PALAGONITE-LIKE ALTERATION PRODUCTS ON THE EARTH AND MARS 2: SECONDARY MINERALOGY OF CRYSTALLINE BASALTS WEATHERED UNDER SEMI-ARID CONDITIONS.

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Introduction: The Martian surface may be mineralogically altered from its pristine, igneous state. Aqueous alteration on Mars would lead to formation of secondary minerals, which could occur in soils, weathering rinds, rock coatings, or sedimentary cements. In order to understand the alteration state of the Martian surface, it is crucial that we anticipate what secondary minerals might have formed on Mars. It is also critical that we understand how secondary materials affect remote observations. In particular, we must understand spectral observations of secondary minerals in geologic context: How do these materials appear when they occur as weathering rinds, soils, cements, or coatings?

Small amounts of weathering could produce significant differences between fresh rock and weathered rock spectra. Previously, we investigated thermal infrared spectra of silica-coated rocks and showed that small amounts of amorphous silica coating basalt greatly influenced spectra, with silica coatings thicker than 7-10 μm completely obscuring the basalt's thermal infrared spectral signature [1]. In weathering rinds, fine-grained, secondary silicates tend to coat primary minerals, and can be thought of as discontinuous, rock-penetrating coatings. Consequently, we expect thermal infrared spectral effects of weathering rinds to be similar to those seen with silica coatings, in that small volumes of secondary products will have large effects.

To test this hypothesis and to address the concerns outlined above, we are performing combined mineralogical-spectral analyses of basaltic weathering rinds to begin to address these concerns. Lander chemical data of Mars suggest that the surface is, broadly, basaltic [e.g. 2-3], and spectroscopic data indicate that primary minerals exist in the relatively dust-free dark regions of Mars [e.g. 4-6]. Thus, secondary products on Mars would likely occur in association with primary igneous minerals. We are studying weathering rinds because they represent incipient stages of weathering, which may be important for Mars if it is generally weakly altered. Weathering rinds are a natural-case example of mixed primary and secondary minerals, and can be used as a proxy for the spectroscopic effects that might occur in other mixed-mineral materials such as soils. This study and others like it will be critical for understanding spectral observations of natural geologic surfaces and for understanding surface alteration on Mars.

Methods: We are studying a set of subaerially weathered rocks of the Columbia River Basalt (CRB) Group. We are characterizing the mineralogy of the rocks and their weathering rinds using a suite of techniques: optical petrography, powder X-ray diffraction (XRD), back-scattered electron (BSE) imaging, electron-probe microanalysis (EPMA), semi-quantitative energy-dispersive X-ray spectroscopy (EDS), and electron diffraction and imaging by transmission electron microscopy (TEM). Petrography, BSE imaging, EPMA, and EDS are performed on thin sections cut normal to and including the weathering rinds of several rocks. XRD and TEM analyses are performed on the <2-μm size fraction separated from the weathering rinds by particle settling and centrifugation. Further TEM analyses of *in situ* secondary products will be performed on TEM mounts prepared from thin sections. Additionally, we are collecting thermal emission and visible/near-infrared reflectance spectra for fresh and weathered surfaces of the CRB rocks, discussed in a companion abstract by *Michalski et al*. [7].

CRB mineralogy: Unweathered portions of the CRBs are comprised of plagioclase feldspar, augite, olivine (Fo_{32}), titanomagnetite and high-silica interstitial glass, with accessory orthopyroxene and apatite.

Weathering rind mineralogy: The process of aqueous alteration disintegrates primary minerals, mobilizing elements that go on to form secondary minerals. Because these are silicate rocks, the most important constituent is SiO_2, and we are principally concerned with secondary silicate phases.

Anticipated mineralogy. We expected to see a general absence of well-crystalline clay minerals. We hypothesized that we would, instead, encounter poorly crystalline silicate weathering products. In his report on basalt and andesite weathering, *Colman* found little XRD evidence for crystalline clay products [8]. Basalt weathering commonly leads to the formation amorphous or short-range order (SRO) silicate weathering products [9-11]. SRO aluminosilicates, such as allophane, occur in many volcanic soils, with clays being a product of further pedogenic processing [12-13].

Preliminary findings. Petrographic analyses of several rocks show that their weathering rinds have a high density of thin microfractures, probably resulting from a combination of volume expansion and dissolution. Secondary products have formed within the fractures and voids (Figure 1). Preliminary BSE/EDS analyses show the secondary products are Si-Al-Fe rich. XRD analysis from oriented powder mounts of the <2-µm size fraction indicate a lack of crystalline clay minerals. TEM analysis of the <2-µm size fraction shows that the Si-Al-Fe-rich material is amorphous to poorly crystalline (Figure 2). Some of the poorly crystalline products seen in TEM bright field images show clay-like structure over short range, and we interpret these to be clay-precursor phases. Overall, the secondary particles observed with TEM are consistent with allophane or SRO protoclays. The high Fe content is likely due to poorly crystalline Fe-oxide/hydroxide phases that are intimately associated with SRO aluminosilicate secondary phases.

