

# Cation-ratio dating of rock varnish: a geographic assessment

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The study of long-term landscape evolution is at a watershed. New methods have been developed in the last few years to estimate the length of time a landform has been exposed at the surface of the earth. Surface-exposing dating (SED) can provide numerical age control where little existed before on cuesta escarpments, bornhardts, alluvial fans, stream terraces, glacial till, sand dunes, patterned ground and other landforms. The potential for increasing our understanding of geomorphic systems is immense. One SED method, cation-ratio (CR) dating of rock varnish, has been the subject of a three-year study of its potential and limitations. The results of this research are reported here.

CR dating can be classified as a calibrated, biochemical age-determination method (see Colman *et al.*, 1987). Chemical changes in rock varnish are calibrated by established numerical ages for the subaerial exposure of the underlying rock. The cation ratio of  $(K^+ + Ca^{2+})/Ti^{4+}$  decreases with time. This is because potassium (K) and calcium (Ca) are more mobile than titanium (Ti). Other cations can serve in the numerator (e.g., Na, Mg) or in the denominator (e.g., Zr), but K, Ca and Ti are easily measured and yield the best empirical correlations with time.

Since its first presentation (Dorn and Oberlander, 1981; Dorn, 1983), the theory and implementation of CR dating has been investigated by Soviet (Glazovskiy, 1985), Canadian (Clarkson, 1985), US (Harrington and Whitney, 1987; Krinsley and Anderson, 1989), South African (Pineda *et al.*, 1988; Jacobson, 1989), Chinese (Tanzhuo and Yuming, in press) and Australian (Dragovich, 1988) researchers. Its application to geomorphology includes such topics as glacial chronology (Glazovskiy, 1985; Dorn *et al.*, 1987b), aeolian history (Dorn, 1986), lacustrine events (Dorn and Oberlander, 1981; Dorn, 1988), alluvial-fan evolution (Dorn, 1988), stream terraces (Whitney *et al.*, 1988), rates of faulting (Harrington, 1987; Dorn, 1988; Tanzhuo and Yuming, in press), colluvial development (Dorn, 1983; Whitney and Harrington, 1988) and rates of erosion (Dethier *et al.*, 1987). Its application to archaeology has been for dating stone artifacts (Dorn *et al.*, 1986), petroglyphs (Dorn and Whitley, 1984; Whitley and Dorn, 1987; Dorn *et al.*, 1988a; Nobbs and Dorn, 1988; Jacobson, 1989) and ground drawings (Clarkson, 1985). CR dating is also being used to assess the suitability of Yucca Mountain, southern Nevada, as a high-level nuclear waste

repository (Harrington and Whitney, 1987; Dorn *et al.*, 1988b; Dorn, 1989a).

The burgeoning interest in CR dating is due to the presence of rock varnish in places where other datable materials, such as charcoal for  $^{14}\text{C}$  measurements, are not usually available. Rock varnish is a paper thin coating of mostly clay minerals and manganese and iron oxides (Potter and Rossman, 1977; 1979; Raymond *et al.*, 1988) that forms on stable rock surfaces. Although found in almost all terrestrial weathering environments (Dorn and Oberlander, 1982), rock varnish has been of most interest in arid regions where its 'desert varnish' facies is most stable biogeochemically. By dating the onset of rock varnish formation, a limiting age is obtained for the exposure of the underlying rock surface, whether the exposure is from human or natural causes.

The purpose of this paper is to provide an assessment of the state of the art in CR dating of rock varnish. A geographical perspective is critical to the practical success of CR dating. For those trying to apply CR dating using empirically derived calibrations, there are three geographical constraints.

- 1) *CR dating requires calibration.* Accelerator mass spectrometry (AMS)  $^{14}\text{C}$  dating of varnish (Dorn *et al.*, 1986; 1987b; 1989) allows calibration anywhere varnish is present, to the limit of the radiocarbon time scale at about 40 ka. Typically, K-Ar dates on volcanics have been used for the time period beyond 40 ka. Quaternary volcanic fields are relatively common in southwestern North America. However, K-Ar dated volcanics with original flow features are not present in many arid areas, for example arid Australia or the Negev Desert.
- 2) *CR dating is constrained to desert regions where varnish is biogeochemically stable.* The general alkalinity of deserts promotes its stability (see Elvidge, 1979; Elvidge and Iverson, 1983; Dorn and Oberlander, 1982; Oberlander, 1982; 1988). Varnish is present in environments like Kentucky, Yosemite, Nepal (Dorn and Oberlander, 1982) and Iceland (Douglas, 1987), but acidic conditions prevalent in these more humid regions dissolve the manganese and iron oxides that act as a cement for varnish (Crerar *et al.*, 1980; Dorn and Oberlander, 1982; Douglas, 1987). Dates on varnish in these environments would only indicate when the varnish was last eroded chemically, not necessarily when the underlying rock was first exposed.
- 3) *CR dating is constrained to specific microenvironments where conditions that affect varnish development and CR changes are similar.* It is misleading to compare varnishes from sites where the local physical geography is not similar. CR is a chemical dating method and is highly dependent on the biogeochemical environment.

## I Role of rock varnish in surface-exposure dating

CR dating is based on a conceptual biogeochemical model of varnish formation (Dorn and Oberlander, 1982) and on the differential mobility of minor elements in varnish (Dorn, 1983). Calibrating differential mobility of cations in varnish with numerical dates is supported by a body of empirical data indicating the ratio  $(\text{K}^+ + \text{Ca}^{2+})/\text{Ti}^{4+}$  decreases with time (e.g. Dorn, 1983; Glazovskiy, 1985; Dorn *et al.*, 1986; 1987a; 1987b; 1988a; Harrington and Whitney, 1987; Pineda *et al.*, 1988; Tanzhuo and Yuming, in press). It is perhaps analogous to using soils to obtain ages. How the soil system changes over time is not completely understood, but parts of it can still be calibrated empirically (Switzer *et al.*, 1988). The purpose of CR dating is to assign an age for the onset of rock varnish formation, that in

turn provides a minimum limit. This is of great importance to geologists and processes of landform development and in the cultural implications of the desert.

There are means other than

- 1) *Uranium-series* was presented but have any previous age control to date the varnish.
- 2) Trace metals such as Zn, Cu, Mn, Fe, Ni, Pb, Sr, Ba, and Cs (Jenne, 1968) and increase in concentration with time (Dorn, 1982).
- 3) *Paleomagnetic analyses* were attempted but the underlying rock could not be separated from the varnish.
- 4) *Sequences of alternating layers* of varnish and rock (Dorn, 1978; 1978; Dorn, 1984; 1989b) offer hope for dating.
- 5) *K-Ar dating of clays in varnish* is possible but the one K-Ar date on a lava flow by over an order of magnitude radiogenic argon is probably inherited from the underlying rock into the varnish.
- 6) Other elements have been tried including zirconium. These are present in small amounts and correlations with time than  $(\text{K}^+ + \text{Ca}^{2+})/\text{Ti}^{4+}$ .
- 7) Dragovich (1986a) constrained the age of varnish by  $^{14}\text{C}$  dating associated inorganic carbon.
- 8) *Radiocarbon dating of rock varnish* is a precise and accurate method of dating but if no dates are available, new tests demonstrating the incorporation into the bottom layer of varnish are limited, however, to the last 40 000 years per square metre.

Rock varnish dating provides a minimum limit for when it was deposited. There are a set of elements that can be used for rock varnish dating, that provide a minimum limit at the surface to cosmic rays.  $^{14}\text{C}$  (Dorn *et al.*, 1986; 1987; 1988; Leavy *et al.*, 1988) and  $^{10}\text{Be}$  (Nishiizumi *et al.*, 1988; 1986a; 1986b; Kurz *et al.*, 1987) can be used to accumulate in the upper 50 ± 10 cm of rock, dependent on time and variable erosion rates, are controlled.  $^3\text{He}$  can be measured by several methods; the rest are measured by gas mass spectrometry (Phillips, 1987).

The cosmogenic buildup method is based on cosmic rays (Phillips *et al.*, 1988) and the geomorphic event of interest (e.g. glacial till signal. For this simple circumstance, the glacial till (Phillips *et al.*, 1988) time range is appropriate) and is used for geomorphological research.

turn provides a minimum limiting age for the exposure of the underlying rock. This is of great importance to geomorphologists who are interested in the history and processes of landform development, and to archaeologists who are interested in the cultural implications of artifact and petroglyph development.

There are means other than CR for dating rock varnish that have potential.

- 1) *Uranium-series* was presented by Knauss and Ku (1980). Although the sites dated did not have any previous age control to evaluate the results, this approach has considerable promise.
- 2) Trace metals such as Zn, Cu and Ni are scavenged by manganese and iron oxides (see Jenne, 1968) and increase in concentration in varnishes over time (Dorn and Oberlander, 1982).
- 3) *Paleomagnetic analyses* were attempted by Potter (1979), but the stronger signal from the underlying rock could not be separated from the weaker varnish signature.
- 4) *Sequences of alternating layers of Mn-rich and Mn-poor laminations* (Perry and Adams, 1978; Dorn, 1984; 1989b) offer hope for relative stratigraphic correlations.
- 5) *K-Ar dating of clays in varnish* from Coso Range indicates the presence of radiogenic argon, but the one K-Ar date on clays in varnish predated the K-Ar date of the underlying lava flow by over an order of magnitude (D. Lynch, personal communication, 1987). The radiogenic argon is probably inherited from the detrital fraction of the clays incorporated into the varnish.
- 6) Other elements have been tried in cation ratios such as sodium, phosphorus, rubidium and zirconium. These are present in smaller concentrations, are harder to analyse, and yield lower correlations with time than  $(K^+ + Ca^{2+})/Ti^{4+}$ .
- 7) Dragovich (1986a) constrained the age of varnish at a site in New South Wales, Australia, by  $^{14}C$  dating associated inorganic carbonate.
- 8) *Radiocarbon dating of rock varnish* (Dorn *et al.*, 1986; 1987b; 1989), is presently the most precise and accurate method of dating rock varnish. At sites where conventional  $^{14}C$  ages are available, new tests demonstrate the reliability and accuracy of dating organic matter incorporated into the bottom layer of the varnish (Dorn *et al.*, 1989). Radiocarbon dating is limited, however, to the last 40 000 years and is limited to large surfaces, on the order of a square metre.

Rock varnish dating provides an age for when a rock surface was last eroded or deposited. There are a set of new cosmogenic SED methods, complementary to rock varnish dating, that provide the length of time a rock has been exposed at the surface to cosmic rays. *In situ* produced isotopes such as  $^{36}Cl$  (Phillips *et al.*, 1986; 1987; 1988; Leavy *et al.*, 1987),  $^{14}C$  (Lal, 1988; Jull *et al.*, 1989),  $^{26}Al$  and  $^{10}Be$  (Nishiizumi *et al.*, 1986; 1989; Klein *et al.*, 1987; Lal, 1988),  $^3He$  (Kurz, 1986a; 1986b; Kurz *et al.*, 1987; Cerling, in press) and  $^{129}I$  (Kubik *et al.*, 1987) accumulate in the upper  $50 \pm$  cm of an exposed rock. The rate of buildup is dependent on time and variables such as altitude and latitude, that can be controlled.  $^3He$  can be measured by difficult conventional-mass spectrometry methods; the rest are measured by accelerator-mass spectrometry (Elmore and Phillips, 1987).

The cosmogenic buildup methods address the history of exposure of a clast to cosmic rays (Phillips *et al.*, 1986; Lal, 1988). If a clast was not exposed prior to the geomorphic event of interest, the buildup of *in situ* isotopes yields a clear age signal. For this simple circumstance of no prior exposure history, such as dating glacial till (Phillips *et al.*, 1988), radiocarbon dating of rock varnish (when the time range is appropriate) and *in situ* SED methods are superior to CR dating for geomorphological research. They do not require a calibration and can be

applied in areas without established age control. *In situ* cosmogenic isotopes are not limited to arid-alkaline regions. They do not suffer from difficulties associated with controlling biogeochemical variables, and the upper few centimetres of rock can spall off and still not significantly affect the surface exposure age.

If a clast had a history of isotopic buildup prior to the event of interest, for example exposure on a hillside before transport and deposition in a fluvial system, varnish dating can have several advantages. Several *in situ* isotopes with different half-lives would be required to constrain the timing of the most recent exposure of the rock. This could be extremely expensive and might not yield definitive results. Consider the history of aeolian abrasion on boulders or the manufacturing of an artifact. Removing a flake scar or aeolian abrasion would remove any prior varnish; varnish formed afterwards would date the flaking (Dorn *et al.*, 1986) or the cessation of aeolian abrasion (see Dorn, 1986). *In situ* isotopes, in contrast, would record when the raw tool material or ventifacted boulder was first exposed to cosmic rays. The varnish clock is readily reset by abrasion. This is an advantage if the timing of this abrasion is of geomorphological or archaeological interest.

## II General limitations and assumptions of CR dating

Probably the most critical step in all SED methods is the collection of samples. If the age of a depositional or erosional landform is to be determined, the rock surfaces collected must reflect the timing of the process(es) in question. Any age estimate for the varnish is only a minimum-limiting date for the exposure of that rock surface. If the underlying rock or the varnish experienced mechanical or biochemical erosion, the varnish clock would be reset, and any CR obtained would reflect the time of last erosion.

The only type of rock varnish used for CR dating is black, rich in manganese (Mn:Fe ratio of about  $\geq 0.3$ ), and formed in subaerial environments exposed to only aeolian fallout. There are many different types of rock varnishes (Dorn and Oberlander, 1982), including orange varnish (manganese-poor) found in soil, rock crevices, and subaerial environments; dusky red varnish (manganese-intermediate) found in soil, rock crevices, and subaerial environments; and black varnish (manganese-rich) found where water runs over cliff faces, in rock crevices, in soil, in regolith, and in humid environments such as point bars of perennial streams. CR variations in these other rock varnishes have not been sufficiently tested to be included in this paper.

Any CR date is based on a calibration, called a cation-leaching curve (CLC). CR dates are only as good as the calibration. All CLCs show CR changes in a linear fashion while age changes as  $\log_{10}$ . That varnish CRs appear to decrease regularly on a semilog scale is reasonable; weathering phenomena in geomorphology tend to be related to age in a log or semilog fashion. A small change in CR results in a large change in age. The least precise CR dates are, therefore, those for the oldest samples. The only realistic solution is to examine the central

tendency of mean dates (several complications are added, as have been shown by the use of a variety of dating methods are used to constrain the dates).

Varnish development on a surface is a complex process. While colonization appears to be rapid in arid and semiarid regions (see Oberlander, 1982; Dorn, 1983), it can produce a complete varnish in periglacial environments where organisms such as lichens have a paucity of moisture slows the varnish development (see Oberlander, 1982; Oberlander, 1982; 1988). A transgressive pattern of varnish development is also possible. For example if a boulder is composed of quartz is quite slow (Dorn, 1983) for microbial colonization and starts to form first yield the best surface.

