

## CATION-RATIO DATING OF PETROGLYPHS USING PIXE

David S. WHITLEY

*Rock Art Research Unit, Archaeology Department, University of the Witwatersrand, P.O. WITS, 2050 Republic of South Africa*

Ronald I. DORN

*Department of Geography, Arizona State University, Tempe, AZ 85287, USA*

A central problem in archaeological research has been the chronometric dating of petroglyphs (rock engravings). Recent improvements in the understanding of the chemistry of rock varnish (or patina) that develops on rock surfaces in arid regions has resulted in the development of a calibrated dating technique, cation-ratio (CR) dating. This is based on calibrating chemical changes in minor and major trace elements in the varnish over time. PIXE is used to determine the bulk chemical constituents of small samples of varnish mechanically removed from within petroglyphs. Recent applications in western North America have yielded petroglyph dates of great importance in understanding the origins of art and the antiquity of human settlement in the western hemisphere. In particular the CR dates on petroglyphs suggest that humans moved into the New World about 10 K yrs earlier than previously believed, and that the making of petroglyphs was one of the most ancient and long-lived cultural traditions in aboriginal North America.

### 1. Introduction

A primary archaeological problem has involved the chronometric placement of petroglyphs (or rock engravings). These are found worldwide and are considered associated with prehistoric hunter-gatherer societies, representing the earliest stage of human cultural evolution. Geochemical analysis of the rock varnish coatings that develop within petroglyphs in western North America has enabled us to derive the first suite of calibrated dates on this form of rock art, and has provided insight into the first appearance of humans on the western hemisphere and the origins of art.

Rock varnish (sometimes called “desert varnish” or “patina”) is a coating composed of clay minerals, manganese and iron oxides, and a variety of minor and trace constituents (including organic matter). Major elemental components include O, H, Si, Fe, Al, Mn and sometimes Ca; minor elements are Ca, K, Mg, Na, Ti, Rb, Sr and sometimes Ba and Cu, with an additional 30 identified trace elements [1]. Recent research has shown rock varnish to be the metabolic product of mixotrophic manganese- and iron-oxidizing organisms; the oxides cement clay particles to a rock surface, thereby resulting in a slow accumulation of the coating on the surface over time. Trace elements are incorporated as debris in the cementation process [2], and airborne dust is the major source of the varnish constituents [3]. Cation exchange complexes are present in the illite-montmorillonite clays and manganese and iron oxides which are dominant in the varnish [4].

Although rock varnish is found in humid areas, it is most common in arid and semi-arid regions, where it frequently forms a very dark purple to black coating on exposed lithic formations, stable landforms such as pavements or talus slopes and archaeological artifacts [5]. Pecking or scratching through this dark coating exposes the typically lighter heartrock underneath, thereby providing a useful visual contrast and medium for the creation of petroglyphs. Subsequently the manganese-oxidizing micro-organisms recolonize the engraved area of the design and the varnish formation process begins again. Although the potential for using rock varnish in chronological studies has been long-recognized by archaeologists and geomorphologists, earlier research typically attempted to assess relative age by a comparison of the darkness of various varnish surfaces. While some relationship between darkness and age may hold within a limited microenvironment, color of varnish is also greatly affected by the relative abundance of manganese and iron present in a sample, with iron-rich coatings (typically developing on the underside of rocks) tending towards orange and the manganese-rich varnishes blacker in color [6].

Some variations in the microchemistry of varnish, however, are a function of time. Mn : Fe appears to vary unsystematically, but other minor elemental constituents can be used to assign ages to varnish samples, when regional changes in varnish chemistry are related to an independent time scale [7]. Specifically, we use  $(K + Ca) : Ti$  for the cation-ratio (CR) [8] dating of petroglyphs.

CR dating is based on the fact that there is a progressive lowering of the ratio of mobile to immobile cations in rock varnish over time. Over time K and Ca, for example, are removed more rapidly in the cation-exchange complexes of varnish than Ti. This lowering process can be used to provide chronometric dates by the establishment of a regional cation-leaching curve (CLC), which calibrates CRs against a numerical time scale [9]. The resulting CR dates are, therefore, minimum age estimates for the samples.

