A MICROSCOPISTS VIEW OF DESERT VARNISH FROM THE SONORAN DESERT. Laurence A.J. Garvie, Center for Meteorite Studies, Arizona State University, Tempe, Arizona 85287-1404, lgarvie@asu.edu, Donald M. Burt, School of Earth and Space Exploration, Arizona State University, Tempe, Arizona 85287-1404, Peter R. Buseck, Department of Chemistry and Biochemistry, Arizona State University, Tempe, Arizona 85287-1604.

Introduction: The current interest in Mars, especially in relation to water [1-4], has prompted the search for target materials that can provide insights into past and current environmental conditions. One such material is desert varnish (Fig. A), which on Earth has the potential to provide information on past surface conditions in arid environments [5-7], and has been proposed to occur on Mars [8,9]. Desert varnish is a microlaminated surface coating composed of wind-blown dust cemented by fine-grained Mn and Fe-bearing materials [10-12]. This layering reveals an accretionary process, with new layers added onto the surface of existing varnish. There is evidence for a relationship between the chemistry of individual laminations and past climate, with Mn-rich layers representing wetter times [5-7], although such a direct relationship has been questioned [13]. The recent explorations of Mars have prompted a reassessment of varnish characteristics primarily because there is the hope that if terrestrial-style varnish occurs on Mars then it too would record past, possibly wetter and warmer conditions. In order to examine the possibility of terrestrial-style varnish on Mars, we report on new studies that reveal the fundamental mineralogical and structural characteristics of desert varnish.

Materials and Methods: We used the high spatial resolution of transmission electron microscopy (TEM) coupled with the analytical capabilities of electron energy-loss spectroscopy (EELS) and energy-filtered TEM imaging (EFTEM) to reveal the desert varnish characteristics. Samples were studied from areas in southwestern Arizona with different lithologies and geomorphologic settings. Our observations show that varnish develops in regions that are neither totally devoid of water nor even moderately humid and suggests its use as a rough indicator of past climates.

Results: Ultrathin petrographic sections (Fig. B) show alternating Fe- and Mn-rich layers roughly parallel to the varnish surface. The contact with underlying rock is generally sharp. TEM of a sample thinned using a focused ion beam (FIB) provides a large-scale, detailed view of the relationship between the varnish minerals and structure such as microvugs and cross-cutting veins. Clay flakes and mottled material dominate the FIB section, with minor amounts of rounded, presumably detrital particles. Individual clay particles are separated by mottled electron-dense material that is tens to hundreds of nanometers thick. Compositional maps made using EFTEM imaging show the nanometer-scale segregation of Mn and Fe (Fig. C). Stringers of Mn-rich material cut across the varnish roughly perpendicular to the rock surface. The Fe- and Mn-rich material between the clay flakes is typically low in Si. Pores rimmed by Mn-rich material occur. Silicon is in the clay flakes and thin stringers parallel to the Mn- and Fe-rich layers. Nanometer-sized, presumably detrital, Ti-rich grains are distributed throughout (Fig. C).

The TEM data show that the Mn-bearing minerals are extremely fine grained, typically 10 to 500 nm. Their forms include grains that range from stubby to elongated, tissue-like aggregates, shapeless to fluffy coatings on clays, and sparse anhedral crystals. Based on EELS analyses, electron diffraction, and morphology, we believe these are, respectively, members of the hollandite/todorokite groups (including romanechite and cryptomelane), birnessite and buserite, poorly crystallized phyllomanganates of unspecified type, and Mn, Fe spinel. Manganese is most abundant as fluffy coatings on clays. Sparse but ubiquitous euhedral barite and strontiobarite are evident in the mottled material. Analyses of individual Mn-oxide particles indicate that they contain varied concentrations of Ba and Ce, reflecting their role as repositories of trace elements.

Models of varnish formation range from abiotic to biotic to a combination of the two [14-16]. Our data are consistent with formation through repeated wetting and drying of surfaces, and leaching and oxidation of reduced Fe and Mn derived from desert dust. These observations also suggest an important role for diagenesis, by analogy with normal layered sedimentary rocks. That is, the varnish undergoes mineralogical and structural changes after deposition. The Mn and Fe in varnish could have been leached from clays in dust, originated from the substrate, or derived from soluble salts in aerosols. Previous studies show no evidence for the substrate as the source, and clay particles appear inadequate, so the remaining possibility is Mn- and Fe-bearing aerosol particles. Some aerosols contain a soluble Mn component [17,18]. The nanometer-scale segregation of Fe and Mn suggests growth involving evaporation and oxidation of soluble Fe^{2+}- and Mn^{2+}-bearing fluids to insoluble high-valence oxides, with Fe precipitating first followed by Mn, which is more difficult to oxidize. An unknown factor in the varnish Mn and Fe cycle is the role of micro-organisms.