**Table 1** Initial cation ratios of rock varnishes analysed by energy dispersive analysis of X-rays (EDAX) using the SEM-EDEX method presented as semi-quantitative approximations

Site (nearest curve)

Fort Piute, Mojave Desert, CA  
(Mojave Curve)

Kearsarge, Owens Valley, CA  
(Owens Valley Curve)

Bodie, eastern CA. (environment most similar to Lunar Crater Curve)

Franklin Mines, Chloride Cliff, CA.  
(Crater Flat Curve)

Swansea, Owens Valley, CA  
(Coso Curve)

near Springfield, CO.  
(Southeast Colorado Curve)

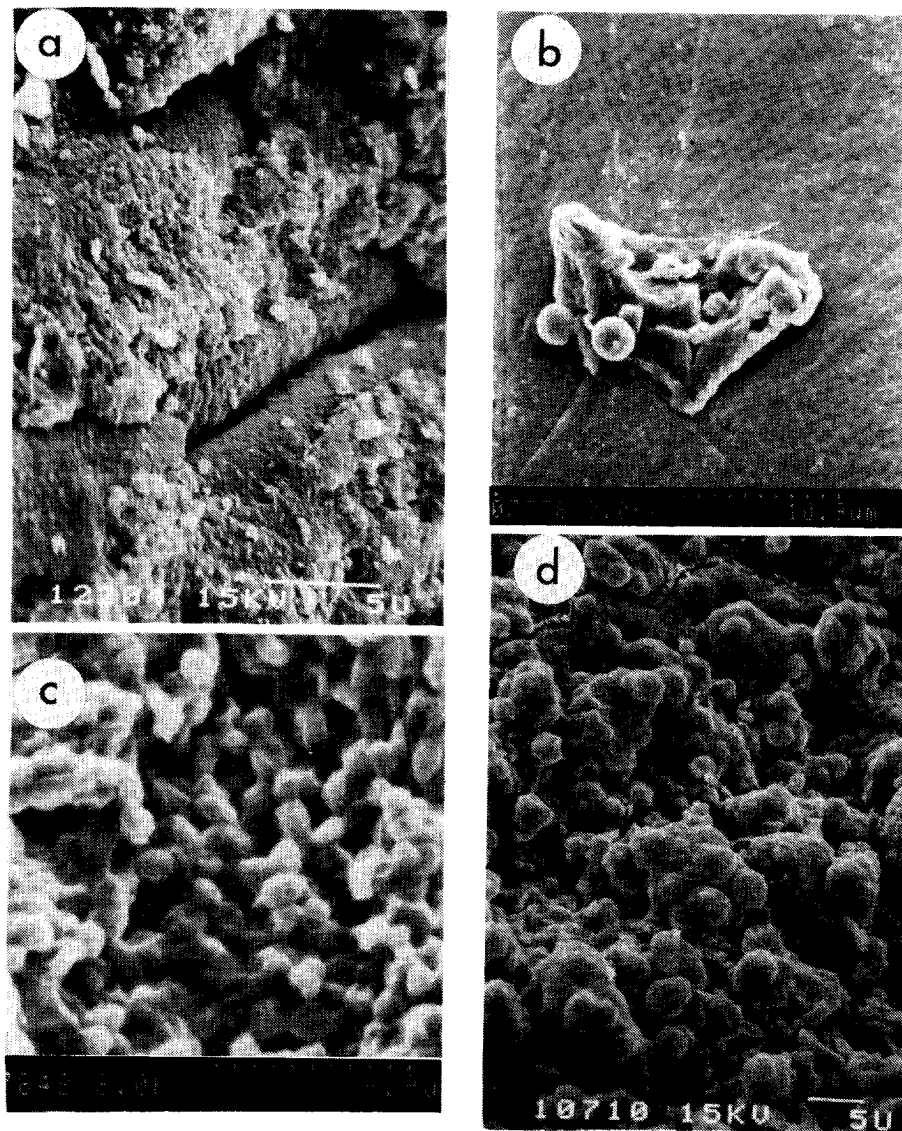
near Yunta, South Australia  
(Oulnina Curve)

tendency of mean dates (see Dorn *et al.*, 1987b; Dorn, 1988). Further complications are added, as Harden *et al.* (1988) note, if several different types of dating methods are used to calibrate CRs over the same time range.

Varnish development on a substrate is not necessarily uniform (Dorn and Oberlander, 1982; Dorn, 1983), illustrating why a CR date is a minimum age estimate. The rate of development varies with microenvironment and rock type. While colonization appears to start on a microscopic scale after about 100 years in arid and semiarid regions (see Figure 1A-C and Table 1), less than a century can produce a complete varnish coating on a rock in periglacial environments (Figure 1D), because varnish-forming organisms are much more active on rocks in periglacial environments where water is abundant and where competing organisms such as lichens have not colonized. In arid regions, alkalinity and the paucity of moisture slows the varnish-forming process (Dorn and Oberlander, 1982; Oberlander, 1982; 1988). CR dating can be influenced by a time-transgressive pattern of varnish growth. The solution is proper sampling. For example if a boulder is composed of quartz, varnish development on smooth quartz is quite slow (Dorn, 1983). Cracks in the quartz, however, are good spots for microbial colonization and varnish quickly; micropositions where varnish starts to form first yield the best estimates for the exposure of the underlying surface.

**Table 1** Initial cation ratios of rock varnishes formed on historical surfaces, analysed by energy dispersive analysis of X-rays (EDAX). Due to the uncertainties of the SEM-EDEX method presented in the text, these results should be viewed as semi-quantitative approximations of varnish CRs.

Site (nearest curve)	Date surface exposed	EDAX CR of dust at site	EDAX CR of incipient varnish
Fort Piute, Mojave Desert, CA (Mojave Curve)	c. 1884	8.7 ± 0.7	8.8 ± 0.5
Kearsarge, Owens Valley, CA (Owens Valley Curve)	c. 1867	9.5 ± 0.5	9.0 ± 0.7
Bodie, eastern CA. (environment most similar to Lunar Crater Curve)	c. 1900	8.9 ± 0.4	8.6 ± 0.5
Franklin Mines, Chloride Cliff, CA. (Crater Flat Curve)	c. 1916	10.0 ± 0.6	9.8 ± 1.1
Swansea, Owens Valley, CA (Coso Curve)	c. 1872	9.3 ± 0.4	8.8 ± 0.7
near Springfield, CO. (Southeast Colorado Curve)	1905	9.8 ± 1.0	9.2 ± 0.6
near Yunta, South Australia (Oulnina Curve)	1884	10.3 ± 0.8	9.9 ± 1.2



**Figure 1** Scanning electron micrographs of varnishes  $\leq 120$  years old. Arid varnishes (A-C) develop slowly and are observable only with an SEM after about 100 years. Periglacial varnishes (D) can develop a complete coating within a few decades (Dorn and Oberlander, 1982). Scale (in microns) in all SEM images reflect either length of solid bar or lengths of dots. A - Varnish on a faced surface of Fort Piute, constructed 1868, Mojave Desert, California; B - Varnish on 1884 engraving, near Mannahill, South Australia; C - Mn concentrating bacteria on surface of incipient varnish, from stone in a foundation at Swansea constructed about 1872, near the Coso Range, eastern California; D - Varnish completely coating boulder on glacial moraine younger than about 1930, Khumbu, Nepal.

The assumptions and inherent uncertainties in Dorn (1983), have been tested and grouped together into three general

1 *First general assumption:* The particle size that is incorporated into varnish on semi-arid sites compared sites for the period of

The particle size that is incorporated into varnish (Dorn, 1986). Hence, subaerial varnishes are composed of fine-grained material. The results of Rabenold (1986) on airborne fallout may be reasonable for Texas. Péwé *et al.* (1981) argue that Quaternary in central Arizona and large regions is not typical (e.g. Dorn, 1986).

Present airborne fallout, however, is affected by anthropogenic modifications of the atmosphere. Amounts of Ca and K in the atmosphere basins for water diversion substantially reduced (Barone *et al.*, 1981; Eldred *et al.*, 1981). Anthropogenic effect, dust has been reduced, deep depressions on rock surfaces, and a horizon. CRs of the  $< 2 \mu\text{m}$  fraction have been relatively similar within a region to region. Where the results differ with the CRs derived from the present airborne collectors placed in Denver, Nevada (6 times), Providence Mountain, Nevada Range, California (8.5 times). The results are a generation and perhaps some local deposits.

The CR of this initial ratio is a function of the curve, based on SEM observations of the historic surfaces. Varnishing starts within a few years in the southwestern USA and the CRs of these microscopic varnishes are high (see Table 1). These semi-quantitative varnishes may be approximated by the natural sites of dust accumulation.

What is most uncertain regarding the relationship of this IR and the abundance of dust is the amount of all compared samples. Short-term samples, years or less are less likely to accumulate and are quite slow in arid and semiarid

The assumptions and inherent uncertainties in CR dating, originally presented in Dorn (1983), have been tested in this study. Extant concerns and new data are grouped together into three general assumptions.

1 *First general assumption: the initial ratio (IR, airborne fallout that is incorporated into varnish on subaerial rock exposures) has been similar at all compared sites for the period of time under examination*

The particle size that is incorporated into varnish is typically  $<2 \mu\text{m}$  (Dorn, 1983; 1986). Hence, subaerial varnishes should have IRs that have the CR of this material. The results of Rabenhorst *et al.* (1984) suggest an assumption of similar airborne fallout may be reasonable at present for the Edwards Plateau of west Texas. Péwé *et al.* (1981) argue that this is not unreasonable for much of the Quaternary in central Arizona. However, a similar chemistry for fallout over large regions is not typical (e.g., Cahill *et al.*, 1981).

Present airborne fallout, however, may not reflect natural conditions due to anthropogenic modifications of the aeolian environment that generally increase amounts of Ca and K in the atmosphere. For example, drying of natural lake basins for water diversion substantially changes the chemistry of airborne fallout (Barone *et al.*, 1981; Eldred *et al.*, 1984; Cahill and Gill, 1987). To minimize the anthropogenic effect, dust has been collected from sites of long-term accumulation, deep depressions on rock surfaces or the uppermost part of the Av soil horizon. CRs of the  $<2 \mu\text{m}$  fraction of these natural sites of aerosol accumulation have been relatively similar within each CLC area, but somewhat different from region to region. Where the results of airborne collectors have been compared with the CRs derived from these natural dust traps, the CRs are higher in airborne collectors placed in Death Valley, California (1.5 to 10 times), Schurz, Nevada (6 times), Providence Mountains, California (6.5 times) and in the Coso Range, California (8.5 times). This is probably due to anthropogenic dust generation and perhaps some leaching that has occurred in the natural dust deposits.

The CR of this initial ratio is assigned an age of 100 years on a cation-leaching curve, based on SEM observations of microscopic varnish development on historic surfaces. Varnishing starts to be seen with an SEM after about 60 to 100 years in the southwestern USA and arid south Australia (see Figure 1A-C). The CRs of these microscopic varnishes tend to be similar to the IRs collected nearby (see Table 1). These semi-quantitative observations suggest that the IR of varnishes may be approximated by the  $<2 \mu\text{m}$  fraction of airborne fallout in natural sites of dust accumulation.

What is most uncertain regarding this first assumption is that the chemistry of this IR and the abundance of dust fallout has remained similar over time and for all compared samples. Short-term changes in airborne fallout over hundreds of years or less are less likely to affect a 'desert varnish' because rates of accretion are quite slow in arid and semiarid environments (Dorn and Oberlander, 1982;

Whalley, 1983). During the period of accretion of rock varnishes under study, however, major variations in lake levels, vegetation changes and climatic fluctuations have occurred on the scale of  $10^4$  years.

2 *Second general assumption: rock varnish serves as a cation-exchange complex where rates of (K+Ca)/Ti change have been similar for compared samples*

Mixed-layer illite-montmorillonite clays in varnish (Potter, 1979) and Mn-Fe oxyhydroxides (Jenne, 1968) act as cation-exchange complexes. Potassium and calcium are also recognized to be far more mobile than Ti in the biogeochemical environments where varnish develops (e.g., Polynov, 1951; Marchand, 1974; Yaalon *et al.*, 1974; Colman 1982; 1986).

The complexities of rock varnish, however, make the mechanisms of cation-exchanges difficult to model. Micromorphological structures in varnish differ over short distances (Dorn, 1986). Variations in varnish thickness, interlayer and intralayer cementation, organometallic compounds, permeability, and other disparities also influence varnish CRs. A serious uncertainty is the micron-scale behaviour of K, Ca, and Ti in varnish (Dragovich, 1988; Raymond *et al.*, 1988; Krinsley and Anderson, 1989). At a simplistic level, the CRs of K:Ti and Ca:Ti should have a similar trend of a decrease with time, and the CRs of K:Ti, Ca:Ti and (K+Ca)/Ti should decrease with greater depth (time) in the varnish (Figure 2A). These changes do occur, but not always. It is not uncommon for two varnishes from the same site to have a similar (K+Ca)/Ti ratio, but have the relative abundances of K and Ca vary considerably. Figure 2B illustrates that the (K+Ca)/Ti, K:Ti and Ca:Ti ratios show no relationship with depth in a single microprobe transect. Similar results of extreme variability are reported by Dragovich (1988) and Krinsley and Anderson (1989). A further complexity is the behaviour of titanium. Ti may be enhanced in varnish by the development of authigenic dome features (Dorn, 1983). It may also be possible to enhance titanium by other diagenetic mechanisms (Sudom and St. Arnaud, 1971; Morad and Aldahan, 1986; Harden, 1988).

There is a great hazard in trying to generalize from data acquired by micron-scale measurements to the bulk chemistry of rock varnishes. Varnish chemistry is extremely variable on a micron scale (see Figure 2 and Dorn and Oberlander, 1982; Dragovich, 1988; Dorn, 1989b; Krinsley and Anderson, 1989). The causes of these variations include micron-scale mineralogical variations (see Raymond *et al.*, 1988) and the mechanics of CR change. The CR dating method examines bulk chemical trends in large enough samples to average this variability. Making CR measurements on a micron scale would be an extremely time-consuming (and expensive) process, requiring probably hundreds to thousands of measurements to average enough material to be remotely comparable to a single bulk chemistry analysis.

A substantial uncertainty is how varnish CRs are influenced by climatic changes. The semilog shape of a cation-leaching curve (CLC) indicates it becomes progressively more difficult to remove the K and Ca relative to the Ti with time.

This change occurs while new climatic changes. That only one curve suggests that the CR system is influenced in part to the cumulative nature of the micron-scale mechanics of cation-exchange of detrital minerals in the varnish.

