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A review of the history of dating rock varnishes

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Abstract

The history of rock varnish dating spans almost 20 years from the initial suggestion to use uranium series isotopes through the use of a geochemical ratio (cation-ratio dating) to the current application of accelerator mass spectrometry radiocarbon dating (AMS ^{14}C). Uranium isotopes were ignored while other dating methods were tested exhaustively on several continents. Evidence of the unreliable dating of the formation of varnishes using cation-ratios was demonstrated by examples of environmental and textural observations reflecting localised leaching, and by chemical analyses that contradicted the fundamental assumptions of the method. The radiocarbon dating of substances embedded in varnishes is also problematic where carbon compounds and sources are not identified. The incompatible coexistence of different carbonaceous components, a recent controversial issue, is explained with reference to different environments of formation. The future of AMS ^{14}C dating of rock varnishes centres around overcoming the practical limitations of sampling and analysing extremely small quantities of carbon-bearing substances. Future directions for dating varnished rock surfaces may include innovative refinements to the U-series, cosmogenic isotope and luminescence methods. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: dating; rock varnish; radiocarbon; cation-ratio; uranium series

1. Introduction

Accumulations of naturally occurring thin, rock surface deposits have been used to estimate the ages of petroglyphs in North America (Dorn and Whitley, 1984; Whitley and Dorn, 1987, 1993; Dorn, 1993; Francis et al., 1993) and Australia (Nobbs and Dorn, 1988; Watchman, 1992a). They have also been used to date geoglyphs at Nazca (Dorn et al., 1992a) and in Colorado (von Werlhof et al., 1995), landforms (e.g., Dorn et al., 1986, 1987a,b, 1992b; Whitney and Harrington, 1993; Peterson et al., 1995) and Nazca puquios (Clarkson and Dorn, 1991, 1995). Many debates have arisen about the results of the methods used in these rock surface dating investigations because of concerns about their accuracy and reliability. This paper reviews the history of rock surface dating as it has been applied to rock varnishes, and in particular the dating of petroglyphs, so as to provide insights into the current status of rock surface dating.

Rock varnishes are a category of a wide range of sub-aerial rock coatings including amorphous silica films (skins or glazes), reprecipitated carbonates, and various sulphate and oxalate-rich crusts. Potter and Rossman (1977) identified clay particles as the major

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component of rock varnishes. They considered atmospheric fallout as the source of the clay and other components. Rock varnishes are usually black or dark brown and contain high percentages of either manganese or iron that are either dispersed through the thin rock surface coatings or concentrated in fine laminations which persist for short distances or are disrupted by post-depositional processes (Fig. 1). The inorganic components are fixed to physically stable exposed surfaces through biological processes (Dorn and Oberlander, 1982; Dorn, 1991a). Rock varnish was previously called desert varnish because the thin coatings were thought only to form in desert or semi-desert terrains (Engel and Sharp, 1958; Krumbein and Jens, 1981; Staley et al., 1983), but rock varnishes also occur in many other microsites and environments (Dorn, 1989). Scanning electron microscope (SEM) observations and X-ray diffraction (XRD) analyses of thin varnish films reveal that they are formed by sequential deposition of inorganic components, including quartz and clay, as well as iron and manganese oxides and hydroxides.

Varnishes offer a way for dating recognisable archaeological, geomorphological and geological events because the original bare rock has been covered by a thin film after the creation of petroglyphs and geoglyphs, the construction of stone structures, the deposition of geomorphic units, or the movement along faults. In 1980, it was suggested that uranium series isotopes could provide a means for determining the age of formation of rock varnish (Knauss and Ku, 1980). This was realised after it was found that the uranium content and activity ratio $^{234}U/^{238}U$ were distinctly different in samples of varnish, altered weathering rind and heartrock from the Colorado Plateau. These preliminary analyses suggested that rock varnish could form a closed system for U, Th and Pa, but this conclusion still requires systematic testing. It was also shown that the amounts of daughter products, ^{230}Th and ^{231}Pa, from natural

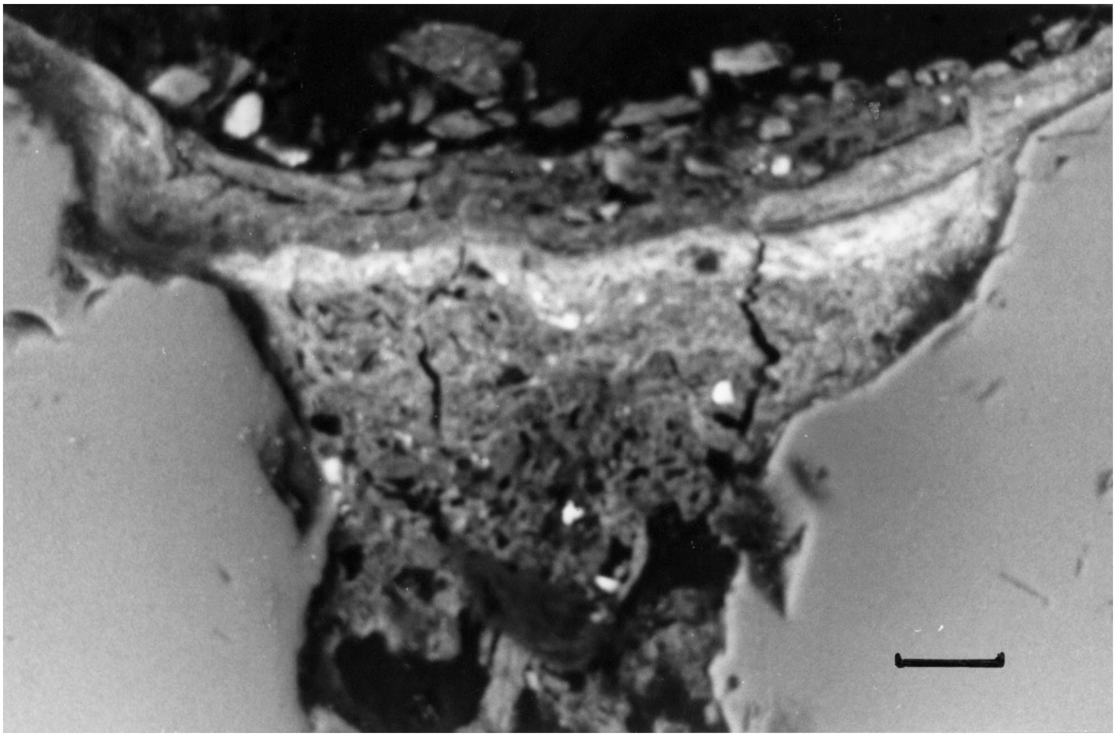

Fig. 1. Backscattered electron microscope image of a polished cross section of rock varnish formed over Nubian Sandstone, Egypt, showing typical textural and compositional variability. A bright manganese-rich layer near the surface overlies porous silty iron-rich varnish (scale bar is 10 μm).

uranium decay were a function of time and initial uranium content. Application of this dating method to archaeological and geomorphological problems has unfortunately not been attempted and the issue of whether uranium exists in a closed varnish system remains unconfirmed.

