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In situ weathering rind erosion

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Abstract

The use of cosmogenic nuclide dating methods place in doubt the long-term future of weathering rinds (WRs) as a chronometric tool. Why estimate ages when radiometric control is possible? This paper presents evidence that WRs can provide invaluable clues about what particular sample would provide the most accurate cosmogenic age by avoiding "inheritance" of cosmogenic nuclides and by avoiding boulders undergoing spalling. The key to this new use requires testing the occurrence and nature of WR erosion. Back-scattered electron microscopy reveals that ignimbrite, andesite, basalt, and granitic clasts experience WR erosion in all subsurface and surface contexts thus far studied in Arizona, California, Hawaii, Oregon, and Washington. To understand the magnitude of WR erosion, we measured WR thicknesses, all while controlling the cosmogenic and surface stability ages of clasts by chlorine-36 and rock varnish microlamination dating methods. Our data reveal that traditional methodologies of sampling cobbles remove two-thirds of the true thickness of weathering rinds, calling into question many beliefs including the notion that clay minerals are not produced during weathering-rind formation. Comparisons of optical and electron microscope measurements support concerns that measurement of WRs by color changes, while useful as a pedagogical tool, creates serious biases in underestimating the true dynamics of WRs. In the end, we found that concordance of WR and rock coating "age trends" indicates the ideal boulder for cosmogenic nuclide dating. Offsets reveal either ongoing boulder erosion, invalidating "zero erosion" model ages, or a potential problem with "inheritance" of cosmogenic nuclides.

Keywords: Geomorphology; Glacial; Organ Pipe; Quaternary; Sierra Nevada; Weathering

1. Introduction

When it comes to presenting visual evidence of rock and mineral decay, weathering rinds (WRs) represent one of the most recognizable weathering features not tied to differential erosion. Students of geomorphology find WRs easy to comprehend: perhaps because it is so intuitive that the outer portions of rocks should have a ring of chemical alteration; perhaps because distinct visual differences (Oguchi, 2001) make WRs easy to identify in the field; or perhaps because WRs tend to thicken over time in surface (Chinn, 1981) and subsurface (Colman

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and Pierce, 1986) settings—helping students visualize the pace of geomorphic time.

The study of weathering rinds has long been a part of basic research in geomorphology. A concern over biogeochemical changes in rims around rocks occurs in scholarship related to biblical interpretations (Krumbein and Jens, 1981), classic field observations (von Humboldt, 1812), early geographical and geological surveys (Blake, 1855; Jutson, 1914), and studies in the glory years of the U.S. Geological Survey in the mid-twentieth century (Hunt, 1961; Marchand, 1974). More recent basic research themes include developing general models to explain rind formation (Oguchi, 2001), analyzing factors involved in rates of rind growth (Oguchi and Matsukura, 2000; Sak et al., 2000), connecting rind processes to observed forms (Turkington, 1998; Campbell, 1999; Matsukura and Tanaka, 2000; McBride and Picard, 2000; Whalley and Turkington, 2001), and detailed analyses of biogeochemical changes (Gislason et al., 1996; Austin and Vitousek, 1998; Etienne, 2001).

Few would argue, however, that the bulk of interest rests in rinds as an indicator of long-term processes. Table 1 provides a partial list of applied research. Although these studies also expand our basic knowledge of WRs, the primary research focus of Table 1 rests in using WR changes to understand different phenomena.

Of the variety of applications in WR research, use as a time indicator dominates the applied WR literature. Since Cernohouz and Solc (1966) noted that logarithmic functions best describe the growing thickness of WRs over time, rind thickness has provided relative or, when tied to radiometric ages, calibrated ages. Most often used to understand glacial chronology (see review in Oguchi and Matsukura, 2000), rind thickness dating has seen use in a variety of other contexts including: dating ancient shorelines (Keating and Helsley, 2002); correlating stream terraces to glacial moraines (Pinter et al., 1994) and sea level change (Pazzaglia and Brandon, 2001); and just about every geomorphic setting imaginable. A

Table 1
Use of weathering rinds (WRs) in different geomorphic subfields and cognate research areas

Use	Discussion	Reference
Climate change influence	WR development includes an important climate function, that can be extracted when all parameters are identified and quantified	(Sak et al., 2000, 2001; Thorn et al., 2001)
Early Earth	Pre-Silurian regolith and properties of its WRs is a major uncertainty in understanding Earth history	(Drever, 1994)
Global warming	Absorption of carbon dioxide is a key factor in Earth's biotic habitability, where WR studies constrain models	(Brady, 1991; Brady et al., 1999)
Initial condition	Other processes can generate WRs that affect post-rind landform development	(Conca, 1985; Golden et al., 1993; Dorn, 2003)
Order of mineral weathering identifies stage of weathering	Accessory calcite in granitic rock WRs rapidly decline in abundance in rinds; ratios of biotite to plagioclase in rinds decline over time; olivine does not necessarily weather first in basalt rinds in arid settings—with implications for interpreting olivine abundance on Mars	(Wasklewicz, 1994; Blum and Erel, 1997; Bullen et al., 1997; White et al., 1999)
Rock art	Weathering rinds influence long-term joint face stability, dating, analysis of tools making the art, and often control the aesthetics of art context	(Sharp et al., 1994; Whitley et al., 1999)
Rock coating interactions	Concern over offset between laboratory and field weathering rates has led to concern over rock coatings	(Dorn, 1998; Darmody et al., 2002; Dixon et al., 2002)
Soil skeletons	Most soil analyses do not include rock fragments or "soil skeleton" (>2 mm fraction), but WRs of these clasts influence nutrient, moisture, and pollution movement	(Ugolini et al., 1996; Austin and Vitousek, 1998; Corti et al., 1998)
Stone monument and building conservation	Initial processes of WR formation greatly impact culturally important structures	(Turkington and Smith, 2000; Paradise, 2002; Pope et al., 2002)
Time indicator	Visual rinds thicken at rates ranging from mm/10^2 years to mm/10^5 years in a variety of lithologies including basalt, andesite, granodiorite, sandstone, gneiss, and hornfels	Table 1 in (Oguchi and Matsukura, 2000)
Waste storage	WR pores influence long-term stability of the storage of hazardous waste	(Gordon and Brady, 2002)

quick glance at citation indices for major papers (e.g., Colman and Pierce, 1986) reveals that chronometric field applications of WRs represent the greatest measurable (Dorn, 2002) impact of WR research.

The growth of cosmogenic nuclide dating in settings normally dominated by WR dating (Dorn and Phillips, 1991; Evenson et al., 1994; Brook et al., 1995; Phillips et al., 1996; James et al., 2002) begs the question over the future of WRs as a chronometric tool: why estimate a general age for a moraine, for example, when radiometric results are possible? If cosmogenic nuclides terminate WR utility, the future of this subfield of geomorphology turns on basic research and other applications listed in Table 1.

