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**Title:** Investigating the role of anhydrous oxidative weathering on sedimentary rocks in the Transantarctic Mountains and implications for the modern weathering of sedimentary lithologies on Mars

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## **Abstract**

Alteration of the uppermost surfaces of geologic materials is a pervasive process on planetary surfaces that is dependent upon factors including parent composition and the environment under which alteration is occurring. While rapid and pervasive in hot and humid climates on Earth, chemical weathering of rock surfaces has also been found to dominate in some of Earth's coldest and driest landscapes as well. Specifically, surfaces dominated by resistant fine-grained igneous rocks in the Antarctic preserve evidence of oxidative weathering processes, which represent the initial immature surface alteration processes that stagnate due to the lack of available water and kinetics necessary for the production of more mature alteration phases. In this study, we test the hypothesis that oxidative weathering also dominates the surfaces of sedimentary rocks throughout the Antarctic. We investigated the chemistry and mineralogy of a suite of sedimentary rocks from the Transantarctic Mountains ranging from fine-grained tuffs to coarse-grained sandstones and conglomerates. Our results show that, like the previously studied fine-grained igneous rocks in the Antarctic, sedimentary rocks generally showed only minor chemical weathering signatures at their surfaces relative to their interiors. However, unlike the igneous rocks in this earlier study, the sedimentary rocks exhibited a wide variety of non-systematic differences between surface and interior compositions. This variability of surface weathering signatures is equally as complex as the physical properties and compositions inherently present within these different sedimentary lithologies. Based on these analyses, it is apparent that oxidative weathering products do not dominate the surfaces of sedimentary rocks throughout the Transantarctic Mountains, which instead exhibit a wide array of weathering signatures that are likely dependent on both lithological and environmental factors. Considering that sedimentary lithologies are widespread across a significant fraction of the martian surface, our results suggest that observed alteration signatures limited to the surfaces of martian sedimentary rocks are most likely to be minor and to vary as a result of the lithological properties of the specific rock unit and not as a result of the widespread influences of the modern cold and dry climatic conditions.

# 1 **Introduction**

2           The modification of parent rock materials as a result of subaerial exposure often produces  
3 alteration phases that can be used to infer the paleoenvironmental conditions present during their  
4 formation. For example, the formation of heavily leached laterite sequences and their  
5 preservation in the geologic record suggest tropical conditions, while caliche hardpans indicate  
6 desert environments (e.g., Sheldon and Tabor, 2009). Weathering coatings (deposits on the  
7 surfaces of rocks derived from external sources), patinas (deposits on the surfaces of rocks  
8 derived from elements source from the rock itself), and rinds (a zone of chemical alteration on a  
9 rock's surface from preferential removal of elements that penetrates to some depth within the  
10 rock) also preserve important paleoclimatic information, particularly in desert environments  
11 where aqueous alteration is minimal (Liu and Broecker, 2000; Dorn, 2009a, 2009b; Mahaney et  
12 al., 2012). Specifically in Antarctica, alteration rinds have been shown to preserve evidence for  
13 oxidative weathering processes in the absence of significant aqueous alteration, demonstrating  
14 that the rocks have been exposed to cold, dry, and stable environmental conditions for long  
15 durations (Weed and Ackert, 1986; Weed and Norton, 1991; Chevrier et al., 2006; Staiger et al.,  
16 2006; Salvatore et al., 2013; Cannon et al., 2015).

17           While relatively immature and mineralogically insignificant (Weed and Ackert, 1986;  
18 Salvatore et al., 2013; Cannon et al., 2015), the alteration rinds generated and preserved on  
19 Antarctic rocks significantly modify the spectral signatures of rock surfaces relative to their  
20 unaltered interiors. These rinds also preserve minor yet consistent elemental variations relative  
21 to their interiors, including a relative increase and decrease in monovalent and divalent cations,  
22 respectively. Salvatore et al. (2013) showed that similar elemental trends are preserved at the  
23 surfaces of igneous rocks in Gusev crater on Mars, and subsequent spectral investigations

24 suggested that oxidative weathering products may be a globally significant component of the  
25 martian surface (Salvatore et al., 2014). With the exception of just a few studies (e.g., Weed and  
26 Ackert, 1986; Weed and Norton, 1991; Cannon et al., 2015), however, previous investigations in  
27 the Antarctic have not focused on the formation or preservation of surface alteration in  
28 sedimentary lithologies. Sedimentary rocks are typically more friable and permeable than  
29 igneous rocks, and their compositions are also much more variable than the relatively  
30 homogeneous dolerites (diabase, or shallow intrusive basalt) that were previously studied  
31 (Salvatore et al., 2013).

32         To improve our understanding of rock weathering in cold, dry, and stable terrestrial  
33 environments, our study tests the hypothesis that oxidative weathering processes are the  
34 dominant alteration process acting on the surfaces of sedimentary rocks throughout the  
35 Transantarctic Mountains (TAM). We do so by characterizing the chemical, mineralogical, and  
36 spectral variations associated with carefully selected sedimentary samples collected from  
37 throughout the TAM. Should oxidative weathering processes dominate, we anticipate these  
38 compositional signatures to be consistent with those identified in Salvatore et al. (2013) for  
39 Antarctic dolerites. Should other trends be observed, we can confidently refute this hypothesis  
40 and instead investigate whether some other alteration process dominates sedimentary rocks in the  
41 cold and dry Antarctic. Our investigation specifically focuses on the wide variety of sedimentary  
42 rocks found throughout the TAM, and does not consider the effects of oxidative weathering  
43 processes on the diverse range of igneous (e.g., Kirkpatrick Basalt, Granite Harbour Intrusives)  
44 or metamorphic lithologies (e.g., Skelton Group, Duncan Formation) present throughout the  
45 Antarctic.

46         It is necessary to consider that the work of Salvatore et al. (2013) only focused on clasts

47 of the Ferrar Dolerite within the confines of Beacon Valley, a stable geologic surface (Marchant  
48 et al., 2002) located at high altitudes within the stable upland microclimate zone (Marchant and  
49 Head, 2007). We extrapolate the work of Salvatore et al. (2013) to a broader suite of geologic  
50 materials over a broader range of micro- and macro-environments within the TAM in an effort to  
51 understand the role of continental-scale oxidative weathering. Previous investigations have  
52 qualitatively described and documented the enhanced oxidation of older surfaces relative to  
53 younger surfaces throughout the TAM, even those dominated by sedimentary lithologies (e.g.,  
54 Campbell and Claridge, 1987; Bockheim et al., 1989; Bockheim, 1990), which suggests that  
55 oxidative weathering is an important weathering process in the cold, dry, and stable Antarctic  
56 environments. However, is oxidative weathering the most dominant alteration process in these  
57 cold and dry environments, or are other processes equally as influential?

58 Our analytical methods were designed to be comparable to those on the Mars Science  
59 Laboratory (MSL) Curiosity rover. Gale crater, the site of Curiosity's explorations on the  
60 martian surface, is dominated by sedimentary rocks deposited in ancient alluvial, deltaic, and  
61 lacustrine environments (Grotzinger et al., 2014). If successful in identifying the dominant mode  
62 of "modern" surface alteration in the TAM using these analytical methods, it may be possible for  
63 Curiosity to distinguish between different modes of modern surface alteration on Mars. Such a  
64 capability could help to constrain the relative roles of physical erosion and chemical alteration in  
65 the modern martian environment.

66

## 67 **Oxidative Weathering Processes on Earth and Mars**

68 Subaerial oxidative weathering, like that dominating surfaces of dolerites in the  
69 McMurdo Dry Valleys (MDV) of Antarctica, is observed as discolored alteration rinds at the

70 surfaces of dolerite (shallow intrusive basalts, or diabase) clasts. The rinds appear reddish  
71 brown, while the rock interiors appear grey or black. No evidence for coatings or patinas is  
72 found on rock surfaces, which would indicate the deposition of materials at the surfaces. Instead,  
73 the alteration rinds penetrate to some depth into the rock where they eventually fade into the rock  
74 interior. Such morphologies indicate diffusion into the rock surface from the outside  
75 environment, with the depth of penetration a result of both the diffusivity of the rock itself as  
76 well as its exposure age. Staiger et al. (2006) showed that the approximate rate of oxidative  
77 weathering rind growth is  $1.5 \text{ mm My}^{-1}$  when compared to uncorrected cosmogenic nuclide  
78 exposure ages of glacial moraine sequences in Vernier Valley, Antarctica. These rinds represent  
79 modern and ongoing chemical weathering in the cold, dry, and stable Antarctic environment.  
80 While others have identified and characterized older episodes of chemical alteration in Antarctic  
81 lithologies, most are associated with more active geologic processes including magmatic  
82 intrusion (Vavra, 1989), continental-scale rifting (Fleming et al., 1992), and major glaciations  
83 (Passchier, 2004).

84 A brief summary of oxidative weathering products and processes in the Antarctic is  
85 provided below, and more detail can be found in Salvatore et al. (2013). Within the alteration  
86 rind, individual mineral phases and morphologies are preserved and relatively unaltered, which is  
87 consistent with X-ray diffraction (XRD) measurements that indicate no significant changes  
88 between rock surfaces and rock interiors. Chemically, alteration rinds exhibit elemental  
89 signatures that are inconsistent with typical aqueous alteration. For example, surfaces exhibit no  
90 appreciable variation in  $\text{SiO}_2$  or  $\text{Al}_2\text{O}_3$  abundances. In addition, cations that are typically mobile  
91 in aqueous environments behave differently in environments dominated by oxidative weathering.  
92 Monovalent (e.g.,  $\text{Na}^+$ ,  $\text{K}^+$ ) and divalent (e.g.,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ) cations are both commonly mobile in

93 aqueous environments. However, during oxidative weathering, divalent cations are  
94 preferentially removed from the rock's surface relative to monovalent cations (with the exception  
95 of  $\text{Fe}^{2+}$ , which is preferentially oxidized to  $\text{Fe}^{3+}$ ), as the oxidation potential from the removal of  
96 divalent cations is twice as large. The result is a relative enrichment of monovalent cations in  
97 rock surfaces relative to their unoxidized interiors, which is not typically observed as a result of  
98 aqueous alteration. At visible/near-infrared (VNIR) wavelengths, reflectance spectra of rock  
99 surfaces exhibit strong charge-transfer absorption features associated with ferric iron at  
100 wavelengths shorter than  $\sim 0.7 \mu\text{m}$ . Absorption features associated with hydrated mineral phases,  
101  $\text{OH}^-$ , and  $\text{H}_2\text{O}$  are weak and comparable to those observed in rock interiors, suggesting minimal  
102 hydration during oxidative weathering.

