LETTERS TO THE EDITOR

UNCERTAINTIES IN THE RADIOCARBON DATING OF ORGANICS ASSOCIATED WITH ROCK VARNISH: A PLEA FOR CAUTION

Ronald I. Dorn
Department of Geography
Arizona State University
Tempe, Arizona 85287-0104

With the advent of ^{14}C dating involving accelerator mass spectrometry, it has become possible to measure ages on rock surfaces. Datable material has been found associated with rock paintings (Russ et al., 1990; Valladas et al., 1992; Loy, 1993), natural coatings of calcium oxalate (Russ et al., 1996), natural coatings of silica glaze (Watchman, 1994, 1995; Stasack et al., 1996), and manganiferous rock varnish (Dorn et al., 1986; Dorn, 1994). The purpose of this paper is to warn interested readers about serious uncertainties in the radiocarbon dating of organic matter associated with rock varnish and perhaps other rock coatings.

In the case of rock varnish, a dark manganiferous coating on rock surfaces, there are many different types of organics in close spatial proximity, including fungi and lichens (Fig. 1), charcoal (Fig. 2) perhaps from rubbing on petroglyphs or perhaps from natural fires (Dragovich, 1994), and a variety of unidentified organics (Fig. 3). Organics rest on top of varnish, directly underneath, in the rock beneath, but only rarely within the coating (Dorn et al., 1992a). Usually, the material underneath the varnish is combined together to collect enough material for a radiocarbon measurement—with the assumption that the different components measure the same age (Dorn, 1994).

Over the last 10 years of accumulating ^{14}C data, I have encountered hard-to-explain anomalies. Although I reported these ages, their significance was not appreciated. For example, on the shoreline of Searles Lake, eastern California, fibrous (fungal?; Fig. 1) material yielded younger ages (13,610 ± 110, AA 2229; 13,290 ± 116, AA 2230) than did dense shiny particles with a vitrinite-like appearance after processing (25,200 ± 400, AA 2321) or a sample that contained a mixture of different forms (15,510 ± 130, ETH 12815). On the highstand of Lake Mojave, eastern California, a similar divergence occurs between fibrous (fungal?, lichen?) material (2,230 ± 45, AA 2231) and denser organics (11,630 ± 150 AA 2318). On glacial moraines at Bishop Creek, in the Sierra Nevada of California, weathering-rind samples (containing abundant denser particles) yielded ^{14}C ages of ~24,000 ^{14}C years (Dorn, 1996). As noted in the Dorn paper, these ^{14}C ages are much older than ^{36}Cl ages of ~17,000 calendar years; if anything, they should be younger. Artifact varnish entombing a charcoal-like substance yielded a ^{14}C age of 8100 ± 80