Conclusions: Nanometer-scale element mapping and spectroscopy of desert varnish reveals a dynamic disequilibrium system characterized by post-depositional mineralogical, chemical, and structural changes, activated by liquid water. Lack of equilibrium is indicated by the large variety of coexisting Mn phases. Our data indicate that terrestrial-style varnish cannot form on present-day Mars although other types of rock coatings might well be expected.

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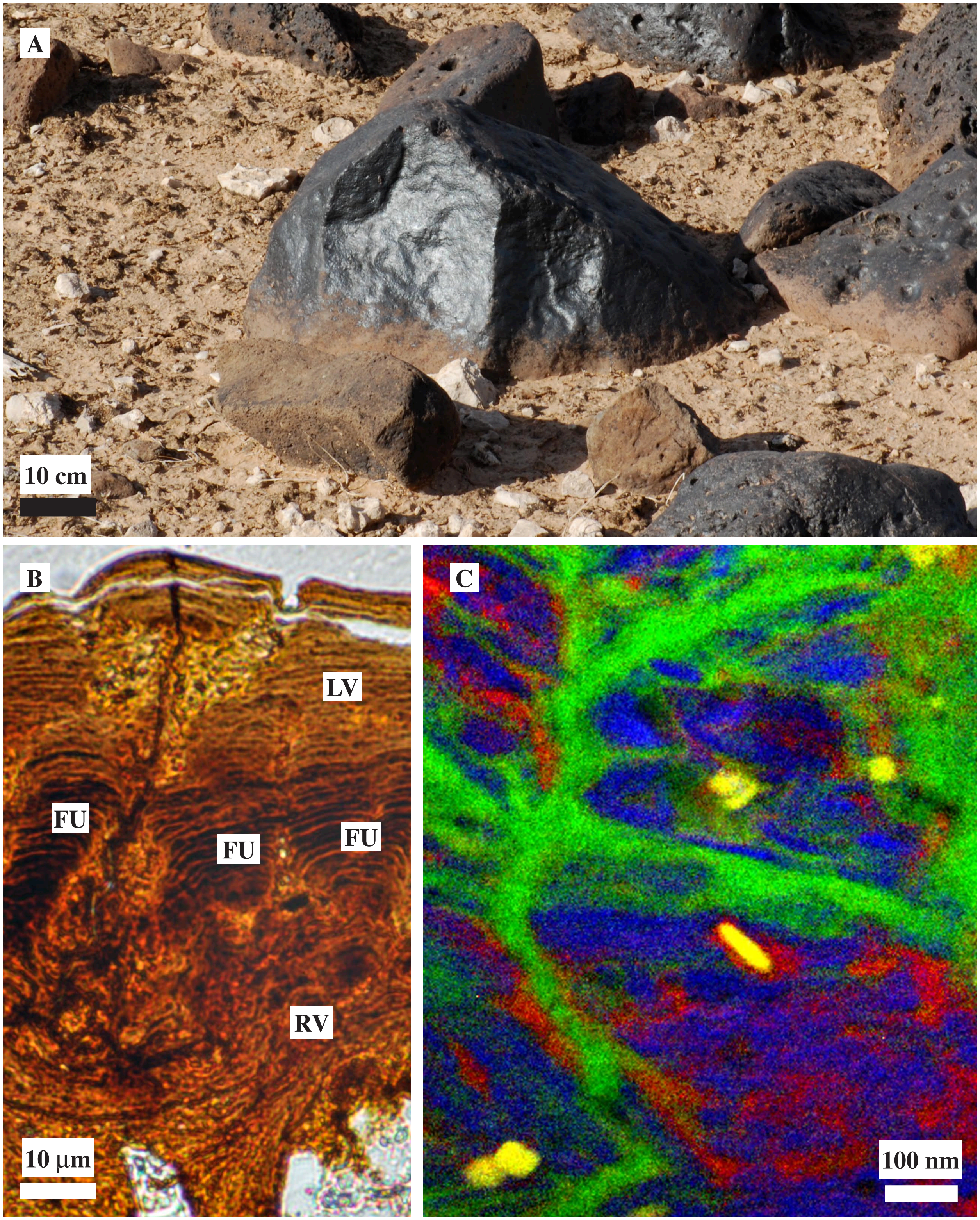

A) Photograph of a varnish-covered boulder from southern Arizona. B) Ultrathin section of desert varnish showing the layered flaring-upward structures (FU), layered varnish (LV) parallel to the air-varnish surface (LV), and rubbly bottom between varnish and underlying rock (RV). C) Energy-filtered TEM image from a thin section of desert varnish prepared using a focused ion-beam and showing the distribution of Fe (red), Mn (green), Si (blue), and Ti (yellow).