Two other approaches have been used for dating rock varnishes: (1) the cation-ratio and (2) accelerator mass spectrometry radiocarbon methods. In the sections that follow each method is described and the assumptions and problems associated with them discussed.

2. Cation-ratio dating

Cation-ratio dating was developed out of the apparently consistent and systematic trends in the ratio of elements in some rock varnishes. The early observations about the chemistry of varnishes implied that the original amounts of cations were generally in the same relative proportions and that minor subsequent variations in cation amounts became apparent over time. While discernible temporal shifts in elemental composition within varnish seemed empirically sound (Dorn and Oberlander, 1981), there were signs indicating complexities, particularly in relation to the origins of titanium compared to calcium and potassium (Gillespie, 1999, pers. comm.). In 1983, a method was proposed for dating rock varnishes (Dorn, 1983), which was based on the variation in elemental ratios (referred to as *cation-ratios*) and not of the elements themselves. It was suspected that leaching of soluble minor elements occurred in varnishes over time and that these variations were not overly sensitive to factors that affect manganese deposition. ''The premise of cation-ratio dating is that with time the leachable cations in varnishes, such as Na, Mg, K, and Ca, are gradually replaced by and/or depleted relative to less mobile cations, such as Ti. The decreasing cation ratio of Na + Mg + K + Ca:Ti, or any component thereof (e.g., Ca:Ti), provides an indication of the length of time that the varnish has been exposed to cation leaching'' (Dorn, 1983: p. 50).

Analyses of varnishes from the shorelines of Searles Lake and slopes of Death Valley (USA), and cobbles from the Negev Desert indicated a trend of decreasing cation ratio with increasing relative age of the geomorphological feature (Dorn, 1983). To test the hypothesis that varnish cation ratios can be calibrated with independently dated surfaces, Dorn also sampled and analysed varnishes from rocks of known ages in the Coso volcanic field in southeastern California. Black varnishes on rhyolite domes and basalt flows were radiometrically dated from more than 3 million years to 39,000 years ago using the K/Ar method. They were analysed for their minor element contents and each cation ratio (K + Ca:Ti) was plotted against the K/Ar age of the underlying rock. Decrease in the ratios versus increasing age followed a linear-logarithmic distribution and permitted the construction of a cation-leaching calibration curve (Fig. 2; Dorn, 1983: p. 63, fig. 7). By measuring the cation ratio of a varnish its age could then be determined.

In 1983, Dorn believed there were only four theoretical assumptions that had to be met before cation ratios could be used to determine the age of a rock varnish. These were:

(1) the components of rock varnishes are derived from essentially the same sources and the cation ratio of airborne fallout has remained constant during the Quaternary;

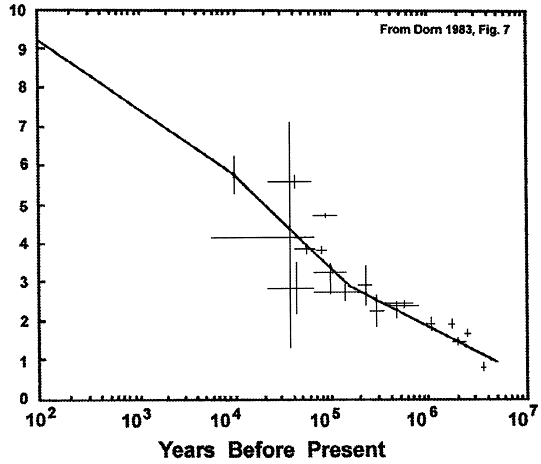

Fig. 2. Semi-logarithmic regression lines of the measured cation ratios of varnishes with the K–Ar ages of volcanic deposits for the Coso region, CA (from Dorn, 1983: p. 63, Fig. 7). The horizontal and vertical bars represent the uncertainties and standard deviations in ages and ratios, respectively.

(2) the rock varnish is a surface deposit serving as a cation-exchange complex whose capacity is similar across all samples being compared;

(3) sodium, Mg, P, K and Ca are more mobile in the varnish exchange complex than Ti; and

(4) the leaching rates of cations in varnishes are similar for all compared samples, or changes affecting the leaching rate are contemporaneous and of the same magnitude for all varnish samples in a region (Dorn, 1983: pp. 53–56).

A problem with the first assumption, that all the components come from the same source, is evident in the Searles Lake and Death Valley varnishes where the amounts of titanium were influenced by up-wind volcanic activity, while Ca and K were affected by pluvial and fluvial processes (Gillespie, pers. comm.). The cation-ratio dating method was further constrained because the four assumptions required verification by field sampling and laboratory analysis. Problems started to be found. For example: cation-exchange processes in rock varnishes were complex; and micro-site environments caused variabilities in varnish composition which resulted in local chemical, micro-stratigraphic and morphological anomalies. There were also compositional effects produced by pluvial history and regional environmental changes through time. Despite these complexities the cation-ratio dating method gained wide acceptance amongst many archaeologists, geomorphologists and geographers.

Although independent testing of cation-ratio dating was not done the method was applied to estimating the relative and absolute ages of various geomorphological and geological surfaces (Dorn et al., 1986, 1987a, 1990), petroglyphs (Dorn and Whitley, 1984; Dorn et al., 1988) and lithic artefacts (Bamforth and Dorn, 1988). Apparently reliable results were obtained using varnish cation-ratios in southeastern Colorado (Loendorf, 1991), China (Zhang et al., 1990) and South Africa (Pineda et al., 1988, 1990). These results tended to provide scientific validation that the method could be used with careful sampling under most circumstances.

For example, Harrington and Whitney (1987) developed the scanning electron microscope analytical method for measuring cation ratios in polished cross-sections of laminated rock varnishes from the Española Basin, NM and Yucca Mountain, NV. They confirmed the linear decrease in cation ratios in those varnishes with the logarithm of their relative ages. The cation leaching curves for varnishes from these sites, although different from that originally produced by Dorn (1983), appeared to support the use of cation-ratio dating ‘‘to determine the minimum time since a surface stabilized’’ (Harrington and Whitney, 1987: p. 970).

