Stable Carbon Isotope Ratios of Rock Varnish Organic Matter: A New Paleoenvironmental Indicator

Abstract. *Stable carbon isotope ratios of organic matter in rock varnishes of Holocene age from western North America and the Middle East show a strong association with the environment. This isotopic variability reflects the abundance of plants with different photosynthetic pathways in adjacent vegetation. Analyses of different layers of varnish on late Pleistocene desert landforms indicate that the carbon isotopic composition of varnish organic matter is a paleoenvironmental indicator.*

Rock varnishes are natural accretions of manganese and iron oxides, clay minerals, trace elements, and small quantities of organic matter that form dark coatings on stable surfaces in terrestrial weathering environments (*1, 2*). Varnish in deserts is characterized by biogeochemical stability and slow rates of formation (*2, 3*), features that allow it to be used in dating (*3*) and to record fluctuations in alkalinity (*4*). We now show that stable carbon isotopic analysis of organic matter extracted from rock varnish provides paleoenvironmental and paleoecological information.

One strategy to determine whether the organic matter in rock varnish contains an environmental signal would be to sample historic varnish films and relate their isotopic compositions to recorded climate. However, varnish forms too slowly and does not contain enough organic matter to make this approach feasible (*5*). We therefore sampled thicker varnish deposits that were formed during long periods of relative climatic constancy. We chose Holocene age varnishes (*6*) because the present gross environmental regimes (desert, semiarid, or montane humid) have been well established since the early Holocene in the areas where we sampled (*7*). There is a strong correlation between local environment and the $\delta^{13}C$ values (*8*) of organic matter (*9*) in these varnish samples (Table 1). The $\delta^{13}C$ values for varnishes from arid sites range from −12 to −19 per mil [negative values represent depletion relative to PDB standard (*8*)], whereas samples from more humid locales have values around −23 per mil, with one exception that is discussed below. The $\delta^{13}C$ values for varnishes collected along two altitudinal transects also show a correlation with environment, becoming more negative as elevation increases (Table 1). Large shifts (−17.0 to −22.2 per mil at Kitt Peak and −14.8 to −22.3 per mil in the Mojave Desert) occur at elevations where the transitions from arid to more humid conditions are demarcated by vegetation changes, with desert scrub being replaced by chaparral and by sage, pinyon, and juniper.

Table 1. The $\delta^{13}C$ values of organic matter in rock varnish sampled at sites in western North America, Israel, and the Sinai Peninsula. Samples marked with an asterisk came from Holocene age landforms; unmarked samples were collected by scraping only the very surface layer from varnish deposits whose oldest layers may predate the Holocene. Negative $\delta^{13}C$ values represent depletion.

Site	$\delta^{13}C$ (per mil)
Semiarid to humid	
Galilee (Israel)	−23.5
Sunflower, northern Arizona	−22.5
Pinal, northern Arizona	−23.9
Schulman Grove, White Mountains, California	−23.9
*Lake Louis, Canada	−23.4
Alpine, west Texas	−23.1
Amistad Reservoir, west Texas	−23.6
37 km west of Davis, west Texas	−15.4
Hyperarid to arid	
*Searles Lake, California, west shoreline	−11.8
*Silver Lake, California, west shoreline	−14.1
*Timna Valley, Negev Desert (Israel)	−14.5
*Searles Lake, California, east shoreline	−15.4
*Pyramid Lake, California, north shoreline	−15.5
*Shoreline Butte, Death Valley, California	−15.6
Marsa Muqbila (Sinai Peninsula) east margin	−15.8
Salt Springs, Mojave Desert, California	−16.0
Piedmont of Gila Mountains, Arizona	−17.9
Copper Creek, talus cone, Death Valley, California	−19.3
Altitudinal-climatic transects	
Kitt Peak, Arizona	
914 m	−16.2
1219 m	−17.0
1524 m	−22.2
1890 m	−24.1
Central Mojave Desert, California	
Bristol Dry Lake, 366 m	−14.6
Clipper Valley, 817 m	−14.8
Hole-in-the-Wall, 1250 m	−22.3
Mid Hills, 1585 m	−22.7
Providence Mountains, 1646 m	−23.3

The following model can be used to explain the relation between $\delta^{13}C$ values of varnish organic matter and environment. Varnish organic matter is derived from micrometer-sized airborne plant material that accumulates on rock surfaces (Fig. 1A) (*10*). Some of this plant material is metabolized by bacteria (Fig. 1B) (*2, 11–13*), microcolonial fungi (Fig. 1C) (*13*), and other microorganisms (Fig. 1D) (*12*) that are ubiquitous inhabitants on varnish. The isotopic composition of the microbial organic matter, which is incorporated into varnish along with plant debris (*14*), is similar to that of the plant debris (*15*). The $\delta^{13}C$ values of incoming plant material reflect the relative abundance of C_3 plants versus C_4 and CAM plants (*16*) in the adjacent vegetation. Since C_4 and CAM plants are more abundant in warm arid environments than in the cool moist environments where C_3 plants predominate (*17*), $\delta^{13}C$ values of varnish organic matter reflect the local environment.