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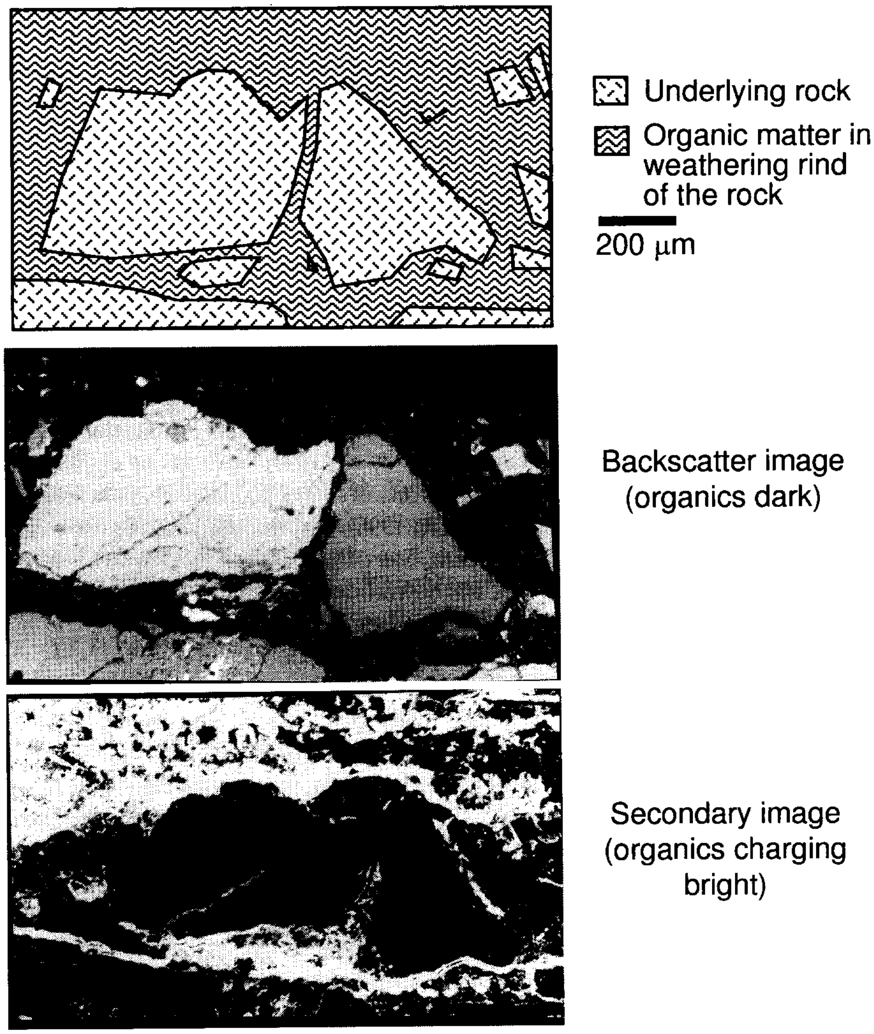

Fig. 1. Backscattered (BSE) and secondary (SE) electron microscope images of what may be a fungal mat, within the weathering rind of a cobble at the Poison Canyon high shoreline of Searles Lake, eastern California. The varnish was first polished away, and the view is from the top, looking down into the rock. Note that the organics are charging in the SE image, but are dark in the BSE image. These images appear similar to iron-coated organic matter reported by Bisdom et al. (1983).

years (ETH 13208)—over 7,000 years older than associated geoglyph ages (von Werlhof et al., 1995). A geoglyph in Chile with a historic motif yielded a ^{14}C age of ~700 years (P. Clarkson, pers. comm., 1996).

The genesis of this paper was the combination of the aforementioned anomalies and the isolation of two very serious problems identified by petroglyph research in Portugal (Dorn, 1997). However, I was able to submit this summary of my concerns only after the article on the site in Portugal had been accepted for publication.

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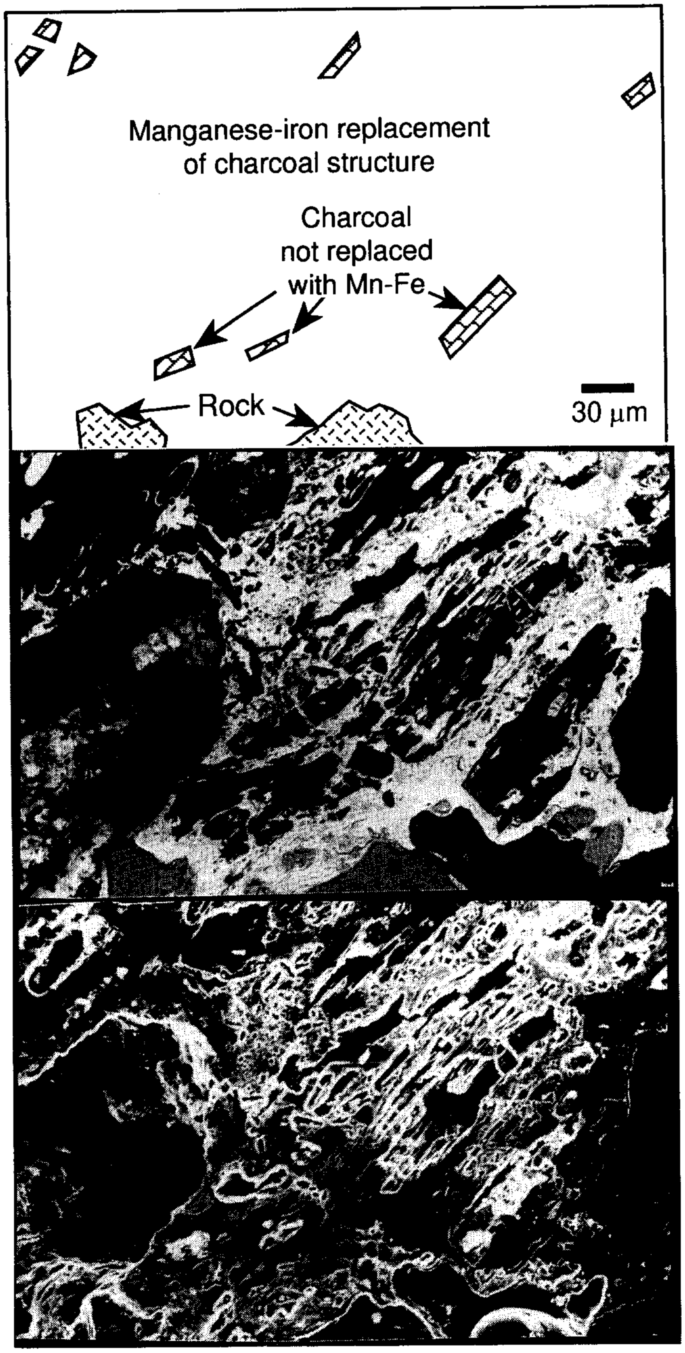