Up to this point advocates thought the calculated cation-ratio ages were valid estimates of surface ages, although the problems that had been highlighted when the method was proposed (Dorn, 1983: p. 67) had still not been addressed. The number of problems increased as the method was used in different locations. For example, information about the compositions of aerosols, soils and dust trapped in rock surface depressions and their time histories were needed at each site because local chemical anomalies could affect cation ratio measurements of modern varnish components. The inclusion in varnishes of particles larger than clay-size also affected the chemistry of varnishes. Details of the extent and rate of cation exchanges in varnishes in which Mg replaced Ca and Na replaced K had not been studied. The effects of Eh, pH, porosity and solution chemistry on the rate and extent of cation leaching had also not been thoroughly investigated. In fact, evidence for a cation leaching mechanism where Ca and K were dissolved from varnish had not been adequately demonstrated.

Factors other than loss or exchange of cations over time could also influence the estimation of a cation ratio. For example, if titanium replaced some exchangeable cations, potassium was preferentially fixed to a clay lattice, organic matter formed complexes with cations or the pH-Eh conditions changed because of fluctuations in climate, then the cation ratio would be unreliable and not simply be related to systematic leaching. These variables had not been considered when the general theory had been developed. In fact, the dating method assumed that the rate of cation exchange was constant for a given sampling area. In reality, depositional structures, varnish micromorphology (ranging from lamellate to botryoidal), coating thickness and environmental factors were found to vary between sites. Sampling varnishes from different micro-topographical locations could therefore lead to potential dating problems (Dorn, 1983: p. 67). The thicknesses of varnishes were highly variable, even on surfaces with similar ages, because of the influence of micro-ridges, cracks and micro-depressions. This was especially true in places of variable aeolian abrasion and concentrations of manganese-oxidizing bacteria. In hindsight, though, it seems that because detailed studies into these and other problems were not undertaken the dating method was doomed to fail.

3. Unreliability of cation-ratios

By 1991, sceptics sounded warnings about the use of cation-ratio dating. Errors had been identified in the analysis of titanium because of the overlapping effect of barium (Bierman and Gillespie, 1991; Harrington et al., 1991). Curiously, this did not seem to affect the data, which would apparently all be wrong if any barium were present. This created a scenario in which the cation-ratio method allegedly worked even when quantities of Ba and Ti were inadvertently determined as an inaccurate Ti analysis, implying that the method would not work so well when Ti was measured accurately. Harrington and Whitney (1995) went further in supposing that Ba might be a better denominator than Ti. While Ba occurs widely in analyses of varnishes its concentration in dust is neither likely to be geographically uniform nor temporally constant. Cation-ratio variability with depth in varnish had also been measured suggesting geochemical heterogeneity and complex localised leaching or exchanges (Dragovich, 1988, Clarke, 1989, Krinsley and Anderson, 1989). Modifications and refinements to the method continued (Dorn et al., 1990; Krinsley et al., 1990; Dorn, 1991a). These changes were accompanied by attempts to use major element variations in varnishes as environmental indicators (Dorn, 1990, 1991a). After 6 years of research and experimentation Dorn (1989: p. 590) had reassessed the cation-ratio (CR) dating method and concluded that: ‘‘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.’’

In addition to this large number of environmental variables, and in an attempt to demonstrate the feasibility of using cation ratios for dating rock varnishes, nine principal factors were proposed as affecting sample selection for cation-ratio dating (Dorn et al., 1989; Dorn, 1990; Krinsley et al., 1990). Those requiring field observations before sampling were identification of unstable surfaces, different types of varnishes and certain environments. Specialised laboratory analyses and observations were required to find evidence of the effects of microorganic activity, anomalous elemental abundances, micro-topographic features, sub-surface cracking, remobilisation of elements and physical deformation structures. To reduce anomalous age determinations samples were also screened using textural and compositional properties before measuring cation ratios.

To increase accuracy, the way that cation ratios were measured was also modified. These refinements were meant to reinforce justification of the basic premise of the dating method, that cation ratios were dependent on age. Instead of analysing scrapings of whole varnish, as had been done before, it was considered more reliable to perform microanalyses of layers in varnishes adjacent to the underlying rock surface in a polished cross-section. Choice of the SEM/EDXA (scanning electron microscopy/energy-dispersive X-ray analyses), for micro-analysis (Dorn, 1990), contradicted the earlier view that using the SEM method gave inaccurate cation-ratio measurements (Dorn et al., 1989).

Other serious doubts about the universal application of the cation-ratio dating method gradually emerged as geochemists and geomorphologists examined varnish chemistry and processes of varnish formation. Some measurements, aimed at obtaining cation-ratio ages from rock varnishes, highlighted analytical imprecision (Bierman et al., 1991) and inaccuracy (Bierman and Gillespie, 1991; Harrington et al., 1991). While the precision obtained in calculating an average cation-ratio was found to depend on the number of analytical points and the volume of material sampled, inaccurate measurements could arise because titanium concentrations were overestimated when a varnish contained barium. This happened when the analyses were made using the proton-induced X-ray emission method (PIXE). The analytical problem was caused by the overlap in the X-ray energy spectra of titanium (Kα) and barium (Lα). This was resolved either by deconvolving the barium spectrum, using SEM/EDXA or ICP analyses (inductively coupled plasma; Bierman and Kuehner, 1994).

In addition, Reneau and Raymond (1991) found from their SEM analyses across varnishes on Cima volcanic rocks (California) that there were no systematic changes in Ca:Mn and K:Si ratios from the lower, older microlaminations to higher, younger layers as would be expected if Ca and K were preferentially leached with time. This contradicts the findings of Harrington et al. (1991), and poses the question as to whether Ba is the only element in varnishes that changes systematically. It was also proposed from SEM observations and energy dispersive analyses that in varnishes with silty, porous textures and low concentrations of Mn, adjacent to well stratified Mn-rich varnish, that extensive localised leaching could have removed both Ca and K (Dorn and Krinsley, 1991). Publication by Dorn and Krinsley of photographic evidence of varnish textures that they believed indicated post-depositional leaching at microsites in laminated varnishes were, however, also interpreted as representing constructional or sedimentary depositional features and not reflecting secondary chemical solubility (Watchman, 1991). While acknowledging that ‘‘a constructional cause for chemical differences is certainly plausible’’ (Dorn, 1990, 1991b), the argument about evidence of localised leaching of cations from varnishes essentially revolved around subjective assessment of varnish textures. This question remains unanswered because ‘‘the critical assumption that these adjacent layers with different textures were originally deposited with the same texture and composition was not evaluated’’ (Reneau et al., 1992: p. 717).

