Highly resolved Mn/Fe microanalyses in desert varnish for paleoclimate reconstruction

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Desert varnish is a dark and thin (< 250 µm) layer on rock surfaces. The main components are Mn and Fe oxides as well as clay minerals. We investigated the structure at the nm scale to test whether desert varnish is suitable as an archive for paleoclimate information. For these investigations we used femto- and nanosecond LA-ICP-MS and the results of STXM with FIB milled ultra-thin sections [1]. Samples came from Mojave Desert (California), Death Valley (California), Negev Desert (Israel), Knersvlakte (South Africa) and Yatib (Saudi-Arabia).

Special settings of the LA-ICP-MS system have to be applied for the high resolution measurements, such as a small fluence of about 0.2 J cm^{-2} for low sample ablation and the Escan mode of the Thermo Element2 mass spectrometer for fast measurements, a mass resolution of 2000 for the separation of interferences from the ions of interest using a flat top peak as well as small spot sizes of 12 µm for high spatial resolution. Using these conditions it was possible to measure Mn/Fe ratios with a precision better than 1 - 3 % (RSD) at a resolution of 10 nm in samples from Death Valley, covering a 15 µm thick varnish layer and about 5 µm of the host rock. Our results demonstrate significant variations of Mn/Fe ratios between less than 0.1 at the surface and 1.6 in the interior, caused by microlamination of Mn- and Fe-rich layers. This is confirmed by the investigation of FIB slices, where ~0.2 µm thick layers of Mn-, Fe- and C-rich material were found in Californian desert varnish samples [1]. In these, low and high Mn/Fe ratios may be related to dry and wet climate [2].

[1] Macholdt et al. (2015) *Chem. Geol.,* subm. [2] Liu and Broecker (2013) *Geomorphology* **187**, 38-60.