3 *Third general assumption: rock varnish CRs are similar for compared samples from similar environments*

Table 2 presents microenvironmental data for two varnishes. If these contemporary environments are compared, they offer two major challenges to the CR dating method. Whether major episodes of past climatic change (D and Figure 4B), it is probable that these influences that could have influenced the CR system. Climatic fluctuations must have influenced the CR system in an ambiguous way when cation-leaching curves are compared. The Coso curve of Dorn (1983), for example, appears to have been influenced by the same factors (Smith, 1976; 1984) as a calibration curve. The calibrations used here. A small number of samples presented later, but not for the CR dating method where a greater density of radiometric dates in different regions are compared.

### III Methods of measuring varnish CRs

Different methods have been used to measure varnish CRs. The method referred to here as scraping involves scraping the varnish off the rock and cleaning it. These samples are then analysed to the limit of detection (usually 10<sup>-12</sup> g) by PIXE emission (PIXE) by the Air Cation Analysis Laboratory, University of California at Davis. The CRs of (Ca+K)/Ti are calculated from the ratios of (Ca+K)/Ti are calculated from the ratios of (Ca+K)/Ti. Scrapings have also been analysed by X-ray fluorescence, ICP and other methods. The method used to analyse the varnish CRs is PIXE. The advantage for establishing calibration curves is important when only small amounts of material are available. Pineda *et al.*, (1988) analysed varnish CRs to analyse varnish CRs.



This change occurs while new varnish is being deposited and during major climatic changes. That only minor slope breaks are present on most CLCs suggests that the CR system is largely buffered against climatic changes. This is due in part to the cumulative nature of the deposit. It may also be due in part to the micron-scale mechanics of cation exchange on clays, oxides and weathering of detrital minerals in the varnish.

3 *Third general assumption: rock varnishes that are compared for CRs must be from similar environments*

Table 2 presents microenvironmental factors that have caused a CR to deviate. If these contemporary environmental disparities are controlled, climatic changes offer two major challenges to this assumption. First, while it is possible to identify whether major episodes of past varnish erosion had taken place (see Figure 3C-D and Figure 4B), it is probably impossible to detect all microenvironmental influences that could have influenced varnishes in the past. Secondly, major climatic fluctuations must have affected CR processes. This effect, however, is ambiguous when cation-leaching curves (CLC) are examined. A major break in the Coso curve of Dorn (1983) at the Pleistocene-Holocene transition, for example, appears to have been exaggerated by using the Searles Lake highstand (Smith, 1976; 1984) as a calibration point, instead of the more local radiocarbon calibrations used here. A small break is still present in the new Coso Curve presented later, but not for the Cima-Mojave Desert curve (Dorn *et al.*, 1987a) where a greater density of radiocarbon calibrations are available. CLCs from different regions are compared in a later section.

### III Methods of measuring varnish CRs

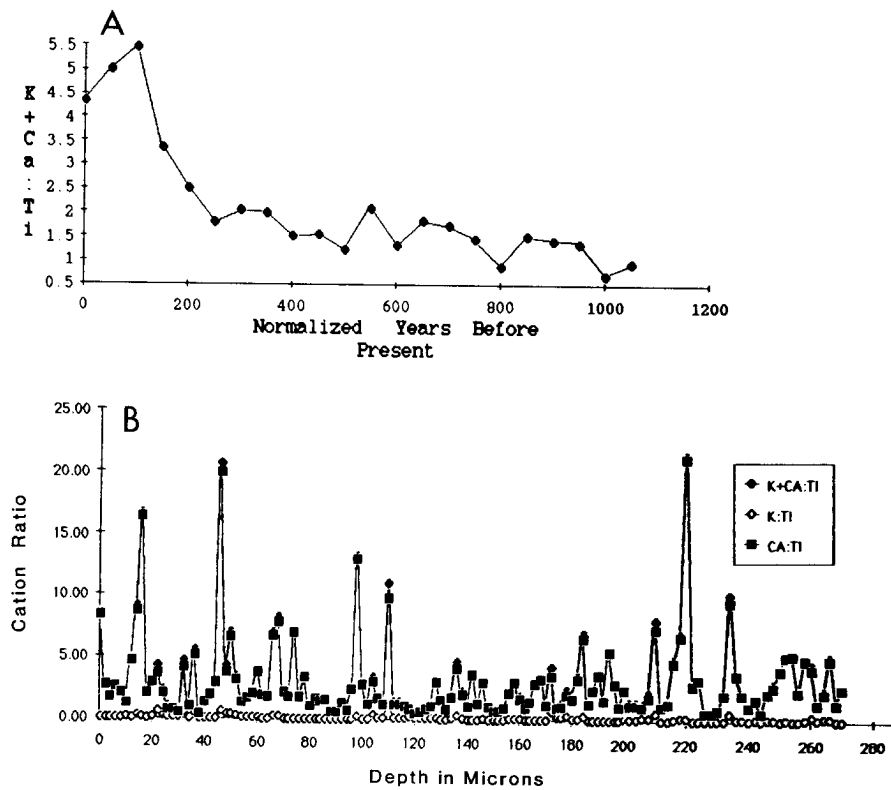
Different methods have been used to establish a varnish CR. I primarily use a method referred to here as scraping-PIXE, where the varnish is first mechanically scraped off the rock and cleaned to remove any material from the underlying rock. These samples are then analysed for the abundance of all elements above the limit of detection (usually over 15 elements) by proton-induced X-ray emission (PIXE) by the Air Quality Group at Crocker Nuclear Laboratory, University of California at Davis (Cahill, 1980; Cahill *et al.*, 1984). Elemental ratios of (Ca+K)/Ti are calculated for each PIXE measurement. Varnish scrapings have also been analysed by neutron activation, microprobe, EDAX, X-ray fluorescence, ICP and other means. The key to this approach is not in the method used to analyse the varnish, but that the varnish is removed from the rock. The capability of PIXE to analyse extremely small samples is not an advantage for establishing calibrations or working with landforms, but it is important when only small amounts of varnish are present on small archaeological samples. Pineda *et al.*, (1988) and Tanzhuo and Yuming (in press) also use PIXE to analyse varnish CRs.

**Table 2** Twenty-three microenvironmental factors that have been found to alter varnish CRs in the Coso Range, eastern California, as compared to CRs determined for varnishes on only constructional surfaces of the different lava flows. 374 PIXE measurements were made in the construction of this table.

Factor (number of flows in parentheses)	Effect on CR Average percent higher or lower (and range) in parentheses)	Comments
<b>On constructional flows – environments that lower CRs</b>		
Lichens (7)	-43% (-23 to -62%)	Avoid varnish near lichens completely. In stream environments, however, lichens are associated with an increase in cation ratios.
Microcolonial fungi (9)	-31% (-5 to -47%)	Avoid concentrations exceeding 5% on a surface or where microcolonial fungi erode into varnish.
Runoff and water collection (5)	-12% (+27%, -11 to -35%)	Water running over rock faces lowered the CR for all but one site. Ratios are also lowered for sites with large depressions that collect water.
Organic matter (3)	-11% (-9 to -13%)	Contact with abundant organic matter, such as leaf litter, tends to lower the CR.
Titanium anomaly (6)	-57% (-28 to -77%)	Local environments can contain abundant titanium detritus, that once incorporated into varnish lowers the CR significantly.
Northeast aspect (5)	-8% (-4 to -12%)	In semiarid environments, varnishes on N-NE aspects have slightly lower ratios than varnishes on the top of a boulder or S-SW facing. This is probably due to the cumulative effect of more mesic conditions promoting the development of fungi and cyanobacteria not detected in examinations of varnish cross-sections. In more arid sites, aspect had no significant effect on a CR.
Filamentous fungi (5)	-10% (-5 to -16%)	Where filamentous fungi have concentrations greater than 5% over a surface, CRs are lowered in deserts.
Acid pH (4)	-9% (-8 to -12%)	When varnishes have acidic pH values <6, CRs are lowered slightly.
Paleoerosion episodes (4)	-13% (-12 to -16%)	Where thin-section and SEM reveals past episodes of erosion from lichens, microcolonial fungi or cyanobacteria.
Ground-line band effect (3)	-8% (-5 to -12%)	At sites where dust collects in a depression creating a cumelic soil and a shiny ground-line band varnish.

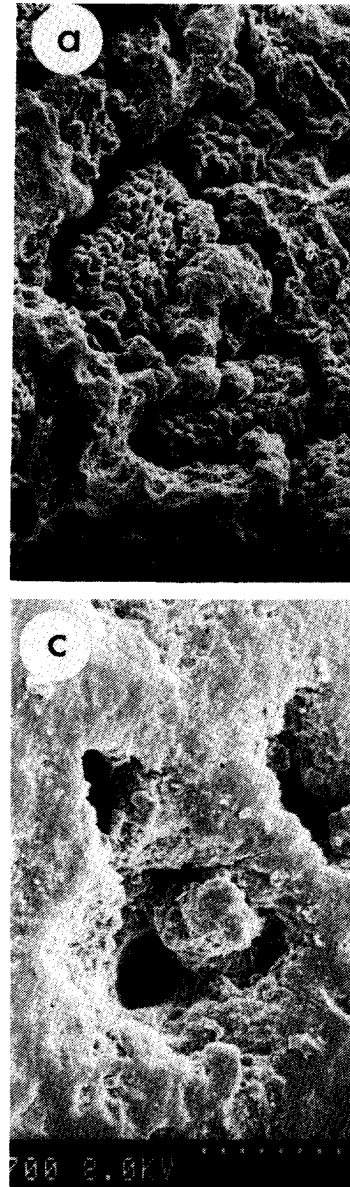
Factor (number of flows in parentheses)	Effect on CR Average percent or lower (and range in parentheses)
Cryptogamic soil (2)	-30% (-26, -35%)
Soil proximity (8)	+35% (4 to 71%)
Calcium anomaly (6)	+66% (30 to 126%)
Potassium anomaly (2)	+62% (32 to 93%)
Alkaline pH (3)	+5% (-3 to 8%)
Overhang (3)	+41 (11 to 89%)
Abundant botryoids (4)	+5% (0 to 12%)
Rough surface (2)	+10% (9 to 10%)
Spalls (8)	+29% (5 to 79%)
Talus (14)	+37% (8 to 172%)
Flaking (4)	+131% (29 to 255%)
Granular disintegration (5)	+39% (16 to 97%)
Massive forms (7)	+30% (9 to 51%)

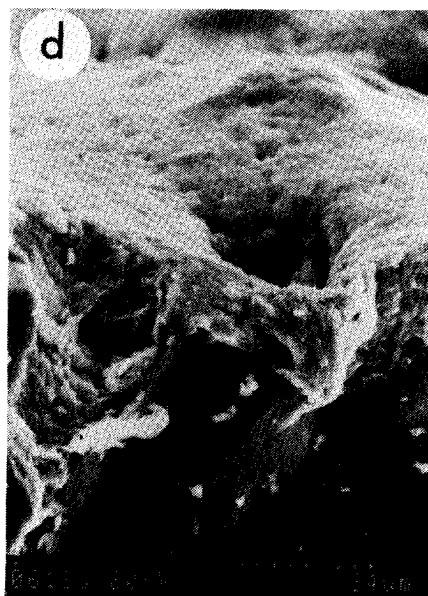
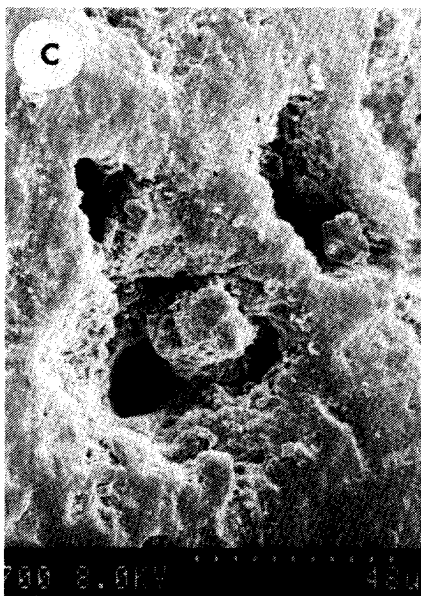
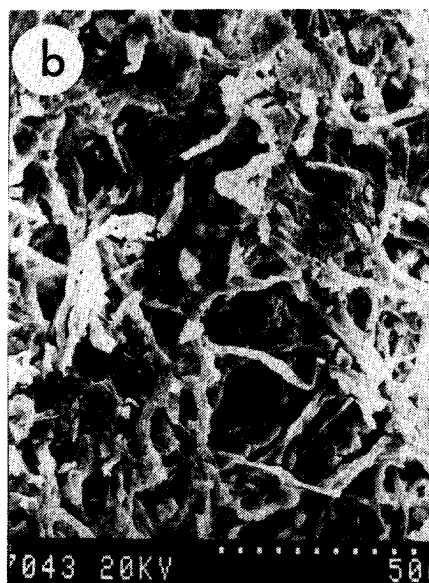
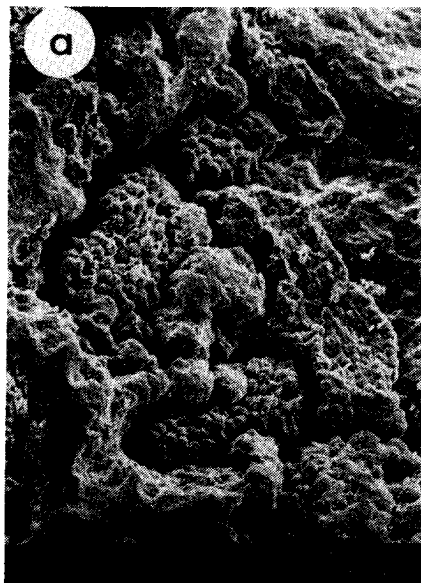
Factor (number of flows in parentheses)	Effect on CR Average percent higher or lower (and range) in parentheses	Comments
Cryptogamic soil (2)	-30% (-26, -35%)	Varnishes collected close to the soil surface, when the soil surface consists of cryptogamic algae, fungi, lichens, and mosses.
<b>On constructional flows – environments that increase CRs</b>		
Soil proximity (8)	+35% (4 to 71%)	Varnishes collected within a few centimetres of a soil surface, that is not cryptogamic.
Calcium anomaly (6)	+66% (30 to 126%)	Local environments can contain abundant calcium carbonate detritus, that once incorporated into varnish increases the CR significantly.
Potassium anomaly (2)	+62% (32 to 93%)	More rare than Ca or Ti anomalies, a few sites contain abundant K at concentrations, from K-feldspar at one site and an unidentified mineral phase at another site.
Alkaline pH (3)	+5% (-3 to 8%)	When varnishes have alkaline pH values, greater than 9, CRs are increased slightly.
Overhang (3)	+41 (11 to 89%)	Where varnishes are collected from the undersides of overhangs, on constructional lava flow features.
Abundant botryoids (4)	+5% (0 to 12%)	Where varnishes have an uncommonly great abundance of botryoids.
Rough surface (2)	+10% (9 to 10%)	From constructional flow features that are particularly irregular and rough.
<b>On flows that have experienced erosion</b>		
Spalls (8)	+29% (5 to 79%)	Where crevices are exposed to the subaerial environment after being previously varnished in a rock crack environment where dust collects.
Talus (14)	+37% (8 to 172%)	From varnish on talus adjacent to constructional flow features.
Flaking (4)	+131% (29 to 255%)	Where flows have appearance of being eroded by the process of cm-scale flaking, likely related to salt weathering.
Granular disintegration (5)	+39% (16 to 97%)	Where flows have the appearance of undergoing granular disintegration into mm-sized angular pieces (see Figure 9A).
Massive forms (7)	+30% (9 to 51%)	Where flow has been eroded less than 1/2m to massive, usually smoother structures (see Figure 9C).

