FORMATION OF SILICA GLAZE ROCK COATINGS
THROUGH WATER VAPOR INTERACTIONS

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Abstract: Manganiferous rock varnish (desert varnish) is common in subtropical deserts, but coatings of amorphous silica glaze dominate rock surfaces of the same lithology and exposed to similar amounts of annual precipitation in the rain shadows of the large tropical shield volcanoes such as those in Hawaii. Lacking an explanation for this contrast, a two decade-long laboratory experiment tested importance of high water vapor content in silica glaze formation. Twenty years of exposing basalt rock chips to 80% and 90% levels of relative humidity revealed that water vapor alone can generate silica glaze and may be an important factor in explaining why silica glaze is the dominant rock coating in humid warm drylands. In addition to adding a new dimension to the formation of terrestrial rock coatings, these findings may have importance in interpreting any coatings of amorphous silica found on Mars. [Key words: desert geomorphology, rock coatings, rock varnish, Mars, silica glaze, water vapor, weathering.]

INTRODUCTION

The geography of rock coatings has been of interest to humans from the days of the earliest artists who used pigments to manufacture anthropogenic coatings and who used natural coatings as a medium to record engraved images (Whitley, 2008). An unanswered question surrounding terrestrial rock coatings (Dorn, 2009) is why accretions of mostly amorphous silica (silica glaze) dominate rock surfaces in drylands that have high relative humidities, such as rain shadows of tropical volcanoes and fog deserts (Farr and Adams, 1984; Curtiss et al., 1985; Dorn, 1998; Bishop et al., 2003; Schiffman et al., 2006; Minitti et al., 2007; Chemtob et al., 2010). In contrast, manganiferous rock varnish (also called desert varnish) dominates in subtropical deserts with much lower relative humidity (Dorn, 1998, 2009).

Similar annual amounts of precipitation exist in the rain shadow deserts of Hawaii dominated by silica glaze (Farr and Adams, 1984; Giambelluca et al., 1986; Brady et al., 1999; Bishop et al., 2003; Schiffman et al., 2006; Minitti et al., 2007; Chemtob et al., 2010) and areas of North American (Engel and Sharp, 1958; Dorn, 1990) and Australian (Dorn and Dragovich, 1990) subtropical deserts dominated by rock varnish. Consider an example of two coatings formed at same annual isohyet of 250 mm on Hawaii (Fig. 1A) and at Florence, Arizona (Fig. 1B). Both locales experience the precipitation during a mixture of summer and winter. Both locales have sub-aerial surfaces of basalt. Yet, two very different types of rock coatings dominate in
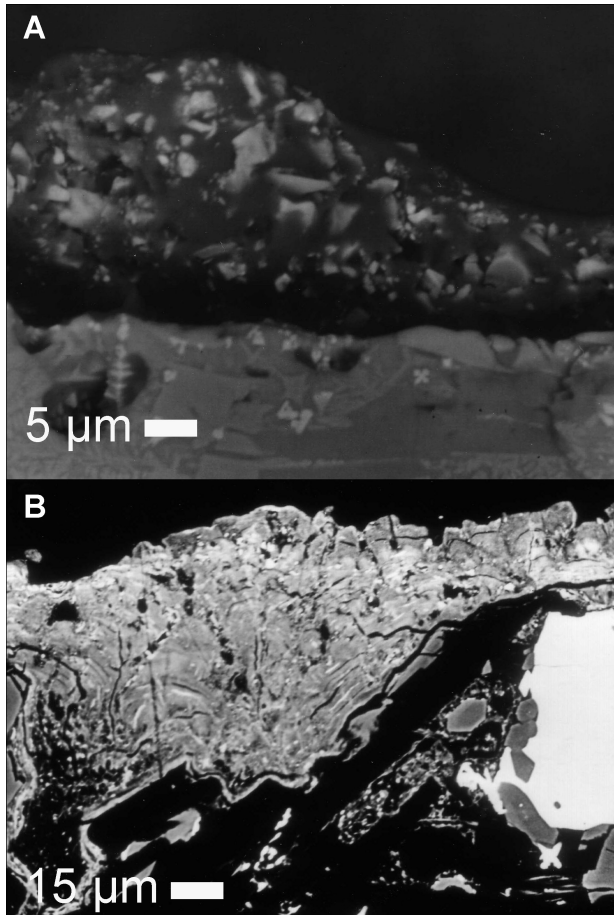
Fig. 1. Silica glaze and rock varnish formed at the same annual precipitation of approximately 250 mm, where both locations experience a mixture of winter and summer precipitation (Giambelluca et al., 1986; Western Regional Climate Center, 2005). (A) Silica glaze coating formed on the 1859 A.D. lava flow of Maua Kea, Hawaii, where the darker silica glaze entombs brighter mineral fragments. (B) Rock varnish formed on basalt in a desert pavement on a stream terrace alluvium near Florence, Arizona.

these different settings. Annual precipitation alone cannot explain the dominance of silica glaze over manganiferous rock varnish in Hawaii.

