sediments, but came from some point on the surrounding basin slope.

The existence of the Orca brine in an open continental slope setting is a phenomenon that can provide an in situ laboratory for testing and developing physical and geochemical models, and its availability and ease of sampling should facilitate future work in these areas. Recent articles on the long-range potential of salt gradients for use in both electrochemical concentration cells and osmotic pumps as energy sources (*12*) indicate a potential economic importance for the Orca brine. Furthermore, it is possible that similar conditions exist in other areas of the northern Gulf of Mexico or elsewhere in the world's oceans. Efforts to locate such occurrences could be greatly aided by use of the seismic technique employed in this study.

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Desert Varnish: The Importance of Clay Minerals

Abstract. *Desert varnish has been characterized by infrared spectroscopy, x-ray diffraction, and electron microscopy. It is a distinct morphological entity having an abrupt boundary with the underlying rock. Clay minerals comprise more than 70 percent of the varnish. Iron and manganese oxides constitute the bulk of the remainder and are dispersed throughout the clay layer.*

Desert varnish is a dark, manganese- and iron-rich coating up to 100 μm thick, which occurs on exposed rock surfaces in dry regions. Associated with this dark coating is an orange coat, which develops in contact with soil on the bottom of desert pavement stones. Detailed physical descriptions of these phenomena are found elsewhere (*1*).

Desert varnish is important not only for its widespread occurrence and, at times, striking appearance, but also for its possible application to relative age dating. Previous studies have been concerned with field observations, bulk chemistry, and chemical variation within the varnish (*1–3*), yet the mechanism of varnish formation remains uncertain, and it is still not possible to use varnish with confidence for dating (*4*). The detailed mineralogical and structural information on which formation theory and dating techniques might be reliably based is unavailable. This report presents the results of the application of infrared spectroscopy, x-ray diffraction, and electron microscopy to such a mineralogical and structural characterization of desert varnish.

We collected varnished rocks of diverse lithology from localities in the Mojave Desert, California, which were previously studied in detail (*1*). Milligram quantities of varnish were scraped from the rock surface with a tungsten needle under × 20 magnification. A comparison of the infrared patterns of varnish and of its underlying rock indicates a minimum sample purity of 93 percent, based on the intensity of quartz bands near 800 cm^{-1}. Samples for in situ examination were millimeter-sized chips broken from larger samples and examined at × 40 to ensure an undisturbed surface.

Sheet silicate absorption dominates the infrared spectra of desert varnish. The spectra of the black and orange coats shown in Fig. 1 are representative

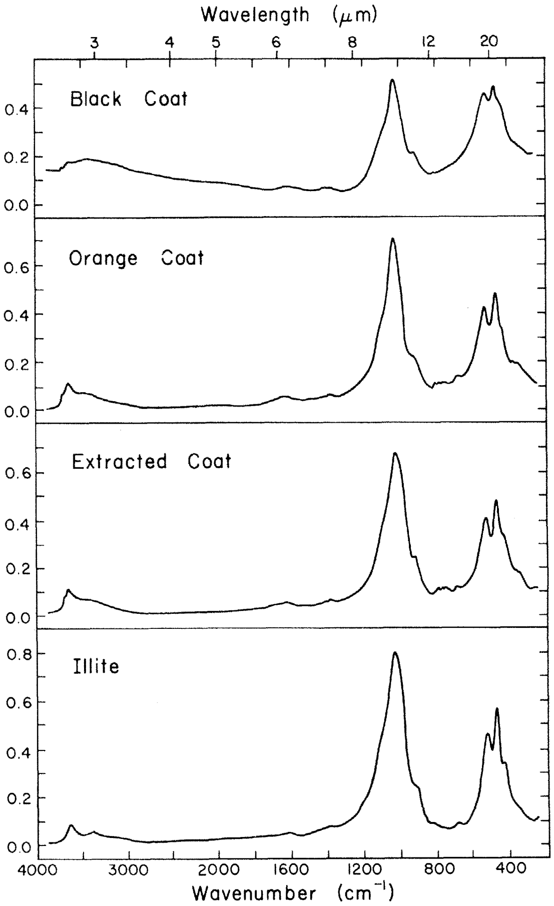

Fig. 1. Infrared spectra of desert varnish showing major features attributable to clay minerals. The spectrum of an illite standard (*16*) is included for comparison. A 0.5-mg portion of powdered sample was dispersed in a 200-mg KBr pellet, 13 mm in diameter, which was heated to 100°C under vacuum to remove water adsorbed on the KBr.