We firmly believe, however, that the low-cost strategy of WR analyses increases the power of the more expensive analytical cosmogenic nuclide strategies. For example, WR analyses show mappable trends that would help identify clasts with "inherited" nuclides (Gore et al., 1994; Haeberli et al., 2003). WRs, when used in conjunction with other chronometric tools, can help isolate paleoclimatic signals (Nicholas and Butler, 1996). Great power, in addition, rests in identifying targets for cosmogenic dating; for example, WR applied research identified the oldest fan deposits in the Blue Ridge Mountains (Mills and Allison, 1995) that could then be analyzed with cosmogenic nuclides and correlated with a 1.5 my glacial advance forming the Ohio River Valley (Mills and Granger, 2002). Where single cosmogenic ages have real costs exceeding US$2000, WR analyses offer a means to increase the efficiency of this extraordinarily expensive technique. In addition, WRs can catch systemic biases in a cosmogenic dating strategy, such as the prior exposure history of boulders. Thus, WRs can provide key supplemental data to enhance both sample selection and the interpretative power of cosmogenic nuclide analyses.

Before geomorphologists and researchers in cognate fields rethink the methods by which WR data can enhance the "bang for buck" in cosmogenic nuclide analyses, we believe that there is a complication in applied WR research that also needs to be restrategized. A growing literature suggests that rind erosion creates interpretative complications. Fig. 1 presents Etienne's (2002) conceptual model for the formation and erosion of WRs, whereby the logarithmic function (Cernohouz and Solc, 1966; Colman and Pierce, 1981) of WR growth reflects a dynamic equilibrium of growth and erosion processes:

> Considering the evolution of weathering rind thickness curves, it can be deduced that chemical weathering (mostly biochemical) is the dominant process in the first century of exposure of morainic sediments [in Iceland]. Curves reach a maximum in the second century whence they plateau and eventually decline. This temporal pattern can be explained in several ways: (1) chemical weathering cannot progress inside the rock due to reduced humidty levels; (2) microorganisms do not penetrate deeper than their minimum photic requirement; (3) weathering rind development still progresses inside the rock but, at the same time, is destroyed at the outer side, so that the apparent thickness remains the same (Etienne, 2002, p. 82).

Erosion of rinds occurs from a variety of processes including: biological weathering (Viles, 2001; Bjelland and Thorseth, 2002); microtextures within minerals (Lee and Parsons, 1995); intramineral primary dislocations (Lee et al., 1998); incongruent weathering

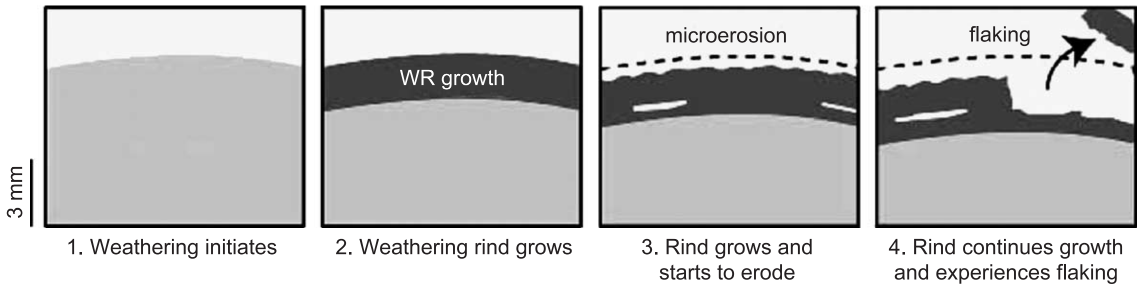

Fig. 1. Etienne's conceptual model for the formation and erosion of weathering rinds. Although the original timescale for these stages is 0–200 years for basaltic moraines in Iceland (adapted from Etienne, 2002), we observed similar stages in desert environments lasting 10^3–10^4 years.

where differential weathering of primary minerals results in enormous variability over small volumes (Gislason et al., 1996); interactions with trace and rare elements (Wray, 1997; Tripathi and Rajamani, 1999); and opening of fractures (Etienne, 2002).

Erosion of WRs, if it is a universal process, would pose considerable complications for prior literature. Consider the method used to measure weathering rinds in one of the classic studies (Colman and Pierce, 1981): clasts are first hit with a rock hammer prior to field measurement. Given Etienne's spectacles, any weaknesses in stages 3 and 4 (Fig. 1) provide ready avenues for rind erosion. Complications go beyond underestimating WR thicknesses. The shortage of clay minerals formed *in situ* in WRs (Colman, 1982) could simply be due to a systematic exclusion of WR products by the very act of pulling a clast from the soil and subjecting it to hammering or even abrasion during sample transport to the laboratory. Our intention is not to question the validity of prior results, but only to note that a sampling methodology that excludes the eroded portion of a WR must deal with such inherent limitations.

Our paper focuses on obtaining measurements of WR erosion, where our dual purpose rests in understanding processes and rates of WR erosion and how WRs might be used to complement cosmogenic nuclide measurements. We take a three-fold strategy to understand WR erosion in subsurface and surface contexts. First, we use back-scattered electron microscopy to understand textures of WR erosion—making sure that we freeze *in situ* WR relationships prior to subsurface clast disturbance. Second, we compare "frozen" rind thicknesses with normally sampled rind thicknesses at sites of known cosmogenic nuclide age. Third, we explore surface WR erosion rates constraining the age of the host clast with ^{36}Cl ages and the age of the WR through rock varnish microlaminations. In the discussion, we explore the broader implications of these findings in rethinking the role of WR thickness studies in the age of cosmogenic nuclide analyses.

2. Study sites and methods

We start with our most important overarching methodological concern. Those involved in detailed laboratory analyses recognize the importance of sample treatment in altering results. Even mild treatment such as sonification and sieving, for example, results in enhanced weathering (Suarez and Wood, 1996). To minimize sampling and laboratory effects, our strategy focuses on freezing *in situ* all weathering prior to sampling by the addition of "superglue." Superglue application takes place as soon as a clast is exposed by very gentle removal of adjacent clasts from the wall of a soil pit. All subsequent handling, therefore, does not artificially erode a clast surface.

A second overarching methodological concern is the way that WRs interact with rock coatings. Even though a considerable proportion of WR researchers collect and analyze WRs from surface contexts, and even though few surface boulders lack one or more rock coatings (Dorn, 1998), only a small number WR publications even acknowledge the presence of rock coatings (e.g. Dixon et al., 2002). Thus, little is known about how rock coatings influence weathering rinds. In conducting one of the few studies on the topic, we can only assume here that all prior studies of surficial weathering rinds may have been influenced by rock coatings, and we explicitly assume that all surficial samples collected here interact with rock coatings.

2.1. Qualitative study of the style of weathering rind erosion

The first part of our study examines the texture of WRs in B horizon subsurface clasts, freezing—prior to sampling—the rind in place. We start with documenting detailed textural evidence of WR erosion in a particular location: ignimbrite cobbles collected from soil pits on alluvial fans of the Ajo Mountains in Arizona (Liu et al., 1996a,b). Back-scattered electron (BSE) microscopy (Krinsley and Manley, 1989; Reed, 1993; Dorn, 1995) is a potent technique to understand delicate structures in WRs frozen in the field and then placed in epoxy molds—all prior to polishing.

