

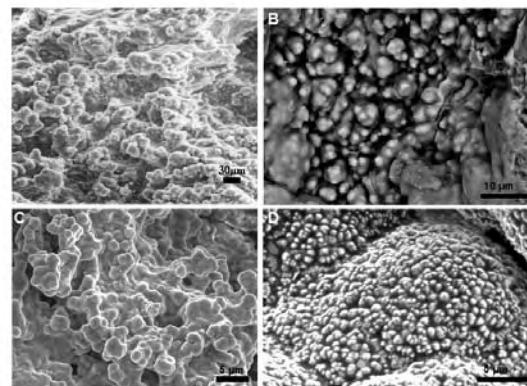
**NEW INSIGHTS INTO NATURAL RECORDERS OF PLANETARY SURFACE ENVIRONMENTS: THE ROLE OF SILICA IN THE FORMATION AND DIAGENESIS OF DESERT VARNISH AND SILICEOUS SINTER.** R. S. Perry<sup>1</sup> and B.Y. Lynne<sup>2</sup>, <sup>1</sup>Impacts and Astromaterials Research Centre, South Kensington Campus, Imperial College, University of London, London, SW7 2AZ, U.K. and Planetary Science Institute, 6920 Roosevelt Way NE 177, Seattle, WA 98115, U.S.A., r.perry@imperial.ac.uk, rsp@psi.edu <sup>2</sup> University of Auckland, Geology Department, Private Bag 92019, Auckland, New Zealand, b.lynne@auckland.ac.nz

Desert varnish and siliceous sinters form in extreme environments and silica plays a significant role in the formation and diagenesis of both. Desert varnish forms coatings ( $\sim 200 \mu\text{m}$  thick) on rock surfaces [1] as silica is dissolved by water from rain, dew or fog. The varnish source materials are primarily airborne dust including detrital grains of silicates and amorphous silica present in soils. While many silicates at low temperature are not generally thought to be soluble, their solubility is particle-size dependent. For example, three micron-sized grains approach 0.1% solubility at 38 °C [2] and solubility begins to increase as pH approaches 9 [3]. Amorphous silica present in soils, colloidal silicates and paracrystalline opal (A/CT, CT, and C) is more readily soluble than silicate detrital grains such as quartz and feldspars. As the water evaporates in micro-sedimentary basins on rock surfaces, pHs rise and increasing amounts of silica are brought into solution until saturations reach levels where polymerization begins and small amounts of silica are deposited [4]. Desert varnish forms where daytime air temperatures can be elevated to  $> 40^\circ\text{C}$  and rock surfaces reach temperatures  $> 60^\circ\text{C}$  [4]. Sinters are hot-spring deposits and form as near-neutral alkali chloride waters discharge at the surface. As the thermal fluids cool to  $< 100^\circ\text{C}$ , silica precipitates [5]. The polymerization process coats and entombs all biotic and abiotic components within the spring water such as microbes, pollen, plant and sinter fragments. In the same way desert varnish entombs soil material, detrital grains and microbes [6] making both rock types valuable environmental recorders. Although sinters form rapidly and desert varnish forms over hundreds to thousands of years, both materials probably preserve paleoenvironmental biosignatures by similar mechanisms.

As with any rock type, mineralogical changes occur with time. Desert varnish experiences natural weathering, due to its slow formation process and exposure to changing environmental conditions such as hot baking temperatures and cool desert nights. Sinters undergo silica phase transformations during diagenesis from opal-A to opal-A/CT to opal-CT to opal-C and ultimately to microcrystalline quartz [7,8]. We surmise that desert varnish and other silica glazes

also undergo similar phase changes. However, the initial source of silica for each organomineral [10] rock type varies. Direct deposition of silica carried in thermal fluids results in sinter deposits. Dissolution of soil minerals, plant (and microbial?) [6] biominerals and previously formed desert varnish, with subsequent reprecipitation of silica as opal-A, results in desert varnish.