One hypothesis is that the ubiquitous water vapor in Hawaii might play a role in allowing silica glaze to form rapidly enough to effectively outcompete manganiferous rock varnish—coating rock surfaces with amorphous silica before varnish even gets a chance to start to form. Thus, a 20-year laboratory experiment to test the role of water vapor in the formation of silica glaze rock coatings began in September of 1989. Two observations initially justified the experiment. First, considerable uncertainty existed (Dorn and Oberlander, 1982) and currently exists as to why manganese-rich rock varnish dominates in subtropical deserts and yet is only rarely

found as a rock coating in rain shadow deserts in the lee of Mauna Kea, Mauna Loa, and Haleakala volcanoes in Hawaii (Farr and Adams, 1984; Curtiss et al., 1985; Bishop et al., 2003; Minitti et al., 2007; Chemtob et al., 2010). Second, the literature (Curtiss et al., 1985) and personal field and electron microscope observations of Mauna Ulu and other historic lava flows in Hawaiian rain shadows (Gordon and Dorn, 2005) revealed that microns of silica glaze can form within a few decades—making a long-term laboratory experiment potentially insightful. This experiment was, thus, begun to answer a specific terrestrial weathering question. The findings also provide a new perspective on silica glaze formation in such settings as rock shelters (Butzer et al., 1979), Antarctica (Weed and Norton, 1991), and possibly Mars (Dorn, 1998; Kraft and Greeley, 2000; Bishop et al., 2003; Minitti et al., 2007; Chemtob et al., 2010).

METHODS

Approximately 300 cm-sized basalt rock chips were manufactured by fracturing a boulder of Makanaka glacial till from Mauna Kea, Hawaii (Dorn et al., 1991; Wolfe et al., 1997) after rock chips with surface rock coatings had been removed. Back-scattered electron microscope (BSE) and High Resolution Transmission Electron Microscope (HRTEM) imagery indicated that none of the 15 randomly selected chips had any observable rock coatings on mineral surfaces. For this experiment, 130 basalt rock chips were covered by dust from the Sonoran Desert (pH of 8.1; mixed-layer illite-montmorillonite clays) in order to provide an opportunity for interaction between rock chips and the dominant clay mineralogy of rock varnish (Potter and Rossman, 1977); dust thicknesses ranged from 5 to 10 μm in BSE imagery of chips placed in epoxy and polished normal to the dust coating. The remainder of the rock chips were not exposed to dust, but were just cleaned with deionized water and air dried.

The experiment involved eight sealed vessels with a small fan underneath a metal grate. Four of the vessels hosted 30 basalt chips coated in dust, and another four contained the uncoated basalt fragments. The two vessels, dusted and undusted, were sealed at the normal room temperature where the experiment was conducted (18°C) with a relative humidity of 15%. Two vessels were sealed in conditions where this room temperature would have a relative humidity of 70%; two vessels at 80% relative humidity; and two vessels at 90% relative humidity. During the experiment, there were times when the power went out during the summer or when Arizona State University transformers went down and room temperature rose to as high as 32°C, but room temperature never lowered to the point where dew would form in any of vessels.