In 1992, further potent arguments arose against the use of cation ratios for dating because of the discoveries by Reneau et al. (1992). They found that the constant initial ratio of (Ca + K):Ti and the proposed progressive leaching of Ca and K (the major premises of this method) were not supported by analytical data on Cima volcanic field varnishes, in California. The concentrations of Ca and K in those varnishes were related to the abundances of Mn and Si, because both Ca and K had showed strong positive correlations with the respective major elements. Furthermore, the critical assumptions used to make palaeoenvironmental interpretations of varnish chemistry were not supported. In a region with essentially the same history of climatic variations a wide range in major element chemistry could be found in the uppermost varnishes, indicating that varnishes which accreted on different rocks may not necessarily share similar elemental compositions. Climatic conditions were therefore not the only factors controlling stratigraphic changes in varnish compositions (Reneau et al., 1992: p. 721). It is probable that some compositional differences were artificially introduced during the sampling of basal layers of varnish by the accidental incorporation of weathered fragments of the underlying rock.

In Australia, an attempt to replicate the construction of a calibration curve in the Olary region of South Australia did not support the cation-ratio dating method. Varnishes from the same calibration site, Pepuarta Bluff, as that which was reported in Nobbs and Dorn (1988) and Dorn et al. (1988), were selected for radiocarbon dating and cation-ratio measurements. Samples that met the stringent field and laboratory prerequisites were processed according to the published procedures at that time (Watchman, 1992b). A usable calibration curve could not be constructed from the radiocarbon age and cation ratio determinations. Dating was measured on plant material that was hand picked from the varnish residue after hydrofluoric–hydrochloric acid digestion and potassium hydroxide neutralisation. The respective varnish cation-ratios and the measured ‘initial ratio’ (representing modern dust scrapings) of two Pepuarta Bluff samples were approximately the same (ranging from 4.51 ± 0.12 to 5.05 ± 0.47). However, there was considerable radiocarbon age differences for the entrapped organic matter (34,590 ± 560 and 21,550 ± 240 years BP; Nobbs and Dorn, 1988) and plant material (1375 ± 60 and 3415 ± 70 years BP; Watchman, 1992b). This made for an ineffective calibration curve (Fig. 3A).

Instead, explanations were provided by Dorn and Nobbs (1992) to counter the anomalous results obtained using cation-ratios from three engraved motifs at the Karolta site in the same region as the calibration site (Watchman, 1992a). The Olary calibration

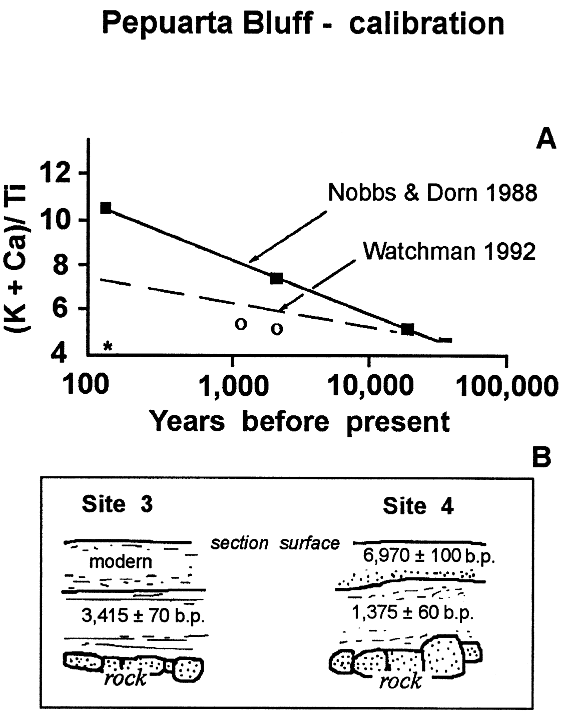

Fig. 3. (A) Reproduction of two cation-ratio calibration curves for Olary varnishes, South Australia (solid boxes are from Nobbs and Dorn, 1988, the open circles are the ages of plant fibres in varnishes of measured cation-ratios and the asterisk is modern dust as in Watchman, 1992a). (B). Schematic illustration of the measured AMS ^{14}C age estimates (years b.p.) for plant fibres in varnish at two of the Pepuarta Bluff calibration locations (from Watchman, 1993).

curve of Nobbs and Dorn (1988) was used as the basis for estimating the age of rock varnish in petroglyphs at Karolta (in the same region) because the attempt to validate the construction of a reliable cation-ratio leaching curve had failed (Watchman, 1992b). Measurements on five varnish samples from within pecked depressions of a circular petroglyph produced cation-ratio ages that were substantially older (44,760 ± 3390 years BP) than a similar set of five samples from off-art varnishes adjacent to the petroglyph (13,140 ± 2950 years BP; Watchman, 1992a: p. 54). This numerical result contradicted a fundamental assumption implicit in cation-ratio dating theory, that once varnish begins to form on a stable exposed surface it continues to form and is not physically lost.

Varnish in a petroglyph should be younger than on the surrounding rock, but the Olary example demonstrated that they are not. Finding rock varnish that is apparently three times older in a petroglyph compared with the surrounding varnish through which the petroglyph was presumably pecked strongly undermined the premise supporting this method. Similar results were also obtained in two other motifs at Karolta. A parallel example was described using varnished artefacts and adjacent bedrock in the Mojave Desert (Bierman and Harry, 1992). These well separated, independent and consistent results indicated that in some settings the processes of varnish formation and subsequent modification were not consistent with the cation-ratio dating theory.

Dorn and Nobbs (1992: p. 59) made the very strong point that ‘‘for varnish dating to work, layered varnish must be used. When the right type of varnish is used, it is possible to obtain reliable ages.’’ This became the basis of their objection (Dorn and Nobbs, 1992: p. 58) to the anomalous and ‘‘irrelevant’’ results at Karolta obtained by Watchman (1992a,b). Their accusation was founded on the basis that the varnish was ‘‘unlaminated and *no* ‘lowest layer’ could be discerned’’ (Nobbs and Dorn, 1992: p. 59). The factual evidence and descriptions of ‘‘continuous, silty laminations’’ (Watchman, 1992a: p. 53 and plate 1) invalidated their objections. The Karolta results do indeed invalidate the cation ratio calibration curves and they also raise the issue of the importance of compositional layering in varnishes.

Compositional layering in varnishes represents sequential or continual accumulation of components over time and it therefore indicates regular accumulation of dust and other ingredients on an undeformed stable surface. However, ‘‘for a varnish date to reflect the true age of the landform requires a condition of no erosion for the microsite where varnish was sampled. Also, a requirement of the cation-ratio dating theory is that the varnish itself must form continuously as a synsedimentary deposit, but this is contradicted by only sampling and analysing the basal varnish. Uninterrupted deposition is frequently not the case in Australia’’ (Dorn and Dragovich, 1990: p. 26), making it impossible to satisfy a condition of the dating method. Evidence of layering was one of the factors in the continually revised list of criteria considered essential for accurate cation-ratio dating (Dorn, 1993, table 1). Nobbs and Dorn (1992: p. 59) acknowledged the independent work at Olary and commented that despite what looks like the ''use of unlayered varnish, we find it encouraging that he (Watchman, 1992a) found numerical values for cation-ratios in the same range as ours for the region.'' This statement that any varnish, layered or unlayered, can still give useful dating results also contradicted the refined sampling strategy and laboratory screening of varnishes to select material considered appropriate for dating. The proposed conclusion, despite all the previous investigations and analyses, was in fact that layering was not a critical factor in obtaining reasonable cation ratios. This was a stunning revelation confirming for many people the incomprehensible complexities of using cation ratios to date the onset of formation of rock varnishes and highlighting internal contradictions in varnish literature.