Fig. 2. Charcoal-like material underneath rock varnish on a "Kachina-face" petroglyph in Petrified Forest National Park. The middle image is BSE, revealing brighter areas of manganese and iron that have partially replaced the charcoal. The bottom image is of secondary electrons, showing a structure similar to woody tissue (cf. Goldberg et al., 1994).

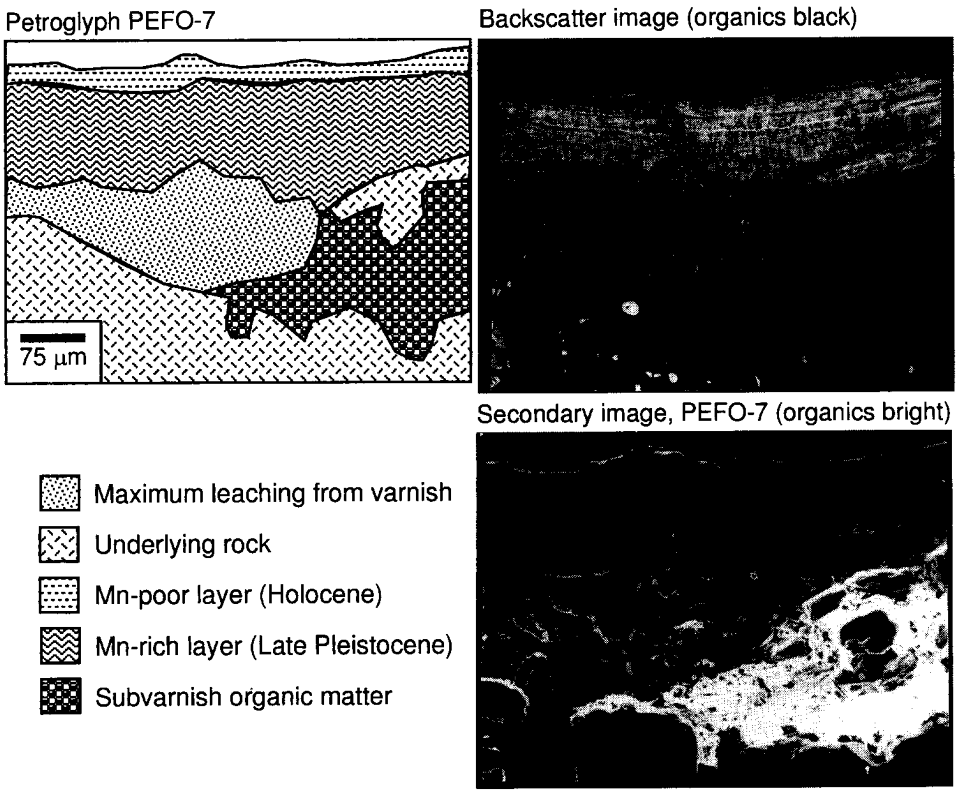

Fig. 3. The context of organic matter trapped under varnish on a grid petroglyph (PEFO-7) at Petrified Forest National Park. Although the organics are dark in BSE, they are charging and show topography with SE. When the material was mechanically scraped from the cross-section under 10–45× magnification, it shattered and the edges appeared shiny and dense, almost like vitrinite. I speculate that the organic matter underwent some diagenesis.