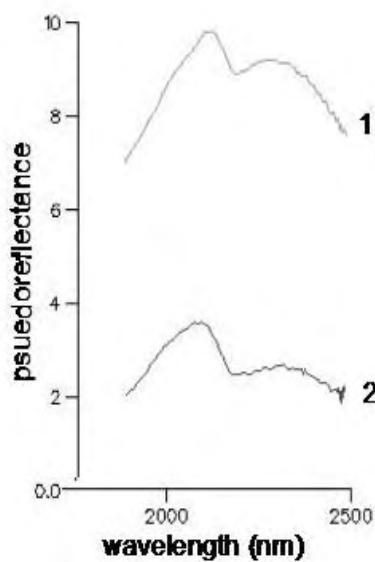
A preliminary comparative study revealed similarities between desert varnish and siliceous sinter (Figs. 1 and 2). Desert varnish samples were from Death Valley and the Mojave National Preserve, California, U.S.A. Opal-A sinter samples were from Opal Mound, Roosevelt Hot Springs, Utah, U.S.A., Steamboat Springs, Nevada, U.S.A. and the Wairakei Power Plant drain, Taupo Volcanic Zone, New Zealand [7,11].



**Figure 1.** SEM images of desert varnish from the Sonoran Desert north of Phoenix, AZ (Plate A) and Death Valley, CA, U.S.A. (Plate B). Botryoidal structures enlarge, coalesce, and are succeeded by new mounds as varnish accretes. SEM images of siliceous sinter from Steamboat Springs, NV, U.S.A., core depth 21' 2" (Plate C) and 37' 1" (Plate D).

Desert varnish and sinter samples were analyzed by X-ray powder diffraction analysis (XRPD), laser Raman microscopy, infrared spectroscopy and scanning electron microscopy (SEM). All samples were found to contain opal-A silica. All XRPD traces

revealed characteristic opal-A broad bands with points of inflection around 15 and 30 degrees  $2\theta$  [7,8,11]. The lower maximum intensity traces produced for the desert varnish samples are due to iron content and are comparable to iron-rich sinter samples. Laser Raman analyses produced similar shaped patterns indicating the presence of silica in sinter and desert varnish coatings. These patterns appear to be characteristic of opal-A and differ from other amorphous silica-rich materials such as glass. Infrared spectroscopy of sinter and desert varnish produced different shaped spectra through the 0 – 1400 nm wavelengths but from 1400 to 2500 nm similar shaped spectra were recorded with nearly identical water features e.g. 2250 nm (Fig. 2). Typical infrared spectra for opal-A sinters show a broad depression centered at 2250 nm. Desert varnish samples revealed almost identical patterns to opal-A sinters. Sinter samples consisting of other silica phases (opal-CT or quartz) produce different shaped infrared spectra. SEM observations of siliceous sinter (Fig. 1) reveal that opal-A morphology consists of microspheres up to 5 microns diameter [7,8,11]. Initial deposition of opal-A silica in sinters results in the formation of spheres, which coalesce with time. SEM observations of desert varnish (Fig. 1), however, show coalesced silica areas draped on botryoidal structures, rather than spheres. These results suggest that silica plays a similar role in the formation and diagenesis of both rock types.



**Figure 2.** Infrared spectra of similar water features at 2250 nm in desert varnish (1) from Death Valley, CA, U.S.A. and siliceous sinter (2) from Opal Mound, Roosevelt, UT, U.S.A.

In the search for the origin of life on Earth and other planets, hydrothermal environments have been implicated as possible sites where early life began [12] and it has been suggested that desert varnish-like rock coatings also exist on Mars [13]. This makes the preservation potential of biological signatures in these rock types of great interest. The role of silica in silica glazes such as desert varnish has only recently been suggested [4,14,15] as has the silica phase diagenetic transformations of sinters. If rock glazes follow similar diagenetic pathways to sinter, it is important to understand how biosignatures within them could be overprinted or changed with time. Only then can we make an accurate analysis and extract valuable paleoenvironmental information from organo-based silica minerals.

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