In 1993, Dorn wrote a comprehensive rebuttal to the severe criticisms of the cation-ratio dating method (Dorn, 1993). The paper was noteworthy for two reasons; it gave detailed explanations of the highly refined selection, extraction and processing method used since about 1992 for cation-ratio dating and it was accompanied by descriptions of the accelerator mass spectrometry radiocarbon method (AMS ^{14}C) to date organic matter in the varnish. So much chemical, textural and environmental evidence had accumulated against cation-ratio dating that even the

Table 1
A summary of the major carbon-bearing components found in rock surface deposits and typical ranges of their usual environments and ages of formation

Carbon component	Formation conditions	Formation age range
cellulose	plants grow on the Earth's surface, leaf, stem and bark can be transported from one sedimentary environment to another. ^{14}C age reflects atmosphere at time of growth.	Quaternary
lichen	grow on stable surfaces or hyphae penetrate the underlying rock. Dead fragments can be transported. ^{14}C age either reflects atmosphere at time of growth or component from rock nutrient.	Quaternary
algae (diatoms)	live in meteoric water on rock surfaces. ^{14}C age either reflects atmosphere at time of growth or contribution from bicarbonate ions from 'hard' water	Quaternary
fungi	live on stable rock surfaces and in cracks. ^{14}C age either reflects atmosphere at time of growth, old 'dead' micro-organism, bicarbonate ions or nutrient components from rock	Quaternary
oxalate salts	produced from fungi, lichen, algae, bacteria on dusty stable surfaces. ^{14}C age reflects atmosphere at time of growth and/or substrate contribution	Quaternary
charcoal	derived from the burning of wood cellulose at the surface	Quaternary
organic matter	unknown substances from unknown processes and origins. Unreliable ^{14}C age	Quaternary or older
coal	metamorphism of plant remains at elevated temperature and pressure at depth beneath the Earth's surface	Mesozoic/Paleaozonic
graphite	metamorphism of carbon-bearing substances at high pressure and temperature at depth beneath the Earth's surface	Mesozoic/Paleaozoic

revised method seemed untenable. The emphasis for dating rock varnishes now shifted from using cations to carbon leaving a huge pile of literature and dates that must be re-evaluated. This daunting task leaves the researcher in a quandary: either to accept all the previous cation-ratio dating results and disregard the criticisms or to critically review the literature pertaining to their region realising the likelihood and extent of the problems and uncertainties they face.

By 1994, the use of cation-ratio dating, perhaps with the exception of replacing Ti by Ba (Harrington et al., 1991), as a means for estimating the ages of varnish on geomorphological, geological and archaeological surfaces was approaching its end. Bierman and Gillespie (1994: p. 82) had ''found no consistent relationship between varnish cation-ratios and the relative ages of chert artefacts. Moreover, in situ analyses gave systematically higher cation ratios and lower Ti abundances than bulk analyses of scraped varnish or microprobe analyses of varnish in cross-section.'' These findings together with more negative results obtained on artefacts, desert pavements and bedrock sealed the end of cation-ratio dating. Harry (1995: p. 126) concluded that the practicalities of selecting appropriate varnishes for dating made it difficult or impossible to date surfaces reliably. The occurrence of cation leaching was also questionable. The chemical variability of cation ratios across varnished surfaces could also significantly affect the discerned temporal patterning of varnish formation.

To establish the cation-ratio calibration curves in Australia (Nobbs and Dorn, 1988), AMS ^{14}C measurements had been made using the organic matter in rock varnish scraped from the lower 10% of the layer. After the imprecision of this sampling strategy was pointed out (Reneau et al., 1991) the published method changed to collecting organic matter, such as endolithic algae trapped beneath varnish (Francis et al., 1993; von Werlhof et al., 1995). This new radiocarbon dating technique appeared to offer a better alternative to the cation-ratio method, which was becoming increasingly seen as highly unreliable because of the complex nature of varnish structures and the variable chemical compositions that were created by diverse environments. Some petroglyphs were dated using both the cation-ratio and AMS ^{14}C methods, apparently to demonstrate the potential of the new chronometric method, and also in a desperate effort to salvage the chemical-leaching approach (Francis et al., 1993).

By the time of publication of the highly controversial paper concerning evidence for peopling of mainland North America prior to about 12,000 ^{14}C years B.P. (the Clovis versus Pre-Clovis debate; Whitley and Dorn, 1993) the seeds had already been sown for yet another rock varnish dating controversy. Fertile ground for a debate, which continues to this day, is manifest in the nature, source and age of carbon used in the AMS ^{14}C method. In their Clovis versus Pre-Clovis discussion paper, Whitley and Dorn (1993) used both AMS ^{14}C and cation-ratio age determinations on varnished artefacts to provide evidence of pre-Clovis occupation. They used cation-ratio dating ''only as supporting evidence for our AMS ^{14}C varnish dates'' (Whitley and Dorn, 1993: p. 635). How reliable is AMS ^{14}C dating if cation-ratio dating is unreliable? Before this question is answered it is worth looking at the AMS ^{14}C dating method and at the various sources of carbon.

4. AMS ^{14}C dating of rock varnishes

It is generally assumed that carbon-bearing substances or 'organic matter' in rock varnishes have been deposited at the same time as the inorganic components. It is these materials that are selected for radiocarbon dating the timing of deposition. Extraction of 'organic matter' using chemical pre-treatments of acid/base/acid digestions followed by water washes leads to a carbon-bearing residue which is first combusted in oxygen and then the resulting gas is reduced to form a small graphite target suitable for AMS radiocarbon analysis (Linick et al., 1989).

The fundamental premise of the AMS ^{14}C dating method applied to rock varnishes is that the age of carbon-bearing substances at the base of a varnish indicates the time when a varnish started to form. In theory, measuring the radiocarbon age of varnish formation therefore gives an estimate of the minimum time since a petroglyph was created or rock surface exposed. The principal assumptions of the AMS ^{14}C dating method are that the 'organic matter' at the base of a varnish is the sole source of the analyzed carbon, that it comes from a single source, that it is not intrusive, and that the varnish and organic matter started to be deposited shortly after the surface was exposed. The fundamental problem of AMS ^{14}C dating is definitive identification of the ‘organic matter’ in varnish.