103         Based on these observations, analytical results, and earlier lab experiments, Salvatore et  
104 al. (2013) concluded that oxidative weathering of dolerite surfaces in the MDV is driven by the  
105 migration of cations towards the rock surface (and replaced by the inward flux of electron holes)  
106 in response to the oxidizing environment. Divalent cations are preferentially mobilized relative  
107 to monovalent cations because of their greater charge, which allows for more oxidation to occur  
108 relative to the number of cations removed. As the cations reach the surface, they form soluble  
109 and friable oxide phases that are easily removed through aeolian abrasion and aqueous  
110 dissolution, which is why they are not observed at rock surfaces exposed to the environment.  
111 What remains is an oxidation rind and oxidation front that penetrates to some depth within the  
112 rock interior, determined largely by rock hardness/permeability and exposure age.

113         The rinds observed by Salvatore et al. (2013) are significantly different from weathering  
114 rinds that have been shown to form in Arctic environments (e.g., Dixon et al., 2002), which form  
115 as a result of dissolution and often result in significant disaggregation and fracturing and indicate

116 the significant influence of liquid water during the weathering process. This is consistent with  
117 the hypothesis that the primary difference between weathering processes in the Antarctic and  
118 other terrestrial environments is the lack of moisture and liquid water (Balke et al., 1991;  
119 Meiklejohn and Hall, 1997; Hall et al., 2002).

120 Salvatore et al. (2013) also showed how oxidative weathering processes appear to  
121 dominate the modern weathering of basaltic surfaces in Gusev crater. Specifically, they used  
122 data from the Alpha Particle X-Ray Spectrometer (APXS, Gellert et al. (2006)), the Mössbauer  
123 spectrometer (Morris et al., 2006), and the Pancam imaging system (McSween et al., 2004) on  
124 rocks that were both brushed and ground into by the Rock Abrasion Tool (RAT) on the Mars  
125 Exploration Rover (MER) Spirit to show that the geochemical and spectral relationships between  
126 rock surfaces and interiors are identical to those observed in Antarctic dolerites. Salvatore et al.  
127 (2014) followed this initial investigation with a global martian VNIR and TIR spectroscopic  
128 investigation to determine whether oxidative weathering processes contribute significantly to the  
129 global spectral signatures observed on the planet. Their results demonstrated that most of Mars'  
130 classic low-albedo regions contain spectrally significant abundances ( $> \sim 10\%$ ) of oxidative  
131 weathering products, indicating the dominance of cold and dry oxidative weathering processes at  
132 play on the "modern" martian surface.

133

## 134 **Methods**

135 To relate our work to that of Salvatore et al. (2013), we utilized the same sample  
136 preparation methods and conducted a similar suite of spectral, chemical, and mineralogical  
137 analyses on our samples. In addition to the analyses from Salvatore et al. (2013), we also  
138 performed laser induced breakdown spectroscopy (LIBS) to measure sample chemistry and for



**Table 1.** Measurements performed on Antarctic sedimentary rocks in this investigation and their relevance to analytical techniques onboard the Curiosity rover.

Analytical Technique, Laboratory	Relevant Analytical Instrument, Curiosity Rover
Visible/Near-infrared reflectance spectroscopy	Mastcam, ChemCam (passive)
X-ray diffraction	CheMin
Laser-induced breakdown spectroscopy	ChemCam (active)
Inductively coupled plasma-optical emission spectroscopy	APXS, ChemCam (active)
Mössbauer spectroscopy	(None)

139 comparison to results from the Chemistry and Camera (ChemCam, Wiens et al., 2013)  
 140 instrument on the Curiosity rover. All other analytical methods were selected for their  
 141 comparability to instruments onboard past and present Mars rovers, specifically Curiosity in  
 142 Gale crater (**Table 1**), allowing us to compare our results to measurements of the martian surface  
 143 as well.

144

145 *Sample Suite*

146 We initially selected a total of 211 rock samples from throughout the Transantarctic  
 147 Mountains, Marie Byrd Land, and the  
 148 Antarctic Peninsula. Samples were originally  
 149 selected to ensure a wide diversity of  
 150 sedimentary rock types and depositional  
 151 environments as well as volcanic rocks for  
 152 comparison. The rock samples were retrieved  
 153 from the Polar Rock Repository (PRR) at the  
 154 Ohio State University, which is the National  
 155 Science Foundation’s repository for Antarctic



**Figure 1.** The location of 22 down-selected samples obtained from the Polar Rock Repository. Colors are representative of specific rock types.

156 samples collected during prior field seasons. The samples consisted of 30 siltstones/mudstones,  
 157 40 sandstones, 26 conglomerates, 59 tuffs and tuffaceous mudstones, 50 basalts, and 6 assorted  
 158 sedimentary and igneous clasts. We then down-selected 22 representative samples from our  
 159 initial collection of 211 for more detailed spectral, chemical, and mineralogical analyses (**Fig. 1**,  
 160 **Table 2**). Our goal was to maintain a representative collection of different lithologies that were  
 161 distributed throughout the Transantarctic Mountains during the down-selection process. Selected  
 162 samples showed clear visual evidence for surface weathering, specifically oxidation, and  
 163 preference was given to those with accompanying field notes that provided additional contextual  
 164 information regarding field setting and reason for collection. We were also cognizant of  
 165 identifying any samples with evidence for lichen or other biological materials present on the  
 166 surface in an effort to avoid geochemical and mineralogical effects from biological weathering

**Table 2.** The 22 samples down-selected for further investigation in this study.

Type	Sample ID	Latitude/Longitude	Geographic Region	Geographic Feature
Basalt	13197	72.98° S, 162.90° E	NVL	Mt. Masley
Conglomerate	20642	63.42° S, 57.02° W	AP	Mt. Flora
	25796	84.23° S, 162.42° E	CTAM	Coalsack Bluff
Mudstone/ Siltstone	12393	86.37° S, 159.25° W	STAM	Roaring Cliffs
	12798	85.33° S, 119.20° W	STAM	Victor Cliff
	23553	85.20° S, 174.30° W	STAM	Thrinaxodon Col
	26210	76.88° S, 159.40° E	SVL	Carapace Nunatak
	30224	86.28° S, 147.27° W	STAM	Mt. Blackburn
Sandstone	05483	84.35° S, 164.70° E	CTAM	Mt. Falla
	26160	77.80° S, 160.55° E	SVL	Aztek Mountain
	26909	84.55° S, 163.60° E	CTAM	Kenyon Peaks
	27111	84.58° S, 164.00° E	CTAM	Storm Peak
	36193	75.62° S, 158.63° E	NVL	Shappard Rocks
Tuff	25633	85.73° S, 176.73° E	CTAM	Mauger Nunatak
	25908	84.52° S, 164.07° E	CTAM	Elliot Peak
	26951	84.37° S, 164.92° E	CTAM	Mt. Falla
	26975	84.37° S, 164.92° E	CTAM	Mt. Falla
	27109	84.85° S, 164.00° E	CTAM	Storm Peak
	34531	84.33° S, 164.43° E	CTAM	Golden Cap
	36150	75.62° S, 158.63° E	NVL	Sheppard Rocks
	36241	75.70° S, 158.78° E	NVL	Ricker Hills
39262	76.73° S, 159.65° E	SVL	Allan Hills	

AP = Antarctic Peninsula, CTAM = Central Transantarctic Mountains, STAM = Southern Transantarctic Mountains, NVL = Northern Victoria Land, SVL = Southern Victoria Land

167 processes, although no evidence for biological materials were present on any of the originally  
168 selected 211 samples. Through this down-selection process, we identified 9 tuffs, 5 sandstones,  
169 5 siltstones/mudstones, 2 conglomerates, and 1 basalt for further investigation.

170 Selected samples were acquired primarily from Northern and Southern Victoria Land,  
171 and the Central and Southern Transantarctic Mountains, with one conglomerate sample from the  
172 Antarctic Peninsula. With the exception of the Antarctic Peninsula, all sampling locations fall  
173 within the “Cold katabatic” climatic zone as defined by Dalrymple (1966), where mean annual  
174 temperatures range from  $-30^{\circ}\text{C}$  to  $-40^{\circ}\text{C}$ , and mean annual precipitation ranges between 0 mm  
175 and 45 mm. The one sample from the Antarctic Peninsula was collected from Mt. Flora, which  
176 is located approximately 5 km from Hope Bay and the Argentinian Esperanza Base, with a  
177 recorded mean annual temperature of  $-4.6^{\circ}\text{C}$  and a mean annual precipitation of 28.6 mm.  
178 These climatological data confirm that all samples were collected from hyper-arid polar desert  
179 environments.

180 While analyzing rocks that were previously collected and returned from the Antarctic is  
181 efficient and allowed us to perform this research without the need for costly field work, the use  
182 of these samples creates two causes for concern. First, the clasts originate from throughout the  
183 Antarctic and correspond to a wide range of environments, from low-elevation coastal regions to  
184 high-elevation mountainous and polar environments. Second, the exposure histories of these  
185 clasts are largely unknown, which precludes our ability to determine the length of time over  
186 which surface alteration processes have been occurring. Regardless, if we assume that the  
187 entirety of the Antarctic hosts cold, dry, and stable environmental conditions, and that surface  
188 alteration proceeds along the same alteration trends regardless of clast location or exposure  
189 history, we are still able to determine whether oxidative weathering processes dominate these

190 sedimentary clasts, whether oxidative weathering is overprinted by more mature alteration  
191 processes, or whether any alteration is seen at all.

192

### 193 *Sample Preparation*

194 Rock surfaces and interiors were subdivided into small (~3 cm<sup>2</sup>) chips and fragments  
195 using a rock hammer to preserve natural surfaces and to avoid artificial cut surfaces. These chips  
196 were prepared for VNIR reflectance spectroscopy and LIBS analyses. Rock powders were  
197 created using a diamond-tipped rotary drill, which was used to extract material from rock  
198 interiors and rock surfaces in an identical manner. Material from rock interiors was acquired  
199 from near the center of the sample, well beyond any visible evidence for oxidation or other signs  
200 of alteration. When preparing rock surfaces, only the uppermost material was removed from a  
201 relatively large area of the rock surface, which minimized the sampling depth and ensured that  
202 only the outermost altered material was extracted (to a depth of ~0.5 mm, Salvatore et al., 2013).  
203 Surface and interior powders were then ground using a mortar and pestle and sieved to < 150 μm  
204 size fractions, which is the same size fraction analyzed by the Chemistry and Mineralogy  
205 (CheMin) XRD instrument on Curiosity (Blake et al., 2012), and prepared for powder XRD, bulk  
206 chemistry measurements, and Mössbauer spectroscopy.