This model is supported by most of the data shown in Table 1. Varnishes from semiarid and humid sites have $\delta^{13}C$ values that reflect the dominance of C_3 plants at present and throughout the Holocene. The only exception, with a $\delta^{13}C$ value of −15.4 per mil, came from near a predominantly C_4 grassland that contains some C_3 grasses. Varnishes from arid sites have $\delta^{13}C$ values that reflect the presence of C_4 or CAM plants or both in nearby vegetation. Among these locales, those with the least negative $\delta^{13}C$ values are areas currently dominated by C_4 or CAM plants or both (for example, *Atriplex confertifolia*, a C_4 shrub, at Searles Lake), whereas those with the most negative $\delta^{13}C$ values (Salt Springs, Piedmont of Gila Mountains, and Copper Creek) are areas where the C_3 plant creosote, *Larrea tridentata*, together with some C_4 and CAM plants, make up most of the plant cover.

There are exceptions to the correlation between the abundance of photosynthetic types that make up present-day vegetation and $\delta^{13}C$ values of varnish organic matter. For example, C_3 shrubs are common now at Pyramid Lake in the western Great Basin and at Salt Springs and Clipper Valley in the Mojave Desert, but the varnishes from these localities yield C_4-CAM isotopic signatures (Table 1). Because most rock varnishes have not accumulated much organic matter since European colonization (*5*), the disparities between the $\delta^{13}C$ values of Holocene age varnish and the composition of the present plant cover may be useful in deciphering ecological changes accompanying European settlement in the New World.

Table 2. The $\delta^{13}C$ values of organic matter in different layers of rock varnish from sites in the western United States and in Israel. Negative values represent depletion.

Site	K-Ar age (10^3 years)	$\delta^{13}C$ (per mil)
Coso Range volcanic 1*	81 ± 8	
Surface layer		−19.5
Basal layer		−22.3
Cima volcanic h_1†	60 ± 30	
Surface layer		−15.3
Basal layer		−21.2
Talus Flatiron, Timna Valley, Israel‡		
Surface layer		−14.2
Middle layer		−23.5
Basal layer		−15.4
Entire varnish coat		−17.8

*Sampled from the top of a rhyolite dome (*20*). †Sampled from a basalt flow (*21*). ‡Site discussed in (*3, 18*).

To explore the possibility of obtaining paleoenvironmental information from isotopic analysis, we sampled surface and subsurface layers of varnish on late Pleistocene volcanic deposits in eastern California. The $\delta^{13}C$ values indicate the basal layers were formed under more humid conditions than the surficial layers (Table 2). These results are consistent with observations that more moist conditions occurred in the southwestern United States during the last major glacial interval compared with the greater aridity of the Holocene (*7*).

Isotopic analysis of different layers of varnish from the middle talus flatiron in a sequence of three flatirons in the Timna Valley, Negev Desert of Israel (Table 2), indicate sequential arid, humid, and arid periods. This sequence is consistent with Gerson's (*18*) climatic geomorphology model for the evolution of talus flatirons in deserts—that is, a talus cover is deposited during a long wet period and, as the environment becomes arid, erosion separates the talus cover from the talus source, producing a flatiron. At this point, varnish would have started to form on the flatiron that we sampled. The basal layer of varnish has a $\delta^{13}C$ value corresponding with this arid period. The subsequent humid and arid periods indicated by $\delta^{13}C$ values for the middle and surface layers of the varnish correspond to the climatic changes which, according to Gerson's model, would have produced the youngest flatiron at the site.