## 2. Techniques

We have dated a total of 36 petroglyphs from the Coso and Cima volcanic fields, eastern California, USA (fig. 1). Twenty of these dates are previously reported [10]. Here we revise seven of our previous Coso dates and report 16 additional dates from this region. The technique and rationale for dating these are as follows:

(i) Varnish was removed mechanically from within the engraved or pecked-out surfaces of the petroglyphs by abrasion using a tungsten needle under  $18\times$  magnification. This produced homogenized samples of varnish in powder form.

(ii) The recovered samples were then cleaned in a laboratory under  $45\times$  magnification to remove any contaminants (e.g., particles of heartrock) in the samples; and

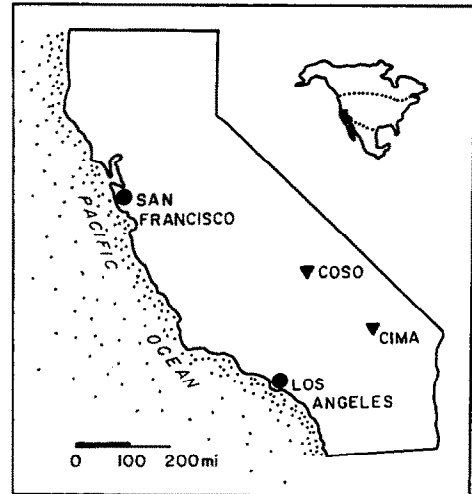


Fig. 1. Sampling locales for petroglyph dating in eastern California. Revised and new dates reported here are from the Coso Range region.

(iii) Samples were mounted on Kapton film and bulk chemical analysis was performed by the Air Quality Group, Crocker Nuclear Laboratory, University of California, Davis, using particle-induced X-ray emission analysis (PIXE) [11] to determine the (K + Ca):Ti ratios. The derived ratios, thus, represent average chemical values for each sample. Because our interest was the

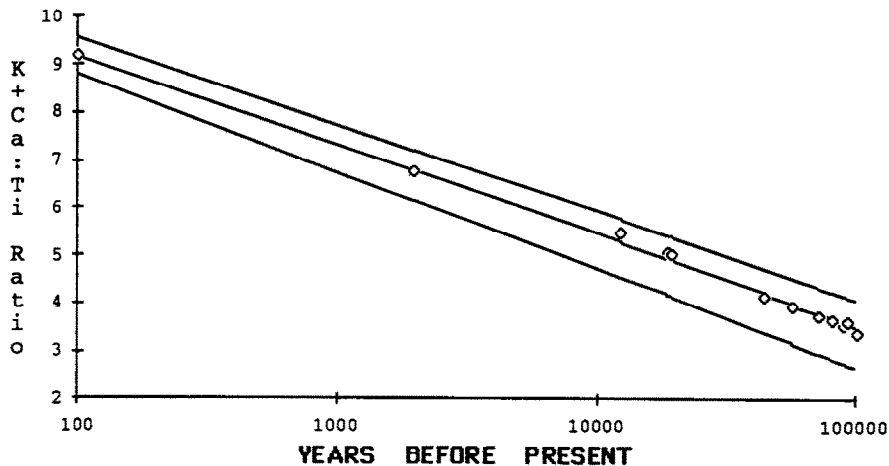


Fig. 2. Revised CLC for the Coso Range region. Calibration points on the semilogarithmic curve are listed in table 1, with this central line representing mean (minimum) age for dated samples. Outside lines represent two-sigma confidence envelope around the CLC curve, calculated using semilogarithmic least-squares regressions through the 2 SE CRs for the calibration points. The central curve is described by the following equation:

Varnish CR

$$= 12.67 - 1.76 \log(\text{AGE}); \text{ where AGE} < 12000 \text{ radiocarbon yr BP; or}$$

$$= 12.53 - 2.21 \log(\text{AGE}); \text{ where AGE} > 12000 \text{ yr BP.}$$

These two separate equations are employed to account for a slope break at approximately  $10^4$  yr BP, the Pleistocene/Holocene transition. This transition involved a major change in climatic regimes, thereby affecting cation leaching rates.

determination of relative values of K, Ca and Ti in samples in finely powdered form, no problems with sample thickness were encountered [12].

K and Ca were chosen for the ratio because PIXE gives reliable readings for these elements [13] and they are not preferentially adsorbed by iron and manganese oxides [14]. Ti was employed because of its relative immobility in arid and semi-arid environments [15]. Further, it is not affected by manganese-concentrating micro-organisms, is present in measurable quantities [16] and is also not preferentially adsorbed by iron and manganese oxides [17].