207

### 208 *Reflectance Spectroscopy*

209 VNIR spectroscopy was performed on rock chips of all 22 samples using an Analytical  
210 Spectral Devices (ASD) FieldSpec4 spectroradiometer in a well-calibrated laboratory setup, a 0°  
211 illumination angle, and a 30° exitance angle outside of the plane of illumination (to avoid  
212 specular reflection). The instrument was calibrated every 10 minutes using a Spectralon white

213 reference in the same viewing and illumination geometry as the measured samples.

214

#### 215 *Mineralogy Measurements*

216 XRD analyses were performed on 21 pairs of sample powders at the University of  
217 Michigan's Electron Microbeam Analysis Laboratory using a Rigaku Ultima IV diffractometer  
218 ( $3^\circ - 65^\circ 2\theta$ ) using a Cu-K $\alpha$  radiation source at 40 kV and 44 mA. The goniometer radius is 285  
219 mm, and the divergence, scattering, and receiving slits are  $0.67^\circ$ ,  $0.67^\circ$ , and 0.6 mm, respectively.  
220 Data were acquired at a step of  $0.05^\circ$  at a speed of  $1^\circ$  per minute. Rietveld refinement was  
221 performed using the MDI Jade software subsequent to these analyses to quantify variations in  
222 mineralogy between sample interiors and surfaces.

223

#### 224 *Elemental Chemistry*

225 Bulk chemistry of all 22 sample pairs was measured at Brown University using  
226 inductively coupled plasma-optical emission spectroscopy (ICP-OES) and the flux fusion  
227 dissolution method (Murray et al., 2000). Powdered samples were divided into 40 mg aliquots,  
228 mixed with 160 mg of LiBO<sub>2</sub> flux, and fused for 10 minutes at 1050° C. Melts were  
229 subsequently quenched in 20 mL of 10% HNO<sub>3</sub> and agitated to ensure thorough dissolution.  
230 Liquid samples were then filtered and diluted again prior to being analyzed using a JY2000  
231 Ultrace ICP Atomic Emission Spectrometer. Samples, powdered standards, and blanks were run  
232 concurrently and analyzed for Si, Al, Fe, Mg, Ca, Na, K, P, Mn, and Ti. All samples were run  
233 and analyzed in triplicate to determine ensure accuracy and to determine analytical uncertainty.

234 Chemistry was also determined on rock chips using LIBS analyses at Los Alamos  
235 National Laboratory (LANL). The LANL instrument is a replica of the ChemCam instrument on

236 the Curiosity rover, and uses a pulsed 1067 nm laser (repetition rate of 3 Hz, energy of 13  
237 mJ/pulse, and stand-off distance of 3 m) to generate a plasma on the sample surface, the light  
238 from which is collected by the unit's telescope and directed to three spectrometers spanning from  
239 240.1 nm through 906.5 nm. A total of 150 laser pulses (and, subsequently, spectra) were  
240 generated at three locations on each sample surface and interior. Each laser pulse bores slightly  
241 deeper into the rock, resulting in the generation of small depth profiles (on the order of ~100  $\mu\text{m}$ ,  
242 Lanza et al., 2012, 2015). The samples were measured under martian environmental conditions  
243 ( $\text{CO}_2$  atmosphere at 7 Torr) to quantify elemental chemistry, a technique that is well-calibrated  
244 for Curiosity's ChemCam unit under martian environmental conditions. The lower atmospheric  
245 pressure also allows for the plasma to more effectively expand within the environmental  
246 chamber. Spectra were subsequently processed and converted to elemental chemistry using the  
247 techniques described in Wiens et al. (2013), Lanza et al. (2015), and Clegg et al. (2017).

248 Mössbauer spectroscopy was used to determine  $\text{Fe}^{3+}$  abundances in 5 sample interiors  
249 and surfaces (3 tuffs and 2 sandstones) and to quantify the distribution of iron among its ferric  
250 and ferrous phases. Analyses were performed at Mt. Holyoke College. Powder aliquots of 75  
251 mg were analyzed at 295 K on a WEB Research Co. model WT302 spectrometer using a  $^{57}\text{Co}$   
252 source.

253 Elemental chemistry and comparisons between unaltered interiors and weathered surfaces  
254 can provide important clues regarding the alteration processes at work. Alteration processes and  
255 their resultant alteration products follow diagnostic pathways that allow for these processes to be  
256 identified and interpreted. For example, typical aqueous alteration under near-neutral conditions  
257 will preferentially leach divalent (e.g.,  $\text{Fe}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ) and monovalent cations (e.g.,  $\text{Na}^+$ ,  $\text{K}^+$ )  
258 out of a material relative to more stable elements like aluminum and silicon. This is the

259 foundation for the Chemical Index of Alteration (CIA, Nesbitt and Young, 1982), which uses  
260 molecular proportions and is defined as:

$$261 \quad CIA = \frac{Al_2O_3}{(Al_2O_3 + CaO^* + Na_2O + K_2O)} \times 100$$

262

263 where CaO\* corresponds solely to the CaO contained within the silicates in the material.

264 Oxidative weathering processes, however, are not easily characterized using the CIA, as divalent  
265 cations preferentially migrate towards the rock surface and are removed from the system relative  
266 to monovalent cations. The result is a relative increase in monovalent cations and decrease in  
267 divalent cations in rock surfaces relative to their interiors, which is unique from most forms of  
268 aqueous alteration. Lastly, the presence of coatings or patinas on rock surfaces is also not well  
269 represented by the CIA, as one or several elements significantly increase in concentration at the  
270 expense of other elements relative to the rock interiors. For example, the presence of a coating  
271 of gypsum (Ca-sulfate) on a rock surface would appear as an increase in CaO at the expense of  
272 most other elemental phases, particularly SiO<sub>2</sub>, which is typically abundant in silicate rocks and  
273 is relatively stable under minor to moderate amounts of alteration. It should be noted that while  
274 we utilize the CIA on the scale of individual hand samples, it was originally developed to  
275 characterize chemical alteration on the landscape-scale (Nesbitt and Young, 1982).

276 While the CIA has long been used to investigate the extent of weathering where aqueous  
277 alteration dominates, it was not designed to differentiate between different types of alteration  
278 processes as described above. To help differentiate between traditional aqueous alteration,  
279 oxidative weathering processes, and the presence of coatings or patinas, we rely on the  
280 Weathering Intensity Scale (WIS, Meunier et al., 2013), which compares the molar proportions  
281 of several cation species. Specifically, the WIS compares M<sup>+</sup> (Na<sup>+</sup> + K<sup>+</sup> + 2Ca<sup>2+</sup>), R<sup>2+</sup> (Fe<sup>2+</sup> +

282  $Mg^{2+}$ ), and  $4Si$  ( $Si/4$ ) on a ternary diagram. The elemental trends between a rock interior and  
283 surface towards or away from any of the three apices can be used to determine the dominant  
284 alteration process at work on the rock surface. To determine the proportion of  $Fe^{2+}$  in each  
285 sample, we utilize the results of our limited Mössbauer spectral analyses to estimate the relative  
286 proportion of  $Fe^{2+}/Fe_{Total}$  in all of our samples.

287

## 288 **Results**

289 The results from our analyses are presented in **Table 3** and discussed in detail in the  
290 sections below.

291

### 292 *Spectral Signatures*

293 Rock samples were originally selected from the PRR due to their visible weathering  
294 signatures (including oxidized red/brown surfaces relative to their less oxidized (less red)  
295 interiors). These oxidation signatures are confirmed through VNIR reflectance spectroscopy,  
296 appearing as strong charge-transfer absorptions at visible wavelengths (shorter than  $0.7 \mu m$ , **Fig.**  
297 **2**). At near-infrared wavelengths, anhydrous oxidative weathering processes typically result in  
298 little if any increase in the strength of absorption features related to hydration/hydroxylation,  
299 which would be seen as sharp absorptions near  $1.4 \mu m$ ,  $1.9 \mu m$ , and between  $2.1 \mu m$  and  $2.5 \mu m$ ,  
300 as well as a general decrease in reflectance towards the longest wavelengths (referred to as a  
301 “blue slope”). A classic oxidative weathering spectrum can be observed in the conglomerate  
302 PRR-20642, which shows

303

304 **Table 3.** Antarctic samples analyzed in this investigation using the full suite of analytical techniques,  
305 sorted by rock type. Reported are the differences observed in the rock surfaces relative to their  
306 corresponding interior measurements. For example, “> Hydration” indicates that the surface is more  
307 hydrated than the interior. The “dominant mode of alteration” is interpreted based on the full complement



308 of analytical techniques and results (see *Discussion* section).

Type	Sample ID	VNIR Spectroscopy	XRD	Chemistry	CIA Difference	Dominant Mode of Alteration
Basalt	13197	> Oxidation ~ Hydration	> Hydrated mineral phases	< CaO < MgO > K <sub>2</sub> O	+2.2	Oxidative
Conglomerate	20642	> Oxidation < Hydration	None	> Al <sub>2</sub> O <sub>3</sub> > FeO <sub>T</sub> > K <sub>2</sub> O < Na <sub>2</sub> O < SiO <sub>2</sub>	+4.2	Oxidative
	25796	> Oxidation > 1 μm crystal field feature ~ Hydration	None	None	+0.9	Oxidative
Mudstone/ Siltstone	12393	~ Oxidation > Hydration < Gypsum	< Gypsum	< CaO > Al <sub>2</sub> O <sub>3</sub> > SiO <sub>2</sub>	+4.1	Aqueous, Bleached*
	12798	> Oxidation ~ Hydration	None	< CaO < MgO > K <sub>2</sub> O	-1.0	Oxidative
	23553	> Oxidation ~ Hydration	None	< CaO < MgO > K <sub>2</sub> O	+1.0	Oxidative
	26210	~ Oxidation > Hydration	> Zeolites and phyllosilicates	< SiO <sub>2</sub> > Al <sub>2</sub> O <sub>3</sub>	+3.4	Unknown
	30224	> Hydration		None	+0.2	Aqueous, Bleached*
Sandstone	05483	> Oxidation > Hydration	> Zeolite	None	+2.0	Aqueous
	26160	> Oxidation ~ Hydration	None	> SiO <sub>2</sub> < Al <sub>2</sub> O <sub>3</sub> < K <sub>2</sub> O	-0.4	Aqueous
	26909	> Oxidation ~ Hydration	< Hydrated phases	None	-1.0	Oxidative
	27111	> Oxidation ~ Hydration	None	None	-0.7	Oxidative
	36193	> Oxidation > Hydration	None	None	+0.5	Unknown
Tuff	25633	> Oxidation > 1 μm crystal field feature ~ Hydration	> Gypsum < Zeolites < Amorphous material	> FeO <sub>T</sub> < SiO <sub>2</sub>	-3.3	Coating (goethite)
	25908	> Oxidation > Hydration	> Gypsum	> CaO > Na <sub>2</sub> O < SiO <sub>2</sub>	-17.8	Coating (gypsum)
	26951	> Oxidation ~ Hydration	None	None	-0.4	Oxidative
	26975	> Oxidation > Gypsum	> Gypsum	> CaO < Al <sub>2</sub> O <sub>3</sub> < SiO <sub>2</sub>	-16.6	Coating (gypsum)
	27109	> Oxidation	> Gypsum	> CaO	-27.3	Coating