We then examine B horizon subsurface clasts at other locales in order to assess if similar WR textures exist in lithoclimatic settings other than the Ajo Mountains. We superglued and observed with BSE microscopy basalt B-horizon clasts from Makanaka-age Mauna Kea glacial deposits (Wolfe et al., 1997) and andesite and granodiorite B horizon clasts from pre-Tioga moraines at Bishop Creek, California (Berry, 1994; Phillips et al., 1996). Two andesite clasts from pre-Tioga moraines at Bishop Creek, California (Berry, 1994; Phillips et al., 1996) were also analyzed with high resolution transmission electron microscopy to assess if the epoxied side of the clast retained clay minerals that might be lost as a consequence of using a hammer to sample WRs.

We also examined a variety of other settings where space limitations prevented us from presenting similar BSE observations from granodiorite B horizon clasts from Tioga-4 age moraines of Bloody Canyon moraines in the Sierra Nevada (Phillips et al., 1996), sandstone B-horizon clasts from Meteor Crater, Arizona (Phillips et al., 1991), and andesite clasts

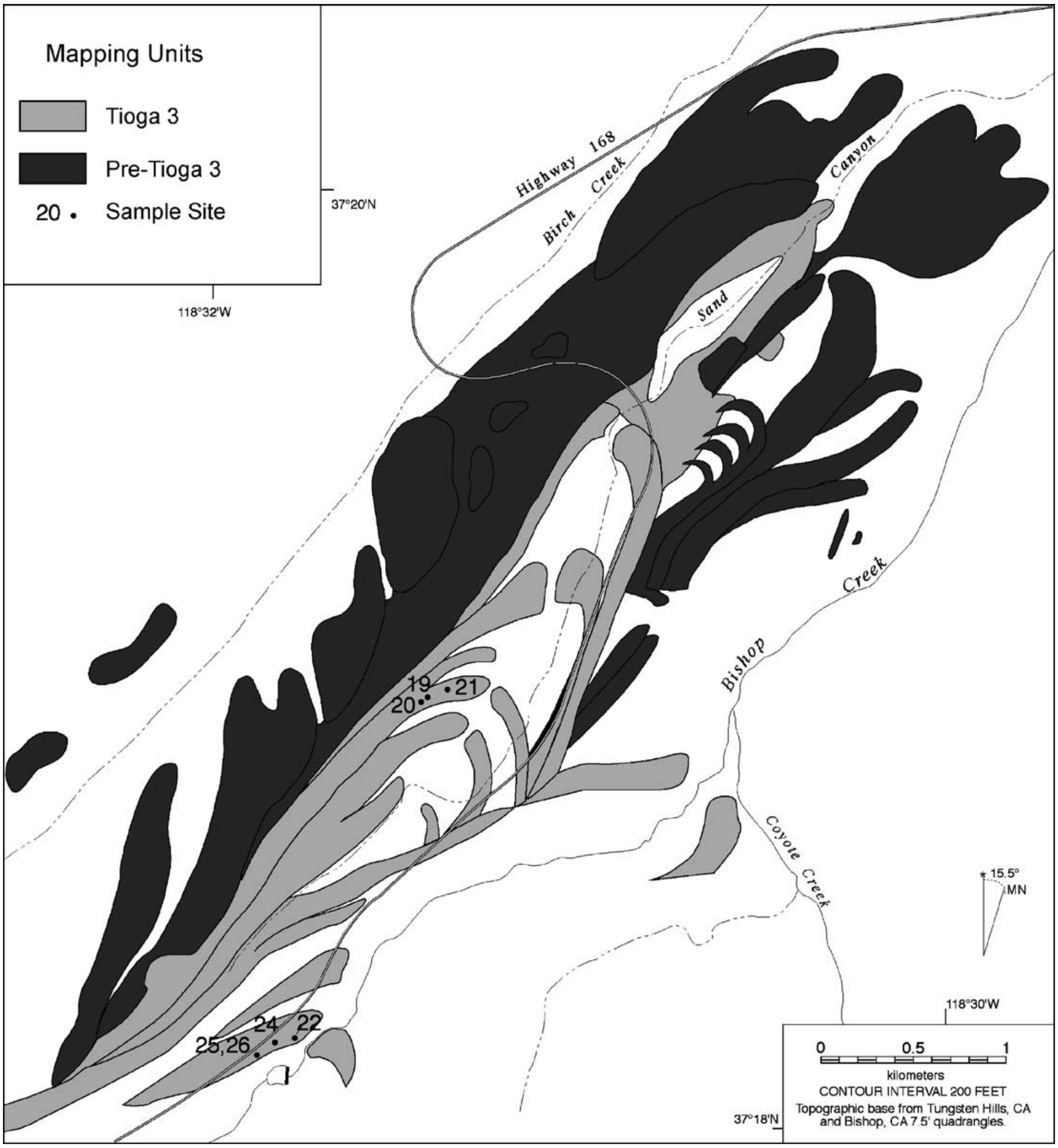

Fig. 2. Moraines at lower Bishop Creek, Sierra Nevada, California. The youngest moraines in lower Bishop Creek rest within the Tioga-3 stage and older moraines. Sample numbers correspond with ^{36}Cl samples that range in 0 mm/ka ^{36}Cl ages of 19 ± 1 (Phillips et al., 1996).

from moraines in the Pacific Northwest (Colman and Pierce, 1981).

2.2. Rates of subsurface rind erosion

The second and third parts of our study concentrated at one study area (Fig. 2), the Tioga-3 moraines of Bishop Creek in the Sierra Nevada of eastern California (Phillips et al., 1996). The younger Pleistocene moraines in the Sierra Nevada yielded ^{36}Cl ages for major advances at 31±1 (Tioga-1), 25±1 (Tioga-2), 19±1 (Tioga-3), and 16±1 (Tioga-4) ka. Our focus rests on the Tioga-3 moraine with sampling of subsurface and surface clasts. We assumed that the WR "clock" started in rough coincidence with moraine deposition at about 19±1 ka ^{36}Cl year.

Subsurface clasts derive from sites 24, 25, and 26 (Fig. 2). WR thicknesses were measured on 30 B horizon clasts. Half of each clast, however, was first epoxied prior to removal from the soil pit. Calipers and a field binocular microscope permitted measurement with significant figures in tenths of millimeters. We do not assume that rind thicknesses reflect only rind growth, but rather Etienne's model of a mixture of growth and erosion.

