

## STXM-NEXAFS and fs LA-ICP-MS Investigations of Rock Varnish

MACHOLDT, D.S.<sup>1,2\*</sup>, PÖHLKER, C.<sup>1</sup>, FÖRSTER, J.D.<sup>1</sup>, WEBER, B.<sup>3</sup>, KILCOYNE, A.L.D.<sup>4</sup>, WEIGAND, M.<sup>5</sup>, MÜLLER, M.<sup>6</sup>, LIEBERWIRTH, I.<sup>7</sup>, JOCHUM, K.P.<sup>2</sup>, KAPPL, M.<sup>6</sup>, HAUG, G.<sup>2</sup>, AND ANDREAE, M.O.<sup>1,8</sup>

- <sup>1</sup> Climate Geochemistry Department, Max Planck Institute for Chemistry, Mainz, Germany  
\*email: d.macholdt@mpic.de
- <sup>2</sup> Biogeochemistry Department, Max Planck Institute for Chemistry, Mainz, Germany
- <sup>3</sup> Multiphase Chemistry Department, Max Planck Institute for Chemistry, Mainz, Germany
- <sup>4</sup> Lawrence Berkeley National Laboratory, Berkeley, CA, US
- <sup>5</sup> Modern Magnetic Systems Department, Max Planck Institute for Intelligent Systems, Stuttgart, Germany
- <sup>6</sup> Physics at Interfaces Department, Max Planck Institute for Polymer Research, Mainz, Germany
- <sup>7</sup> Physical Chemistry of Polymers Department, Max Planck Institute for Polymer Research, Mainz, Germany
- <sup>8</sup> Geology and Geophysics Department, King Saud University, Riyadh, Saudi Arabia

Rock varnishes are black layers of unknown genesis, occurring on rock surfaces of slowly weathering rocks, independent of their lithology. Its main components are poorly crystallized Mn and Fe oxides and clay minerals. This sedimentary material, applicable as paleoclimate archive, accumulates micrometers per thousands of years and grows up to a thickness of approximately 250  $\mu\text{m}$ .

Consequently, femtosecond laser ablation-ICP-MS and STXM-NEXAFS are suitable  $\mu\text{m}$ - and nm-resolving techniques to obtain information about previous climate changes and potential biological signals.

A 200 nm-fs LA-ICP-MS was chosen for high-spatial-resolution geochemical analyses. STXM-NEXAFS analyses were conducted on focused ion beam ultra thin sections (100-200 nm) and microtome slices using the X-ray microscopes at beamline 5.3.2.2 at the Advanced Light Source, Berkeley, CA, USA, and MAXYMUS at beamline UE46-PGM-2 at BESSY II, Helmholtz-Zentrum Berlin, Germany.

Rock varnishes, which cannot be distinguished based on their morphological appearance, differ by their constituent elemental mass fractions, e.g., of Mn, Fe, Ni, Co, Ba, and Pb, and their REE patterns. Dust particles, internal structures such as layers of Mn-, Fe-, Ca-, and C-rich material, layer-free varnishes from non-arid environments, and cavities lined by Mn, C, and Fe were observed in varnishes from different regions in the world.