Several factors may complicate interpretation of $\delta^{13}C$ values in varnish organic matter. First, the presence of autotrophic organisms on rock surfaces could contribute organic matter whose $\delta^{13}C$ value is not related to the abundance of different photosynthetic types in the adjacent plants. Among autotrophic organisms that occur in environments where varnishes form, lichens are inimical to varnish and cyanobacteria, although oc-

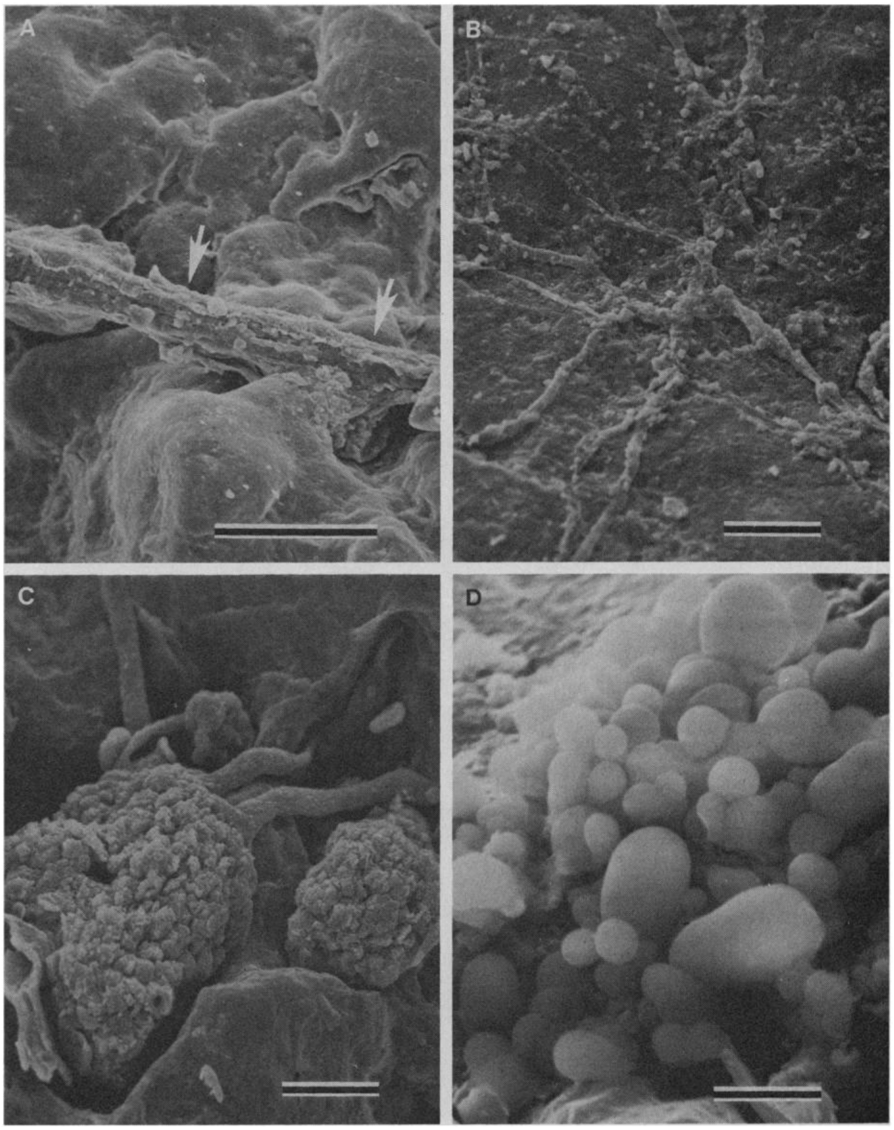

Fig. 1. Sources of organic matter in rock varnish. (A) Incorporation of organic plant detritus (arrows) into varnish from Halloran Springs, Mojave Desert. Scale bar, 50 μm. (B) Filamentous budding bacteria, perhaps *Metallogenium* (*22*), on varnish near Copper Creek alluvial fan, Death Valley. Scale bar, 5 μm. (C) Microcolonial fungi on varnish near Florence Junction, east of Phoenix. Scale bar, 10 μm. (D) Unidentified microorganism on manganese-rich varnish collected by T. M. Oberlander near Copiapo, Atacama Desert, Chile. Scale bar, 2 μm.

casionally present on varnish, are rare (*2*). Although some fungi may incorporate atmospheric CO_2 into their biomass, the microcolonial fungi commonly found on varnish seem to obtain their carbon from airborne organic matter derived from adjacent soil and vegetation (*13*). Second, certain types of plants may contribute more than their share of organic debris to the atmosphere, thus leading to bias in varnish $\delta^{13}C$ values. Third, it is possible that varnish growth is favored during seasons when organic debris is shed by plants with nonrepresentative $\delta^{13}C$ values. Finally, $\delta^{13}C$ values of CAM and C_4 plants may change in response to variations in environmental factors (*19*). Fortunately, the isotopic changes these plants experience are such that the environmental signal in varnish organic matter $\delta^{13}C$ values would be enhanced, rather than weakened, by such changes.

