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STXM-NEXAFS: applying a new technique which helps to unravel the mystery of rock varnish

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Rock varnish is a black shiny layer on rock surfaces, present on slowly weathering rocks, independent of their lithology. Its main components are poorly crystallized Mn and Fe oxides and clay minerals. The latter are thought to be dust particles that have accumulated in this sedimentary structure over time. The genesis of rock varnish has been a matter of debate since its first description in 1812[1]. This material, which can be applied as paleoclimate archive, grows only micrometers per thousands of years and only up to an overall thickness of approximately 250 µm. Consequently, techniques resolving nanometer structures are necessary to observe the information about the past.

In this study, scanning transmission X-ray microscopy – near-edge X-ray absorption fine structure spectroscopy (STXM – NEXAFS) on focused ion beam (FIB) ultra-thin sections (100-200 nm thickness) was used. The FIB Ga^+-ion sputtering (milling) was performed using an FEI Nova600Nanolab dual-beam instrument. The STXM–NEXAFS analysis was conducted using two X-ray microscopes: (1) the instrument at beamline 5.3.2.2[2] at the Advanced Light Source, Berkeley, CA, USA and (2) the MAXYMUS at beamline UE46-PGM-2[3] at the synchrotron BESSY II, Helmholtz-Zentrum Berlin, Germany. Both instruments are equipped with a high energy resolving grating, a Fresnel zone plate providing a spatial resolution of up to 30 nm, and phosphor-coated Lucite photomultiplier tubes for the detection of transmitted photons. Data were evaluated with the Interactive Data Language (IDL) widget "Analysis of X-ray microscopy Images and Spectra" (aXis2000).

With STXM-NEXAFS, nanometer structures can be observed by element distribution mapping[4]. Sensitivity for functional groups and moieties might in addition provide an answer to the genesis of rock varnish (i.e., biogenic vs. abiogenic). Furthermore, oxidation states of elements such as Mn and Fe can be investigated to receive information about the nanocrystalline matrix-minerals of this material. Investigating the FIB sections, layered sequences of Mn- and Fe-rich were observed, which are thought to represent wet and dry climate episodes[5]. Element abundance changes in layers, such as for K and Ca, might display changing dust compositions over time. Cavities in the underlying rock, lined by Mn and Fe, are evidence for dissolution processes and case hardening. Furthermore, variations were observed within varnishes from different landforms, indicating diversity within the varnish genesis. Measurements of South African and urban sandstone varnishes by STXM showed varnishes without layered sequences, which have a Mn- and Ca-rich matrix, where Fe is only present in enclosed mineral particles. Thus,

STXM-NEXAFS results provide detailed insights, but to solve the mystery of rock varnish, a combination of microanalytical techniques is required, since no single technique is able to provide all essential information on its own.

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