There are two subtle issues here: the actual identity of the carbon substance and its relationship to deposition of varnish components that are directly linked to the geomorphological, environmental, geological or archaeological event of interest. For the Clovis versus pre-Clovis debate radiocarbon age estimates were made on ‘‘endolithic algae that was removed from the weathering rinds below varnished flake scars, and unidentified organic matter in an interface position, on the Mojave Desert artifacts, and unidentified organics from petroglyphs’’ (Whitley and Dorn, 1993: p. 637). Carbon-bearing substances are not only present at the interface between the varnish and underlying rock, but they are also found within varnish layers and in the weathering rind just beneath the varnish coated surface.

Unidentified ‘organic matter’ from within Australian varnish layers gave radiocarbon ages ‘‘slightly but consistently younger than independent controls’’ (Nobbs and Dorn, 1993: p. 26), and either older or younger than the age estimates of plant fibres from the rock-varnish interface (Watchman, 1993: p. 40). In the original sampling method ‘‘organic matter extracted from the bottom $\leq 10\%$ of the varnish’’ (Dorn et al., 1992b: p. 20) was used for radiocarbon dating, but because carbon-bearing substances in the varnish contaminated the analysis the revised method sampled only the ‘‘organic matter still attached to the underlying rock’’ (Dorn et al., 1992a: p. 141; Nobbs and Dorn, 1993: p. 26). However, reliability of a measured radiocarbon age is diminished when the carbon-bearing substances in the ‘organic matter’ are not identified (Beck et al., 1998).

5. Carbon sources

A wide range of carbon-bearing substances has been found in rock surface deposits associated with rock art and these have been used for dating petroglyphs and rock paintings. For example, cellulose plant fibres (Watchman, 1992b; Watchman and Cole, 1992; Mazel and Watchman, 1996), oxalate salts (Watchman, 1993), fossilised diatoms and other microorganisms (Watchman, 1995), fatty acids (Watchman, 1992c) and unidentified organic matter (Francis et al., 1993) have been used to date rock art. Of this diverse group, cellulose plant fibres, fossilised diatoms and unidentified organic matter have been used to date petroglyphs. Oxalate salts have only been used for dating rock paintings, but current research is showing that the age of oxalate crystallisation can provide estimates for the antiquity of petroglyphs (Watchman et al., in press a,Watchman et al., in press b). Other carbon-bearing substances have been identified in rock surface deposits, complicating the dating process and leading to controversial interpretations of the age of rock art [for example coal (Beck et al., 1997), charcoal (McDonald et al., 1990; Beck et al., 1997; Llosas et al., 1999) and graphite (Watchman, 1995)]. Unidentified organic matter is not a reliable medium for dating because the relationship between the carbon compounds of unknown origin and the event being dated is uncertain. In 1994, Fleming and Barnes (1994: p. 30) recognised this troubling problem and acknowledged that ‘‘some of the material dated was wind- or water-borne pollen or spores which can remain in the environment for millennia and need have no temporal relationship to the context on which they were deposited.’’

Cellulose plant fibres absorb carbon from carbon dioxide in the atmosphere in which they grew through the process of photosynthesis. When a plant dies, its leaves, stems and roots gradually break up and degrade releasing cellulose fibres into the environment. Some of these can be incorporated into rock varnishes (Watchman, 1992b). They can be removed for radiocarbon dating, but usually only a few small fibres can be extracted after scraping varnish from several square centimetres of rock surface. However, such small quantities (typically one fibre/cm^2) limit the opportunities for identifying the plant from which the fibres are derived and for radiocarbon dating. Research needs to be done to understanding how plant material degrades and how long it remains in the environment before becoming incorporated into rock varnishes.

In the case of algae, carbon can be absorbed from carbon dioxide in the air, through photosynthesis or from carbonate ions dissolved in water. Algae, which take up carbon dioxide, should give reliable age estimates, but those microorganisms that absorb carbon from carbonate ions may give erroneously old radiocarbon ages if the carbon is derived from geologically ancient calcareous rocks. Microorganisms, such as fungi and algae, become fossilised when the aqueous medium in which they live evaporates inducing precipitation of dissolved salts and minerals. The covering of algae, fungi and bacteria by silica, carbonate, clay or iron entraps their organic molecules and insulates them from external degradational processes. Dating the fossil carbon in those molecules gives an estimate for the time of death of the microorganism. Such an age measurement gives a minimum age for a petroglyph covered by a fossiliferous deposit.

It has often been assumed that the ages of fibres and fossilised microorganisms reflect the contemporary atmosphere of their formation and that the carbon molecules are autochthonous. However, as the major inorganic components of rock varnish (manganese and iron oxides and hydroxides, quartz and clay) could have been transported long distances it is possible that some carbon-bearing substances are allochthonous and much older than the varnish age. For example, if the inorganic components have been derived from dust eroded as fine particles from bare soil, clay pans, loose sediments and existing varnishes, then carbon-bearing components may have accompanied them to the site of deposition (Reneau and Harrington, 1988; Reneau et al., 1991). Ways to increase the confidence in a radiocarbon determination for a varnish are to measure a suite of samples, and not just one sample. This can be achieved by comparing the age estimates of different types of carbon-bearing substances from the same varnish layer, determining ages for adjacent layers and sections along a single layer, and measuring ages of varnishes in petroglyphs and on the surrounding surface. While these steps are advantageous there are practical difficulties in selectively removing and processing small quantities of datable materials.

Homogeneous laminations are common, but not very extensive and cannot be traced far even on the same rock. Many rock varnishes do not consist of components of the same age, but mixtures of contemporary and older components. Occasionally inverse age relationships of carbon-bearing components also develop (Fig. 3B; Watchman, 1993).

Diatoms, bacteria, fungi and algae will most likely become fossilised in rock surface deposits because the water in which they live also contains insoluble salts and minerals that precipitate over them. Calcium oxalate salts are so highly insoluble that they precipitate immediately when calcium ions mix with oxalate ions. These carbon-bearing salts reflect deposition at the same time as other inorganic particles. On the other hand unidentified organic matter poses enormous problems because the form of carbon is unknown. Many sources and ages of carbon may be represented in 'organic matter.'

