SI- AND TI- RICH SURFACE COATINGS ON HAWAIIAN BASALT AND IMPLICATIONS FOR REMOTE SENSING ON MARS. S. M. Chemtob, B. L. Jolliff, and R. E. Arvidson, Dept. of Earth & Planetary Sciences, Washington University, St. Louis, MO 63130. (smchemto@wustl.edu)

Introduction: Surface coatings on rocks are common if not ubiquitous on Earth, and now they have been observed and documented on the surface of Mars [1-3]. They occur in a variety of environments, and vary in composition, thickness, and physical properties. Surface coatings are important because they record conditions of alteration mostly owing to exposure to the planet's atmosphere. Coatings are also important in remote sensing applications where they mask the composition and mineralogy of the underlying rocks.

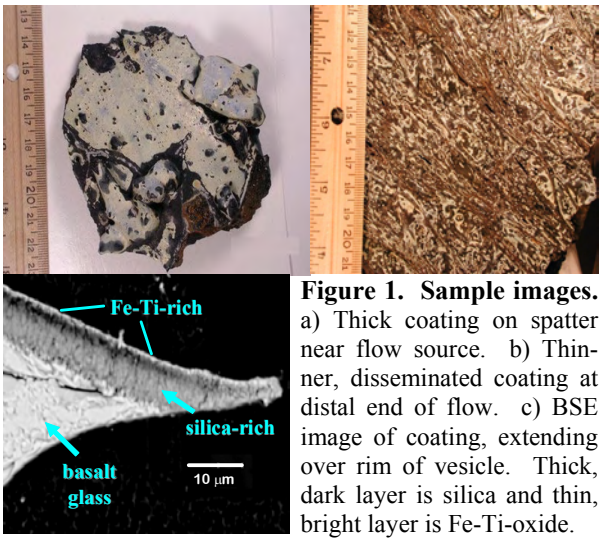

Figure 1. Sample images. a) Thick coating on spatter near flow source. b) Thinner, disseminated coating at distal end of flow. c) BSE image of coating, extending over rim of vesicle. Thick, dark layer is silica and thin, bright layer is Fe-Ti-oxide.

Volcanic rocks, especially basalt, are abundant on the surface of Mars, and thus far, only basalt and ultramafic igneous rocks have been found to occur among the martian meteorites [4]. However, some have used remote sensing spectral signatures and compositional data to infer the presence of andesite or basaltic andesite, a more silica-rich volcanic rock composition [5]. It is important to understand if these rocks are really andesitic or if they have silica-rich coatings and/or weathering rinds. This abstract presents results of analyses of silica-rich coatings on basalt from recent flows at Kilauea, Hawaii, and their implications for remote sensing. (see also [6-7])

Lava flows in the Ka'u Desert, southwest of the Kilauea Caldera on the island of Hawaii, commonly have white, light blue, opalescent, and red coatings. Those of interest to the present study have silica-rich coatings and associated TiO_2-rich white coatings. These coatings occur on spatter at lava vents near the source of flows (Fig. 1a) and are thinner at the distal reaches of flows (Fig. 1b).

We used a suite of analytical techniques to study the composition, mineralogy, and morphology of spatter coatings collected from several locations along the 1974 flows in the Ka'u Desert and near the crater of Mauna Ulu. We used the electron microprobe (EMP) to determine surface elemental compositions and laser Raman spectroscopy (LRS) to determine mineralogy.

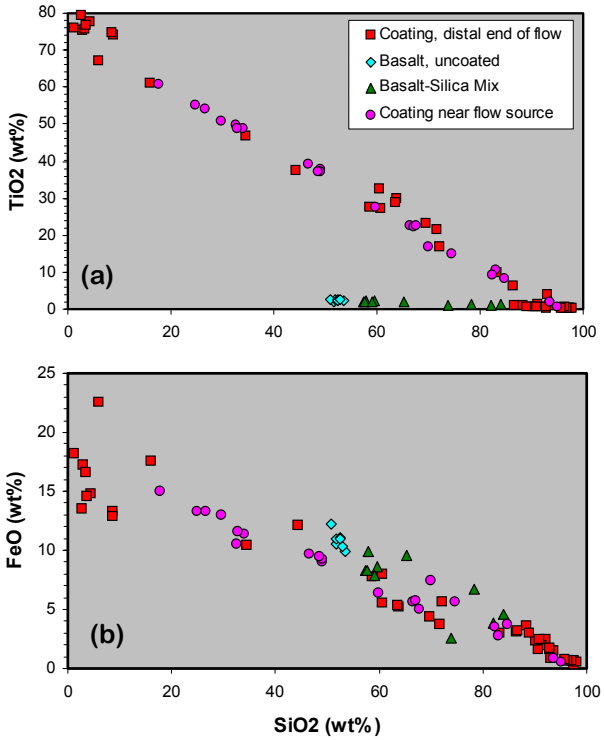

Figure 2. Compositional analyses. a) TiO_2 vs. SiO_2, normalized to 100%. Three endmembers – uncoated basalt, pure silica, and Fe-Ti-oxide - are evident. b) FeO vs. SiO_2, normalized. Basalt FeO concentrations lie along the line, but FeO and TiO_2 are highly enriched in the coating.