Following measurement of CRs, calibrated dates of samples were determined by comparison with a CLC. These have been related to a chronometric scale with a semilogarithmic least-squares regression, which relates CR values ( $y$ ) to years BP ( $x$ ).

Construction of a regional CLC involved, first, the collection of varnish samples from surfaces of known age. These include: (a) K/Ar dated basalt flows; (b) accelerator mass spectrometry radiocarbon dates on the basal-varnish organic material on Late Pleistocene/Holocene geological surfaces [18]; and the  $< 2 \mu\text{m}$  fraction of dust collected in aeolian traps, such as rock cracks. This last has been shown to yield a CR equivalent to an initial value. Based on SEM examination of historical surfaces the initiation of varnish growth is assigned a date of 100 yr BP [19].

These samples were, secondly, cleaned in a laboratory. Chemical analysis of the calibration samples, thirdly, was then performed with PIXE. The recently revised CLC for the Coso region, which incorporates accelerator-radiocarbon calibration points not used in the original curve, is provided in fig. 2.

Although CR dating is, thus, an empirical technique, the CLCs so far developed have provided excellent correlations between CRs, K/Ar dated basalts and accelerator-radiocarbon dated surfaces [20]. Further, they have been verified independently in the Pamirs of the Soviet Union [21], and northern New Mexico and southern Nevada, USA [22]. Because of their empirical derivation, however, a CR date is subject to whatever systematic errors might be present in the calibration technique; since the form of the CLC is a semilogarithmic least-squares regression a minor change in the CR can also have a significant effect on the calculated date [23]. Other limitations of CR dating are discussed by Dorn [24].

### 3. Results

Twenty-three revised/previously unpublished CR dates for petroglyphs from the Coso Range are provided in table 1. These range from mean (minimal) dates of 550 yr BP to 18 200 yr BP, indicating a produc-

Table 1

Calibration data (see fig. 2) for the revised Coso CLC and petroglyph dates derived from this CLC. Because several separate PIXE analyses are combined into one average for the "mean date", large errors may result from the standard errors of this combination (e.g., wp4). Further, CR dates may have asymmetrical errors due to the semi-logarithmic least-squares regression.

Calibration data			
Calibration point	Dating method	Cation-ratio	Date <sup>a)</sup> [yr BP]
Initial ratio	Historical	$9.17 \pm 0.22$	$100 \pm 0$
Fan 1	Radiocarbon	$6.81 \pm 0.16$	$1975 \pm 160$
Fan 2	Radiocarbon	$5.50 \pm 0.11$	$12300 \pm 310$
Fan 3	Radiocarbon	$5.10 \pm 0.11$	$18530 \pm 200$
Cinder conc	Radiocarbon	$5.08 \pm 0.09$	$19380 \pm 300$
Coso 26	K-Ar	$4.19 \pm 0.19$	$44000 \pm 11000$
Coso 17	K-Ar	$3.98 \pm 0.11$	$57000 \pm 16000$
Coso 4	K-Ar	$3.78 \pm 0.12$	$72000 \pm 31000$
Coso 1	K-Ar	$3.69 \pm 0.08$	$81000 \pm 8000$
Coso 25	K-Ar	$3.56 \pm 0.14$	$90000 \pm 25000$
Coso 27	K-Ar	$3.65 \pm 0.12$	$93000 \pm 26000$
Coso 6	K-Ar	$3.39 \pm 0.15$	$101000 \pm 33000$
Coso 28	K-Ar	$3.19 \pm 0.18$	$140000 \pm 40000$
Petroglyph data			
Petroglyph	Cation-ratio <sup>a)</sup>	Mean date [yr BP]	2 SE for date
cm12-bighorn	$5.11 \pm 0.06$	18200	16100–20600
cm5-abstract	$5.20 \pm 0.11$	16600	13200–20900
bss3-abstract	$5.35 \pm 0.13$	14200	10200–18600
cm8-abstract	$5.40 \pm 0.11$	13500	10100–16900
cm15-abstract	$5.44 \pm 0.05$	12900	11200–14300
cm7-bighorn	$5.52 \pm 0.12$	11500	8400–15300
bss2-abstract	$5.87 \pm 0.53$	7300	1800–24900
cm6-bighorn	$5.89 \pm 0.08$	7100	5700– 8700
cm2-bighorn	$5.94 \pm 0.09$	6600	5200– 8400
cm3-bighorn	$6.03 \pm 0.10$	5900	4500– 7600
bss1-abstract	$6.10 \pm 0.21$	5400	3100– 9300
cm4-lizard	$6.14 \pm 0.10$	5100	3900– 6600
wp4-abstract	$6.17 \pm 0.70$	4900	800–26000
cm16-abstract	$6.32 \pm 0.10$	4000	3100– 5200
wp3-abstract	$6.39 \pm 0.50$	3700	1000–13600
cm1-bighorn	$6.61 \pm 0.61$	2800	550–13600
cm10-lizard	$6.68 \pm 0.09$	2500	2000– 3200
cm9-lizard	$6.83 \pm 0.15$	2050	1400– 3100
wp1-abstract	$7.08 \pm 0.06$	1500	1300– 1750
cm13-bighorn	$7.35 \pm 0.08$	1050	850– 1300
cm11-anthrop.	$7.59 \pm 0.04$	750	700– 850
cm14-bighorn	$7.73 \pm 0.06$	650	550– 750
wp2-bighorn	$7.86 \pm 1.18$	550	300–11800