2.3. Rates of surface rind erosion

Our surface study of rind erosion mixes three different chronometric approaches: pre-existing cosmogenic ^{36}Cl ages provide the timing of moraine deposition (Phillips et al., 1996); WR thickness ideally indicates minimum weathering since moraine deposition (Berry, 1994); and rock varnish microlaminations (Dorn, 1990; Liu and Dorn, 1996; Liu, 2003) tell when a WR erosion event took place. In a recent blind test of the varnish microlaminations (VML) approach, the editor of *Geomorphology*, monitoring the test, summarized findings:

> The manuscripts were submitted and reviewed with neither author aware of the results of the other. Once the manuscripts were revised and accepted, the results were shared so each author could compare and contrast results obtained by the two methods. In four of the five cases, dates obtained by the two methods were in close agreement. Independent dates obtained by Phillips and Liu on the Cima "I" flow did not agree as well, but this may be attributed to the two authors having sampled at slightly different sites, which may have in fact been from flows of contrasting age. Results of the blind test provide

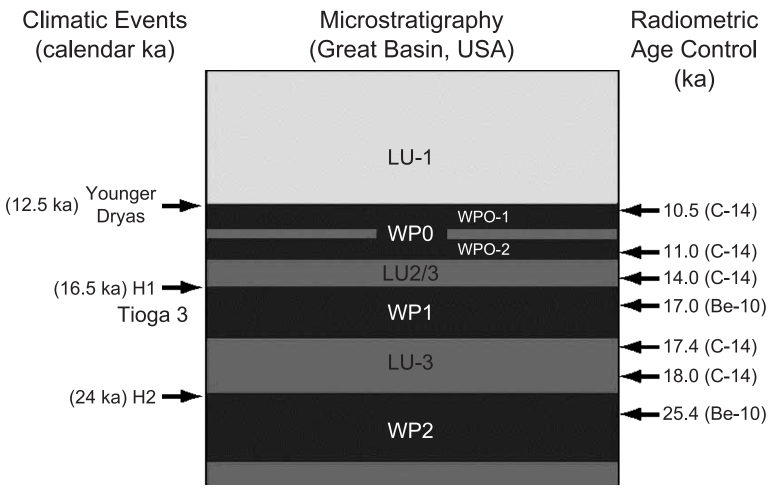

Fig. 3. Varnish microlamination (VML) calibration for the Great Basin (adapted from Liu and Dorn, 1996; Liu et al., 2000; Liu, 2003). Note that most VML units provide only broad time ranges. The "LU" acronym refers to dry period "layering units" with an orange or yellow color, counting downward from the surface LU-1 unit. The "WP" acronym refers to "wet periods". The numbers assigned to wet period were assigned to correspond to Heinrich Events, where WP0 (subdivided into two wet periods where varnish accumulation rates are faster) correspond with the Younger Dryas, and WP1 and WP2 corresponds to Heinrich Events 1 and 2.

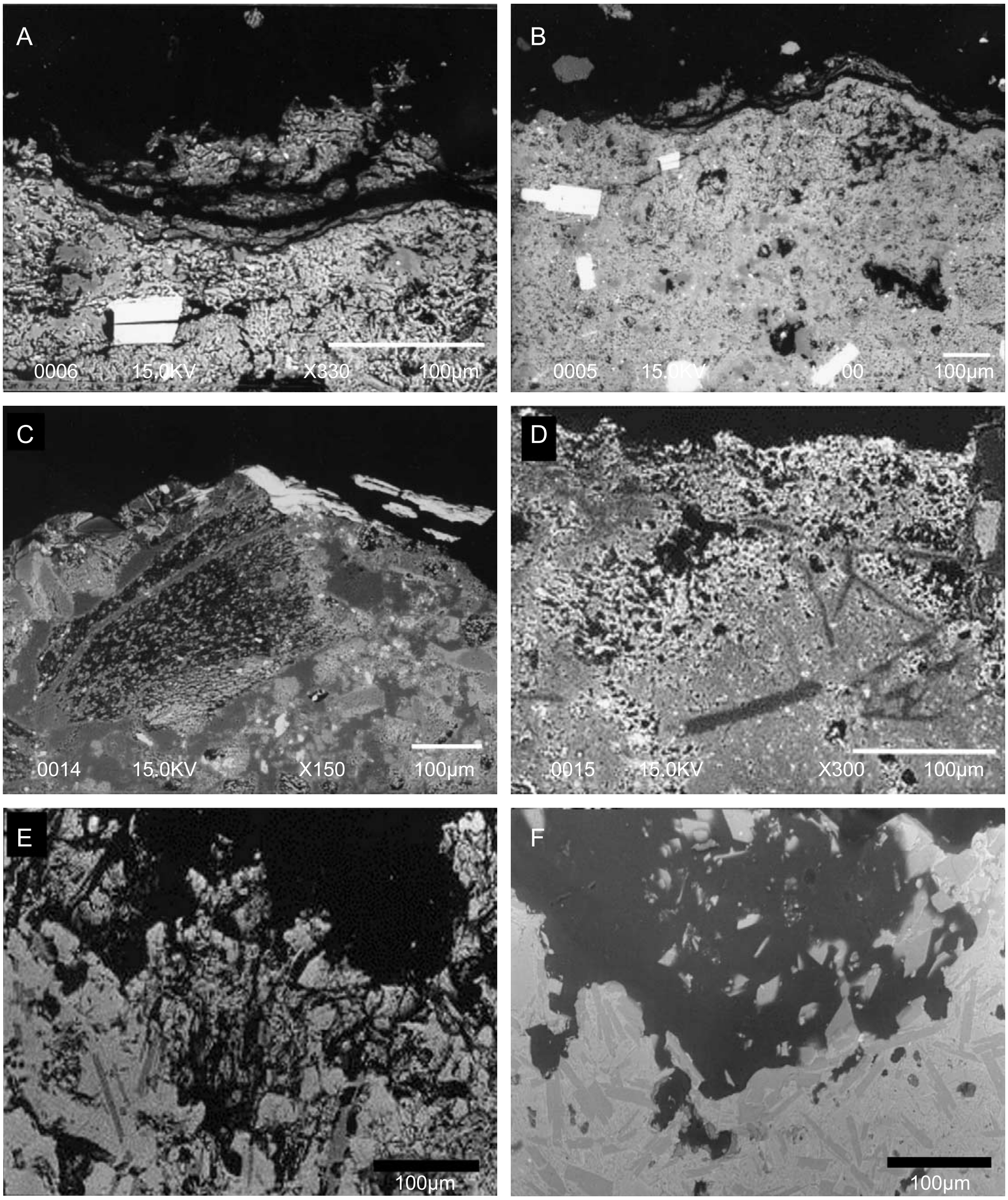

Fig. 4. Textural evidence of WR erosion at lower magnifications. Images (A) and (B) present high and low magnification views of rhyolite rinds from the Qf2 surface in the Ajo Mountains, with ^{36}Cl ages of 49,800–134,000 years (mean 99,700 years) (Liu et al., 1994). Image (C) is from a basalt clast on the paraglacial alluvial fan (Dorn, 1996) derived from glacial maxima Makanaka-age Mauna Kea glacial moraine (Dorn et al., 1991). Image (D) is derived from a basalt clast side in Makanaka till, while image (E) is a BSE image from B horizon basalt clast in Makanaka till. Image (F) is derived from a B horizon andesite clast in a pre-Tioga moraine at Bishop Creek (Fig. 2).

convincing evidence that varnish microstratigraphy is a valid dating tool to estimate surface exposure ages (Marston, 2003, p. 197).