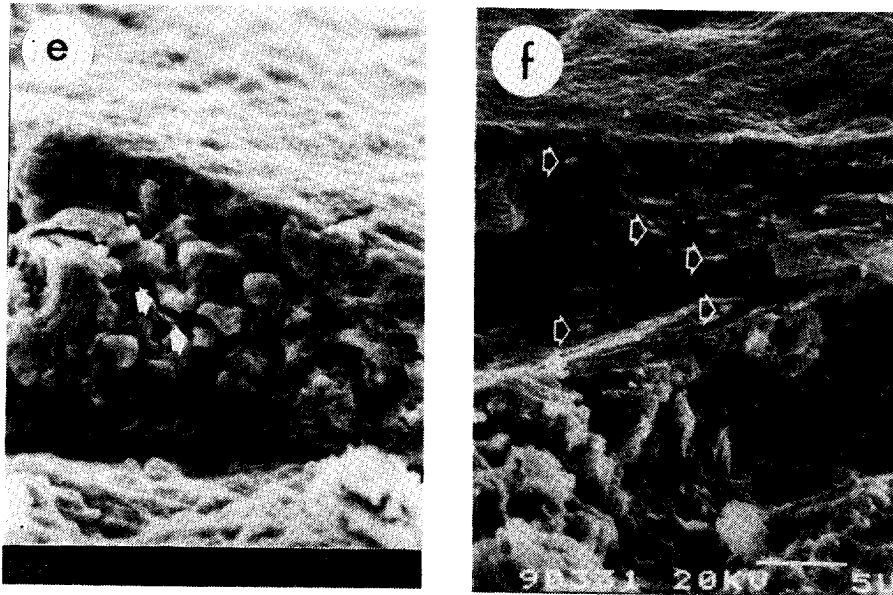


**Figure 2** Variations in varnish cation ratios with depth as measured by electron microprobe, in arid varnish from Coso Range volcanic 32 ( $1.07 \pm 0.12$  myr, Duffield *et al.*, 1980). A – Average of 17 microprobe transects for varnish from Coso 32. Depth variations have been normalized to the K-Ar age. The cation ratio appears to lower with increasing depth (age); B – A single microprobe profile from Coso 32, illustrating considerable variability.

For the scraping-PIXE method used here, manganese-rich black rock varnish is collected from the tops of the larger clasts at a site, preferably over a metre in diameter. Microenvironments listed in Table 2 are avoided. The samples are collected from a combination of different rock surfaces, typically 15 or more boulders. Ideally, a separate CR measurement would be made on each sample. However, this is not very cost efficient. A compromise is reached by placing samples into five groups, based on similarity of microsite variables. This poses problems mostly while searching for the cause of an anomalous CR, for example abundant Ti or Ca detritus (see Table 2).







**Figure 3** Examples of sources of anomalies in varnish cation ratios. A – Microcolonial fungi eroding and lowering CR of varnish on the oldest alluvial-fan unit at Silver Lake, Mojave Desert, California (see Wells *et al.*, 1987); B – Filamentous fungi lowering CRs on varnish on the Bishop Tuff, Owens Valley, California; C – Pits created by biogeochemical erosion of varnish collected from Crater Flat, southern Nevada. These bioerosion pits could have been made by microcolonial fungi or cyanobacteria; D – Paleoerosional pits from Death Valley, California. The pit on the left has been refilled, while the one on the right is more recent and has not been infilled. Note the irregular boundary between the rock and the varnish; E – Titanium-rich detritus (e.g., arrows) incorporated into varnish on the south basalt flow, Lathrop Wells, NV. Arrows identify angular pieces of what may be titanomagnetite detritus. Ti-rich detritus will lower CR anomalously; F – Ca-rich detritus (e.g., arrows) incorporated into varnish developed on a flake scar of an artifact, collected from the Mojave Desert, California. Ca-rich detritus made the CR anomalously high and the CR age too young. The artifact was on the surface an eroding alluvial fan next to calcrete rubble.

In the laboratory, samples are processed for CR determination. Random chips are taken from the varnish. If the sample is not processed for CR determination or where filamentous fungi, microcolonial fungi, or lichens exceed those concentrations listed in the literature (Wells, 1983; Danin and Garty, 1983) has been found. Samples are processed by the following methods:

- 1) Varnishes are scrubbed lightly with a tungsten carbide brush for five to 24 hours.
- 2) Varnishes from the five different sites are crushed at 45x magnification with a tungsten carbide brush, and nucleopore filters of 45, 15, 2 and 0.5 µm are used to separate from the varnish.
- 3) Contamination from the underlying rock is eliminated by chemistry by SEM-EDAX *in situ* analysis. Criteria for distinguishing varnish from rock is provided by chemical (Potter and Rossman, 1987) approach to assess contamination in the laboratory.
- 4) Scrapings of each of the five groups are made for each fixative.
- 5) Analysis for a varnish CR is by PIXE at the University of California at San Diego. This permits very precise determination of the CR.
- 6) At each site, the <2 µm fraction of the varnish is analysed by PIXE. If the CR of this fraction is anomalously high or low, the source of the anomaly. Some sites have extremely high levels of ambient contamination which may lead to or low, and a specific cause can be identified.

Dorn (1983: 58) also tried scanning electron microscopy for energy-dispersive analysis to examine varnish CRs. Glazovskiy (1988), and Whitney and Harrington (1988), and Whitney and Harrington (1988) use of SEM-EDAX in the measurement of CRs are generated when electrons pass through a sample used to measure the elemental composition. Accelerating voltage of the SEM is used to generate. Accelerating voltage is a change in chemistry apparent as a reduction in Mn or and increase in Ca.

Harrington and Whitney (1987) have shown that over scraping the varnish and analysis of the underlying rock cannot be re-examined after scraping. This is not on smooth-surfaced rocks and the underlying rock. The first criticism of this method is to examine *in situ* anomalies. However,

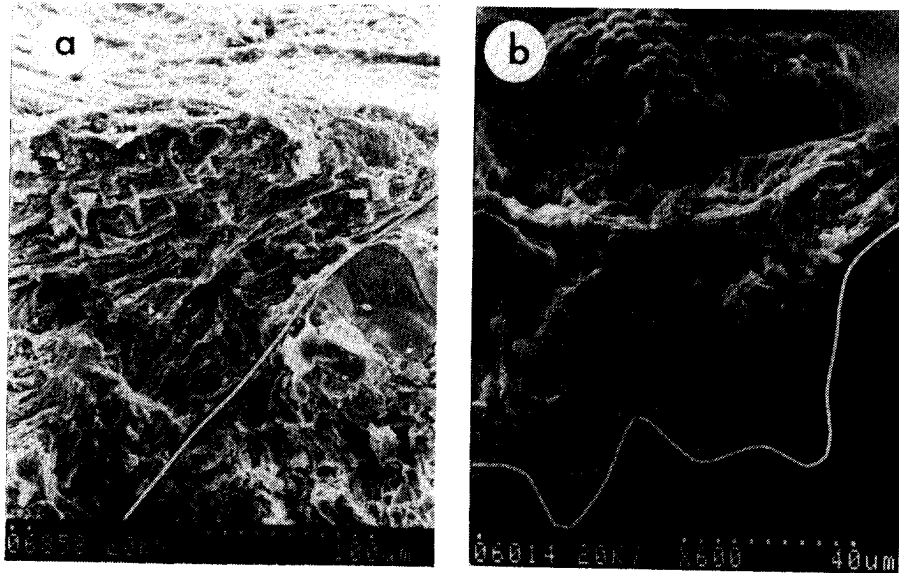
In the laboratory, samples are blown with compressed air to remove loose detritus. Random chips are taken for SEM and thin-section analysis. A sample is not processed for CR determination if any lichens or cyanobacteria are present, or where filamentous fungi, microcolonial fungi or bioetchpits (Figure 3A-D) exceed those concentrations listed in Table 2. The role of cyanobacteria and lichens in the weathering of varnish (Dragovich, 1986b) and rock (see Danin, 1983; Danin and Garty, 1983) has been recognized.

Samples are processed by the following procedure.

- 1) Varnishes are scrubbed lightly with deionized water to remove loose detritus and air dried for five to 24 hours.
- 2) Varnishes from the five different groups are scraped from the underlying rock under 10-45x magnification with a tungsten-carbide needle. The scrapings are passed through nucleopore filters of 45, 15, 2 and 0.2  $\mu\text{m}$ . This allows rock contaminants to be more easily separated from the varnish.
- 3) Contamination from the underlying rock is estimated for volume and by approximate chemistry by SEM-EDAX *in situ* examination of randomly selected scrapings (Figure 5). Criteria for distinguishing varnish from rock fragments is morphological (Dorn, 1986) and chemical (Potter and Rossman, 1977; 1979). Tanzhuo and Yuming (in press) use a similar approach to assess contamination in scrapings.
- 4) Scrapings of each of the five groups are mounted on Kapton film with a lead-free spray fixative.
- 5) Analysis for a varnish CR is by proton-induced X-ray emission (PIXE) by the Air Quality Group at the University of California at Davis (Cahill, 1980; Cahill *et al.*, 1984). PIXE permits very precise determination of elemental ratios with very small quantities of material.
- 6) At each site, the  $<2 \mu\text{m}$  fraction of the dust that has accumulated in natural dust traps is analysed by PIXE. If the CR of this dust is anomalous, the site is carefully examined for the source of the anomaly. Some sites in Death Valley, for example, cannot be dated by CR due to extremely high levels of ambient titanium.
- 7) A PIXE analysis of varnish is not to be used in computing a CR if it is anomalously high or low, and a specific cause can be found (see Table 2).

Dorn (1983: 58) also tried scanning electron microscopy (SEM) to generate X-rays for energy-dispersive analysis (EDAX) and electron-microprobe analysis to examine varnish CRs. Glazovskiy (1985) used SEM-EDAX on varnish on glacial deposits in the Pamirs, USSR. Harrington and Whitney (1987), Dethier *et al.*, (1988), and Whitney and Harrington (1988), however, most actively promote the use of SEM-EDAX in the measurement of CRs. The basic theory is that X-rays are generated when electrons penetrate the varnish. These X-rays are in turn used to measure the elemental CR of  $(\text{K}+\text{Ca})/\text{Ti}$  with automated EDAX. The accelerating voltage of the SEM is varied to control the depth at which X-rays are generated. Accelerating voltage is increased until the EDAX analysis reflects a change in chemistry apparently due to the underlying rock, for example a reduction in Mn or and increase in Mg.

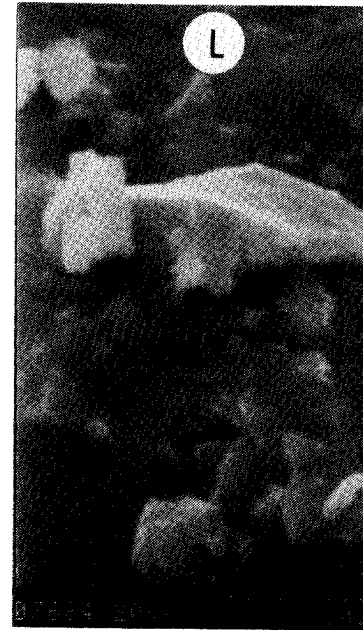
Harrington and Whitney (1987) assert several advantages of the SEM method over scraping the varnish and analysing it by PIXE: 1) the original varnish surface cannot be re-examined after scraping; 2) SEM can be used for varnishes that are not on smooth-surfaced rocks and; 3) there is less contamination from the underlying rock. The first criticism is true. Substitute samples must be studied to examine *in situ* anomalies. However, the scraping sample analysed by PIXE can



**Figure 4** Irregular subsurface of boundary of rock varnish. A – Relatively thick varnish on the northern basalt flow at Lathrop Wells, southern Nevada, USA. While the surface is smooth, the varnish-rock boundary is extremely irregular; B – Varnish on Warm Springs alluvial fan, Death Valley, California. The varnish appears smooth at the surface, but is irregular at depth. Note the two paleoerosional pits that have been infilled. Microcolonial fungi, now seen growing on the surface, could have caused them.

be analysed by SEM-EDAX to determine if the chemical anomaly is concentrated at discrete points or if it is averaged throughout the sample. Proxy samples must also be examined by SEM-EDAX as cross-sections are not from the areas analysed for CR dating. The other criticisms may be reversed. Increased SEM magnification of the surface of the varnish cannot address subsurface irregularities that can be considerable. These irregularities exist even though the surface of the varnish might be smooth (Figure 4). Further, by increasing SEM magnification, the volume of varnish analysed by SEM drops to unrepresentative levels.