		> Gypsum		< Al <sub>2</sub> O <sub>3</sub> < SiO <sub>2</sub>		(gypsum)
	34531	> Oxidation > Hydration	None	> CaO > P <sub>2</sub> O <sub>5</sub> < SiO <sub>2</sub>	-14.7	Coating (amorphous Ca- sulfate)
	36150	~ Oxidation ~ Hydration	None	> CaO < Al <sub>2</sub> O <sub>3</sub>	-0.4	Unknown
	36241	> Oxidation ~ Hydration	None	> FeO <sub>T</sub> > MgO	+0.9	Unknown
	39262	> Oxidation ~ Hydration	> Zeolite > Chlorite	< CaO < MgO > K <sub>2</sub> O > SiO <sub>2</sub>	+0.5	Oxidative

309 \*Surfaces consistent with bleaching due to exposure to ultraviolet radiation, as was first described in  
310 Tasch and Gafford (1969).  
311

312 weakened hydrated absorption features relative to the rock's interior, a strong Fe<sup>3+</sup> charge-  
313 transfer absorption at visible wavelengths, and an overall blue slope at near-infrared wavelengths  
314 (**Fig. 2d**). Only approximately half of the samples measured in this study exhibit VNIR spectral  
315 signatures that are consistent with oxidative weathering processes (**Table 2**).

316 In addition to these oxidized signatures, many sample surfaces also exhibit spectral  
317 signatures that are consistent with more mature alteration processes. For example, PRR-25633, a  
318 tuff from Mager Nunatak in the Central Transantarctic Mountains (CTAM), exhibits broad  
319 absorption features near 0.64 μm and 0.92 μm that are associated with Fe<sup>3+</sup> crystal field  
320 transitions (Morris et al., 1985). Other examples include a suite of tuffs collected from the  
321 Hanson Formation in the CTAM (including PRR-27109 from Storm Peak, **Fig. 2b**), almost all of  
322 which exhibit spectral signatures consistent with the calcium sulfate mineral gypsum at their  
323 surfaces but not in their interiors. Diagnostic gypsum signatures include “saw tooth” absorptions  
324 centered near 1.42 μm and 2.23 μm, as well as a prominent 1.78 μm absorption. These more  
325 mature alteration phases are not predicted for nor observed in the oxidative weathering  
326 previously identified in Antarctic samples (Salvatore et al., 2013, Cannon et al., 2015) and,  
327 instead, are more consistent with more extensive and mature aqueous alteration.

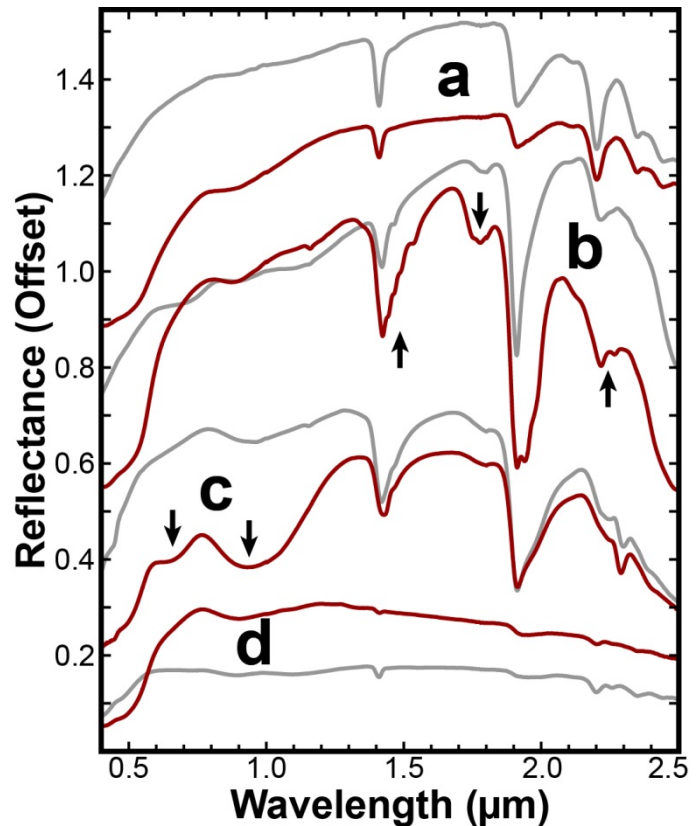
328

329 *Mineralogy*

330 As reported by Salvatore et al.  
331 (2013), XRD patterns of dolerites from  
332 the MDV do not show any significant  
333 variations between rock surfaces and  
334 interiors, suggesting little (if any)  
335 mineralogical variations as a result of  
336 oxidative weathering. This interpretation  
337 was supported through petrographic  
338 analyses, which showed unaltered  
339 minerals at the uppermost surface of  
340 oxidized dolerites in the absence of  
341 significant coatings, patinas, or other  
342 evidence for aqueous alteration.

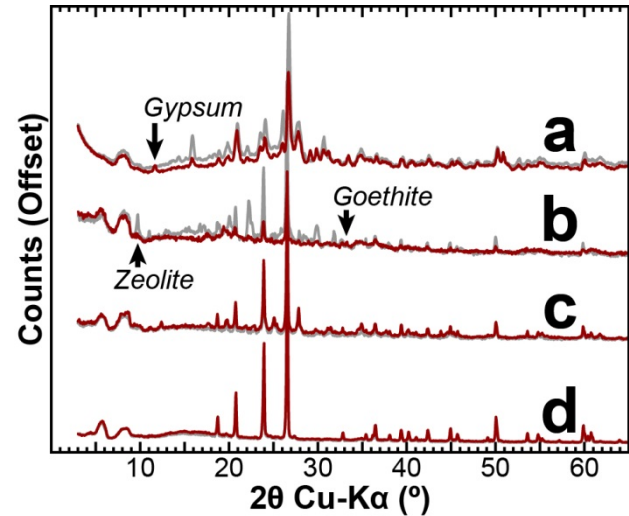
343 Mössbauer spectroscopy also confirmed  
344 this interpretation and suggested that the  
345 increased Fe<sup>3+</sup> in rock surfaces (+14% on average) remains in its original primary mineralogical  
346 phases (most likely pyroxenes) as opposed to producing new crystalline oxides and oxy-  
347 hydroxides.

348 The sedimentary rocks analyzed in this study, however, exhibit a wide diversity of  
349 mineralogical signatures (**Fig. 3**). For example, half (9) of the samples do not show any  
350 appreciable differences between their interiors and their surfaces, suggesting that the alteration



**Figure 2.** Visible/Near-infrared spectra of representative sample interiors (grey) and surfaces (red). Arrows indicate major differences in absorption features between interiors and surfaces. (a) PRR-26160 (Sandstone, offset +0.8) showing a strong ferric iron charge-transfer absorption at the surface; (b) PRR-27109 (Tuff, offset +0.4) showing strong gypsum absorption features at the surface (see arrows); (c) PRR-25633 (Tuff, offset +0.1) showing significant goethite absorptions at the surface (see arrows); and (d) PRR-20642 (Conglomerate, no offset) showing a strong ferric iron charge-transfer absorption at the surface.

351 process acting on the rock's surface did not  
352 remove phases present within the bulk rock,  
353 nor did it produce new alteration phases. Such  
354 signatures are consistent with oxidative  
355 weathering, but can also occur as a result of  
356 congruent leaching or dissolution under  
357 aqueous conditions. Other samples show  
358 evidence for more mature alteration phases at  
359 their surface, including gypsum and goethite,  
360 which is consistent with VNIR spectral  
361 measurements. For example, the surface of  
362 sample PRR-25633 (**Fig. 3b**) exhibits a small  
363 XRD peak associated with goethite, which  
364 supports the VNIR observations discussed previously. The relatively small goethite peak is  
365 likely a result of the Cu-K $\alpha$  radiation source, which causes significant iron fluorescence and a  
366 higher background that creates difficulty in identifying crystalline phases. In addition, the  
367 majority of XRD peaks observed in the interior of this sample are muted or entirely absent from  
368 the surface XRD pattern, suggesting that the surface mineralogy is less complex (dominated by  
369 only a few mineralogical species) than the interior. The surface pattern of sample PRR-26975  
370 (**Fig. 3a**) also shows a weakening of the XRD peaks found in the sample interior in addition to  
371 the appearance of an XRD peak associated with gypsum. This observation is consistent with the  
372 corresponding VNIR spectra that suggest the presence of a gypsum coating on the surface of this  
373 sample and its absence in the sample interior.