Results: Using LRS and EMP analysis, we analyzed coated surfaces along traverses and in selected 1-10 μm spots. Some parts of the surfaces are uncoated and have characteristic basaltic composition, but most spots featured one of two prominent coating phases: a high-SiO_2 phase and a phase enriched in Fe and Ti (Fig. 2). The Fe-Ti-rich endmember has a weight ratio of ~75% TiO_2 to ~20% FeO. Low oxide sums for the Fe-Ti-rich component suggest a hydrated phase, but Raman spectra show no peak corresponding to structural OH. The low sums might also reflect porosity of the coating materials.

Raman spectra of coating materials revealed three principal phases. Uncoated basalt was identified by peaks corresponding to pyroxene and plagioclase feldspar. Opaline silica was identified by a characteristic weak increase in absorption at ~510 cm^{-1}. The third phase produced spectra that resembled that of anatase. However, the peak positions for this phase were commonly significantly shifted away from positions previously determined for anatase. Systematic shifts in peak positions suggest that the third phase is Fe^{3+}-substituted anatase. Such an iron-enriched anatase would be consistent with the Fe-Ti oxide observed in compositional analyses. Synthetic anatase has been precipitated containing up to Fe/(Ti+Fe) 0.1 mol/mol [8].

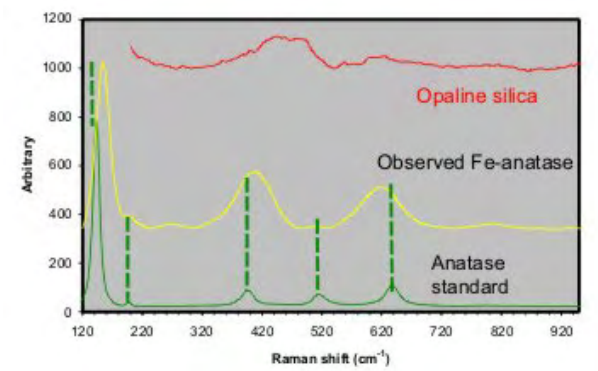

Figure 3. Raman spectra of coating endmembers. Our Raman anatase standard is included to illustrate the peak offsets.

The Fe-Ti-rich phase corresponds to areas of bright white coatings, and the silica-rich phase covers most of the surface, even where it is dark. The coating is divided into at least two layers; silica lines the substrate surface, and a thin Fe-Ti-rich layer is on top (Fig. 1c). A cross section through the coatings shows the silica-rich coating to be thicker, on order 10-20 µm, and the Ti-rich coating to be thin, only 2-5 µm, although this varies locally. Flecks of uncoated basalt occur on the coated surfaces, which implies that the coating was formed soon after eruption, while the lava was still hot and spatter and volcanic gases were being emitted from vents. The coating occasionally extends over the rim of surface vesicles, also implying formation while lava was still hot and gas was escaping (Fig. 1c). Tiny fractures, possibly formed by shrinkage upon cooling, cover the surface and break the coating into polygonal platelets. These cracks split basalt flecks, indicating that cooling occurred after the initial formation of the coating.

Discussion: Several mechanisms have been proposed for the formation of coatings on Hawaiian basalts. One is deposition of silica through leaching of wind-blown tephra; this occurs throughout the Ka'u Desert and at the summit of Mauna Kea [9]. Another mechanism is deposition of silica through evaporation of silica-bearing water vapor; this is observed downwind of Halema'uma'u crater. Our preferred explanation for the coatings observed in this study involves magmatic degassing and vapor deposition. If the gases emitted from erupting vents were rich with metal ions, those metals could be deposited as coatings around the vents. Lava could also contain metal-rich gases as it flows away from the vent, and would continue to degas over time. This explanation is consistent with the observation that coatings are rare on the distal end of new lava flows. Although we find no documentation of vapor transport and deposition on the surface of lava flows, a similar process has been observed in basaltic stalactites in Hawaiian lava tubes [10]. Metal ions can be transported in vapor as chloride, fluoride, and phosphate complexes, all of which are components of volcanic emission. Mauna Ulu coatings have similar morphology as Ka'u Desert coatings, but the composition varies, probably as a function of variable metal content of volcanic gases.

Remotely sensed VNIR spectrometry data of the 1974 Kilauea flows is dominated by the indication of hydrated silica alone [6], despite the fact that the silica coatings are only tens of microns thick and overlie much thicker basalt flows. However, there is a strong spatial correlation between the depth of the Si absorption feature and proximity to the lava flow source, supporting the evidence for thicker coatings near eruption sites. Ti-oxide coatings are not detected by visible spectrometry because there are no diagnostic absorption features in the VNIR range. Awareness of the relationship between coating characteristics and the degree of masking in remotely sensed data will yield more effective analyses of martian remotely sensed data.

Acknowledgements: Support from NASA grant NAG5-12684 (blj) is appreciated. We thank Karla Kuebler and Alian Wang for help in the Raman lab, and Kim Seelos for comments on the abstract.

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