In conclusion, our stable isotope analyses of organic matter in rock varnish reveal that $\delta^{13}C$ values are strongly correlated with environment and that $\delta^{13}C$ values in fossil varnish reflect past environmental conditions. The abundance of plants possessing different photosynthetic pathways in adjacent vegetation governs the carbon isotopic composition of rock varnish organic matter. However, before carbon isotope ratios of varnish organic matter can be used routinely as paleoenvironmental and paleoecological indicators, the method of extracting layers of fossil varnish only a few micrometers thick must be refined.

RONALD I. DORN
Department of Geography,
University of California,
Los Angeles 90024

MICHAEL J. DENIRO
Department of Earth and Space Sciences
and *Archaeology Program, University*
of California, Los Angeles 90024

References and Notes

1. R. M. Potter and G. R. Rossman, *Chem. Geol.* **25**, 79 (1979).
2. R. I. Dorn and T. M. Oberlander, *Prog. Phys. Geogr.* **6**, 317 (1982).
3. R. I. Dorn, *Quat. Res. (N.Y.)* **20**, 49 (1983); R. I. Dorn and D. S. Whitley, *Ann. Assoc. Am. Geogr.* **74**, 308 (1984).
4. R. I. Dorn, *Nature (London)* **310**, 767 (1984).
5. Desert varnish deposits formed during the last 100 years consist of isolated patches only 1 micrometer thick. Since varnish contains less than 1 percent organic matter by weight, on the order of 10^5 cm^2 of varnish would have to be removed to provide enough organic matter for an isotopic determination. We had access to only a few historical varnished surfaces of this size in the western United States.
6. Varnish was removed from the underlying rock as described in (*3*). Temporal control was achieved by removing the entire varnish coat from landforms of Holocene age (for example, shorelines of western U.S. pluvial lakes) or by sampling only surficial varnish.
7. W. G. Spaulding, E. B. Leopold, T. R. Van Devender, in *Late Quaternary of the United States: The Late Pleistocene*, S. C. Porter, Ed. (Univ. of Minnesota Press, Minneapolis, 1983), p. 259; G. I. Smith and F. A. Street-Perrott, *ibid*, p. 190; P. V. Wells, *Ecol. Monogr.* **53**, 341 (1983); D. Neev and J. K. Hall, *Sediment Geol.* **23**, 203 (1979).
8. $$\delta^{13}C = \left[\frac{(^{13}C/^{12}C_{\text{sample}})}{(^{13}C/^{12}C_{\text{standard}})} - 1\right] \times 1000$$
   The standard is the PDB carbonate.
9. Organic matter was concentrated from varnish samples by removing manganese oxides with acidified hydroxylamine hydrochloride, iron oxides with dithionite, carbonates with HCl, and silicates with HF. Carbon isotopic composition was determined as described by D. W. Northfelt, M. J. DeNiro, and S. Epstein [*Geochim. Cosmochim. Acta* **42**, 495 (1981)].
10. Plant residues make up the primary component of organic eolian particulates collected from rural areas [B. R. T. Simoneit, M. A. Mazurek, W. E. Reed, in *Advances in Organic Geochemistry 1981*, M. Bjoray, Ed. (Wiley, New York, 1983), p. 355].
11. R. I. Dorn and T. M. Oberlander, *Science* **213**, 1245 (1981).
12. W. E. Krumbein and K. Jens, *Oecologia (Berlin)* **50**, 25 (1981).
13. J. T. Staley, F. Palmer, J. B. Adams, *Science* **215**, 1093 (1982); S. Taylor-George *et al.*, *Microb. Ecol.* **9**, 227 (1983).
14. B. R. T. Simoneit (personal communication, 1983) found mostly microbial lipids and plant residues in preliminary organic geochemical analyses of varnish from Rainbow Basin in the Mojave Desert.
15. Microorganisms cultured from varnish have not been reported to be autotrophic (*11–13*). Isotopic fractionation occurring during heterotrophic growth of varnish microorganisms is probably small, since, in laboratory culture, the $\delta^{13}C$ values of the cell masses of heterotrophic (nonvarnish) microbes are typically within a few per mil of the $\delta^{13}C$ values of their carbohydrate carbon sources [P. H. Abelson and T. C. Hoering, *Proc. Natl. Acad. Sci. U.S.A.* **47**, 623 (1961); L. O. Ingram, J. A. Calder, C. Van Baalen, F. E. Plucker, P. L. Parker, *J. Bacteriol.* **114**, 695 (1973)].
16. The C_3 plants, in which initial carbon dioxide fixation is catalyzed by ribulose bisphosphate carboxylase, have $\delta^{13}C$ values that range from −20 to −30 per mil, averaging −26 per mil; C_4 and CAM plants, in which phosphoenol pyruvate carboxylase catalyzes initial carbon dioxide fixation, have $\delta^{13}C$ values that range from −9 to −17 per mil, averaging −14 per mil [P. Deines, in *Handbook of Environmental Isotope Geochemistry*, P. Fritz and J. Ch. Fontes, Eds. (Elsevier, Amsterdam, 1980), vol. 1, p. 329].
17. H. A. Mooney, J. H. Troughton, J. A. Berry. *Carnegie Inst. Washington Yearb.* **73**, 793 (1974).
18. R. Gerson, *Israel J. Earth Sci.* **31**, 123 (1982).
19. J. H. Troughton, P. V. Wells, H. A. Mooney. *Science* **185**, 610 (1974); T. F. Neales *et al.*, *Aust. J. Plant Physiol.* **10**, 437 (1983).
20. W. A. Duffield and C. R. Bacon, *U.S. Geological Survey Miscellaneous Investigation Map I-1200* (1981).
21. J. C. Dohrenwend, L. D. McFadden, B. D. Turrin, S. G. Wells, *Geology* **12**, 163 (1984).
22. B. V. Perfil'ev and D. R. Gabe, in *Applied Capillary Microscopy: The Role of Microorganisms in the Formation of Iron-Manganese Deposits*, B. V. Perfil'ev, Ed. (Consultants Bureau, New York, 1965), p. 9.
23. We thank L. Sternberg, S. Ambrose, A. Orme, and anonymous reviewers for comments, R. Gerson and J. Dohrenwend for field assistance, B. R. T. Simoneit for organic geochemical analyses of rock varnish, and H. Ajie and D. Winter for isotopic measurements. Supported in part by UCLA and NSF grant ATM 79-24591. This report is dedicated to Bernard Annenberg, who started the first author in the ways of science.