Once a year, the eight vessels were unsealed and a basalt chip extracted from each, placed in an epoxy mold and examined with BSE for evidence of any rock coating formation. Once a year, the eight vessels were resealed under the same conditions described in the previous paragraph. All of the small recirculating fans were also replaced annually. When rock coating formation was detected through BSE, focused beam wavelength dispersive detectors were employed with an electron microprobe to measure elemental abundances, reported in the convention of
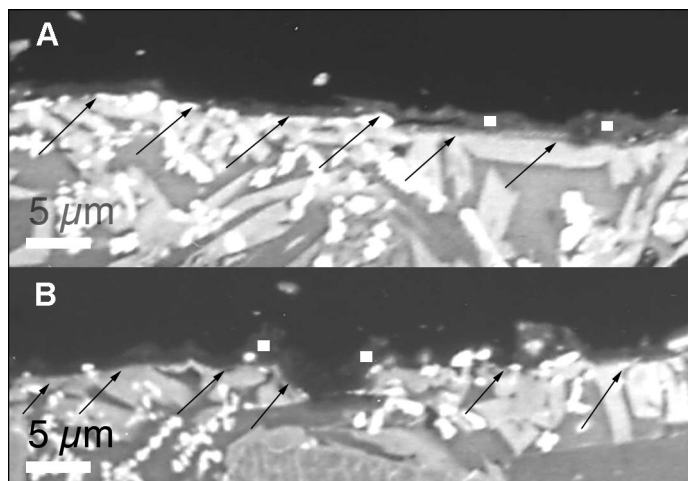
Fig. 2. Silica glaze formed on basalt rock chips after exposure to only air with a relative humidity of (A) 90% and (B) 80% at 18°C in a 20-year-long laboratory experiment. The white dots indicate the positions of focused beam electron measurements #1 and #2 reported in Table 1. Arrows show contacts between the silica glaze and the underlying basalt. The image was acquired through back-scattered electron microscopy.

oxide weight percent (Reed, 1993). The approximate diameter of the focused-beam measurements was about 2μm, and thus only the thickest portions of the silica glazes were analyzed. Once it was determined that silica glaze formation was detectable at the micron scale through BSE, HRTEM was then employed to assess whether rock coatings could be detected earlier than in BSE.

RESULTS

Uncoated basalt chips exposed to 90% relative humidity air developed silica glaze detectable at the micron scale by BSE after 18, 19 and 20 years (Fig. 2A). After 19 and 20 years, uncoated basalt chips exposed to 80% relative humidity air also developed detectable micron-scale silica glaze (Fig. 2B). No change observable in BSE took place on the basalt rock chips coated with dust. No change observable in BSE took place on uncoated chips exposed to 15% and 70% relative humidity.

A preliminary examination with HRTEM of samples formed under 80% relative humidity suggests that tens of nanometers of silica glaze started to accumulate after only three years of exposure to just water vapor. Thicknesses appear to slowly increase through the first 12 years of analyses of these samples. Preliminary HRTEM analyses suggest that a jump in thickness appears at 15 years of exposure to just relative humidity (Fig. 3). However, these HRTEM observations are preliminary, based only on observations of single samples exposed for 3, 5, 10, 12, and 15 years.

Focused beam wavelength dispersive electron microprobe measurements were collected at the white dots in Figure 2, in addition to other coating locations where thicknesses were greater than 2 μm. These data (Table 1) indicate that only Type I
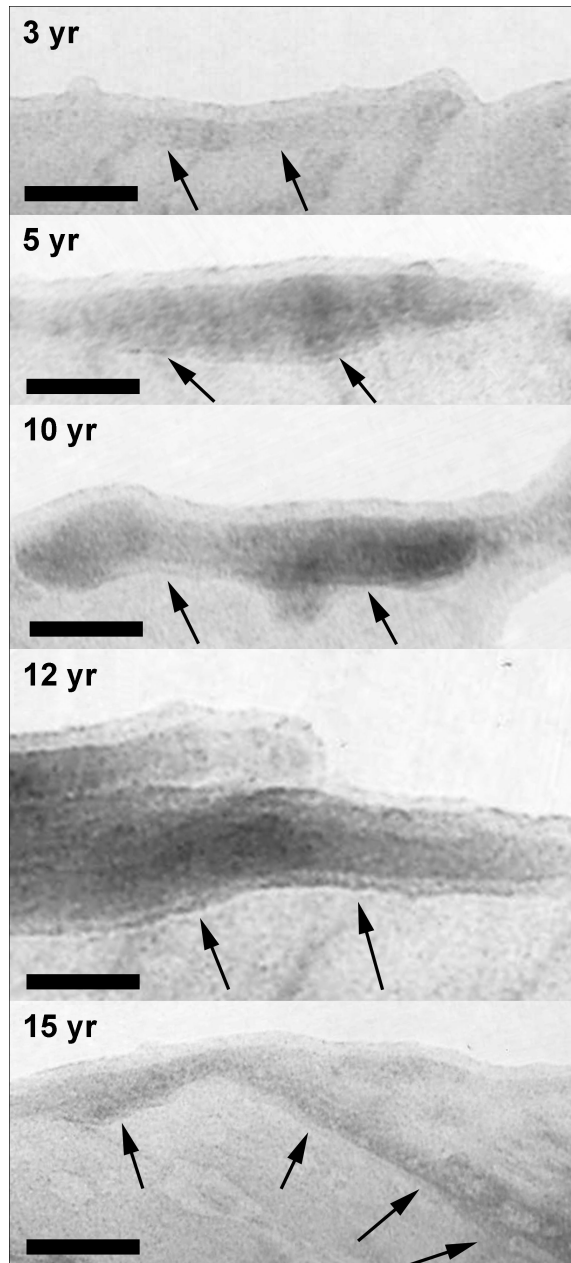
Fig. 3. Silica glaze formation in a laboratory experiment after exposure to air only with relative humidity of 80% at 18˚C. The label for each micrograph indicates how many years the basalt chip was exposed to the water vapor. Arrows point to the boundary between the darker silica glaze and the underlying plagioclase. The thickness appears to slowly increase and then there is jump in thickness after 15 years of exposure to water vapor. The imagery was acquired through High Resolution Transmission Electron Microscopy. The scale bar for 3, 5, 10, and 12 years of exposure is approximately 30 nanometers long, but the 15-year scale bar is approximately 60 nanometers long. The very thin lighter band at the outer (upper) edge of each image is an artifact.

