Gordon and Dorn, 2005b; Langworthy et al., 2010). However, it appears as though nanoscale movement of inorganic and possible organic components starts in dust deposits on rock surfaces—prior to envelopment inside a rock coating.

3.09.7 From nanoscale to landscape scale: Applications of meteoric $^{10}$Be and $^{10}$Be/$^9$Be to the study of Earth’s surface

Meteoric $^{10}$Be is a cosmogenic radionuclide with a half-life ($t_{1/2}$) of 1.39 million years (Chmeleff et al., 2010; Korschinek et al., 2010). Cosmogenic $^{10}$Be produced within minerals is very different in that it builds up within minerals like quartz. Also, the concentration of in situ produced $^{10}$Be is negligible compared to much greater meteoric $^{10}$Be concentrations. Meteoric $^{10}$Be is more like $^{14}$C that is produced within the atmosphere by nuclear reactions and delivered by snow, rain or by dry deposition to Earth’s surfaces (Fig. 32A). Unlike radiocarbon that is best dated in association with preserved organic matter (e.g., tree wood), meteoric $^{10}$Be...
that rains out of the atmosphere rapidly adsorbs to soil or river, lacustrine, and marine sediment particles (Willenbring and von Blanckenburg, 2010).

Geomorphologists have been struggling to determine how best to use meteoric $^{10}$Be that is strongly adsorbed to smaller particles at pH > 6 (Willenbring and von Blanckenburg, 2010; You et al., 1989). A key strategy is comparing $^{10}$Be with the stable isotope $^9$Be to circumvent an issue associated with grain size dependency and retentivity (von Blanckenburg et al., 2012). One way that geomorphologists have used this cosmogenic nuclide is to study seafloor deposits underneath ice shelves or ice sheets (Yokoyama et al., 2016; White et al., 2019) that impede the delivery of meteoric $^{10}$Be to the seafloor providing a proxy for ice sheet retreat (Jeong et al., 2018).

Meteoric $^{10}$Be and authigenic $^{10}$Be/$^9$Be ratios can provide a powerful tool for dating lacustrine, marine sediment and floodplain deposits (Bourles et al., 1989; Seong et al., 2016). Age calculations are performed as follows:

$$ t = - \left( \frac{1}{\lambda} \right) \times \ln \left( \frac{N(t)}{N_0} \right) $$

where $\lambda$ is decay constant ($\ln(2)/t_{1/2} = 5 \times 10^7$ year$^{-1}$) of $^{10}$Be, $N_0$ [atoms g$^{-1}$] is the meteoric $^{10}$Be concentration measured in the sample, $N(t)$ is the initial meteoric $^{10}$Be concentration, $R(t)$ is the measured authigenic $^{10}$Be/$^9$Be, and $R_0$ is the initial authigenic $^{10}$Be/$^9$Be.

There are two prerequisites for applying $^{10}$Be/$^9$Be for the age calculations (Lebatard et al., 2010; Sujan et al., 2016): (1) the initial authigenic $^{10}$Be/$^9$Be ($R_0$) should be accurately determined; (2) the samples should have remained in closed system which means that any beryllium isotopes should not enter or escape the sample after deposition. Globally, $R_0$ in ocean deposits have been relatively constant over the last 12 Ma (Willenbring and von Blanckenburg, 2010), and locally it was confirmed that the $R_0$ remains stable in large continental basins like Lake Chad (Lebatard et al., 2010) and in the northern Danube Basin (Sujan et al., 2016) over the last 8 and 11 Ma, respectively. The $R_0$ should always be measured in recent samples deposited in similar environmental settings (Lebatard et al., 2010), because meteoric $^{10}$Be flux is dependent on latitudes (Masarik and Beer, 2009) and $^9$Be inputs are depending on the geological composition of the drainage basin and on sedimentary environments (Sujan et al., 2016).

The second prerequisite of a closed system (or approximating a closed system) is where nanoscale weathering processes become important. As a dating method, the authigenic $^{10}$Be/$^9$Be particularly useful when biostratigraphical data is scarce due to the interaction of complex processes (lacustrine, deltaic and alluvial) to deposit and supported by limited geochronological data with only a few grams of fine grained sediment (Sujan et al., 2016). Authigenic $^{10}$Be/$^9$Be is also very useful because it can be used to date sediments that include the Quaternary and Pliocene.

The deposits of an ancient lake could hold the key to the origin of the Grand Canyon of the Colorado River, southwestern USA, as an example of the importance of nanoscale processes. Meek and Douglass (2001) hypothesized that overflow of Lake Bidahouchi led to the formation of the Grand Canyon. Although this hypothesis is consistent with available geomorphic criteria (Douglass et al., 2009), confirming or disconfirming evidence has been difficult to obtain including the age of Lake Bidahouchi’s youngest deposits. Douglass et al. (2020) used $^{87}$Sr/$^{86}$Sr to document that these youngest preserved deposits have a Colorado River signal. Douglass et al. (2020) also compared Bidahouchi $^{10}$Be/$^9$Be to Bouse Formation (lacustrine) deposits along the lower Colorado River (Pearthree and House, 2014). For the lake overflow hypothesis to be possible, the youngest Lake Bidahouchi deposits must slightly post-date the youngest lacustrine deposits far downstream (Bouse Formation). The hypothesis is that Bidahouchi over-aged to initiate Grand Canyon incision, and this then led to a through-flowing Colorado River that then breached closed basin lakes (cf. Bouse Formation) downstream.