I argue here that the SEM method has serious flaws that need to be evaluated. First, it is destructive of archaeological samples, requiring the mechanical removal of the rock underlying the varnish by coring or breaking a sample with a hammer. In contrast, scraping varnish from an archaeological feature does very little to affect its appearance (Whitley and Dorn, 1987; Nobbs and Dorn, 1988). Secondly, there is no evidence that the SEM method controls the level of contamination as claimed by Harrington and Whitney (1987). They did not present an independent test to determine if X-rays are generated from the underlying rock. Establishing a criteria on *assumed* differences in chemistry

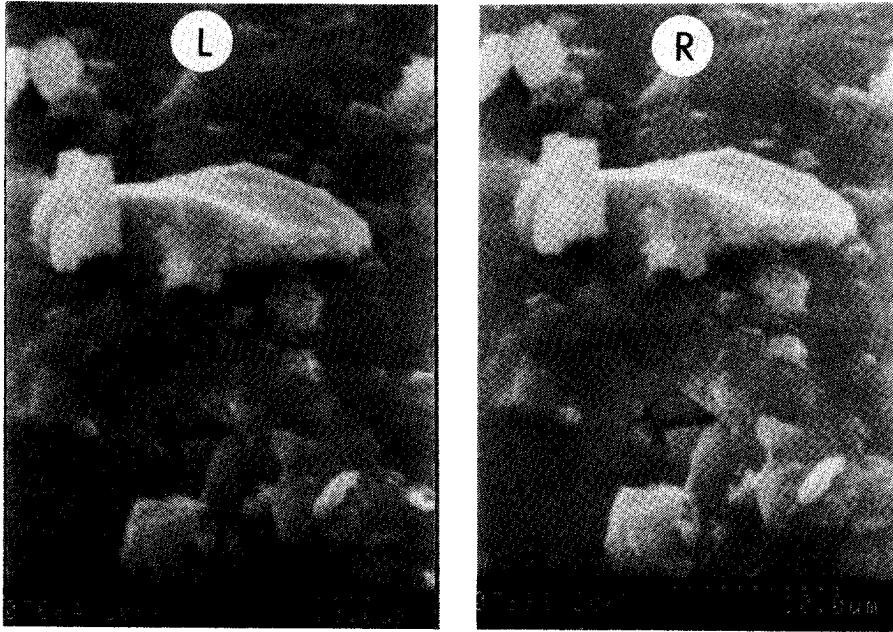


**Figure 5** SEM stereopair of desert varnish from Crater Flat, NV. The large piece of quartz is described in the text. It is quartz. The smaller pieces are varnish. By electron microscopy, volume and chemistry of the varnish can be determined independent tests.

between a varnish and the underlying rock, meeting the criteria, and concluding that it is an independent test. The scraping method and chemical contamination from the underlying rock. Thirdly, SEM-EDAX results can be compared with such as XRF, PIXE or neutron activation analysis. It has been analysed by other tests. The SEM method is biased towards the surface layer generated from the surface layer of the varnish. This bias results towards the surface of the varnish in roughly equal amounts (Whitley and Dorn, 1988). Energy-dispersive X-rays are generated from titanium when they are in the varnish. This is significant because any given sample is proportionally off by an unknown amount.

There is a difference in sample

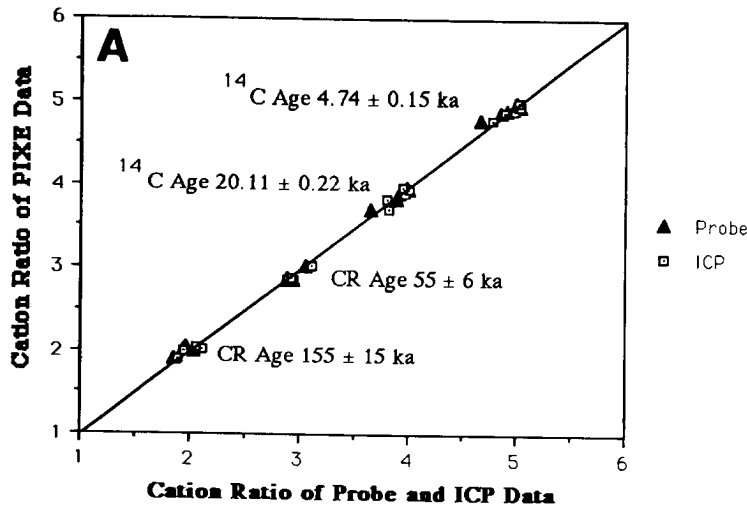




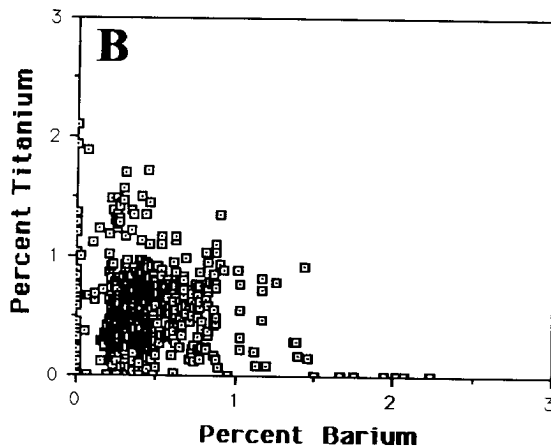
**Figure 5** SEM stereopair of detritus scraped from the rock underlying varnish from Crater Flat, NV. The large piece of detritus was not removed by the cleaning process described in the text. It is quartz, so it would offer no chemical contamination. The smaller pieces are varnish. By evaluating random scrapings with SEM-EDAX, the volume and chemistry of the contamination can be assessed quantitatively by independent tests.

between a varnish and the underlying rock (e.g., Mn or Mg concentrations), meeting the criteria, and concluding minimal contamination does not constitute an independent test. The scraping-PIXE method, in contrast, does assess volume and chemical contamination from the underlying rock by an independent test. Thirdly, SEM-EDAX results cannot be reproduced by other analytical methods such as XRF, PIXE or neutron activation. The same material analysed by PIXE has been analysed by other techniques (see Figure 6(a)). Fourthly, the SEM method is biased towards the surface layer of the varnish. More X-rays are generated from the surface layers of the varnish than from lower layers in the varnish. This bias results towards a net higher CR. Finally, Ba and Ti are present in varnish in roughly equal amounts (see Figure 6(b) and Bard, 1979; Dragovich, 1988). Energy-dispersive X-rays analysed with a SEM cannot separate barium from titanium when they are in similar concentrations at levels around 1%. This is significant because any given CR ratio determined by SEM is, therefore, proportionally off by an unknown amount of Ba.

There is a difference in sampling philosophy implicit in the approach of using



**Figure 6(a)** Comparisons of CRs from the same scrapings from four different sites in the Mojave Desert, California. These scrapings were analysed by PIXIE, ICP (inductively coupled plasma) and wavelength dispersive electron microprobe (probe) after sample homogenization with a flux of lithium metaborate. The regression is significant at  $p < 0.001$ .



**Figure 6(b)** Concentrations of barium and titanium (% weight) in PIXE analyses from the Coso Range, eastern California. This illustrates that barium and titanium are usually found together and typically at levels  $\leq 1\%$  similar to Bard (1979) and Dragovich (1988). Since the SEM-method cannot discriminate between Ba and Ti at these concentrations, the CR of the SEM method is proportionally distorted by the amount of Ba.

submillimetre measurements as analysis of varnish removed together relatively large volumes of rock (centimetres). Even with a large area, it is difficult to conduct hundreds to thousands of analyses. The best method is to avoid gross anomalies (Harden *et al.*, 1982). If a large enough area/volume is available to slip through the screening processes that reduce the cation ratios, the time and hour investments, it is not practical to use these methods to take this dual approach.

#### IV Local variations in varnish

This section presents the first results of microenvironmental variables on varnish in the field is perhaps the most important. The samples collected from sites that have been studied here were collected from microenvironments on K-Ar dated basalt in California (Duffield *et al.*, 1980). The first cation-leaching curve (Duffield *et al.*, 1980) were completely rejected as valid because they were not reconfirmed. They were reaffirmed.

Table 2 summarizes these results. The CRs were evaluated from 20 K-Ar dated sites. It was found that microenvironmental variables do not affect a cation ratio in a significant way. The CRs examined did not appear to affect the CRs in micromorphology; south- and north-facing slopes of a boulder; slope variations of a boulder; microtopography of a basalt flow; or as the Mn:Fe ratio was greater than 0.1, CRs do not change. CRs below 0.1, CRs do not change. CRs above 0.1, CRs are a stronger cementing agent. CRs influence the kinetics of CR change. CRs (0.3) black varnishes collected from the Coso Range (Harden *et al.*, 1982) paper.

Table 3 presents data used in this paper. The mean CRs are compared with the CRs from the squares regression.  $^{14}\text{C}$  dates of the mean CRs from these sites are compared with the regression. As Harden *et al.* (1982) paper.

submillimetre measurements as opposed to scraping the varnish. A bulk chemical analysis of varnish removed from the rock, for example by PIXE, averages together relatively large volumes of varnish collected over tens of square centimetres. Even with a large spot size, SEM or microprobe methods must conduct hundreds to thousands of measurements to analyse the same volume as a single bulk chemical analysis. Part of the philosophy behind the scraping-PIXE method is to avoid gross anomalies that are known to change a CR (see Table 2). If a large enough area/volume of varnish is analysed, the anomalies that are able to slip through the screening process might be an important part of the net processes that reduce the cation ratio over time. Due to machine costs and human hour investments, it is not practical for the SEM or other small-area analytical methods to take this dual approach.

#### IV Local variations in varnish cation ratios

This section presents the first quantitative assessments of the effects of microenvironmental variables on varnish CRs. The collection of varnish samples in the field is perhaps the most difficult part of CR dating. Varnishes must be collected from sites that have comparable CR leaching environments. The approach used here was to recollect and re-evaluate manganese-rich varnishes from microenvironments on K-Ar dated volcanics of the Coso Range, eastern California (Duffield *et al.*, 1980; Duffield and Bacon, 1981) used to construct the first cation-leaching curve (Dorn, 1983). In some cases, previously used flows were completely rejected as valid calibration sites. In other cases, the older results were reaffirmed.

Table 2 summarizes these results. Twenty-nine microenvironmental variables were evaluated from 20 K-Ar dated flows. Twenty-three of these variables were found affect a cation ratio in a statistically significant fashion. Six of the variables examined did not appear to affect a cation ratio significantly: minor differences in micromorphology; south- and west-facing aspects as compared with the top of a boulder; slope variations on a boulder (except where runoff occurs); microtopography of a basalt flow surface; and manganese concentration, as long as the Mn:Fe ratio was greater than about 0.3. When manganese concentrations drops below 0.1, CRs do not change with time in a regular manner. Manganese oxides are a stronger cementing agent than iron oxides, and their reduction influences the kinetics of CR changes over time. Only manganese-rich (Mn: Fe  $\geq$  0.3) black varnishes collected from subaerial environments are evaluated in this paper.

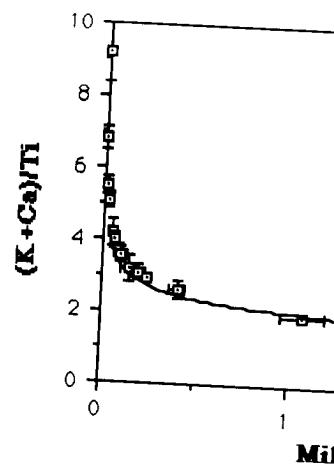
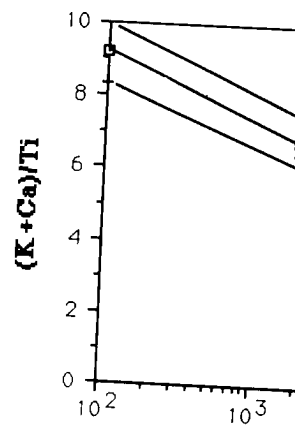
Table 3 presents data used in the new Coso curve (Figure 7). In Figure 7A mean CRs are compared with K-Ar ages of Coso lava flows in a semilog least-squares regression.  $^{14}\text{C}$  dates on varnishes in the Coso area are compared with the mean CRs from these same sites in a separate semilog least-squares regression. As Harden *et al.* (1988) note, the meaning of CR dates using a mixture

**Table 3** Calibration data for the Coso cation-leaching curve. AMS radiocarbon dates are uncorrected. K-Ar dates are from Duffield *et al.* (1980). Errors are 2 sigma. RD refers to rhyolite dome and BF to basalt flow.

Material	Method	Varnish CR	Numerical Age in ka
Initial Ratio	Historical	9.17 ± 0.44	0.1
Fan 3	<sup>14</sup> C	6.81 ± 0.32	1.975 ± 0.32 (Beta 18877;ETH 2416)
Fan 2	<sup>14</sup> C	5.50 ± 0.22	12.30 ± 0.62 (Beta 18250;ETH 2695)
Fan 1	<sup>14</sup> C	5.10 ± 0.22	18.53 ± 0.40 (Beta 17173;ETH 2411)
Red hill	<sup>14</sup> C	5.08 ± 0.18	19.38 ± 0.60 (Beta 17867;ETH 2482)
Coso 26 <sup>RD</sup>	K-Ar	4.19 ± 0.38	44 ± 22
Coso 17 <sup>RD</sup>	K-Ar	3.98 ± 0.22	57 ± 16
Coso 1 <sup>RD</sup>	K-Ar	3.69 ± 0.16	81 ± 8
Coso 6 <sup>RD</sup>	K-Ar	3.58 ± 0.22	101 ± 33
Coso 28 <sup>BF</sup>	K-Ar	3.19 ± 0.36	140 ± 89
Coso 34 <sup>BF</sup>	K-Ar	3.08 ± 0.22	188 ± 35
Coso 36 <sup>BF</sup>	K-Ar	2.91 ± 0.10	234 ± 22
Coso 30 <sup>BF</sup>	K-Ar	2.61 ± 0.26	399 ± 45
Coso 32 <sup>BF</sup>	K-Ar	1.95 ± 0.14	1070 ± 120
Coso 52 <sup>BF</sup>	K-Ar	1.31 ± 0.20	2510 ± 50
Coso 42 <sup>BF</sup>	K-Ar	1.21 ± 0.20	3670 ± 160

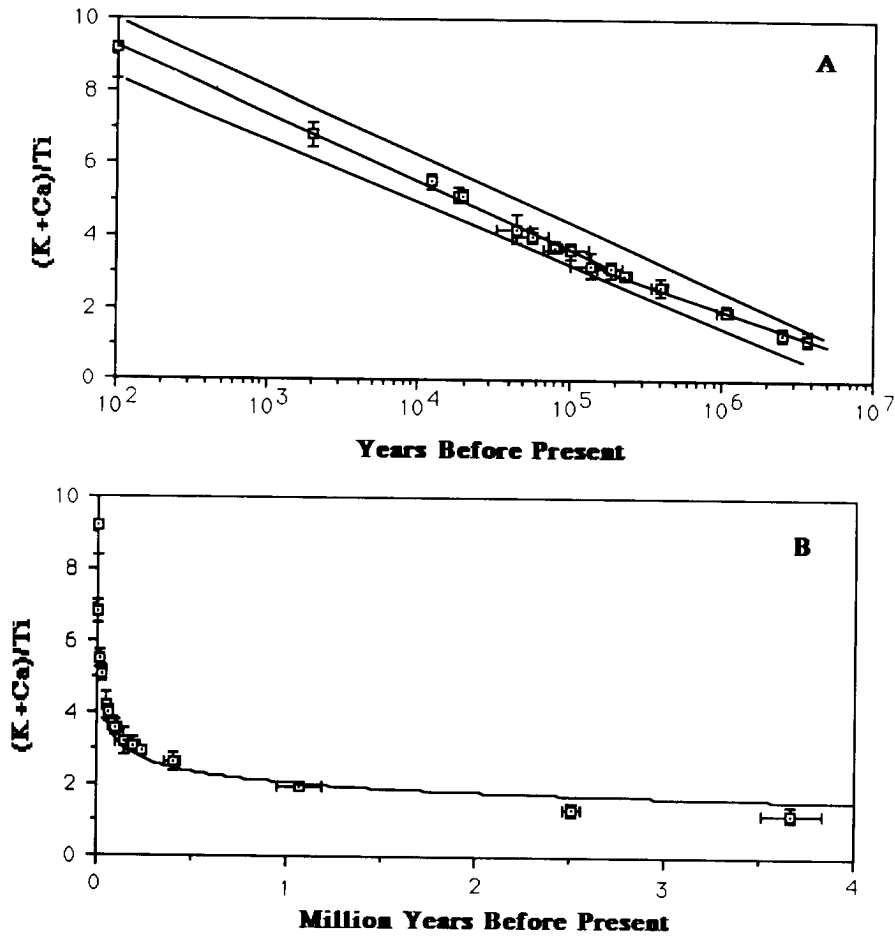
of different dating methods for calibration would be unclear. However, since the least-squares regression for the <sup>14</sup>C and the K-Ar time scale rest on the same line, they are combined. CRs compared with the Coso CLC in the radiocarbon range (≤20 ka) reflect radiocarbon calibrations. CRs compared with the Coso curve in the K-Ar range (≥44 ka) reflect K-Ar calibrations. CRs compared with the Coso curve from 20 to 44 ka are hybrids. Of note, Coso 26 has a K-Ar date of 44 ± 22 ka (Duffield *et al.*, 1980); the varnish radiocarbon age on this same dome is similar 42.9+3.9/- 2.6 ka (Dorn *et al.*, 1987b). Higher correlation coefficients are found when the curve is broken in the K-Ar range at 140 ka and in the radiocarbon range about 13 ka. The equation for the central curve in Figure 7A is:

$$CR = \begin{cases} 12.67 - 1.76 \log_{10}(\text{age}) & \text{where age is } \leq 13 \text{ ka} \\ 14.36 - 2.17 \log_{10}(\text{age}) & \text{where age is } \geq 13 \text{ ka } \leq 140 \text{ ka} \\ 10.80 - 1.47 \log_{10}(\text{age}) & \text{where age is } \leq 140 \text{ ka} \end{cases} \quad (1)$$