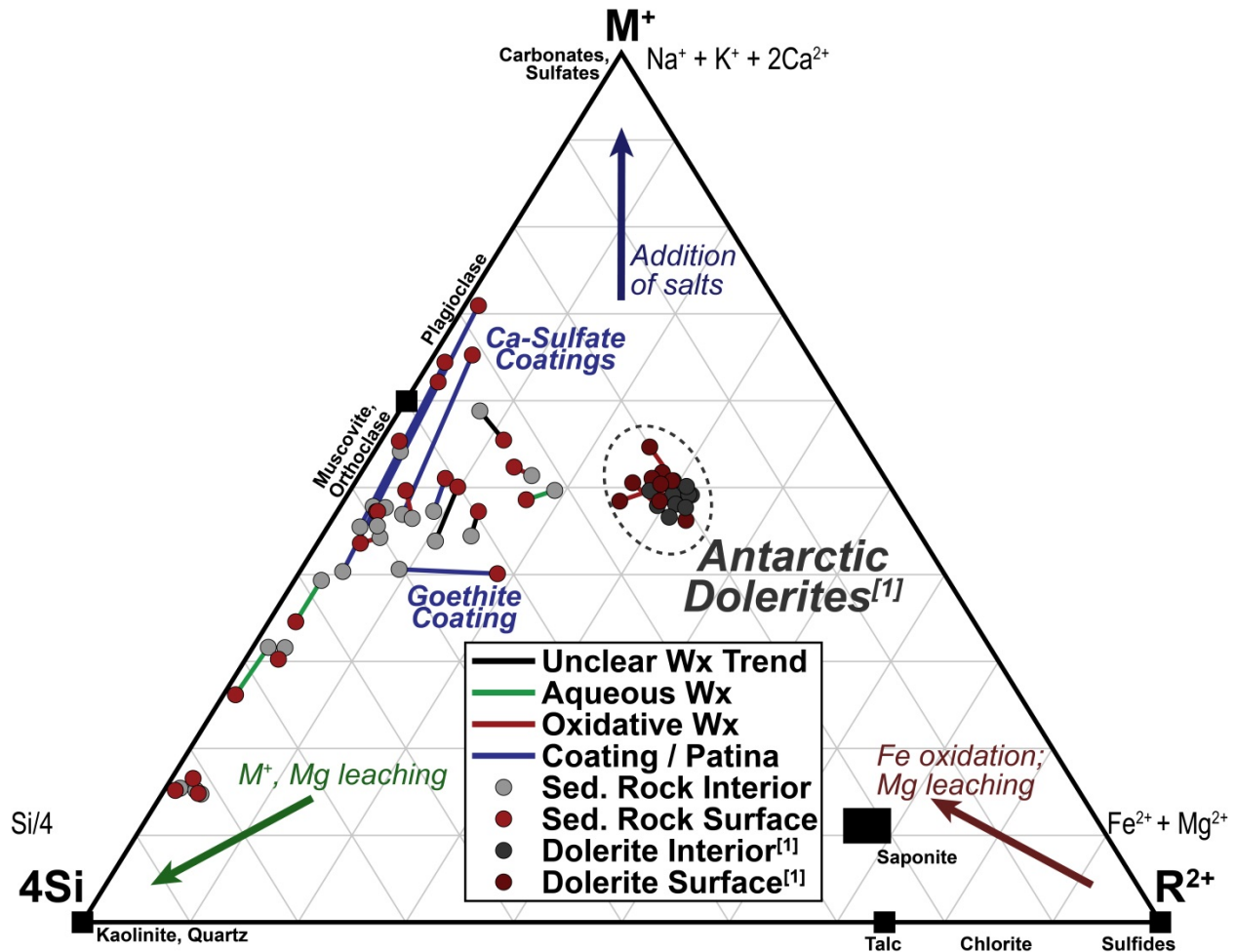
**Figure 3.** X-ray diffraction (XRD) patterns of representative sample interiors (grey) and surfaces (red). Patterns are offset for clarity and arrows represent significant differences between patterns. (a) PRR-26975 (Tuff) showing the presence of gypsum at the surface; (b) PRR-25633 (Tuff) showing the presence of zeolite and goethite in the interior and at the surface, respectively; (c) PRR-20642 (Conglomerate) and (d) PRR-26160 (Sandstone), both showing no significant mineralogical differences between the surface and interior.

374           Lastly, some samples also exhibit evidence for crystalline alteration phases within their  
375 interior (e.g., zeolites), with significantly weaker signatures at the surface. These interior  
376 alteration phases are likely indigenous to the sedimentary rocks and prevalent throughout the  
377 sedimentary unit. One possible reason for why these alteration minerals are not present at the  
378 rock surface is due to their dissociation by ultraviolet radiation, which has been previously  
379 observed in the Antarctic and shown to have significant influences on both the clay mineralogy  
380 and organic content of organic-rich sedimentary rocks (Tasch and Gafford, 1969).

381

### 382 *Chemical Signatures*

383           The diversity of the derived rock chemistries reflect the diversity of sedimentary rocks  
384 characterized in this investigation. This is demonstrated in the CIA values for rock interiors  
385 calculated using ICP-OES data, which range from 45.7 (sandstone sample PRR-26909) to 83.6  
386 (siltstone sample PRR-30224). These CIA values reflect the concentration of mobile cations  
387 inherent within the parent lithologies, and indicate that some of these lithologies have  
388 experienced significant aqueous alteration prior to their most recent exposure to the Antarctic  
389 environment, while others likely did not. While CIA variations among interiors represent rock  
390 alteration prior to modern exposure, the CIA value of each rock surface relative to its interior  
391 identifies any cation removal within the current rock surface. Differences in CIA values between  
392 rock surfaces and their corresponding interiors are reported in **Table 3**. However, as previously  
393 noted, CIA is not ideal for identifying oxidative weathering processes.



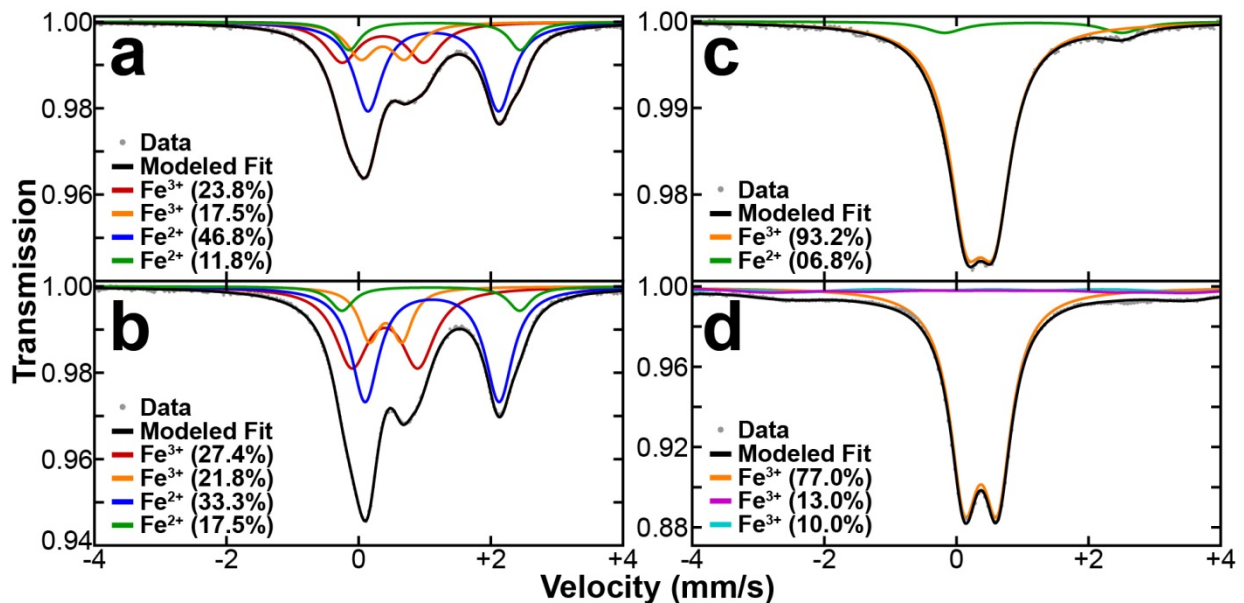
**Figure 4.** A Weathering Intensity Scale (WIS) ternary diagram showing the ICP-OES-derived chemistry and relationships between rock interiors (grey dots) and surfaces (red dots) for the Antarctic samples investigated in this study. The color of the joins between rock interior-surface pairs indicate the dominant weathering process interpreted based on available data. Antarctic dolerite interiors and surfaces are also shown for comparison, highlighting the trends caused by oxidative weathering in basaltic materials.

394 The dominance of oxidative weathering processes in dolerites from the MDV can be  
 395 more clearly seen in a WIS ternary diagram (**Fig. 4**), where rock surfaces trend away from the  
 396  $R^{2+}$  apex as  $Fe^{2+}$  is oxidized to  $Fe^{3+}$  and  $Mg^{2+}$  is preferentially removed from the rock surface.  
 397 Some dolerite surfaces also trend slightly towards the  $M^+$  apex, indicating that the relative  
 398 increase in  $Na^+$  and  $K^+$  is greater than the relative removal of  $Ca^{2+}$  in the dolerite surfaces. The  
 399 relative distance between rock interiors and surfaces is small, which is consistent with the  
 400 relatively minor elemental variations observed in rock surfaces that have undergone oxidative

401 weathering relative to their interiors. Each sample surface was assumed to have 14% more  $\text{Fe}^{3+}$   
402 than their corresponding interior, a result based on the average difference in  $\text{Fe}^{3+}/\text{Fe}_{\text{Total}}$  of the  
403 three representative samples measured with Mössbauer spectroscopy in Salvatore et al. (2013).

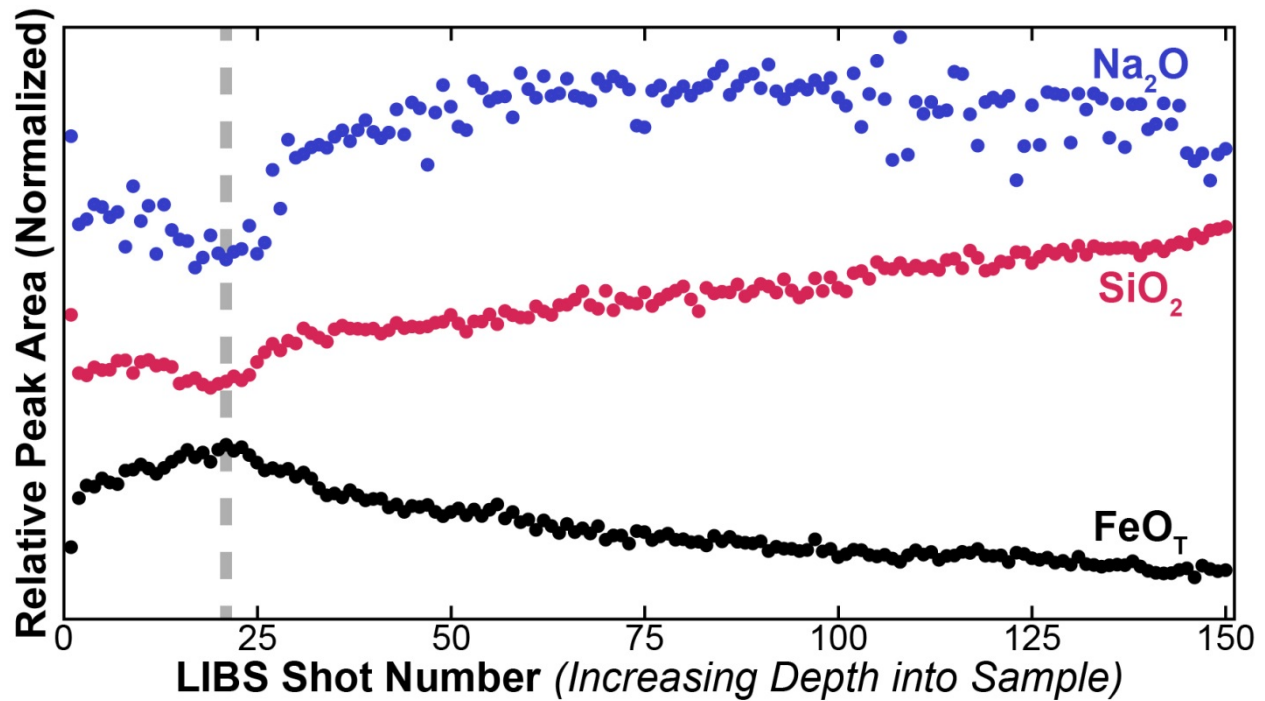
404 In contrast to the tight clustering observed in the dolerites from the MDV, the lithologies  
405 investigated in this study span a wide range of interior and surface compositions (**Fig. 4**). The  
406 interior compositions reflect the wide variety of lithologies selected for this investigation, from  
407 siliceous clastic sedimentary rocks towards the bottom-left of **Fig. 4**, to the basalts and basaltic  
408 tuffs found towards the center of **Fig. 4**. Similarly, the surface compositions reflect a wide  
409 variety of alteration trends relative to the unaltered interior. The relationship between chemical  
410 signatures in some surfaces relative to their interiors point to dominance by oxidative weathering  
411 processes, which follow a similar path away from the  $\text{R}^{2+}$  apex as the dolerites. The oxidation of  
412 some samples without a significant change in mineralogy is also confirmed by Mössbauer  
413 spectroscopy in samples like PRR-39262 (**Fig. 5a-b**). However, oxidative weathering was not  
414 found to be the dominant alteration process in these sedimentary samples. Several samples also  
415 exhibit alteration trends that are more consistent with typical aqueous alteration, which trends  
416 towards the 4Si apex as mobile cations are leached from the rock surface (**Fig. 4**, Meunier et al.,  
417 2013). In addition, significant trends towards either the  $\text{R}^{2+}$  or  $\text{M}^+$  apices indicate an enrichment  
418 of mobile cations at the rock surface relative to its interior, which is not predicted for either  
419 aqueous alteration or oxidative weathering. Instead, these trends are most consistent with the  
420 presence of coatings or patinas on the surfaces (Meunier et al., 2013), which supports the spectral  
421 and mineralogical observations discussed above.