for varnish on all lithologies studied. The spectrum of the extracted coat is representative of varnish after iron and manganese oxides were removed by sodium dithionite (*5*). The major peaks occurring at 3620, 1030, 530, and 470 cm^{-1} arise from illite, montmorillonite, or mixed-layer illite-montmorillonite (*6*).

Studies of reference clays (*7*) and their mixtures place an upper limit of 20 percent on the amount of discrete octahedrally substituted montmorillonite present in the varnish clays; however, we found infrared spectroscopy insensitive to the illite/montmorillonite ratio in mixed-layer clays (*8*). Peaks not due to these clay minerals are attributable to water (3400 and 1625 cm^{-1}), quartz (800, 400, and 370 cm^{-1}), and kaolinite (3700 cm^{-1}). The spectra of the orange coat do not differ significantly from that of extracted varnish. Spectra of the black coat show decreased resolution in the region 800 to 400 cm^{-1} due to absorption by ferromanganese oxides.

X-ray diffraction patterns of dithionite-extracted varnish oriented by sedimentation from water suspension indicate that varnish clay contains major amounts of discrete illite and mixed-layer illite-montmorillonite with small amounts of kaolinite and, in some instances, chlorite (*9*). The patterns of the unextracted varnish have a weak kaolinite peak at 7 Å and a broad band with maximum intensity in the region 11 to 14 Å. A 10-Å illite shoulder is generally visible on this band. The diffuseness of the pattern of unextracted varnish accounts for previous reports that varnish is x-ray amorphous (*1*, *10*). The orange coats show some expansion after glycolation; with the black coats, little or none occurs. The influence of the manganese and iron oxides on clay expansibility requires that they be located either in the interlayer position or as an external coating on the clay particles. It seems likely that the oxides are present mainly as external coatings. Iron oxides associated with expandable clays are known to favor the external position (*11*), and the presence of manganese or iron oxides in the interlayer position would require a basal spacing of 14 Å or more.

The major element composition of desert varnish was determined by electron microprobe analyses of varnish surfaces of high natural polish before and after removal of the oxides by sodium dithionite. Normalization of the cations on the basis of ten oxygens and two hydroxyls gave the following sheet silicate formula representing the average composition of the complex clay mixture in extracted varnish (*12*): $\mathrm{Na_{0.2}K_{0.3}(Al_{1.6}Mg_{0.3}Fe_{0.2})(Si_{3.5}Al_{0.5}O_{10})(OH)_2}$. The oxide content of the untreated varnish surfaces was calculated by subtracting the clay components from the chemical analyses, assuming that all the silicon was present in clay of the overall composition found in the extracted varnish. The orange coat gave a residue of approximately 10 percent, consisting predominantly of iron (*13*). The black coats gave residues of approximately 30 percent, consisting of manganese and iron in a variable ratio with small amounts of other elements (*14*). Clays thus comprise at least 70 percent of the varnish material.

Scanning electron microscopy of the desert varnish surface showed no evidence of crystallinity to the 100-Å resolution of the instrument. The surface views shown in Fig. 2 are characteristic of desert varnish surface morphology. In transverse view, varnished rocks have a coating with fabric parallel to the rock surface and morphology distinct from that of the rock (Fig. 2, A and C). This coating is the varnish itself, not a general weathering feature in which the varnish is found. This can be seen most clearly on quartz, where dendritic growths of varnish have abrupt, easily visible boundaries. Identification of these boundaries in the light microscope followed by examination in the electron microscope (Fig. 2B) shows that varnished areas are associated with the surface layer seen in transverse view (Fig. 2C). The unvarnished areas (Fig. 2D) show a relatively clean surface.

No change in thickness of the varnish coating was measurable in the electron microscope after the oxides were extracted with sodium dithionite. This indicates that the bulk of the oxides are dispersed throughout the clay layer rather than present as a local concentration at the surface. In the samples we studied there is no evidence of the oxide-rich layer which Hooke *et al.* (*3*) reported for some of their samples.