Thus, Bidahouchi and Bouse lacustrine deposits were evaluated for $^{10}$Be/$^9$Be, with reasonable assumption that the production rate in this same region and in same general timeframe of the late Pliocene would have been the same. While the Bouse deposits had a $^{10}$Be/$^9$Be ratio consistent with the cessation of deposition ca. 5 Ma, the Lake Bidahouchi youngest deposits had mixed $^{10}$Be/$^9$Be results (Douglass et al., 2020). One group of Lake Bidahouchi deposits had $^{10}$Be/$^9$Be ratios with a tight cluster that is slightly older than the Bouse deposits, consistent with the idea of lake overflow leading to Grand Canyon’s formation. Another group of Lake Bidahouchi deposits had variable $^{10}$Be/$^9$Be ratios.

A nanoscale analysis reveals why. Fine grained Lake Bidahouchi deposits with minimal internal porosity at the nanoscale (e.g., Fig. 32A–C) provide a closed system for the beryllium. In contrast, Lake Bidahouchi deposits with textures more susceptible to diagenesis (Fig. 32D–F) increase the ability of groundwater to move through the sediment and mobilize beryllium taking it out of a closed system. Without this sort of nanoscale insight, it would not be possible to distinguish open from closed Lake Bidahouchi sediment.

### 3.09.8 Conclusion

Rock decay (weathering) is a multidisciplinary arena explored by geochemists, soil scientists, geomorphologists, hydrologists, civil and environmental engineers, archaeologists, planetary geologists, and others interested in the breakdown and decay of rocks. Geomorphologists were among the first to explore the importance of nanoscale processes in rock decay (Eggleton, 1980; Krinsley et al., 1995; Pope, 1995), even though nanoscale research in weathering has been dominated by geochemists over the past two decades.
decades (Banfield and Eggleton, 1988; Banfield et al., 1999; Hochella, 2002a; Hochella et al., 2008; Waychunas et al., 2005). A consequence of a general lack of attention to the nanoscale by geomorphologists has resulted in a situation where few connections exist between Earth’s landforms and the nanoscale.

Certainly, rock decay theory in geomorphology is concerned with scale (Hall, 2006b; Phillips, 2000; Pope et al., 1995; Viles, 2001; Turkington et al., 2005). However, the “microscale” in geomorphic theory has been the subject of research at micrometer and more extensive areas. Nanoscale processes operating between one nanometer ($10^{-9}$ m) and 100 nm ($10^{-7}$ m) or 0.1 μm (Fig. 1) do not reflect microscale conditions or processes.

Physical, electrical, magnetic, thermal, and kinetic properties differ dramatically across the nano-micron threshold (Hochella, 2002b; Zhang et al., 2003). The behavior of water in microfractures supporting capillary flow at the micron scale (Dorn, 2003; Dixon and Thorn, 2005; Meunier et al., 2007) does not reflect the behavior of nanoscale water (Kalinichev et al., 2007; Langworth et al., 2010; Lower et al., 2001; Wang et al., 2006; Zhang et al., 2003). An example comes from brucite, a magnesium hydroxide that is a common weathering product (Kalinichev et al., 2007). Kalinichev et al. (2007) modeled three well-defined layers with respect to the behavior of water within 15 angstroms of a brucite surface. There is an inner layer of a few angstroms that is highly structured and contains water molecules with a high atomic density coordinated to the brucite surface. There is a middle transition layer about four angstroms from the surface with a low atomic density, and the outer layer that becomes similar to bulk nanoscale water about 5–15 Å from the surface. A similar result comes from studies of how water adheres to mica (Xu et al., 2010), where the first and second 0.4 nm layers of water behave like ice and accumulates at surface defects, but thicker accumulations of water are liquid-like.

A large realm of considerable challenge in nanoscale weathering research rests in explaining weathering forms such as those displayed in Fig. 33. A biotite grain that is undergoing splintering has split into subparallel fragments as a result of weathering processes by water accumulating at surface defects. The next generation of weathering researchers will link nanoprocesses to such micron-scale forms with such technology as coupled dual-beam focused ion beam electron microscopy (FIB-EM) (Table 1).

Linking nano- and micron-scales will involve exceptionally different and hard-to-predict behavior such as biologically generated particles. In many cases, nanobiominerals are more stable (Tang et al., 2004) than would be expected of inorganic counterparts. In other cases, they are less stable (Dorn, 1998; Krinsley, 1998) than inorganic counterparts, for reasons. Given the dominance of microorganisms on Earth (Reith, 2011), biologically generated particles will be a persistent issue in all aspects of nanoscale weathering.

Further development of theory as it applies to understanding rock decay forms needs to cross the nano-micron threshold. Unfortunately, very little research exists connecting nanoscale processes and geomorphic forms. For example, Hall (2006a: 388) argued that “little or no recognition has been given to either the processes or the measuring of attributes influencing the [freeze-thaw] processes or the measuring of attributes influencing the weathering processes, at the micro-scale, let alone the nano-scale.” Until nanoscale observations are woven into the fabric of understanding such basic processes as frost weathering, it would be premature to develop geomorphic theory further. We do not believe that there exists a sufficient understanding to be able to link the nanomicron threshold with a new theoretical understanding of landforms. Instead, this article represents an attempt to provide empirical case studies exemplifying why nanoscale matters to geomorphology.

![Decay of biotite mineral, Adirondack Mountains, New York. The subparallel fracturing called splintering is a result of weathering that is taking place at the nanoscale.](image_url)
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