422 For example, the presence of a goethite coating on the surface of PRR-25633, as  
 423 supported by spectral, mineralogical, and chemical analyses (e.g., **Fig. 2** and **Fig. 5c-d**). In **Fig.**  
 424 **4**, the surface of PRR-25633 is shown to trend towards the  $R^{2+}$  apex, indicating a significant  
 425 enrichment in iron. Note that this enrichment in iron is predicted as  $Fe^{2+}$  because the average  
 426 Mössbauer  $Fe^{2+}$  value was used in the generation of this figure; in reality, the surface of sample  
 427 PRR-25633 was measured to be 100%  $Fe^{3+}$  using Mössbauer spectroscopy, and so no variation  
 428 in Fe between rock interior and surface should be visible on a WIS diagram because none of the  
 429 Fe is in a ferrous state. However, LIBS analyses confirm the presence of an Fe-rich phase at the  
 430 surface of this sample. As shown in **Fig. 6**, the observed contribution of Fe in LIBS analyses of  
 431 the surface of PRR-25633 generally decreases with increasing depth into the sample, with a  
 432 maximum calculated  $FeO_T$  abundance of roughly 25%. The first ~20 laser pulses in two of the  
 433 three LIBS analyses averaged on the surface of PRR-25633 show a significant increase in  
 434 elemental Fe before decreasing with depth; this initial increase in Fe corresponds with a similar



**Figure 5.** Mössbauer spectra of select samples measured in this study. The interior (a) and surface (b) of sample PRR-39262, exhibiting changes in relative abundances of  $Fe^{2+}$  and  $Fe^{3+}$ , although very little change in host mineralogy, which is consistent with oxidative weathering processes. Alternatively, the interior (c) and surface (d) of sample PRR-25633 exhibit significant spectral differences that are consistent with a coating of goethite on the sample surface.





**Figure 6.** Normalized peak intensities (corresponding to relative oxide abundances) for sample PRR-25633S for elemental Fe, Si, and Na, measured as the peak area at 404.58 nm, 288.16 nm, and 589.59 nm, respectively. The vertical dashed grey line indicates the transition from a Si- and Na-rich coating at the uppermost surface to an Fe-rich coating just below the uppermost coating.

435 decrease in Si and Na before these two elemental phases begin to increase with depth into the  
 436 sample. While the elemental trends after the first ~20 laser pulses are consistent with a goethite  
 437 coating, the initial increase in Fe and decrease in Si and Na suggest that the uppermost ~20  $\mu\text{m}$   
 438 of sample PRR-25633 contains a silicon- and sodium-rich coating that lies above a subsequent  
 439 coating of goethite. This uppermost coating must be sufficiently thin as to not be evident in  
 440 VNIR spectral measurements, or to be incorporated in significant volume into the powdered rock  
 441 surfaces that were subsequently measured by XRD or Mössbauer spectroscopy. While an Fe-  
 442 poor phase may not be visible to Mössbauer spectroscopy, even a non- or nano-crystalline silica-  
 443 rich phase should be detected in XRD analyses through the presence of an amorphous hump.

444 The presence of gypsum coatings on the surfaces of several tuffs from the CTAM is  
 445 indicated by a trend towards the  $\text{M}^+$  apex in **Fig. 4**, as the presence of gypsum preferentially  
 446 increases the concentration of calcium at the surface relative to silicon. LIBS analyses agree

447 with this observation and provide additional insight into the thickness and purity of the coatings  
448 and patinas observed in the other chemical, mineralogical, and spectral data (Lanza et al., 2012).  
449 For example, **Fig. 7** shows the comparison between ICP-OES measurements of sample PRR-  
450 27109 and LIBS measurements of the same sample surface on a WIS ternary diagram. A nearly  
451 identical pattern can be seen using both analytical methods. Consistent with the ICP-OES  
452 measurements, the LIBS analyses trend away from the  $M^+$  apex, which corresponds to the  
453 decreasing concentration of Ca in the rock interior. The trend towards the 4Si apex also  
454 indicates that silicates are becoming more prevalent in the rock interior relative to the sulfate-  
455 dominated rock surface (Meunier et al., 2013). The derived compositions from both the initial  
456 and final LIBS shots are remarkably consistent with the compositions measured using ICP-OES  
457 for the rock surface and interior, respectively. This likely indicates that the LIBS pulses were  
458 able to completely penetrate through the gypsum coating and into the underlying tuffaceous  
459 substrate. A value of 82%  $Fe^{3+}$  was used for all LIBS shots, as that is the value derived from  
460 Mössbauer spectroscopy of the surface of PRR-26975, a similar gypsum-coated tuff collected  
461 from the same geologic unit as PRR-27109.

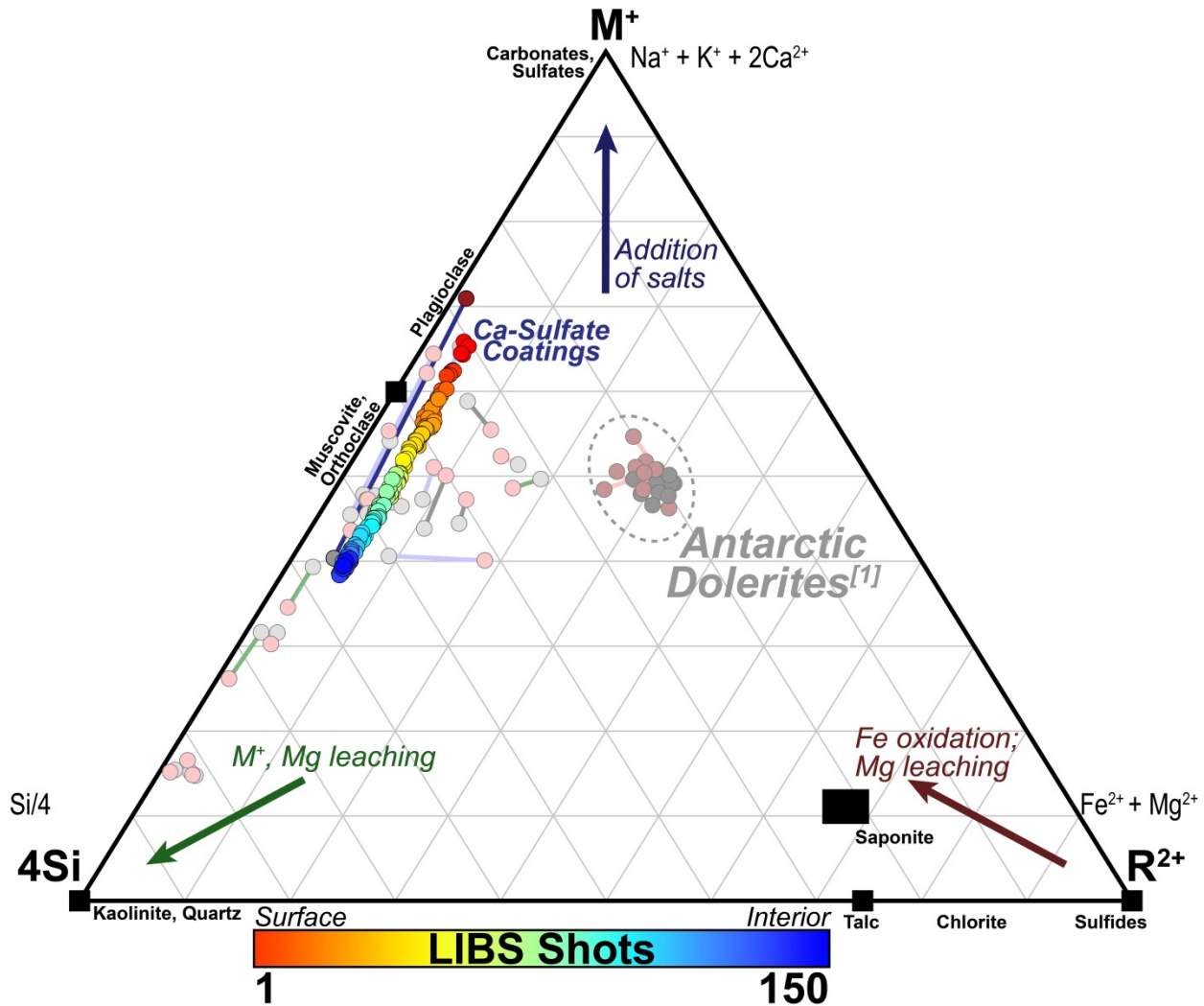
462

## 463 **Discussion**

464

### 465 *Surface Weathering of Sedimentary Rocks in Antarctica*

466 The combination of our spectral, mineralogical, and chemical analyses does not support  
467 the hypothesis that oxidative weathering is the dominant alteration process occurring on  
468 sedimentary rock surfaces throughout the TAM. While the relationship between rock surfaces  
469 and interiors is generally well-defined in Antarctic dolerites (Salvatore et al., 2013), the



**Figure 7.** A Weathering Intensity Scale (WIS) ternary diagram highlighting the laser induced breakdown spectroscopy (LIBS) 150-shot analysis of sample PRR-27109 (tuff), which was shown to have a sulfate-rich coating at its surface. The ICP-OES-derived surface-interior trend is also highlighted for this sample in the background. Both techniques show notably similar chemical trends between the surface and the interior, as the measurements trend away from the M<sup>+</sup> apex with increasing depth into the sample, which is consistent with the presence of a Ca-sulfate coating at the surface and decreasing Ca-rich compositions with depth.

