Oxidation State of Manganese in Rock Varnish

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Rock varnish is generally understood to be a 5-500 micrometer thick nanostratigraphic coating consisting of approximately 70% clay glued together by 30% iron and manganese oxides, which forms on the surfaces of rocks in most semi-arid to hyper-arid climates. Many investigators believe that manganese exists in rock varnish mainly as birnessite, and that varnish has at least a partial biological origin because of the relative abundance of manganese. We have investigated the oxidation state of manganese in rock varnishes from Cima, CA and Parker, AZ. Localized X-ray absorption spectra and chemical maps were obtained using the "Spectromicroscope for PHotoelectron Imaging of Nanostructures using X-rays" (SPHINX), a PEEM III instrument (Elmitec Gmbh, Germany) installed on the High Energy Resolution MONochromator (HERMON) beamline of the Synchrotron Radiation Center in Stoughton, WI [1]. L-edge spectra were obtained for a variety of different Mn oxide minerals of different oxidation states, including a synthetic birnessite. Comparison of the L-edge spectra collected from the two rock varnishes with reference spectra demonstrates that the manganese phase in the varnish is MnO opposed to birnessite as previously shown using the K-edge [Fig. 1] [2]. The presence of Mn$^{2+}$ instead of Mn$^{3+}$ and Mn$^{4+}$ would appear to indicate that the Mn in these varnishes is deposited by abiological means.

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References