This mineralogical and structural description of desert varnish suggests several features that may be important in its

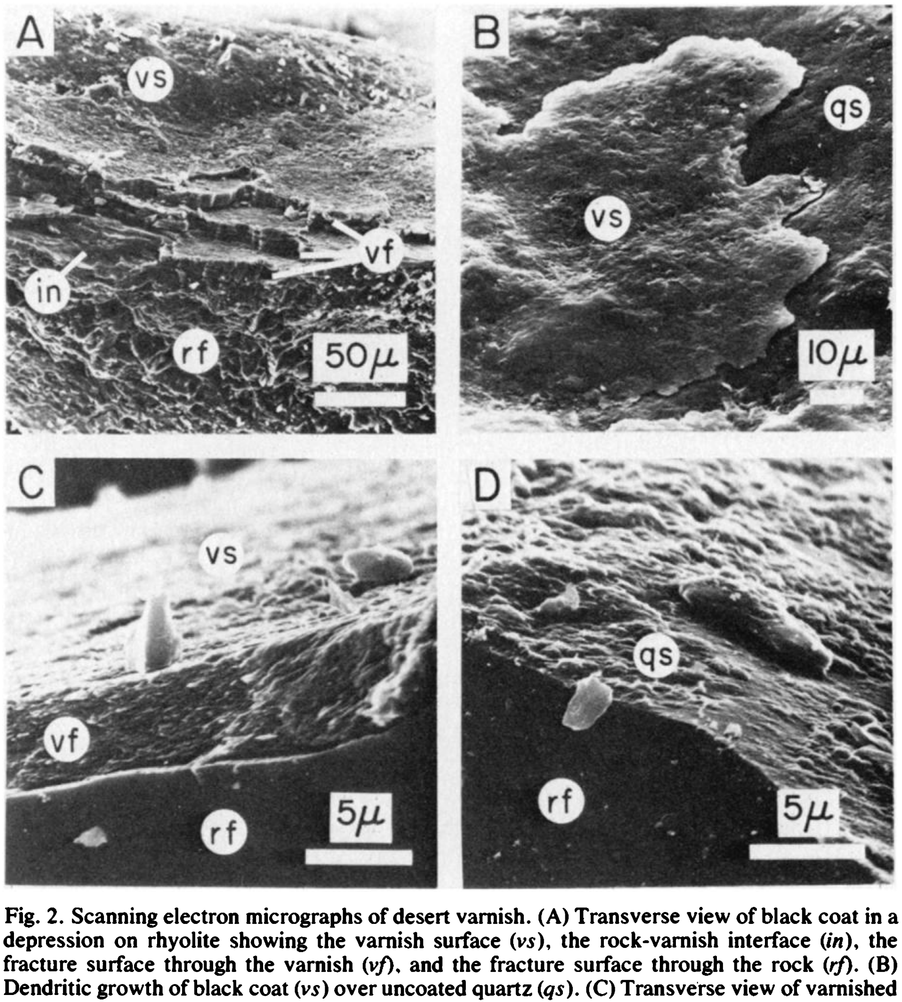

Fig. 2. Scanning electron micrographs of desert varnish. (A) Transverse view of black coat in a depression on rhyolite showing the varnish surface (*vs*), the rock-varnish interface (*in*), the fracture surface through the varnish (*vf*), and the fracture surface through the rock (*rf*). (B) Dendritic growth of black coat (*vs*) over uncoated quartz (*qs*). (C) Transverse view of varnished quartz showing the varnish surface (*vs*), the fracture surface through the varnish (*vf*), and the fracture surface through the quartz (*rf*). (D) Transverse view of unvarnished quartz showing the weathered surface (*qs*) and the fracture surface through the quartz (*rf*).

formation. The abrupt morphological demarcation of varnish from rock indicates that varnish material is derived from sources external to the rock. On coarsely crystalline quartz none of the varnish material can be due to alteration of the underlying rock. The presence of a variety of clay minerals precludes direct synthesis from solution. Thus, the clay must be transported to the rock surface. The dependence of varnish development on the porosity and surface roughness of the underlying rock (*1*) may reflect the importance of capillary movement of water in clay transport. Wind transport of clays may be significant in varnishing of outcrop exposures where large distances make water transport unlikely. In this case, moisture might influence retention of windborne clays.