Cellulose, lichen, algae, fungi, diatoms and oxalate salts can occur together in a rock varnish, but it is incongruous for coal or graphite to exist in rock varnishes together with charcoal, diatoms, oxalate salts, fungi, algae, lichen or plant remains (despite the findings of Beck et al., 1998). Such an occurrence would represent a contradiction between the form of carbon and its primary environment of formation and the existing rock varnish setting. It is unnatural for either coal or graphite to occur in rock varnishes with these other carbon-bearing substances because coal and graphite are geologically old and have formed under metamorphic conditions requiring considerable heat and pressure. The charcoal, algae, fungi and cellulose would have been irreversibly changed into different, yet identifiable, coal components (macerals). Pressure and temperature conditions needed for bituminous coal formation generally exist at more than 2-km depth in the Earth (Berkowitz, 1979: p. 11; Stach et al., 1982: p. 43). At that depth charcoal in sediment is essentially converted to a coal maceral called fusinite or inertinite, wood cellulose changes to vitrinite, spores to sporinite and algae to alginite. Therefore, charcoal and inertinite (coal) should not occur together in an unmetamorphosed rock surface deposit, such as rock varnish or a weathering rind. An unnatural process therefore seems likely where coal and charcoal coexist in laboratory samples of rock varnishes.

One circumstance where coal and charcoal could occur together in rock varnishes is where an exposed coal seam sheds particles of coal into a landscape littered with burnt trees. Coal and charcoal particles could coexist in a varnish formed on stable rocks nearby, but all varnishes in petroglyphs and on natural surfaces in the region should have similar occurrences of these carbon-bearing substances, and this should be easily verified. Alternatively, people who made graffiti over rock varnishes could have used coal and charcoal as pigments; traces of these carbon-bearing substances could have become included in varnishes. Recently, in the extraordinary case described by Beck et al. (1997; Beck et al., 1998)), evidence was presented of coal and charcoal occurring in a sample of varnish collected by Dorn from a single petroglyph in the Petrified Forest, southwest USA. However, except for a few fungal hyphae, no carbon compounds were extracted from a duplicate sample taken by Beck from the same varnish-covered engraving. This intriguing case is highly controversial, even though counter arguments were offered to explain the anomaly (Dorn, 1998), because it is apparent that a natural process was not the only contributing factor by which charcoal and bituminous coal were incorporated in those varnish samples (Dalton, 1998a,b).

Another example that highlights the difficulties of dating rock surface accretions (not necessarily restricted to rock varnishes), is the work done to date petroglyphs in the Côa valley, Portugal. Various carbon compounds were extracted from weathering rinds, siliceous rock surface deposits and the interfaces between coatings and rinds on soft schist. These samples of carbonaceous substances produced radiocarbon ages of similar age, but ones that were different from the expected age estimates (Watchman, 1995, Dorn, 1996). In this case, diatoms, charcoal particles, fragments of grass, leaf and plant litter were dated in silty accretions resembling red-brown weathering rinds that also contained particles of ancient graphite flakes naturally formed in the schist directly under the surface coatings removed for analysis (Watchman, 1996). It seems that components in coatings derived from surface weathering and depositional processes were inadvertently mixed during sample collection with graphite from the underlying schistose rocks. The mixture of young weathered products and ancient graphite gave radiocarbon age estimates that reflected the proportions of ^{14}C activities from the two different fractions. The radiocarbon measurements neither indicated the age of the graphite nor the younger components, but a pooled mean ‘average’ age of all carbon components in the mixture (Watchman, 1997).

6. Other problems

One of the major problems affecting acceptance of rock varnish age determinations based on their radioactive carbon activities is the lack of detail from authors about the sampling site and the process and pretreatments before graphitization into an AMS target. If archaeological, geomorphological or geological information is not reported about a sample, then the reader cannot appreciate whether the age determination actually relates to the event in question or to some other unrelated circumstance. For example, the radiocarbon dating of rock varnish associated with the underground water channels in Peru (*puquios*) is problematic because sampling locations were not precisely identified on varnish-covered cobbles used to build and repair the channels (Clarkson and Dorn, 1991, 1995; Fleming and Barnes, 1994). There is no assurance that varnish samples did not come from naturally varnished cobbles brought to the channel to effect repairs long after the water canal had been built.

Additionally, identification of the carbon components selected for dating must be documented because ‘organic matter’ can come from a wide range of possible sources and ages (Table 1). Simple petrographic observations may be sufficient to recognise plant fibres and other macro-organic substances. Analytical tools (SEM, XRD, infrared spectroscopy, gas and liquid chromatography) are available to observe and characterise inorganic and organic forms of carbon that are incorporated into rock varnishes so that their origin and depositional pathway can be demonstrated.

Under most surface temperature and pressure conditions, implied in the enormous volume of apparently reliable and published radiocarbon age determinations, carbon isotopes are not exchanged between dead organic substances and the atmosphere. If this happened regularly, then the radiocarbon dating method would not be a viable way of finding the age of a carbonaceous material. Occasionally, circumstances exist where the measured radiocarbon ages do not match archaeological or geomorpho-

Table 2
Summary of the amount of dateable carbon extracted from rock varnishes scraped from cobbles and their radiocarbon age estimates, Avawatz Mountains, Mojave Desert, CA

Sample Id. cave spring wash	Weight of varnish powder (mg)	Area of varnish scraped (cm^2)	Weight of graphite (μg)	Carbon in varnish (wt.%)	^{14}C age (years b.p.)
94-19	18.7	9	76	4.06	2390 ± 170
94-2b	6.1	10	19	3.11	14,700 ± 2600
95-1	4.9	6	14	2.85	3350 ± 500
94-16	15.7	8	43	2.93	2910 ± 330
94-15	11.1	8	29	2.61	3540 ± 210

logical theories. For example in the Côa valley, Portugal ''continued exchange of organic matter in an open system'' provides a simple explanation why the age estimates are younger than expected (Dorn, 1997: p. 106). Not only is physical addition of younger carbon possible through epilithic or endolithic microorganic activity, but slow chemical exchange in an open system is also thought feasible. In order to demonstrate that the measured mid-Holocene radiocarbon age estimates for petroglyphs should in fact be Pleistocene, Dorn (1997: p. 108), suggested that ''petroglyph grooves could have received a large influx of then-modern carbon in the Palaeolithic when rock faces were exposed to a subaerial environment. Subsequent slow rates of post-engraving carbon exchange would produce observed Holocene ages.'' Evidence supporting this rationalisation of results comes from a study of radiocarbon dating in open systems affected by chemical processes induced by nuclear explosions (McKay et al., 1986). As there is no evidence from the $\delta^{13}C$ measurements that exchange in two of the three isotopes or selective absorption of ^{14}C has occurred the hypothesis seems improbable.

On the other hand, in a process known as fractionation, the heaviest carbon isotope (^{14}C) can be preferentially depleted or enriched in CO_2 during chemical pre-treatment and processing prior to AMS ^{14}C dating. Artificially reducing the amount of ^{14}C in a sample by controlling the extraction conditions will effectively make the measured age older than the real age because the activity of ^{14}C is less than it was in the starting material. While such a chemical problem does not explain the situation found in the Côa valley (Watchman, 1996, 1997), this form of isotopic fractionation may explain other anomalously old radiocarbon determinations.