**Figure 7** Cation-leaching curves. A - Semilog plot. B - Linear plot. Error bars are displayed. A - Semilog plot is described in the text. Error bars are displayed by using the ± 2 sigma errors of the data set in Table 3, as discussed in the text. B is a power function discussed in the text.

Uncertainties in the x and y variables are included in the empirical relationship. When the data points are compared in one least-squares regression, the upper error curve in Figure 7A is produced for all varnish CRs and calibrations. Figure 7B illustrates the relationship described by a power function.



**Figure 7** Cation-leaching curve for the Coso Range, based on Table 3. 2 sigma errors are displayed. A - Semilog plot of the Coso data. The central regression curve is described in the text. Error curves illustrated are least-squares regressions derived by using the  $\pm 2$  sigma errors of varnish CRs and age uncertainties for the entire data set in Table 3, as discussed in the text; in B - Linear plot of the Coso data; the curve is a power function discussed in the text.

Uncertainties in the x and y variables are treated empirically, since a CLC is an empirical relationship. When +2 standard errors for all varnish CRs in Table 3 are compared in one least-squared regression with +2 standard errors calibration dates, the upper error curve in Figure 7A is generated. When -2 standard errors for all varnish CRs and calibration ages are used, the lower error curve is produced. Figure 7B illustrates a linear plotting of the data; the relationship is described by a power function of  $CR = 32.2 * Age^{-0.20}$ . This illustrates that only

a very small change in Coso CRs after about 200 000 to 300 000 years results in a very large jump in age.

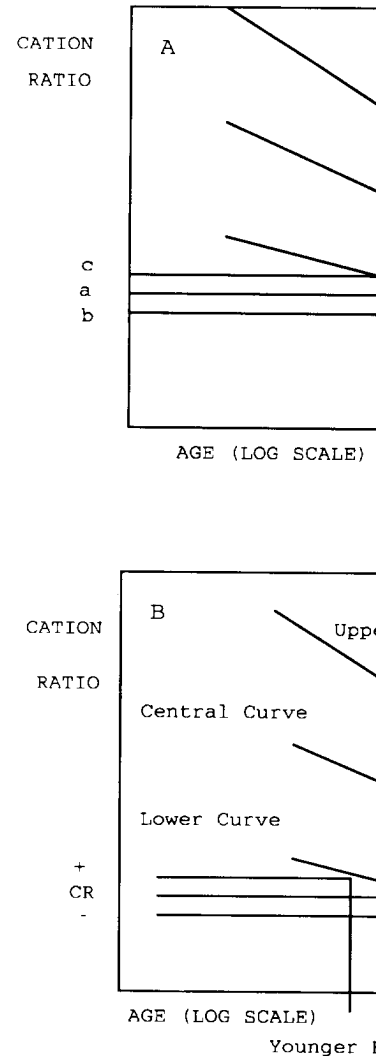
A CR age is assigned by one of two methods. If several PIXE measurements have been made for different varnish samples, mean CRs are compared with the central curve, as illustrated in Figure 8A. The average and standard error of these mean dates yield an estimate of the central tendency. Alternatively, the  $\pm$  error associated with a single sample is compared with the error curves, as in Figure 8B. The first method deals only with central tendencies and it requires multiple measurements. The second method requires only one analysis and is a more conservative approach, incorporating all errors. Both are valid approaches in that they provide the reader with a different perspective on CR variability. Ideally, it would be best to derive several different averages for CRs for multiple samples from a site, and then use the central tendency approach in Figure 8A, as in Dorn *et al.* (1987b; 1988a), Dorn (1988), and Nobbs and Dorn (1988).

## V Importance of surface degradation

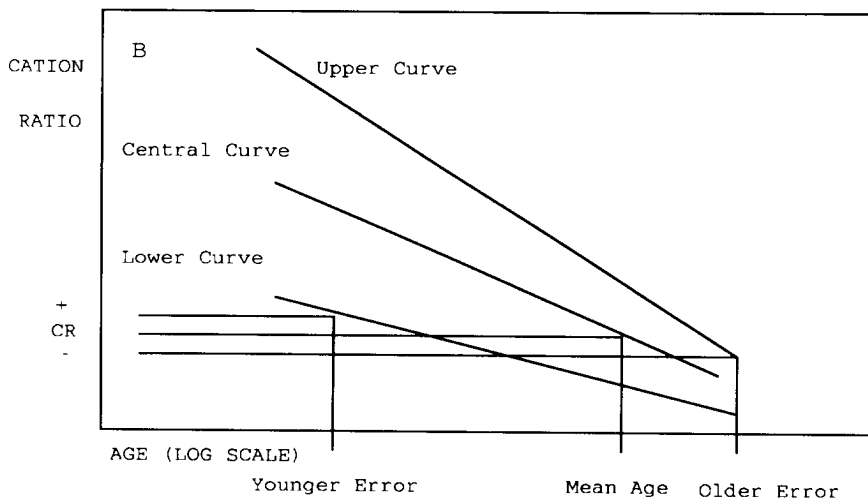
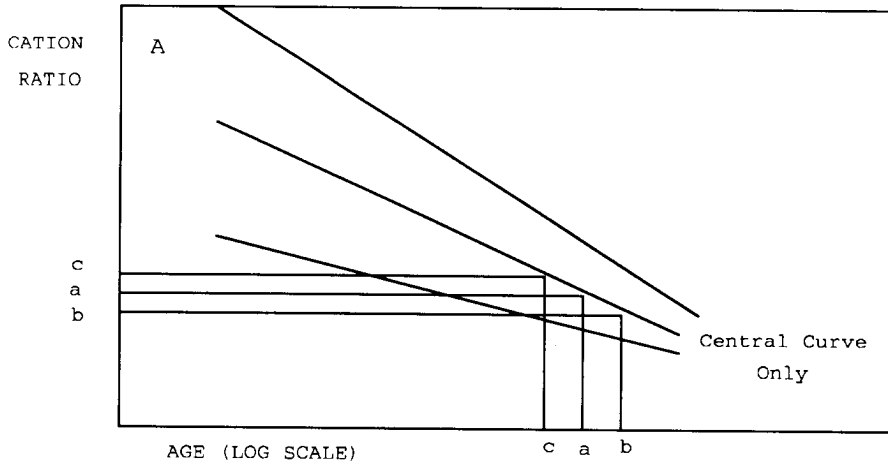
Degradation of a rock surface over time is a critical issue in all SED methods, but particularly for dating rock varnish. The constructional surfaces of lava flows are used to calibrate cation-leaching curves. Preservation of constructional rock surfaces and their rate of erosion have not been topics of substantial concern to geomorphologists and geochemists who study weathering (e.g., Colman and Dethier, 1986; Whalley and McGreevy, 1988). However, it is the unweathered surfaces of rocks that can be used to date landforms. If the outer surface of a rock surface on a landform has weathered, the SED method would only record when the weathering took place. The nature of surface degradation is examined here for the first time by studying the timing of surface degradation on lava flows, and glacial and alluvial-fan deposits.

### 1 Degradation of lava flows in Hawaii

Lava flows start to erode soon after they solidify. Historical basalt flows on Hawaii lose their initial glassy, friable surface after only a few years to decades. After this initial loss, constructional forms in the rainshadow parts of Hawaii and Maui can remain intact for tens of thousands of years.  $^3\text{He}$  (Kurz, 1986a; 1986b; Kurz *et al.*, 1987) and varnish  $^{14}\text{C}$  (Dorn *et al.*, 1989) SED dates closely match conventional radiocarbon dates for the lava flows. Once in a rainforest environment, however, the constructional topography degrades much more rapidly yielding varnish  $^{14}\text{C}$  dates that are much younger than the  $^{14}\text{C}$  age of subflow charcoal.



**Figure 8** Different approaches to age estimates. A - The central tendency approach using multiple measurements (e.g. a, b, c) and calibrated ages. The result is an average age-estimate; B - The conservative approach using a single measurement and lower error curves. The higher (younger) CR error curve is used only when a single CR measurement is available; the lower (older) CR error curve is used when the full range of variability is available.



**Figure 8** Different approaches to using a cation-leaching curve to assign calibrated age estimates. A - *The central tendency approach* uses only the mean CR of several different measurements (e.g. a,b,c) and the central curve to derive three separate calibrated ages. The result is an average (and standard error) of the central-tendency age-estimates; B - *The conservative approach* uses both the  $\pm$  of the CR and the upper and lower error curves. The higher (younger) CR error is compared to the lower curve. The lower (older) CR error is compared to the upper curve. This approach is used only when a single CR measurement or set of measurements is available, or when the full range of variability is to be expressed.

## 2 *Degradation of lava flows in the Coso volcanic field*

Lava flows in southwestern North America can maintain constructional surfaces for over a million years (see Figure 9C and Figure 9D), but not without considerable loss of the original surface (Figure 9A). This is not a contradiction. Remnants of constructional topography remain even while much of the surface weathers. This is supported by Phillips *et al.*, (1986), Leavy *et al.* (1987), Kurz *et al.* (1987) and Cerling (in press) who show a good concordance between  $^{14}\text{C}$  and K-Ar dates on lava flows and the buildup of  $^{36}\text{Cl}$  and  $^3\text{He}$  isotopes on constructional surfaces.

As understanding of how constructional surfaces degrade is important to the application of all SED methods. CRs were measured for varnishes on spalls, talus, surfaces undergoing centimetre-scale flaking, surfaces undergoing millimetre scale granular disintegration and erosion to massive joint surfaces. Twenty K-Ar dated lava flows of the Coso Range, California were evaluated (see Table 2). The differences between the K-Ar ages and the CR ages average 47%, 54%, 78%, 69%, and 46% for these different styles of lava flow degradation (see Table 2). I could detect no systematic trends for these five different styles of erosion on 20 different flows of the Coso Range. It is possible, however, that with additional sampling a climatic influence on this erosion might be detected. The nature of the surface weathering of basalt flows in the Coso Range can be summarized as slow and spatially uneven.

Basalt flows in the Coso Range appear to be more stable than rhyolite domes. Domes 4, 15, 25 and 27 (see Duffield and Bacon, 1981) were dropped from the calibration due to uncertainties as to whether a constructional flow surface was sampled. Fink and Manley (1987) argue that rhyolite domes start out with a surface of finely vesicular pumice. Still, varnishes were sampled from what may be constructional rhyolite flow features from the tops of Coso 1 (see Figure 9B), 6, 17, and 26. To assess the degree of erosion, these domes were first dropped from the CLC in Figure 7, and the CLC (minus these domes) was used to assign ages to the varnishes on these domes. Using the method in Figure 8A with 5 separate PIXE measurements on each flow, the CR ages with 2 sigma errors are  $93 \pm 22$  ka (Coso 6),  $83 \pm 13$  ka (Coso 1),  $60 \pm 14$  ka (Coso 17), and  $49 \pm 10$  ka (Coso 26). These are similar to their K-Ar ages (listed in Table 3). The combination of field observations indicating the presence of flow features and these CR measurements led to the inclusion of these domes in the new Coso CLC (see Figure 7 and Table 3).

## 3 *Degradation of lava flows in the Cima volcanic field*

The basalt flows of the Cima volcanic field, Mojave Desert, California have a different style of degradation. Wells *et al.* (1985) present a model where the surfaces of lava flows less than a million years old maintain constructional forms as topographic highs. These are buried in a mantle of loess that floats a desert

pavement of basalt fragments sampled from basalt clasts making CR dating results support the pavement about 10–25% younger than the model by Wells *et al.* (1985), or is no way of explaining the relatively thin 'floating' mantle

## 4 *Degradation of clasts on glacial*

The degradation of individual rhyolite objects is to date glacial events, morphology of erosional and depositional object is to date glacial events, a rock surface with glacial polish in a site. Conversely, if the object compared to CR dates on various currently available on the issue of constructional boulder surfaces on glacial moraines and alluvial fans

Rock varnish CR and  $^{14}\text{C}$  dates on glacial till at Pine Creek, Sierra Nevada boulders sampled were those with CR ages are significantly younger. central tendency of 143 ka to 156 ka to have a constructional surface ka to <1 ka on 13 boulders at various a younger age are grussification and centimetre-scale sheeting pebbles

Alluvial-fan material in Death Valley towards decay. For example, varnishes dated to be circa 23 ka (Dorn, 1987) uneroded quartzite boulders to 100% disintegration into grus. Alluvial fans indicated by a smooth, rounded surface. Their abundance decreases in alluvial fans probably because of the dominance of Death Valley (Goudie and Day, 1987)

The discrimination between constructional and fluvial surfaces is a subjective field judgement at present a rounding of a fluvial cobble is always obvious. Issues of rates of degradation in different environments will become



pavement of basalt fragments (McFadden *et al.*, 1986; 1987). Varnishes were sampled from basalt clasts making up desert pavements on the loess mantles. The CR dating results support the proposed models. Most of the CR ages are only about 10–25% younger than the K-Ar dates of the basalt flows they mantle. There is no way of explaining the relative antiquity of these pavements other than the model by Wells *et al.* (1985), of a gradual accretion of aeolian loess beneath a relatively thin 'floating' mantle of basalt fragments.