Using all three chronometric indicators allows us to distinguish the signals of WR erosion and WR buildup, because every WR erosion event resets the VML clock.

Surface samples come from the same boulders as ^{36}Cl sample numbers 19, 20, 21, 22, 24, 25, and 26 (Fig. 2). On each ^{36}Cl-dated boulder, 20 varnish microbasins analyzed through light microscopy serve as the host for four separate measurements: the age of VML sequence in that microbasin; the thickness of the WR as indicated by a color change in the thin section; the thickness of the WR as indicated by a change in porosity of the minerals in the thin section; and the depth of microfractures displaying enhanced porosity of minerals along the fracture walls. Each varnish microbasin typically has dimensions at most a few millimeters across and deep.

The VML calibration (Fig. 3) provides a minimum time for the formation of the new weathering rind. This is because there is a lag time for the onset of varnishing and because the WR erosion may not completely reset the WR signal. In other words, WR erosion is probably only partial. So when a varnish microbasin flakes off because of instability of the WR, the erosion of the WR may not be complete. The newer varnish could be forming on a preexisting weathering rind.

3. Results

3.1. Qualitative study of the style of weathering rind erosion

Extrusive igneous B horizon clasts, frozen in place prior to collection, display clear BSE textural evidence of WR erosion. Ignimbrite cobbles in a semiarid setting show evidence of ejected (or perhaps slightly attached) material resting at the edge of weathering rinds (Fig. 4A and B). Lower resolution views (Fig. 4B) show subparallel material as a part of a lateral continuum, while higher resolution views (Fig. 4A) display general trends of progressively greater porosity (darker areas) closer to rind surfaces. Basaltic clasts in semiarid to arid areas of Hawaii similarly show noticeable increases in porosity from the outer edge of the clast inward (Fig. 4C), where the extreme edges of clasts exhibit groups of particles apparently in the process of flaking away from the rind. Micron-size particles show some of the clearest evidence of separation (Fig. 4D). The ejection of loose material from the rind surface, along with an increase in porosity near the rind surface, becomes even more evident at higher magnifications (Fig. 4E). Andesitic clasts show similar features; for example, a pre-Tioga moraine at Bishop Creek shows stringers and fingers of loosely attached particles (Fig. 4F) that would never survive rind-measurement methodologies without the benefit of support from epoxy.

The sorts of textural observations seen at lower magnifications (Fig. 4F) become more apparent at higher magnifications of glacial moraine clasts at Bishop Creek (Fig 5). The space dedicated to a full article of just BSE images would not change the basic electron microscope signal we observe: just about every *in situ* weathering rind appears to show qualitative textural evidence of ongoing erosion.

High resolution transmission electron microscopy (HRTEM) observations of two andesite cobbles from the B horizon of pre-Tioga moraines at Bishop Creek, California (Berry, 1994; Phillips et al., 1996) reveal qualitative differences between the epoxied and unepoxied sides. The unepoxied sides suffered spalling of the outer sections of the rinds, as a consequence of the use of a rock hammer in sampling. The epoxied sides preserved the outer section of the rinds. HRTEM imagery of the eroded, unepoxied side revealed little incipient clay formation at the nanometer scale (Fig. 6A). In contrast, the epoxied side showed extensive clay mineral formation, dominating the outer sections of the rind (Figs. 6B and C).

3.2. Rates of subsurface rind erosion

Soil pits excavated close to ^{36}Cl-dated boulders on the Tioga-3 moraine (Fig. 2) yielded dramatically different results for epoxied and unepoxied clasts (Fig. 7). Protected clast surfaces have rind thicknesses typically three times thicker than the unepoxied side. Since this substudy explores rind thickness, the importance of epoxy rests in freezing rinds prior to sampling. The effect of clast handling, thus, appears to

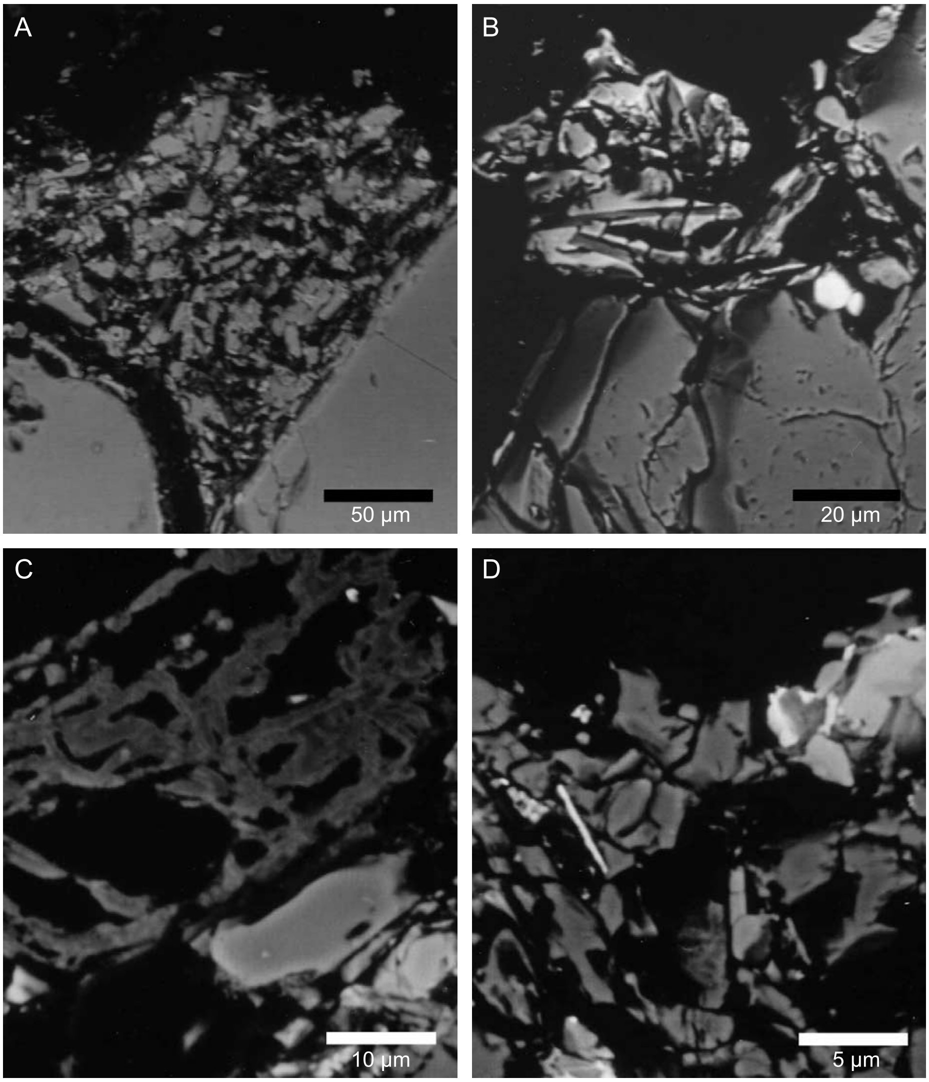

Fig. 5. Textural evidence of WR erosion at progressively higher magnifications, where samples come from andesite collected from the B horizon of pre-Tioga moraines at Bishop Creek (Berry, 1994; Phillips et al., 1996). Image (A) presents highly weathered plagioclase between less-weathered quartz, where the darker areas in the plagioclase could be clay minerals. Image (B) displays highly etched clinopyroxene that appears to be "hanging on by a thread". Image (C) shows extremely delicate clay-sized material of a weathered plagioclase mineral, while image (D) presents fragments that appear to have separated from the main clast, likely held in place by tenuous connections in the *Z* axis.

erode approximately two-thirds of the weathering rinds at these sites.