Table 1. Electron Microprobe Measurements of Type I Silica Glaze that Formed on Basalt Chips through 20 Years of Interactions with Only Water Vapor[a]

Sample	Na_2O	MgO	Al_2O_3	SiO_2	K_2O	CaO	TiO_2	Fe_2O_3
90% RH, 20 year #1	.02	.06	.57	80.22	.04	.22	.08	.06
90% RH, 20 year #2	.03	.07	.51	79.51	.04	.19	n.d.	.07
90% RH, 20 year #3	n.d.	.03	.93	85.26	n.d.	.18	.03	.06
90% RH, 20 year #4	n.d.	.07	.87	89.73	n.d.	.21	.03	.06
90% RH, 20 year #5	.03	.03	.63	68.33	n.d.	n.d.	.05	.09
80% RH, 20 year #1	.04	n.d.	.46	88.35	n.d.	n.d.	n.d.	.17
80% RH, 20 year #2	n.d.	.08	.93	91.02	.05	n.d.	n.d.	.16
80% RH, 20 year #3	.05	.03	.86	89.49	n.d.	n.d.	.08	.38
80% RH, 20 year #4	n.d.	n.d.	.44	85.63	n.d.	n.d.	.08	.82
80% RH, 20 year #5	.04	.06	.33	60.32	.04	n.d.	n.d.	.16

[a]Five measurements were collected at coating positions where thicknesses were equal to or greater than about 2 μm. Measurements are reported here are for chips exposed to only water vapor at 90% and 80% relative humidity for 20 years. P_2O_5 and MnO were also measured, but were below the limit of detection (0.02%). The silica glazes are porous, resulting in totals less than 100%; n.d. means below the limit of detection.

silica glaze formed in the experiment. Type I silica glaze is relatively homogeneous with SiO_2 weight abundances typically two orders of magnitude greater than other measured elements. There was no evidence of the formation of other types of silica glaze: Type II, detrital-rich; Type III, alumina-iron rich; Type IV, alumina-rich; Type V, iron-rich; or Type VI, alumina glaze (see Chapter 13 in Dorn, 1998, for more detailed description of different types of silica glazes).

DISCUSSION

The 20-year long laboratory experiment presented here reveals that it is possible to form coatings of silica glaze through rock-water vapor interactions alone, where no liquid water was involved in the mobilization or reprecipitation of the silica. The weathering literature involving rock-water vapor interaction does discuss the possible role of water vapor in mineral weathering in such diverse settings as on Mars (Gooding, 1978) and in the Arctic (Humlum, 1992). There is also discussion about how the activity of cryptoendolithic organisms increases when relative humidity reaches 70%, and cryptoendolithics are weathering agents (Viles, 1995). Water vapor can also be important in salt weathering (Camuffo, 1995), where direct observations with Environmental Scanning Electron Microscopy reveals that reaction rates increase greatly when humidity cycles above and below 75% relative humidity (Lopez-Arce and Doehne, 2006). Water vapor interactions with amorphous silica has long been known to be important at temperatures far higher than found in the terrestrial weathering environments (McDonald, 1958; Zhuravlev, 2000). However,

I can find no prior discussion on the role of water vapor or even relative humidity in the formation of rock coatings.