Clay may be an active agent in desert varnish formation. It may serve as a medium for capillary movement of varnishing solutions. Deposition of the ferromanganese oxides within the clay matrix could then cement the clay layer. The clay may aid in the deposition. Illite is known to fix manganese under the *p*H and oxidation-reduction conditions at which varnish forms (*15*). In this way the clay and oxide phases may be mutually dependent: the clay depending on the oxides for resistance to erosion; the oxides depending on the clay for transport and deposition. This would explain why neither pure clay nor pure ferromanganese oxide coatings are associated with desert varnish.

Infrared analyses of varnish from diverse localities in Arizona and New Mexico indicate that our varnish characterization from the Mojave Desert can be generalized to these areas.

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12. Although 0.2 sodium atom per 12 oxygens was present in the extracted varnish, there was negligible sodium in the untreated varnish. We assume that the sodium was introduced in the extraction procedure.
13. The percentage composition of the residue was: Fe_2O_3, 65; H_2O, 24; CaO, 7; K_2O, 2; and MgO, 2.
14. The Mn/Fe ratio varied from 10:1 to 2:1; the typical percentage composition of the residue was: MnO_2 + Fe_2O_3, 69; H_2O, 20; BaO, 4; Al_2O_3, 3; CaO, 3; and MgO, 1.
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Great Lakes Eutrophication: The Effect of Point Source Control of Total Phosphorus

Abstract. *A mathematical model of the Great Lakes total phosphorus budgets indicates that a 1 milligram per liter effluent restriction for point sources would result in significant improvement in the trophic status of most of the system. However, because large areas of their drainage basins are devoted to agriculture or are urbanized, western Lake Erie, lower Green Bay, and Saginaw Bay may require non-point source controls to effect significant improvements in their trophic status.*

Accelerated eutrophication, resulting primarily from phosphorus additions due to human activities, is generally regarded as one of the major causes of the deterioration of the Great Lakes water quality (*1*). The governments of Canada and the United States recognized this fact in the Great Lakes Water Quality Agreement between the two countries signed by Prime Minister Trudeau and President Nixon in April 1972. This agreement requires that the phosphorus concentration of effluents from all large municipal waste treatment plants discharging into Lake Erie or Lake Ontario or the international section of the St. Lawrence River be limited to 1 mg/liter (*2, 3*).

Recently, the International Joint Commission, the unitary body set up by the two countries to consider problems related to the boundary waters, suggested carrying this limitation a good deal further. In their *Fourth Annual Report on Great Lakes Water Quality* (*4*), that body recommended to the governments involved that the 1 mg/liter effluent limitation be extended to all point source discharges of phosphorus throughout the entire Great Lakes system.

Implementing a limitation of 1 mg/liter for the point discharges around the Great Lakes is a multibillion dollar proposition. Thus, it is of great interest to determine what changes in water quality can be expected from the imposition of such a limitation. A mathematical model of the total phosphorus budgets for the Great Lakes has been developed that can address this question (*5*).

The model is generally based on Vollenweider's phosphorus loading concept (*6*), the major premise of which is that a lake's trophic state is primarily determined by its phosphorus levels. Recent evidence has lent strong support to this assumption (*7*). While the phosphorus loading concept is typically represented by graphical correlations, the present model takes a more mechanistic approach. As a detailed description of the present approach is published elsewhere (*5*), only a brief overview is given here.

The basic forcing functions of the model are variables, such as population and land use, which represent human activities in each drainage basin. A waste source submodel uses empirical relationships to translate these variables into phosphorus loadings. At present, three categories of waste sources of total phosphorus are considered: domestic sources, land runoff, and atmospheric inputs (*8*).

Domestic sources are the sewered waste water from residences, businesses, and institutions and are primarily due to human waste and detergents. The phosphorus load from domestic sources is computed as a function of human population multiplied by per capita loading factors for both human waste and detergents. The amount of removal achieved