3.3. Rates of surface rind erosion

WRs develop under rock varnishes on the surfaces of Tioga-3 age ^{36}Cl-dated boulders. Progressively more complex VML sequences cover progressively thicker WRs (Table 2). WRs measured by mineral porosity exceeded the thickness of WRs measured by color change, typically by a factor of about 1.5 (Table 2). Microfractures beneath varnish microbasins showed even deeper penetration of weathering rinds—to the limits of the section thicknesses, typically 1 cm deep. Color change thus underestimates the thickness of WRs defined by porosity change.

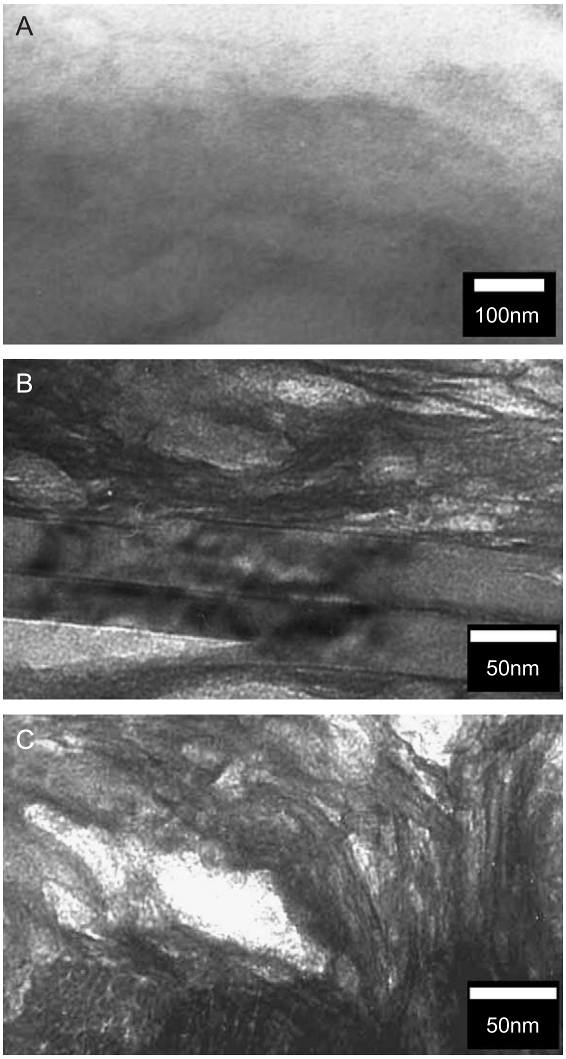

Fig. 6. High resolution transmission electron microscopy reveals great contrasts between the unepoxied (eroded by hammer impact) and epoxied sides of andesite B horizon clasts from a pre-Tioga moraine at Bishop Creek (Berry, 1994; Phillips et al., 1996). Image (A) from the unepoxied side presents the edge of a plagioclase grain, where the progressively lighter upper half illustrates only beam interaction without substantive weathering. In contrast, images (B) and (C) from the epoxied sides exemplify layered clay mineral structures, with spacing consistent with smectite. Despite careful searching, clay-mineral structures seen in images (B) and (C) were not seen on the unepoxied samples.

Rind thickness varies tremendously under microbasins with different VML stratigraphies. The oldest (WP1) microstratigraphy that closely reflects the ^{36}Cl age for the site shows the greatest rind thickness (Fig. 8). Considering just averages, the rate of rind thickening declines from 270 μm/ka underneath the WP1 stratigraphy to 180 μm/ka under the LU2/3 stratigraphy, and then drops even more to 120 μm/ka under WPO-2 and 50 μm/ka under WPO-1. Because the LU-1 stratigraphy could represent any time during the Holocene, rind formation rates are minimums at >14 μm/ka—a pattern seen in the comparatively small rind thicknesses under the LU-1 VML sequence (Fig. 8). Another manifestation of the variability is that a few microbasins show very thick WRs under each varnish stratigraphy; rind thicknesses drop tremendously for the bulk of the microbasins (Fig. 8).

The VML pattern that corresponds with the ^{36}Cl date for the host boulder shows the VML layering unit WP1. Comparatively few varnish microbasins display the full microstratigraphy—only 8%. About half of the varnish microbasins show only a Holocene (LU-1) signal.

4. Discussion

Erosion of WRs is not a new concept but an old realization manifested recently in Etienne's model (Fig. 1). Rind erosion does not interfere with the use of WRs as a chronometric tool (Cernohouz and Solc, 1966; Colman and Pierce, 1981) in so long as rind erosion is non-episodic—thus permitting the use of empirical calibration curves. Future refinement of WR dating methods have been largely halted by the advent of cosmogenic nuclide measurements. In just a few years, precise radiometric ages have become a far more appealing metric than convoluted calibrated ages providing only rough age assignments.

We argue here that the WR chronometric tool need not be abandoned but can be used to maximize the chances of obtaining the most accurate cosmogenic nuclide age. For example, "inheritance" of cosmogenic nuclides (Dorn and Phillips, 1991; Phillips et al., 1998; Fabel and Harbor, 1999) takes place in the same setting as WR production, and hence the presence of anomalously thick WRs could signify a boulder that experienced prior weathering and prior exposure to cosmogenic nuclides. Anomalously thin WRs could reflect boulder surfaces undergoing dramatically rapid erosion—invalidating the "zero