18 October 1984; accepted 21 December 1984

Effect of Vanadate on Elevated Blood Glucose and Depressed Cardiac Performance of Diabetic Rats

Abstract. *The trace element vanadium has an unclear biological function. Vanadate, an oxidized form of vanadium, appears to have an insulin-like action. The effect of vanadate on blood glucose and cardiac performance was assessed in female Wistar rats 6 weeks after they were made diabetic with streptozotocin. When vanadate was administered for a 4-week period to the diabetic rats, their blood glucose was not significantly different from that of nondiabetic controls despite a low serum insulin. In contrast, blood glucose was increased about threefold in the diabetic rats that were not treated with vanadate; these rats also had low insulin levels. Cardiac performance was depressed in the untreated diabetic animals, but the cardiac performance of the vanadate-treated diabetic animals was not significantly different from that of nondiabetic controls. Thus vanadate controlled the high blood glucose and prevented the decline in cardiac performance due to diabetes.*

Vanadium, a trace element in the environment (*1, 2*), is found in plants and animals, but its biological function is unclear (*3*). Studies have shown that vanadium directly affects glucose metabolism (*1–7*). Tolman *et al.* (*1*) reported that vanadate stimulates glucose oxidation and transport in adipocytes, enhances glycogen synthesis in liver and diaphragm, and inhibits hepatic gluconeogenesis and intestinal glucose transport. An insulin-like effect of vanadate was also reported by other investigators (*2–7*). Vanadate can also influence cardiac performance. It induced a positive inotropic effect in the isolated rat heart (*8*) and isolated cat papillary muscle (*9*) and had a negative inotropic effect in most atria (*10*). These observations suggest that vanadate may have a role in regulating glucose metabolism and cardiac performance in vivo. We therefore investigated the possibility that vanadate can affect the elevated blood glucose concentration and depressed cardiac contraction of diabetic rats.

The animals used in this study are described in Table 1. Body weights of rats made diabetic with streptozotocin but not treated with vanadate were significantly lower than body weights of untreated controls. There was no significant difference between the weights of the two groups of vanadate-treated animals but they gained weight more slowly than did the controls; however, the dif-