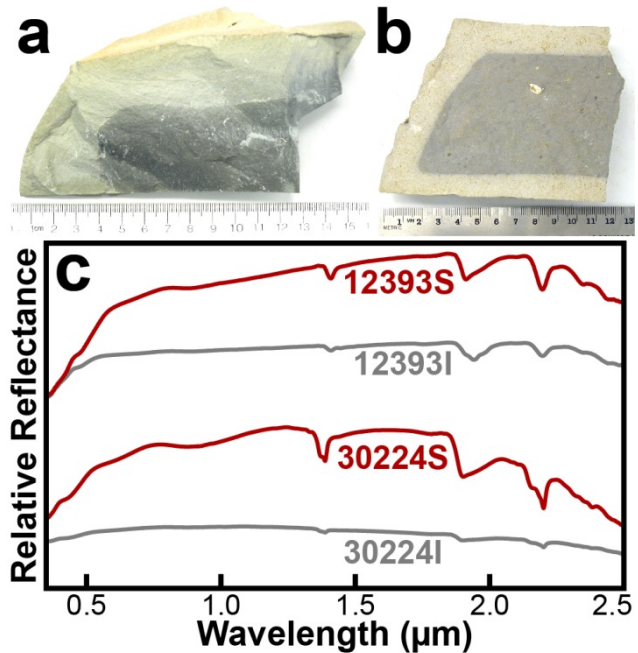
470 relationships observed in sedimentary rocks cannot be explained with a single weathering  
 471 process. Instead, it appears as if at least three separate alteration processes are occurring on the  
 472 22 samples analyzed as part of this investigation (**Fig. 4, Table 3**).

473 Based on our interpretation of the results presented above, we have identified oxidative  
 474 weathering processes preserved at the surfaces of 9 of the 22 samples analyzed in this  
 475 investigation. This process is identified through the presence of Fe<sup>3+</sup> charge-transfer absorption

476 features and the lack of new alteration phases as observed in VNIR spectroscopy, a general  
477 similarity between XRD patterns of rock surfaces and interiors, and chemical signatures that  
478 indicate a depletion of divalent cations relative to monovalent cations at rock surfaces. Evidence  
479 for aqueous alteration is observed in 4 of our samples, which can be identified by strengthened  
480 hydration features at VNIR wavelengths, the presence of crystalline secondary phases (e.g.,  
481 phyllosilicates) in XRD data, and the depletion of both monovalent and divalent cations and a  
482 relative increase in  $\text{SiO}_2$  and/or  $\text{Al}_2\text{O}_3$  at rock surfaces. Lastly, evidence for coatings or patinas  
483 is observed on 5 of the 22 rock surfaces, which can be observed as significant increases in  
484 elemental phases at the surface that should otherwise be mobile under aqueous or oxidative  
485 weathering processes. In addition to these three dominant modes of surface alteration, 4 of the  
486 22 sample surfaces exhibit alteration patterns that are not consistent with any of these three  
487 modes, suggesting that an unknown alteration processes is (or combination of alteration  
488 processes are) dominating these rock surfaces. None of the 22 samples showed evidence for  
489 biological weathering processes, which would lead to the disintegration and physical weakening  
490 of sample surfaces as well as the preferential redistribution of metal cations from the actions of  
491 organic acids (Banfield et al., 1999).

492 Two samples that exhibit evidence for both aqueous alteration as well as an additional  
493 alteration process are PRR-12393 and PRR-30224, two dark grey Permian-aged mudstones with  
494 bright surface rinds more than one centimeter in thickness (**Fig. 8**). The dark nature of these  
495 mudstones is likely due to an abundance of organic carbon within the sample, which is consistent  
496 with other members of the carbon-rich Victoria Group from the southern Transantarctic  
497 Mountains (Barrett et al., 2013). VNIR spectra of both sample surfaces indicate stronger  $2.2 \mu\text{m}$   
498 absorption features associated with Al- or Si-OH bonding, and the PRR-30224 spectra exhibit

499 the diagnostic doublet absorption features at  
500 1.4  $\mu\text{m}$  and 2.2  $\mu\text{m}$  that are diagnostic of  
501 kaolinite (**Fig. 8c**). The strengthening of  
502 vibrational absorption features in the surface  
503 spectra is consistent with aqueous alteration  
504 processes modifying the rock surfaces. The  
505 unique lightening at the surface is most  
506 consistent with the oxidation and bleaching of  
507 the surface under the enhanced ultraviolet  
508 (UV) radiation in the Antarctic due to the  
509 relative depletion of the ozone layer, a  
510 geologic phenomenon that was first identified  
511 by Tasch and Gafford (1969). They showed  
512 that the increased UV radiation is able to bleach, oxidize, and remove essentially all organic  
513 carbon from the rock surface, leaving it in stark contrast to the rock's interior. No other samples  
514 in our suite demonstrate a similar weathering pattern, possibly because PRR-12393 and PRR-  
515 30224 are the most enriched in organic carbon, resulting in both their dark interior as well as  
516 providing the contrast necessary to observe this UV bleaching.



**Figure 8.** Photographs of samples PRR-12393 and PRR-30224, showing the thick bleached rinds and the darker interiors. Images courtesy of the Polar Rock Repository. (b) Visible/Near-infrared (VNIR) spectra of the interiors and surfaces of the two samples, showing the distinct brightening of the surfaces at visible wavelengths and the strengthening of hydration features.

517 There are several possible reasons as to why oxidative weathering processes like those  
518 found in Antarctic dolerites (Salvatore et al., 2013) dominate the surfaces of some but not the  
519 majority of samples studied here. The oxidative weathering products studied by Salvatore et al.  
520 (2013) were found on hard, fine-grained, and impermeable igneous rocks that can readily  
521 preserve alteration rinds (Glasby et al., 1981; Campbell and Claridge, 1987; Staiger et al., 2006).

522 Only a handful of samples analyzed in our investigation share similar physical attributes to those  
523 investigated by Salvatore et al. (2013). Increased erodibility of our samples may allow physical  
524 erosion to outpace chemical weathering, resulting in the rapid flaking and removal of altered  
525 surfaces. In addition, the dolerite samples investigated by Salvatore et al. (2013) had similar  
526 compositions, allowing for the composition of surfaces relative to their interiors to be easily  
527 determined. The samples analyzed in our study vary widely in composition, from basaltic to  
528 silica-rich, which may play a significant role in the availability and behavior of cations as well as  
529 our ability to confidently identify and track the behavior of different cation species using our  
530 analytical techniques. We are confident, however, in our ability to differentiate between typical  
531 aqueous alteration, oxidative weathering processes, and other forms of alteration, because of  
532 their consistent geochemical signatures. For example, nearly all compositions of igneous rocks  
533 have been shown to aqueously weather in the same manner, first with the leaching of CaO,  
534 Na<sub>2</sub>O, and K<sub>2</sub>O, followed by the leaching of FeO<sub>T</sub> and MgO, with a steady enrichment in Al<sub>2</sub>O<sub>3</sub>  
535 and SiO<sub>2</sub> (Nesbitt and Young, 1982, 1984; McLennan et al., 2002; Hurowitz and McLennan,  
536 2007; Meunier et al., 2013). This consistency in weathering trends allows us to differentiate  
537 between alteration processes regardless of the parental chemistry of the rock.

538         Significant differences in parental composition as well as their original formation  
539 environments may also minimize any oxidation gradient that is present between rock interiors  
540 and the surrounding Antarctic environment. For example, the dolerites studied by Salvatore et  
541 al. (2013) were likely emplaced near the quartz-fayalite-magnetite (QFM) redox buffer, which is  
542 extremely reducing relative to the oxidizing Antarctic environment and establishes the oxidation  
543 gradient that is required for oxidative weathering processes to dominate. If these sedimentary  
544 lithologies were deposited under relatively oxidizing environmental conditions, the redox

545 gradient between the rock interior and the Antarctic environment may not be sufficient to  
546 promote surface oxidation and the preservation of oxidation rinds.

547         Lastly, the dolerites studied by Salvatore et al. (2013) were collected from the same  
548 valley and likely underwent similar geologic and alteration histories during their exposure to the  
549 Antarctic environment. The samples investigated in our study, however, were sourced from  
550 throughout the Antarctic continent and were likely exposed to a wide range of environmental  
551 conditions. Although all of the samples were collected from hyper-arid regions of the TAM,  
552 Marchant and Head (2007) showed that microclimatic variations can occur within very small  
553 geographic distances, resulting in significant differences between micro-, meso-, and macro-  
554 scale landscape and lithologic properties. In addition, the micro-geographic settings of these  
555 rocks (e.g., their orientation relative to other rocks or surfaces) and the impetus for their  
556 collection (e.g., were they a “typical” clast or was there some unique characteristic) are also  
557 poorly constrained for most of the samples analyzed here. The result is the inability to control  
558 for or even to confidently identify the relatively minor environmental, geologic, and geographic  
559 variables that might influence the formation and preservation of alteration products on these  
560 rocks.

561         While unlikely, it is possible that the gypsum coatings present on some tuffs are  
562 consistent with oxidative weathering processes. Cooper et al. (1996) were the first to show that  
563 oxidative weathering of basaltic glass in the laboratory resulted in the formation of crystalline  
564 CaO on sample surfaces. The calcium is sourced from the sample interior, as a result of divalent  
565 cations migrating outwards to the sample surface in response to the inward migration of electron  
566 holes (Cooper et al., 1996). However, in field settings where physical erosion and dissolution  
567 influence rock surfaces, the extremely friable and soluble CaO coatings are unlikely to be

568 preserved for any significant period of time (Salvatore et al., 2013). Is it possible that the local  
569 chemical environment promotes the formation of Ca-sulfates at rock surfaces instead of CaO as a  
570 product of surface oxidation? In addition, is it possible that the local microenvironment where  
571 these samples were collected was capable of protecting these rocks from physical erosion and  
572 dissolution to preserve these surface coatings? While no additional evidence suggests that these  
573 gypsum coatings are directly related to surface oxidation (e.g., clear gradients of discoloration, or  
574 significant differences in monovalent cation abundances between surfaces and interiors), we  
575 cannot wholly refute this possibility.