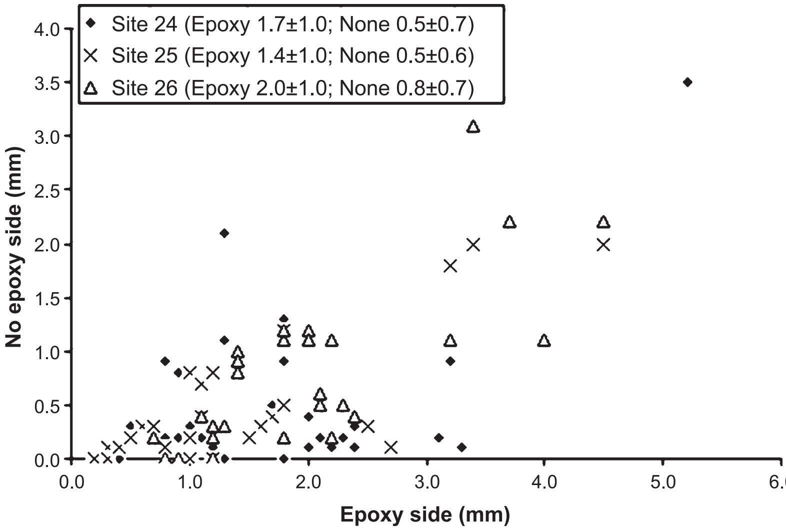

Fig. 7. Variations in the visual weathering rind thicknesses measured from 30 B horizon clasts. One half of each clast was epoxied prior to being hit with a rock hammer to split the clast for rind measurement. The other half was left unepoxied. The R^2 value of 0.44 with a statistically significant (p<0.01) relationship reveals that rind erosion takes place in the process of field rind measurement.

erosion age" assumption and significant underestimation of surface exposure ages. In settings of significant erosion and poor surface stability, cosmogenic sampling becomes extraordinarily complicated (Robinson, 2002)—and catenas (Birkeland and Burke, 1988) of WR analyses could help discern stability problems prior to the comparatively enormous expenditure of cosmogenic nuclide analyses.

Given the new role for WRs in the arsenal of Quaternary dating methods, using calibrated WR curves becomes far less important than understanding the processes of WR occurrence. In other words, if the issue is not surface age (the former use of WRs) but isolating anomalies such as boulders formerly exposed to a WR-producing-and-nuclide-buildup-environment (one of many new uses to complement cosmogenic nuclides), WR researchers must discard conceptual models of logarithmic decline in empirical curves. Discernable anomalies contain far more utility than general trends, since general trends cannot produce the precision or accuracy of radiometric measurements. Our approach here, of not assuming thickness–time relationships obtained by normal sampling strategies, rests in exploring the notion and rates of rind erosion. For only by understanding both aspects of the WR thickness function, growth and erosion, that WRs can be used as a tool to complement cosmogenic nuclide analyses in Quaternary research.

Back-scattered electron microscopy visualizes textures of WR erosion—as long as the investigator is sure that *in situ*—WR relationships are frozen prior to

Table 2
Using ^{36}Cl-dated boulders at Bishop Creek, this table compares the mean and standard deviation of WR thicknesses underneath varnishes of varying age

Layering unit	WP1	LU2/3	WP0-2	WPO-1	LU-1
Age (ka)	16	13	11	10.5	<10
n	11	23	6	31	68
Color WR thickness	4364±1984	2289±967	1333±513	469±317	138±122
Rate color WR (μm/ka)	~270±120	~180±70	~120±50	~50±30	>14
Pore WR thickness	6791±2531	3457±1637	1760±754	718±478	252±202

The varnish layering units refer to the lowest layer of varnish with ages indicated in the first row. WR thickness was measured by color change and change in porosity of minerals, as seen in optical thin sections. Measurements are in microns.

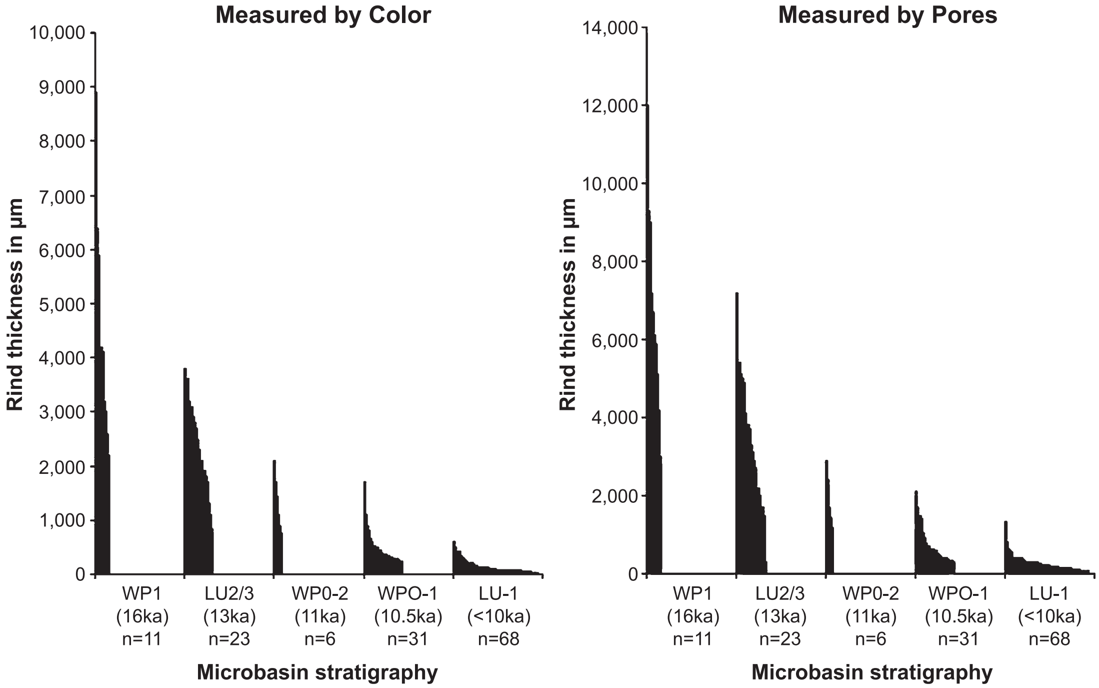

Fig. 8. Distribution of rind thickness under rock varnish thin sections, where rind thickness is based on changes visible in cross sections. The microlamination (VML) calibration for the Great Basin (Liu and Dorn, 1996; Liu et al., 2000; Liu, 2003) provides only broad time ranges, represented here by a date that indicates a "younger than" signal. In other words, the WR thicknesses represent growth since the indicated time.

subsurface clast disturbance. Our results indicate that weathering rinds erode, and indeed micrographs show that much of the highly weathered outer zone of the rind contains a large amount of material that would spall or erode from minimal disturbance (as in Etienne's Stage 3 and especially Stage 4). This disturbance could take the form of removal from the soil context in which a clast lies, or more directly, the splitting of a clast or removal of a sample by striking with a rock hammer. Therefore, standard WR dating techniques, as well as collection of samples for cosmogenic dating, are likely to artificially reduce WR thicknesses. After independently validating Etienne's (Fig. 1) conceptual model (Figs. 4–6), we assessed the effects of artificial rind erosion.