Weathering rind spectroscopy: As predicted, the lightly weathered basalts that we have investigated show considerable thermal infrared spectral differences compared to their fresh-rock interiors. Spectrally deconvolved mineral abundances for weathered CRB surfaces include abundant basaltic glass (see [7]), which is not a real constituent phase. The deconvolution models include glass to model the significant spectral contribution from SRO silicate weathering products. Because allophane and other SRO materials are currently unavailable in the spectral library, deconvolution models must rely on available materials that have similar spectra, such as silicate glasses and clays. The precise glass or glass-clay combination that best models a weathered-surface spectrum depends on the Si/O ratio of the SRO weathering product [7,14]. Importantly, the deconvolved mineralogy of the weathered rocks includes primary phases. Primary plagioclase, pyroxene, and olivine are seen *at the surface* of weathering rinds in BSE images and are notably more abundant than secondary products in the rinds.

Mars may indeed be palagonite-like: Poorly crystalline weathering products can result from subaerial weathering of crystalline basaltic rocks. The mineralogy of the CRB weathering rinds—poorly crystalline aluminosilicates and Fe-oxides/hydroxides—is similar to the mineralogy of palagonite, which has been championed as a possible Martian surface material [e.g. 15-16]. What is important to note is that palagonite-like products can result from weathering not only basaltic glass, but crystalline basalt as well. Poorly crystalline secondary minerals may occur on Mars from weathering of the bulk surface rocks. Thermal infrared spectra of Martian surfaces that have been modeled to contain glasses, including global spectral surface types and materials from the Mars Exploration Rover sites, are consistent with chemically altered surfaces containing SRO silicates.

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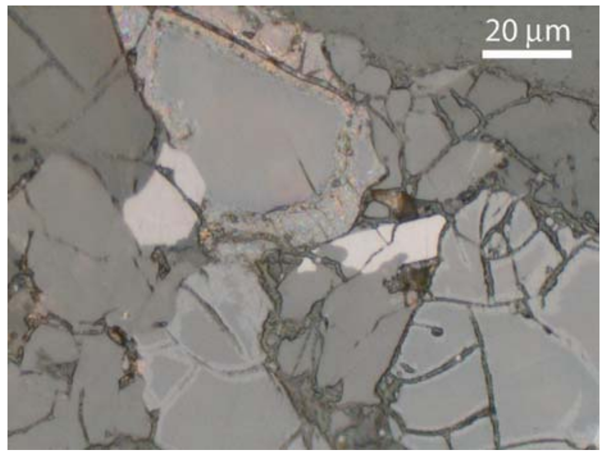

Figure 1. Reflected light photomicrograph of a CRB weathering rind showing microfractures and voids filled with secondary material. From SEM-EDS, the fracture-filling materials are Si-Al-Fe-rich.

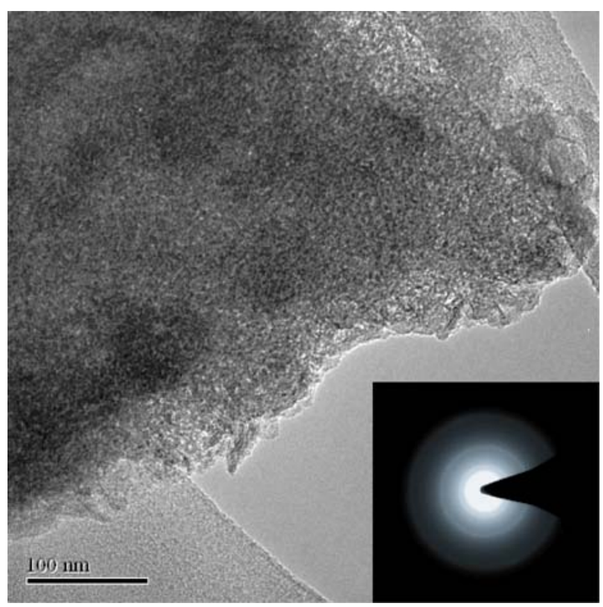

Figure 2. TEM bright field image of a Si-Al-Fe-rich secondary particle showing some degree of short-range order. The diffraction pattern of diffuse rings indicates that the particle is poorly crystalline.