This experiment revealing that silica glazes can form in two decades is not new, since these rates have been reported previously on natural and anthropogenic sub-aerial rock surfaces (Curtiss et al., 1985; Dorn and Meek, 1995; Dorn, 1998; Gordon and Dorn, 2005). Microns of silica glaze accumulation in Hawaii in a few decades are rates are far greater than the microns per millennia for manganiferous rock varnishes in southwestern USA deserts (Liu and Broecker, 2000; Dorn, 2007). The experimental results reported here, however, provide the first evidence that natural accumulations of silica glaze might be explained from interactions of water vapor and rock surfaces alone.

The source of the silica in these water-vapor coatings is not clear, other than it must have derived from the basalt chips themselves. There is no other option. It is also unclear how water vapor might alter basalt mineral surfaces to release and then remobilize silica. There are, however, indications in analyses of alpha-quartz that hydration energies of water vapor absorption range from -90 to -28 kJ mol^{-1} (de Leeuw et al., 1999). Artificial silica powder samples are known alter more under higher relative humidity (Morel et al., 2009). It is possible that silica-water vapor interactions might occur through nanoparticle dissolution (Rimer et al., 2007) and then nanoparticle assembly (Rimer et al., 2008). The preliminary HRTEM analyses (Fig. 3) are insufficient to begin to answer these questions or infer nanoscale processes. However, the absence of a clear explanation of process is an issue distinct from the fundamental contribution of this paper: that silica glaze can accumulate on basalt mineral surfaces in the absence of liquid water.

These results should not infer that liquid water is irrelevant to silica glaze formation. Liquid water is clearly involved in the mobilization of silica from basalt minerals in the rainshadows of Hawaiian volcanoes (Brady et al., 1999). Silica glaze forms in a wide variety of other terrestrial environments in contact with liquid water including hot subtropical deserts (Fisk, 1971; Perry et al., 2006), subglacial and pro-glacial environments (Whalley et al., 1990), the Tibetan Plateau (Langworthy et al., 2010), streams (Alexandre and Lequarre, 1978), temperate humid rock surfaces (Robinson and Williams, 1994; Dorn and Meek, 1995), stone artifacts (Goodwin, 1960), rock art in rock shelters (Butzer et al., 1979), stone monuments (Paradise, 1993), mineral grains (Smith, 1998; Zhu et al., 2006), and even snowmelt and capillary water in Antarctica (Weed and Ackert, 1986; Conca and Astor, 1987; Weed and Norton, 1991; Matsuoka, 1995; Giorgetti and Baroni, 2007).

These results suggest, however, that terrestrial silica glaze formation can be influenced by water vapor. In settings with high relative humidity, such rain shadows of Mauna Kea and Mauna Loa, or fog deserts, silica glaze accretion rates can be among the most rapid of any natural rock coating (Dorn, 1998). In Antarctica, conversely, lower abundances of liquid water and water vapor could potentially play a role in much slower silica glaze development (Weed, 1985; Matsuoka, 1995). The silica glaze formed over pictographs in rock shelters (Butzer et al., 1979) protected from precipitation or spring discharge might also involve water vapor interactions with rock surfaces.

There exists speculation that coatings of silica glaze should exist on Mars (Dorn, 1998; Kraft and Greeley, 2000; Bishop et al., 2003; Minitti et al., 2007; Chemtob et al., 2010). Martian amorphous silica coatings certainly might relate to rainfall events, perhaps in the Noachian (McSween Jr. et al., 1999) or liquid water films on mineral surfaces (Boynton et al., 2009). Alternatively, water vapor interactions around martian springs (Allen and Oehler, 2008) might generate silica glaze.

However, there exists a growing collection of information suggesting water vapor exists in notable quantities at the surface of Mars. Observations collected from the SPICAM instrument (Maltagliati et al., 2011) reveals the "frequent presence of water vapor in excel of saturation, by an amount far surpassing that encountered in Earth's atmosphere" (Malgagliati et al., 2001, p. 1868). Phoenix Landing Site research reveals that H_2O ice and vapor interacts with martian soil particles (Smith et al., 2009) and that water vapor concentrations can vary considerably (Whiteway et al., 2009)—all opening the door to the potential that billions of years of tiny amounts of water vapor interactions might play a role in generating accumulations of amorphous silica on Mars.

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