A further, and more substantial, limitation of AMS ^{14}C dating is the paucity of dateable carbon in rock varnishes. For example, the low amounts of carbon that were extracted from varnish frustrated the study of rock varnish ages in the Avawatz Mountains, Mojave Desert, CA (Watchman and McGill, unpublished data; Table 2). The total amount of extractable carbon in the Cave Spring Wash samples of varnished cobbles is extremely low considering the surface area that was scraped. Ideally, at least 100 μg (0.001 g) of graphite is needed for a reliable AMS ^{14}C age determination, but this is not easy to obtain from some rock varnishes on geomorphological surfaces. It is almost impossible to obtain the ideal amount of graphite that is needed for dating from varnished petroglyphs because of areal and aesthetic constraints.

7. Conclusions

Cation-ratio dating assumes that once a varnish is fixed to a stable rock surface the soluble cations are gradually lost in a process of localised chemical leaching. While repeated speculations have suggested that leaching and chemical loss of cations take place there is no conclusive evidence to demonstrate that this actually occurs. Other processes (Reneau and Raymond, 1991) can explain the apparent time-dependent variations in varnish chemistry.

Localised concentration of cations and complex cation exchange reactions can contribute to inconsistencies between measured cation-ratio ages and the relative ages of varnishes. Components deposited in varnishes do not always come from the same sources within a region, but can reflect local and regional compositional variations in dust, climatic fluctuations, and periodic erosion and redeposition of existing varnishes. Therefore, the apparent relationship in rock varnishes between cation ratios and the time since their formation cannot provide a reliable way for estimating the ages of varnished rock surfaces (Schneider and Bierman, 1997).

The cation-ratio dating method continued to fail various reliability tests even after refining the methods for selectively screening varnishes by using nine field and laboratory factors and by recognising 23 environmental variables that affect varnish chemistry, and by modifying the analytical techniques. Independent researchers could not reproduce calibration curves. Geochemical associations between major elements and cations indicated chemical influences over cation ratios other than slow progressive leaching over time.

Introduction of the AMS ^{14}C method for dating the formation of rock varnishes has suffered from the same lack of rigour that plagued the cation-ratio dating method. This has happened because fundamental research into the nature and properties of the principal component used as the basis for the method was not done. Unidentified organic compounds were radiocarbon-dated on the presumption that they were related to the timing of varnish formation, but subsequent work has shown this is not always the case. Inappropriate samples and poor methodology have also harmed this promising method. Systematic identification of the source of carbon extracted from varnishes for use in radiocarbon dating combined with the dating of stratified varnishes provide opportunities to increase confidence in AMS radiocarbon measurements.

Currently, there is no routine dependable method for dating rock varnishes because cation-ratios are unreliable, and as sample size and the identity and origin of carbon are problems affecting AMS radiocarbon measurements (Schneider and Bierman, 1997). Cation-ratio dating the formation of rock varnishes is not a reliable method because of a diverse and complex range of problems associated with the site environment, geochemical variability, and textural heterogeneity. The lack of a verified physical process to account for the observed variations in chemistry as primarily a function of time (i.e., the absence of proof for preferential leaching of cations) is a key deficiency of the method. There is also no certainty of establishing a dependable calibration curve because the decreasing curve of cation ratios often found in varnishes may not be solely attributable to the effects of time.

Accelerator radiocarbon dating of various carbon-bearing substances in rock varnishes sometimes provides a reliable means for dating, but occasionally anomalous results are obtained. The identification of the source of carbon used for dating is essential; otherwise, a misleading relationship could exist between the measured age and the varnishing event. Whereas different carbon-bearing components can coexist in natural rock varnishes, there is no satisfactory explanation that accounts for large quantities of coal-like and charcoal-like particles in accretions from the volcanic island of Hawaii (Beck et al., 1998; Dorn, 1998). Even if the presence of coal can be explained in the Arizona samples, there is no plausible reason for coal or coal-like substances to exist in the Hawaiian varnishes because there are no local sources of coal on Hawaii. It also seems statistically improbable that coal should exist in all of the stored samples of varnish dating experiments at three AMS laboratories.

8. Future directions

Three types of rock surfaces are associated with petroglyphs; unpatinated, partly repatinated and varnished. Each surface requires special attention in terms of measuring the time of its production. Measuring the AMS ^{14}C age of encapsulated carbon-bearing components at the base of rock varnish will provide an estimate of the minimum age of a varnished engraving. Collaborative research should be carried out in a pilot study to apply uranium series and AMS ^{14}C analyses to determine the age of a varnished geomorphological surface. Additional research should also focus on measuring time-dependent variables in single grains within rock that underlies partly varnished and repatinated surfaces. Single grains of quartz, feldspar or other minerals in rock surfaces beneath varnishes may contain a physical variable, which when measured will indicate the time since the surface was exposed. More research is therefore needed into understanding the properties of crystal lattices in rock-forming minerals and how natural radiation and the impacts of petroglyph production affect them. For example, from studies of luminescence dating we know that nuclear, cosmic and solar radiations affect the electron energy levels in light-trapping centres within quartz and feldspar crystals, but we do not know the full range of effects that these radiations have on deep electron traps and crystal defects.

As with other physical dating methods that have progressively become ‘‘miniaturised’’ through time there may be scope for using microsamples for in situ cosmogenic isotope analyses (^{3}He, ^{10}Be, ^{26}Al and ^{36}Cl). With the invention of sophisticated analytical tools it may be possible in the future to measure the isotopic contents of single grains rather than grams of rock. The problem with in situ cosmogenic dating is that penetration by the energetic particles is vastly greater than the varnish thickness, so the concentrations in a rock varnish are tiny. However, if such advances could be made they would be a major development in the dating of rock varnishes and petroglyphs. It seems more likely that conditions created at a rock surface by sub-atomic particles or photons might provide future dating possibilities. Similarly, advances in analysing small quantities of nuclides may also lead to opportunities for applying the uranium series method (^{230}Th, ^{231}Pa, ^{226}Ra, ^{234}U and ^{235}U) where contamination is not a problem. The inauspicious beginning of rock-varnish dating has not sealed its future, but created cautious optimism and healthy scepticism. Rigorous research based on innovative approaches and inquiries into the physico-chemical variables and fundamental properties of rock surfaces will undoubtedly provide the essential components for future rock-varnish dating studies.

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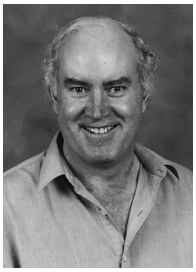

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