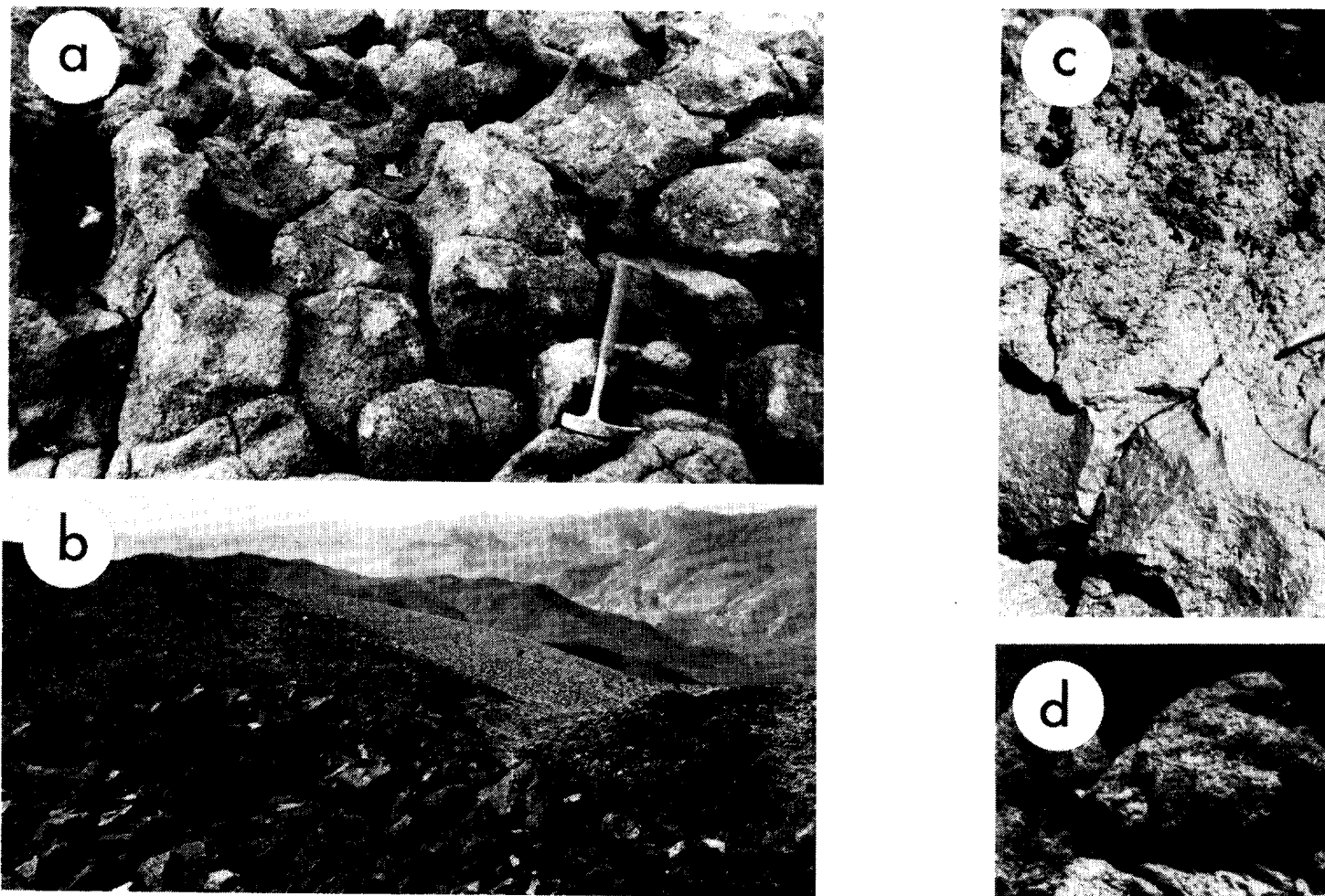
#### 4 Degradation of clasts on glacial moraines and alluvial fans

The degradation of individual rocks associated with the constructional topography of erosional and depositional landforms is also poorly understood. If the object is to date glacial events, for example, there would be little question that a rock surface with glacial polish would be appropriate for SED of deglaciation in a site. Conversely, if the object is to study weathering, a control date can be compared to CR dates on various erosional features. No age determinations are currently available on the issue of rock surface degradation. The erosion of constructional boulder surfaces on two very different depositional landforms, glacial moraines and alluvial fans, are evaluated here.

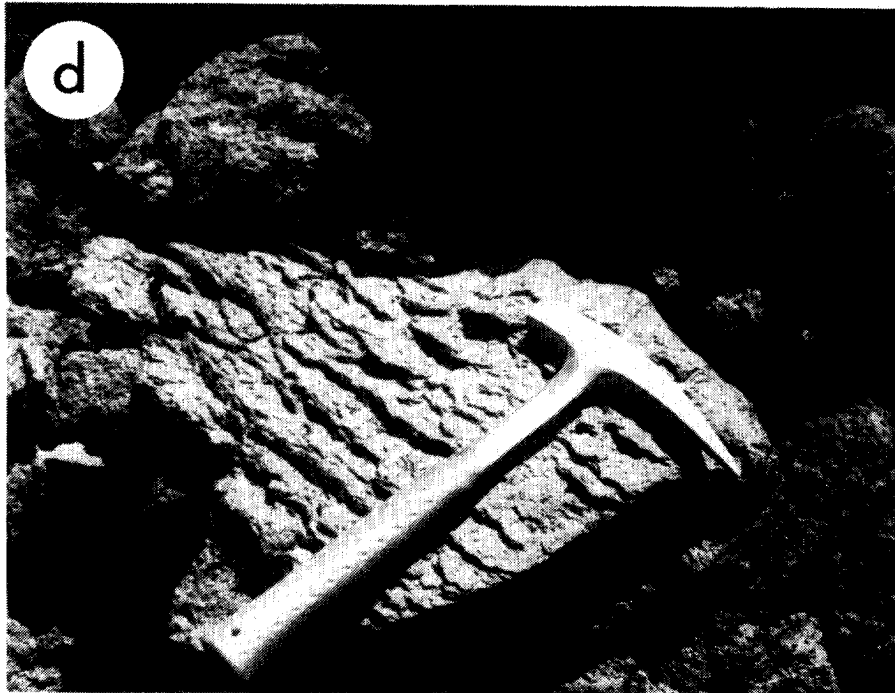
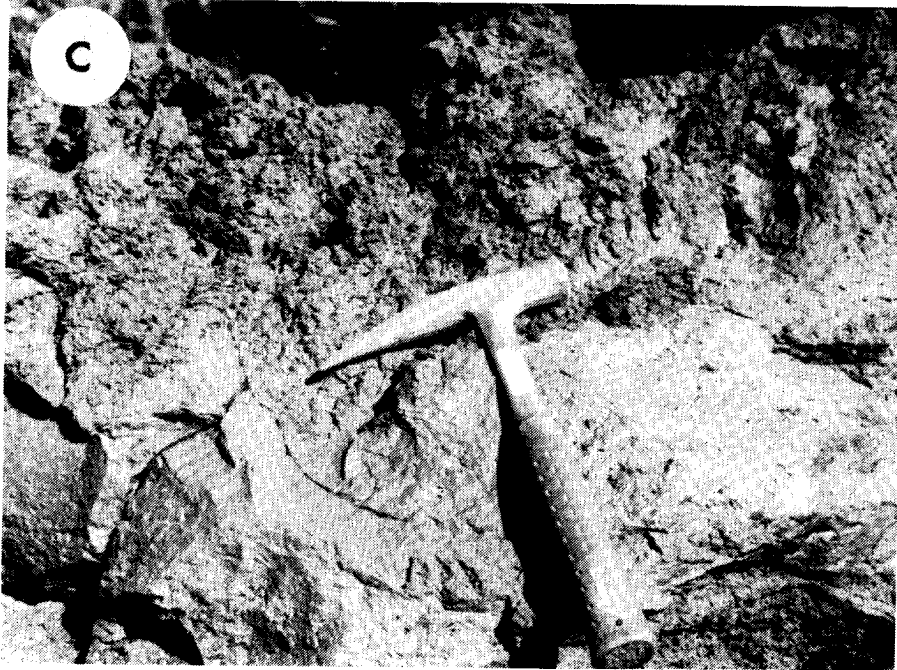
Rock varnish CR and  $^{14}\text{C}$  dating have been used to assign minimum ages to glacial till at Pine Creek, Sierra Nevada, California (Dorn *et al.*, 1987b). The boulders sampled were those with a constructional surface (Figure 10A). Where boulders have experienced postdepositional erosion (Figure 10B), however, CR ages are significantly younger. For example, the Tahoe-age moraines, with a central tendency of 143 ka to 156 ka (Dorn *et al.*, 1987b) for boulders interpreted to have a constructional surface (Figure 10A), have a range of CR ages from 110 ka to <1 ka on 13 boulders at various stages of degradation. Common causes of a younger age are grussification, splitting of large boulders along joint planes, and centimetre-scale sheeting perhaps due in part to brush fires.

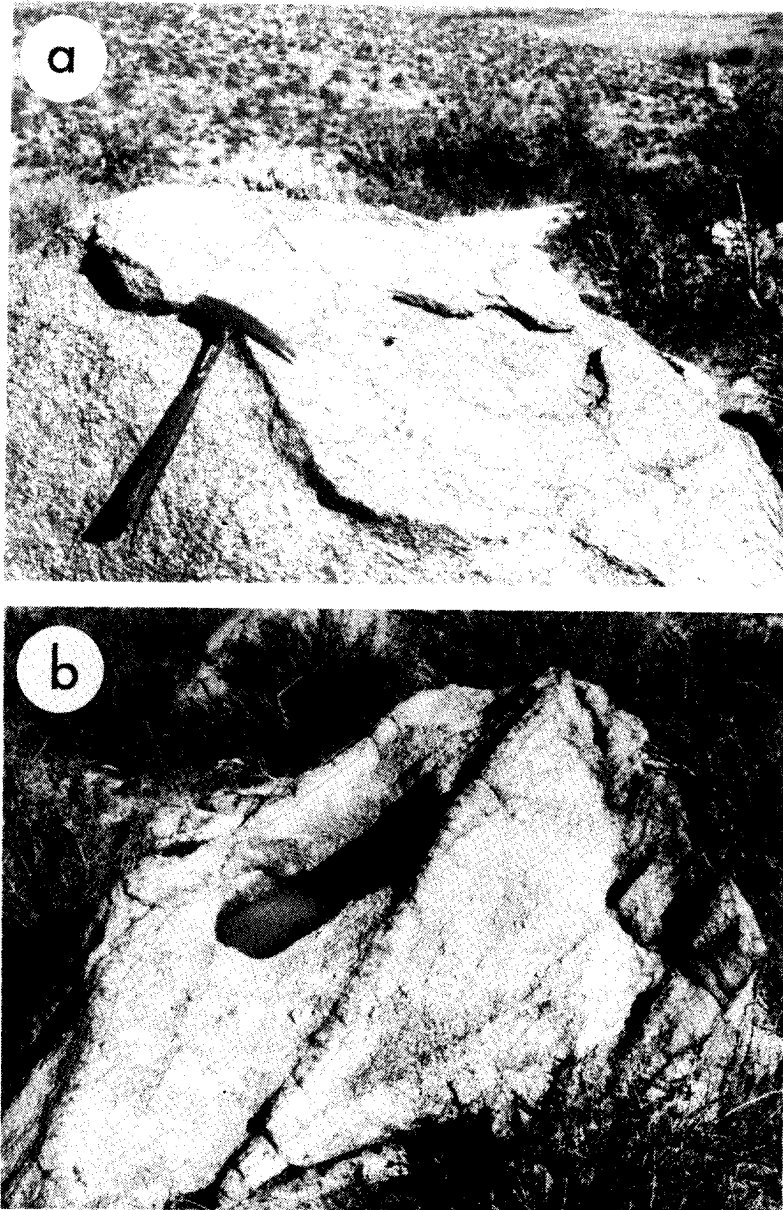
Alluvial-fan material in Death Valley, California shows a similar tendency towards decay. For example, varnish on 18 boulders on the part of a fan unit  $^{14}\text{C}$  dated to be circa 23 ka (Dorn, 1988) yields CR ages ranging from 23 ka on uneroded quartzite boulders to <1 ka on granitic boulders undergoing granular disintegration into grus. Alluvial-fan boulders with constructional surfaces are indicated by a smooth, rounded form without evidence of surface weathering. Their abundance decreases in a negative exponential relationship with time, probably because of the dominance of salt weathering in an environment like Death Valley (Goudie and Day, 1980; Butler and Mount, 1986).

The discrimination between a constructional and an erosional feature is a subjective field judgement at present (see Figures 9 and 10). Tell-tale signs like a rounding of a fluvial cobble or polish for a glacial erosional feature are not always obvious. Issues of rates of weathering for different lithologies and in different environments will become an increasingly serious concern as surface-



**Figure 9** Appearances of lava flows. A - Heavily degraded plot of Coso 30 ( $399 \pm 45$  ka, Duffield *et al.*, 1980) eroded by granular disintegration. The CR on the varnish here is  $3.03 \pm 0.17$  (Ave  $\pm 1$  S.E. of 3 PIXE measurements); with a calibrated age 50% younger than varnish on the constructional surface of the flow; B - Well-varnished flow on Coso rhyolite dome 1 ( $81 \pm 8$  ka, Duffield *et al.*, 1980). If all rhyolite domes are removed from the calibration in Table 3 and Figure 7, the CR of  $3.69 \pm 0.08$  (Ave  $\pm 1$  S.E. of 5 PIXE measurements) yields a CR age of  $83 \pm 13$  ka. While rhyolite domes do erode more rapidly than basalt, the flow structures sampled on Coso 1 are felt to be close to constructive. C - Surface of Coso 42 ( $3.67 \pm 0.16$  myr, Duffield *et al.*, 1980). The part of the flow above the hammer is felt to be constructional surface, with a CR of  $1.21 \pm 0.10$  (Ave  $\pm 1$  S.E. of 5 PIXE measurements) and used in Table 3. The flow below the hammer is not a constructional surface. It is classified here as a more massive subsurface joint. With a CR of  $1.83 \pm 0.23$  (Ave  $\pm 1$  S.E. of 3 PIXE measurements), its CR is 63% higher with a mean age of about 1-1/3 myr; D - Constructional surface of basalt flow No. 29, Cima volcanic field, Mojave Desert ( $990 \pm 70$  ka, Turrin *et al.*, 1985).