<sup>a)</sup> One standard error employed for cation-ratios and calibration points; two standard errors indicated for petroglyph dates.

tion of petroglyphs from the Late Pleistocene into the Protohistoric period. Two cultural implications can be drawn from these CR dates. First, previous impres-

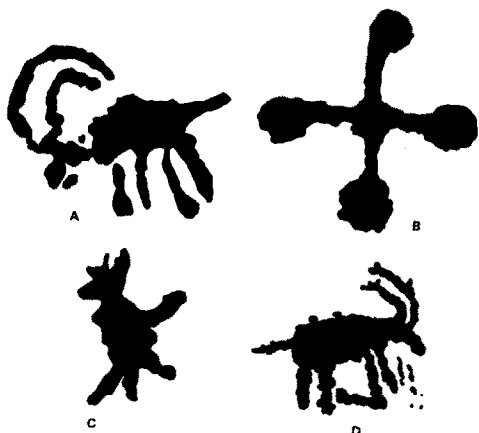


Fig. 3. Tracings of selected petroglyphs. (A) sample CM-7 (see table 1), bighorn sheep; (B) CM-15, abstract; (C) CM-8, abstract (possible zoomorph?); (D) CM-12, bighorn sheep. All motifs to same scale; maximum dimension of (B): 16.4 cm.

sionistic chronologies of North American rock art have argued for stylistic chronologies involving an evolution of art from abstract to representational forms [25]. Although four of our five oldest motifs are abstract designs, our most ancient petroglyph is a representational engraving of a bighorn sheep (*Ovis canadensis*; table 1 and fig. 3). We therefore reject the evolutionary tenets of inferentially-based stylistic chronologies on empirical grounds. Rather, we argue that the production of both abstract and representational motifs probably occurred concurrently for the duration of the art tradition, and that this tradition began approximately 20 000 yr BP.

Second, our petroglyph dates include five with mean dates greater than 11 500 yr BP, the generally accepted date for the appearance of humans in the western hemisphere [26]. In combination with CR dates on surface stone artifacts from eastern California [27], as well as recently reported radiocarbon dates from a stratified cave deposit in Brazil [28] and an open-air site in Chile [29], we feel there is increasing and compelling evidence for occupation of the western hemisphere as early as 20 000 yr BP. Further, our data support the Brazilian radiocarbon assays [30]. These were run on hearths found in stratigraphic association with cave-roof spalls containing evidence of painting, indicating that in South America as in North America, the production of rock art was one of the earliest and most long-lived cultural traditions in the western hemisphere.

Financial support was provided by NSF grant SES 86-01937. This research could not have been conducted without the kind assistance of T.A. Cahill, B. Kusko, R. Eldred, D. Shadoan, T. Gill and the entire Air Quality Group at Crocker Nuclear Lab, U.C. Davis. We thank

them for their aid in this study and our ongoing applications of CR dating. We thank the Commander, NWC China Lake, and W. Eckhardt for permission to take samples from the Coso petroglyphs; and H. Annegarn, M. Tamers, W. Wolfi, D. Dorn, D. Tanner and T.K. Whitley for assistance.

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