The test of artificial WR erosion involves epoxying only one side of a clast, prior to its removal from a soil pit, thus comparing "frozen" rind thicknesses with normally sampled rind thicknesses at sites of known cosmogenic nuclide age. Rind thicknesses on unepoxied sides average 0.5–0.8 mm, only slightly greater (Fig. 7) than average rind thicknesses seen by others in the local area (Berry, 1994) of 0.3–0.4 mm for granodiorite clasts. Observed thicknesses on the epoxied side, however, reveals that approximately two-thirds of the WR is artificially removed—at least for granodiorite clasts in a semiarid moraine setting. With BSE observations (Figs. 4 and 5) showing outer rinds hanging by a proverbial thread, our finding should not be surprising—that WR adhesion would be insufficient to survive being hit with a rock hammer. A natural corollary is to question the current paradigm of clays not forming in semi-arid western USA Quaternary soil settings (Colman, 1982), but being a product of only aeolian import. Clays do appear to be forming in WRs (Fig. 6)—left in the field when the investigator strikes a rock with the hammer, thus leading to the erosion of an outer rind that can contain clay minerals.

Exploration of surface rind erosion is particularly relevant to cosmogenic nuclide dating, in part because cosmogenic dating procedures focus on large boulders that may or may not have eroded during transport, and hence may suffer systemic problems of "inheritance" of a prior exposure signal (Dorn and Phillips, 1991; Nishiizumi et al., 1993; Phillips et al., 1996). In contrast, weathering-rind researchers typically select smaller clasts that are carried in a matrix and are more likely to suffer abrasion during transport.

Our results have two main implications for the interface of weathering and cosmogenic nuclide analyses: (i) less than 10% of a late Pleistocene granodiorite boulder's surface fits the zero-erosion assumption used in reporting cosmogenic nuclide ages; researchers wishing to base their interpretations on a "zero erosion" age would need to supplement their research with varnish VML or WR analyses; and (ii) the pattern of a few very thick WRs under different varnish microbasins could be due to incomplete rind erosion events. Incomplete rind erosion spells problems for cosmogenic nuclide analyses because it suggests prior episodes of weathering and buildup of cosmogenic nuclides. "Inheritance" of cosmogenic nuclides will be a significant issue where these WR anomalies exist because partial erosion of the WR would reset the varnish clock and would create an anomalously thick rind. Put another way, a concordance of WR and rock coating "age trends" would indicate ideal boulders for cosmogenic nuclide dating.

By constraining the timing of WR formation through ^{36}Cl ages and the timing of WR erosion events by varnish microlaminations, our results on surface WR erosion have two counter-intuitive implications. First, accelerating rates of rind formation seen under progressively older VML sequences (Table 2 and Fig. 8) runs contrary to the logarithmic decline in the WR curves so frequently observed (Oguchi, 2001). With the assumption that weathering enhances water retention that in turn enhances greater weathering, a positive feedback should occur to enhance rind formation over time (cf. Viles, 2001)—that is, if rind erosion does not take place. The only way to ensure that the WR thickness does not include WR erosion is to obtain independent age control; the VML sequence constrains the timing of WR erosion unlike all prior WR sampling locales. We are left with the conclusion that a positive feedback of more intense weathering takes place under the protection of rock varnish and that we see no process-based reason why that positive feedback should not occur in other WR contexts. Second, the original interpretation for the relative paucity of complete varnish microstratigraphies was the slow onset of varnishing (Dorn, 1990; Liu and Dorn, 1996; Liu et al., 2000; Liu, 2003). The systematic patterns in WR thicknesses and their relationship to VML observed in this study suggests that WR erosion may be a key player in resetting the varnish clock.

A last discussion point involves nomenclature and a circumstance where pedagogy may have interfered with interpretation. The vast majority of researchers view WR as a color change phenomenon seen in the field, perhaps initiated by teachings in introductory classes. This misconception of color equating to weathering runs counter to detailed process studies (Oguchi and Matsukura, 2000; Oguchi, 2001; Aghamiri and Schwartzman, 2002; Dixon et al., 2002; Etienne, 2002). Our findings similarly illustrate that color change is only a part of the WR story. WRs defined by an increase in porosity are thicker than WRs defined by color, by a factor of 1.5. Similarly, microfractures of more intense weathering extend even deeper into the host clast. The color change so tied to the "weathering rind" nomenclature, although useful as a teaching tool, seriously miscommunicates the true nature of WRs. Even though color-based WR thickness measurements represent the minimum penetration by weathering processes, we do not think enough data exist to justify a "correction factor" that might vary among different rock types and environmental settings.

5. Summary

Weathering rinds (WRs) represent an important part of fundamental research in geomorphology, in as much as WRs represent a widespread interface between earth materials and the broader terrestrial environment. Their ubiquitous occurrence has also led to a number of applications (Table 1), the most widespread being use as a chronometric indicator. Although the large cost of cosmogenic nuclides has not completely replaced WRs as a dating tool, undoubtedly WRs are on their way out as the primary chronometric focus of a research project. Why fuss with guesses, when radiometric control can be had? First, their low cost permits expensive cosmogenic ages to be used as local-area calibrations for WR curves to extend the density of chronometric data. Second, WRs can detect a flawed sample collection scheme involving such systemic biases as a prior exposure history. Third, analyses of WR erosion can aid in the pre-selection of the best clasts for cosmogenic nuclide dating.

This paper explores an irony in WR research: that a fundamental flaw in WR dating methods might be a key to its long-term utility as a chronometric method. An often unstated assumption in the application of WRs in geochronology has been that WR erosion either does not occur or that it is not episodic. Assuming away WR erosion has been practical and permitted its use as a chronometric tool (Cernohouz and Solc, 1966; Colman and Pierce, 1981) in so long as rind erosion is nonepisodic—thus permitting empirical calibration curves. Outliers of rinds too thin from erosion or too thick from "inherited weathering" events wash out in statistical treatments. We believe that it is time for these outliers to take center stage.

The first step in our research involved assessment of the occurrence and magnitude of WR erosion. Qualitative back-scattered and high resolution transmission electron microscopy observations reveal that Etienne's (2002) conceptual model for the formation and erosion of weathering rinds over 10^2 yr in cold wet settings is valid in arid and semiarid environments over 10^3–10^4 yr. One substudy, on granodiorite clasts in the B horizon of a last glacial maxima moraine of the Sierra Nevada in California, reveals that normal sampling procedures for WR dating removes two-thirds of true rind thickness. Furthermore, rind thickness measured solely on the basis of optical color changes underestimates rind thickness measured by porosity by a factor of 1.5.

Establishing the ubiquitous nature and approximate magnitude of WR erosion in soil settings led to a controlled field experiment on the nature of WR erosion in the surface contexts where boulders are sampled for cosmognic dating. Using boulders at Bishop Creek in the Sierra Nevada with known ^{36}Cl ages (Phillips et al., 1996), we knew when the "clock" of WR formation started. Using the varnish microlaminations sequence on top of the WR rinds (Liu, 2003; Marston, 2003), we knew when the last WR erosion event took place. More than 90% of a boulder's surface experienced enough erosion to question the "zero erosion" age used so prevalently in cosmogenic nuclide reporting. Just as troubling, some settings revealed anomalously thick WRs, suggestive of "inherited" weathering and the possibility of "inherited" cosmogenic nuclide buildup. Thus, the outliers to statistical trends that promoted the use of WRs as a chronometric tool offer critical tests of a sample's suitability for use in cosmogenic nuclide dating.

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