**Figure 10** Differential preservation of till boulders, south Tahoe moraine at Pine Creek, Sierra Nevada Mountains, California. (see Dorn *et al.*, 1987b). A – Boulder with partial preservation of the original surface; B – Boulder where the original surface has eroded away completely.

exposure dating techniques are under research.

## VI Comparison of cation-leach

Prior to this study, there were no data of a quantitative biogeochemical process quantitatively how different microorganisms has ascertained how certain biological processes in the Sierra Nevada Range, California. Similar quantitative data was our primary goal. The second obstacle was our poor understanding of cation-ratio changes in varnish. We collected multiple samples from different locations using the ion probe, high-resolution scanning electron microscope. Our understanding of specific controls on cation-ratio changes is due in part to the few number of samples.

Nine CLCs have been constructed (see Figures 11 and 12) and analyzed. Two have been built using the SEM. The first CLC curve is from arid South America (Dorn, 1988); the rest are from southwestern California. They are roughly similar in that CR changes with time in a semilog relationship.

The lack of a substantial Holocene boundary indicates that varnish is not a result of climatic changes, because new varnish is gradually leached relative to Tertiary varnish. This is prominent in the Mojave and Colorado Plateau. Valley and Lunar Crater curves are similar to accessible cation-exchange sites. The lack of a substantial release of mobile cations from *in situ* varnish may be related to the amount of water available. In the southeast Colorado, Texas Panhandle, precipitation is  $\geq 30\%$  of the current precipitation. Precipitation undoubtedly changed during interglacials, but the issue of sea level change is not assessed (Spaulding and Graumlich, 1988).

It is clear from the variety of varnish types that cannot be used to date varnish. The data is not substantially from drainage to the west. However, the Texas Panhandle and Colorado, hundreds of kilometers

exposure dating techniques are used more in geomorphic and archaeological research.

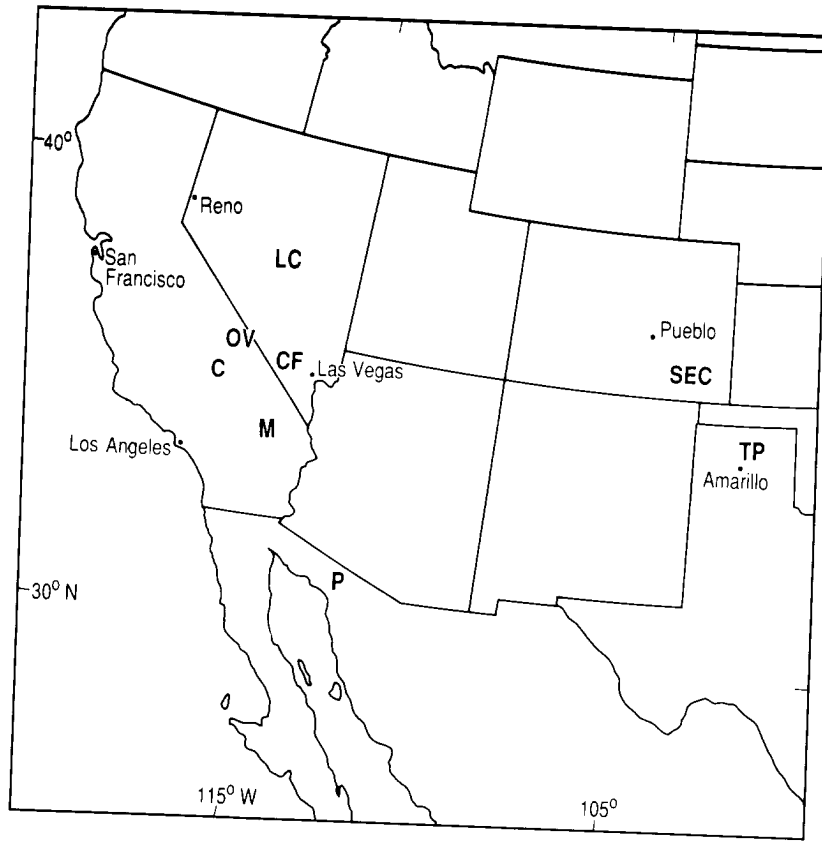
## VI Comparison of cation-leaching curves

Prior to this study, there were three general obstacles to the further development of a quantitative biogeochemical model of CR dating. The first was establishing quantitatively how different microenvironments affect a varnish CR. This study has ascertained how certain biogeochemical conditions affect CRs in the Coso Range, California. Similar quantitative tests need to be carried out in other areas. The second obstacle was our poor understanding of the micron-scale mechanics of cation-ratio changes in varnishes. This remains and will require the analysis of multiple samples from different environments of varnish growth with tools like the ion probe, high-resolution transmission electron microscopy and high-resolution scanning electron microscopy. The third obstacle was an inadequate understanding of specific controls on the shape of a cation-leaching curve. This is due in part to the few number of curves that have been established.

Nine CLCs have been constructed by the scraping-PIXE method for this study (see Figures 11 and 12) and another by Tanzhuo and Yuming (in press). Two have been built using the SEM method (Harrington and Whitney, 1987). The Oulnina curve is from arid South Australia (Dorn *et al.*, 1988a; Nobbs and Dorn, 1988); the rest are from southwestern North America (Figure 12). They are all roughly similar in that CR change over time is best approximated by a negative semilog relationship.

The lack of a substantial change in slope about 10 ka at the Pleistocene-Holocene boundary indicates that all these CLCs are largely buffered against climatic changes, because new varnish is constantly accumulating as K and Ca are gradually leached relative to Ti. The slope change about 130–40 ka is most prominent in the Mojave and Coso curves, and least prominent in the Owens Valley and Lunar Crater curves. It may be from exchange taking place at less accessible cation-exchange sites on older varnishes, and perhaps due to the slow release of mobile cations from *in situ* weathering of detrital minerals. Slope may be related to the amount of warm season precipitation. Curves from Oulnina, southeast Colorado, Texas Panhandle, Pinacate and Mojave are in areas where  $\geq 30\%$  of the current precipitation occurs during the summer. This relationship undoubtedly changed during glacial periods and perhaps during previous interglacials, but the issue of seasonality in prehistoric precipitation is difficult to assess (Spaulding and Graumlich, 1986; Van Devender *et al.*, 1987).

It is clear from the variety of curves in Figure 12 that a CLC from one area cannot be used to date varnishes in a different region. Curves can differ substantially from drainage to drainage in the western Basin and Range. However, the Texas Panhandle does have a very similar CLC to southeast Colorado, hundreds of kilometres away. A major objective of modeling CLCs is

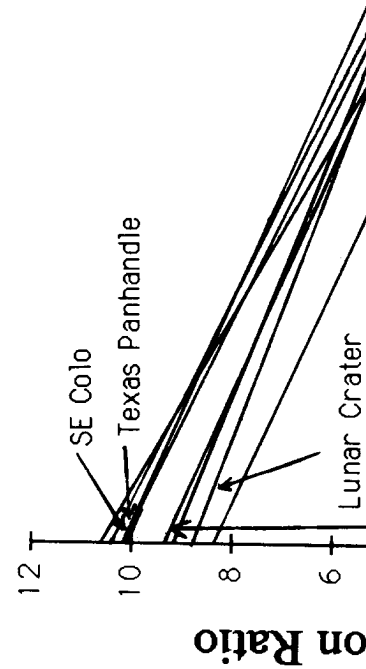


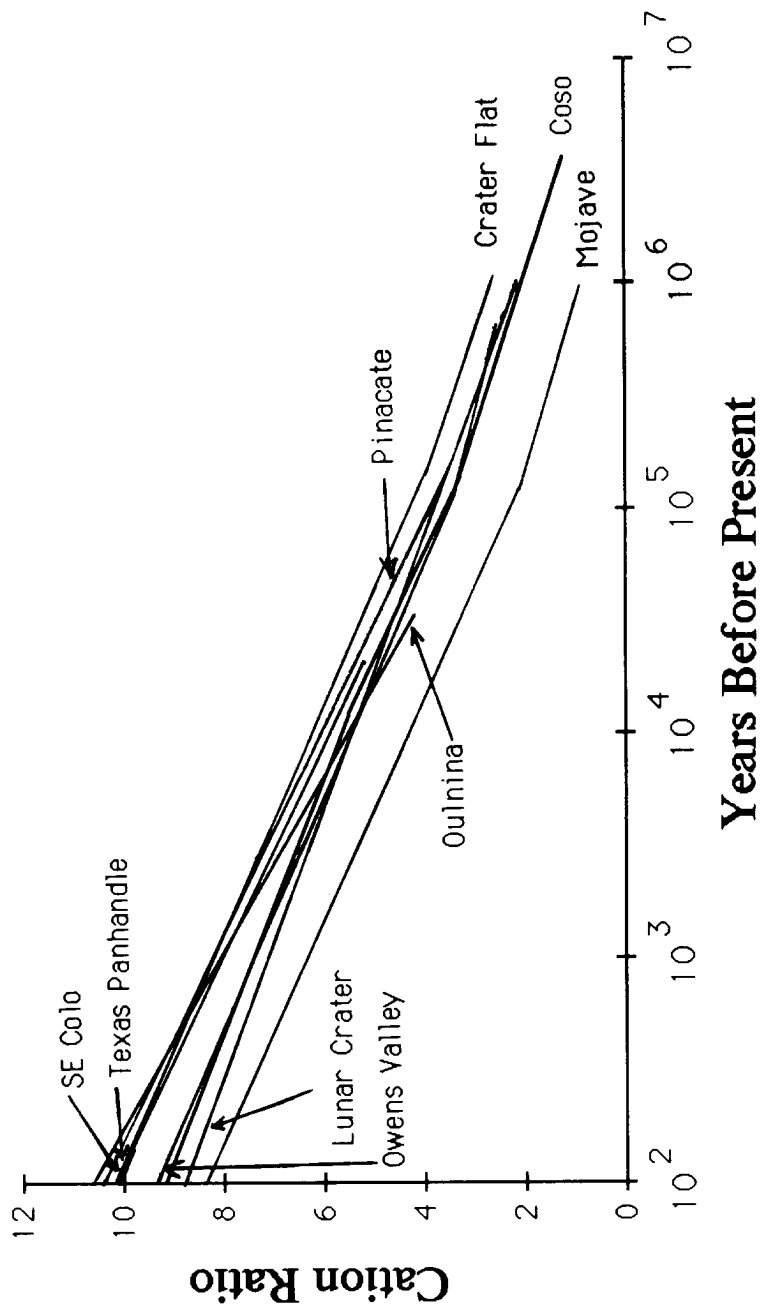
**Figure 11** Location of cation-leaching curves in western North America, discussed in the text and presented in Figure 12.

to transfer a well-documented curve to a region without numerical calibration ages, based solely on environmental factors. This is a distant goal. It will probably be possible in the near future, however, to transfer a well-documented curve to a region that has only a few numerical calibrations, utilizing a quantitative model of biogeochemical factors influencing varnish CRs.

### VII Conclusion

New surface exposure dating techniques are able to estimate when a rock surface first becomes exposed to the atmosphere. Rock varnish dating provides a minimum age estimate of when a varnish started to form on a rock, representing the cessation of deposition or an erosional event. *In situ* cosmogenic isotopes





**Figure 12** Cation-leaching curves constructed by the PIXE-scraping method. Sites for the curve, except Oulmina, are in Figure 11. The Oulmina curve is elaborated in Dorn *et al.* (1988) and Nobbs and Dorn (1988). Data for the Coso curve is in this paper; for the Mojave curve in Dorn *et al.* (1987a); the Crater Flat curve in Dorn (1989a); and for the Owens Valley curve in Dorn *et al.* (1987b). The other curves are based on unpublished data.

provide an independent way of determining how long rocks have been exposed to the subaerial environment, from the radiocarbon time scale to millions of years. The exposure of bedrock on a hillslope, the deposition of a boulder on a river terrace, glacially polished bedrock, and many more land surfaces have not been datable, until now. SED methods offer geomorphologists insight into a wide range of questions that had little hope of an answer less than a decade ago. Like radiocarbon (see Stuiver *et al.* 1986; Shackleton *et al.*, 1988) CR dating and other SED methods will undergo a process of constant refinement. Like radiocarbon, these methods should be utilized in geomorphological research even during the period of development.

This paper presents the results of a three-year study of the potential and limitations of CR dating. Since the inception of this study, the number of CR calibrations has been expanded from one to nine. At least 23 different environmental variables are quantitatively documented to influence a CR; these must be controlled if the time signature is to be deciphered correctly. The SEM-method of CR dating cannot determine a varnish CR accurately; removing the varnish from the underlying rock and analysing it by a bulk chemical method like PIXE is strongly preferred here. Erosion of a rock surface is a serious sampling concern in all surface-exposure dating methods. The timing of degradation of lava flows, as well as alluvial and glacial deposits, is analysed quantitatively for the first time. The unique role of rock varnish as compared to other surface-exposure dating methods is its ability to determine the timing of last abrasion of a rock, whether by human or natural agencies.

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#### Acknowledgements

Funded by NSF grants SES 86-01937 and EAR 87-57014, and the Nevada Bureau of Mines and Geology for the Crater Flat work. I thank D. Dorn and D.L. Tanner for field and laboratory assistance, S. Anderson, J. Bell, D. Elliott-Fisk, D. Krinsley, F. Phillips and B.D. Turrin for discussions, D. Lynch for K-Ar dating of varnish clay, T.A. Cahill, T. Gill and the Air Quality Group at the University of California at Davis for PIXE analyses, B. Trapido for assistance in graphics, J. Stipp and M. Tamers at Beta Analytic and W. Wolfli at ETH Zurich for AMS  $^{14}\text{C}$  measurements on Coso varnishes. Thanks to W.L. Graf, G. Pope and an anonymous reviewer for comments on the manuscript.

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## Salt tectonics and

by A.S. Goudie

### I Introduction

Evaporites are extremely widespread and their distribution (Table 1) covers a quarter of the world's continental shelf or another (Kozary *et al.*, 1986). The most important mineral is halite (sodium chloride), an important geomorphological agent. In this paper, the structures, the production of salt, the effects of salt on drainage modification, the creep of salt, subsidence and karst formation are discussed on the basis of this brief review. References to the origin of salt deposits are provided by Goudie (1986), Jenyon (1986) and Warren (1986).

### II Salt movement mechanisms

Having a low density (generally 2.16 g/cm<sup>3</sup>) and the ease at which it flows as a liquid, salt flows under conditions where the surrounding rocks are even small amounts of water (as in the case of salt domes, *et al.*, 1986), while at temperatures above 100°C (Heroy, 1968). The ability of salt to flow is the basis of the development of the miscible displacement of salt (Jackson (1987a: 58) have expressed

When it is under a continuous stress, salt flows as a liquid and deforms without breaking. . . . It creeps only under the relatively strong stress of salt plates. . . . In contrast, salt flows only when it is one of the least dense of all rocks. . . . when it is buried under other sediments, it is gradually compressed. . . . The