The first problem is that the organics in Portugal are not in a closed system; comparisons of ^{14}C and ^{36}Cl ages for the exact same surfaces reveal much older ^{36}Cl ages. This is best explained by the exchange of organic matter among the rock, the coating, and modern sources. Traditional approaches to radiocarbon dating are accurate only when the carbon decays from an initial "modern" state. In Portugal, younger organics appear to be added periodically to the weathering rinds.

The uncertainty isolated here is not knowing how to interpret the ^{14}C ages. In the case from Portugal, exchange occurs in an open system. In the aforementioned cases, material older than the last surface exposure appears to be incorporated into the dated material. The issue is: Does one try to correct for older material or for younger material? Or, can any correction by made accurately?

The second problem, suggested by the previous data but highlighted by research in Portugal, is that different materials within the same "bulk" sample can yield different ^{14}C ages. A joint face at the Penascosa site at Côa in Portugal (Dorn et al., 1996) yielded a ^{14}C age of 23,550 ± 190 years (CAMS-20498) in a bulk sample. When this bulk sample was split into dense shiny particles and less-dense granular material, the dense particles yielded a ^{14}C age (29,990 ± 240, Beta 86633) older than that of the less-dense organics (17,460 ± 460, Beta 86632).

Materials of different age in the same sample could result from mixing organics at the interface of the varnish and the underlying rock (Dorn et al., 1992a), organics in the weathering-rind (Bonani et al., 1988; Soleilhavoup, 1992), and carbon (e.g., graphite) in the rock itself (Timofeyev et al., 1980). The mixing of different types of organics could explain why basalt flow ^{14}C ages correspond with independent age controls (Dorn et al., 1992b), while the aforementioned examples are more difficult to interpret. Basalt flows have low concentrations of carbon within the rock, and they have not experienced organic weathering prior to their extrusion. In contrast, other samples may have been exposed to a complex history of organic interactions. Organic remains are ubiquitous—even well beneath the earth's surface (Krumbein and Dyer, 1985; Fyfe, 1996).

A mixture of different ages in the same sample could also be from mixing material with different diagenetic histories. In other words, there may be pulses of insertion for organics, followed by alteration. Diagenesis of organic matter associated with rock varnish and other rock coatings could be catalyzed by the manganese mineral birnessite (Wang and Lin, 1993, by clays (Mayer, 1994) in combination with high temperatures on rock surfaces (Collins et al., 1995), or by iron and other heavy metals that occur in varnish (Jones and Jarvis, 1981; Bisdom et al., 1983; Ertel and Hedges, 1984; Bird et al., 1994).

This speculation on diagenesis only highlights the poor state of knowledge on the organic geochemistry of rock varnish. The $\delta^{13}C$ values of varnish-associated organics are in the range of terrestrial plant material (Dorn and DeNiro, 1985), but these organics remain largely uncharacterized—other than by morphological microscope studies (e.g., Figs. 1–3). Preliminary gas chromatography–mass spectrometry (GC-MS) analyses by B.R.T. Simoneit (pers. comm., 1983, 1988) reveal *n*-fatty acids from microbial residues, refractory organics of plant origin, *n*-alkanes, and other material. The GC-MS analyses of varnish-associated organics did not show significant differences between different altitudes, ages, or geographic locations.

The conclusion is that the interpretation of radiocarbon ages associated with rock varnish is unclear, and there may be similar problems associated with other rock coatings. I still hope that it may be possible to obtain reliable ages in the future. That effort, however, must be based on a careful characterization of different types of organic matter associated with rock varnish. In addition, the ages of different types of organics must be measured where there are independent age controls, and in blind tests.

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