576         This work also provides evidence to suggest that some of the coldest and driest terrestrial  
577 environments are capable of aqueously altering the surfaces of sedimentary rocks. Mean annual  
578 temperatures throughout the TAM range from -30° C to less than -50° C (Dalrymple, 1966) and  
579 mean annual precipitation rivals that of the world's most arid deserts (Bull, 1971). The arid  
580 conditions and frequent katabatic winds also result in the rapid sublimation of most snow that  
581 falls onto ice-free surfaces, prohibiting liquid water from interacting with geologic surfaces for  
582 any extended periods of time (Campbell and Claridge, 1987). Despite these conditions that are  
583 adverse to the availability and activity of liquid water, aqueous alteration is possible due to the  
584 seasonal availability of small amounts of meltwater on the surfaces of rocks (Allen and Conca,  
585 1991; Staiger et al., 2006; Marchant and Head, 2007) as well as the stability of the landscapes,  
586 which keeps geologic features and rock surfaces preserved and intact well longer than most  
587 terrestrial environments (Marchant and Denton, 1996). Given enough time, sufficient energy,  
588 and a source of both liquid water and geologic materials susceptible to chemical weathering, our  
589 work has demonstrated that aqueous alteration is possible even in the coldest and driest terrestrial  
590 environments. These are important considerations when studying martian sedimentary



591 landscapes and the degree to which they are chemically altered.

592           This study also helps to reinterpret the work of Salvatore et al. (2013) and their  
593 conclusion that oxidative weathering processes dominate dolerite surfaces in Beacon Valley. Do  
594 these new analyses of other lithologies throughout the TAM suggest that oxidative weathering is  
595 unique to Beacon Valley and/or dolerites, and not as widespread as originally anticipated?  
596 Based on theory and the occurrence of oxidative weathering in other locales, we believe that  
597 while the dolerites of Beacon Valley are uniquely optimized to preserve oxidative weathering  
598 signatures, oxidative weathering processes are still broadly at work throughout the TAM. Our  
599 study and previous work has shown that oxidative weathering can be easily overprinted by more  
600 mature alteration processes, but that oxidative weathering still occurs wherever an oxidation  
601 gradient and sufficient  $\text{Fe}^{2+}$  is present within a rock. While oxidative weathering may initially  
602 dominate rock surfaces throughout the TAM, the interaction of rocks with their local  
603 microclimates (in addition to their individual geologic histories) is far more influential on the  
604 overarching alteration signatures than the easily overwhelmed oxidative weathering processes  
605 that may also be at work. The composition, hardness, and exposure histories of the dolerites of  
606 Beacon Valley, along with the cold, dry, and stable microclimatic environment, are perfectly  
607 suited to form and preserve oxidative weathering signatures while retarding the progression of  
608 more mature alteration processes. While this perfect combination of physical, chemical, and  
609 environmental properties may be present elsewhere throughout the TAM, our study demonstrates  
610 that such conditions are not the norm and, instead, more mature alteration processes are able to  
611 overprint oxidative weathering signatures in many Antarctic environments.

612

613 *Implications for the Weathering of Sedimentary Rocks on Mars*

614 Chemical weathering of rocks at the martian surface has been investigated in the past,  
615 particularly using the results of the Mars Exploration Rovers Opportunity and Spirit. McSween  
616 et al. (2004, 2006) and Haskin et al. (2005) identified evidence for minor amounts of surface  
617 alteration on the olivine-bearing basaltic clasts on the floor of Gusev crater, suggesting that  
618 chemical weathering is occurring in the modern martian environment. Salvatore et al. (2013)  
619 showed that the elemental chemistries and trends between rock interiors and surfaces are  
620 consistent with the dominance of relatively immature anhydrous oxidative weathering processes,  
621 and Salvatore et al. (2014) demonstrated that global spectral signatures are also consistent with  
622 the presence of doleritic oxidative weathering products. Furthermore, the investigation of  
623 meteorites on the martian surface confirms that chemical weathering on Mars is relatively minor  
624 with little evidence for significant recent aqueous alteration (e.g., Schröder et al., 2008; Fairén et  
625 al., 2011). Studies also suggest that physical erosion is likely to significantly outpace chemical  
626 weathering in the modern martian environment, which should result in the identification of  
627 chemical weathering products on rock surfaces being the exception rather than the norm  
628 (Golombek and Bridges, 2000; Golombek et al., 2006).

629 Few studies have investigated the role of modern chemical alteration on the surfaces of  
630 sedimentary rocks on Mars. Knoll et al. (2008) identified and investigated the presence of  
631 veneers and thick rinds in Meridiani Planum that were investigated by the Opportunity rover and  
632 showed that rock surfaces differed significantly in composition relative to their interiors. These  
633 veneers were interpreted to form through the interaction of these rock surfaces with small  
634 amounts of liquid water that resulted in an increased Si and NaCl concentration at rock surfaces  
635 (Knoll et al., 2008). Cannon et al. (2015) investigated oxidative weathering processes in an  
636 Antarctic sandstone and suggested that similar processes may be at work in sedimentary

637 landscapes on Mars, particularly in Meridiani Planum.

638           The rocks under investigation in Gale crater by the Curiosity rover are dominantly  
639 sedimentary in nature (e.g., Grotzinger et al., 2014). These sedimentary units were emplaced in  
640 alluvial, deltaic, lacustrine, and aeolian environments several billion years ago, and were likely  
641 re-exposed as a result of physical erosion and landscape evolution in the more recent geologic  
642 past. CIA values associated with these sedimentary units vary from  $< 35$  (Hurowitz et al., 2017)  
643 to  $> 60$  (Frydenvang et al., 2018) which, if assumed that all sedimentary rocks were basaltic to  
644 start (Taylor and McLennan, 2009), indicates little to moderate amounts of aqueous alteration  
645 has likely occurred under fluctuating climate and environmental conditions during transport,  
646 deposition, and lithification (Hurowitz et al., 2017). Based on these and additional data from the  
647 instruments onboard Curiosity (Vaniman et al., 2014; Johnson et al., 2016; Treiman et al., 2016;  
648 Hurowitz et al., 2017; Rampe et al., 2017; Wellington et al., 2017; Frydenvang et al., 2018), it is  
649 clear that the oxidation state of sedimentary rock interiors in Gale crater varies widely (**Fig. 9**).  
650 Should we expect oxidative weathering to dominate the sedimentary rock surfaces under  
651 investigation by the Curiosity rover in Gale crater and, if so, might these weathering processes  
652 influence our ability to accurately characterize surface compositions?

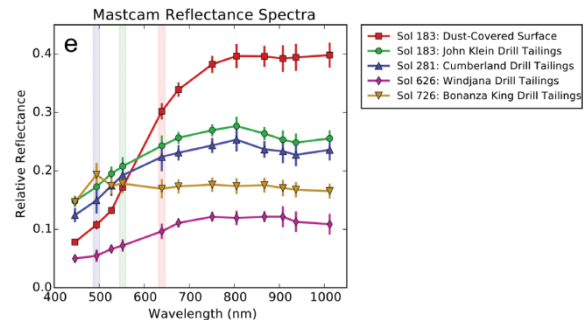
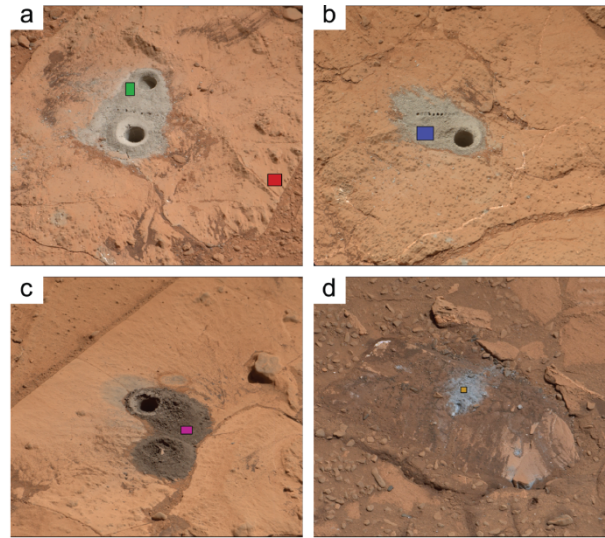
653           Unfortunately, determining the specific role of oxidative weathering in Gale crater is a  
654 difficult task, as Curiosity's payload does not include a Mössbauer spectrometer and is thus not  
655 capable of quantifying the  $\text{Fe}^{3+}/\text{Fe}_{\text{Total}}$  ratio of geologic materials. This makes it impossible to  
656 quantify the oxidation gradient present between the rock interiors and the current martian  
657 environment. In addition, estimates of physical erosion in Gale crater are surprisingly high  
658 ( $\sim 0.75 \text{ m My}^{-1}$ , Farley et al., 2014) and comparable to (and, in some cases, far greater than) those  
659 found in parts of the Antarctic interior (e.g.,  $\leq 0.31 \text{ m My}^{-1}$ , Margerison et al., 2005). This

660 suggests that the likely low rates of oxidative  
661 weathering (the current martian atmosphere is  
662 more than two orders of magnitude less  
663 oxidizing than Earth's atmosphere, Owen,  
664 1992) would probably be outpaced by  
665 physical erosion, preventing the formation of  
666 measurable oxidative weathering rinds on the  
667 surfaces of sedimentary rocks in Gale crater.

668 While observing and measuring  
669 oxidative weathering products similar to those  
670 observed on Antarctic dolerites would be  
671 difficult in Gale crater using the Curiosity  
672 rover, our work discussed above suggests that  
673 oxidative weathering is unlikely to dominate  
674 sedimentary lithologies in the first place.

675 Considering the observed diversity in rock  
676 chemistry, physical properties, exposure

677 histories, and the environmental conditions present during sediment deposition, lithification, and  
678 burial, we hypothesize that the products of oxidative weathering are unlikely to dominate the  
679 composition of sedimentary rock surfaces in Gale crater. Additional work is necessary to  
680 critically evaluate compositional differences between rock surfaces and interiors as measured by  
681 the Curiosity rover. However, given the inability for Curiosity to quantify ferric vs. ferrous iron,  
682 the only way to definitively identify oxidative weathering products would be through the subtle



**Figure 9.** Mastcam multispectral data derived from various drill tailings in Gale crater. Spectra of drill tailings (representing rock interiors) are compared to the dust-covered surface (red spectrum). The depth of the short wavelength (< 600 nm) absorption feature and steepness of the slope between 550 and 700 nm indicate the relative spectral contribution from Fe<sup>3+</sup>. Drill holes are approximately 1.6 cm in diameter for scale. From Wellington et al. (2017).

683 chemical patterns identified by Salvatore et al. (2013). Our work shows, however, that such  
684 chemical patterns are not preserved in the diverse suite of Antarctic sedimentary lithologies  
685 investigated here.

686         The hypothesis that oxidative weathering is not expected to dominate the surfaces of  
687 sedimentary rocks in Gale crater is supported by the only documented case of surface alteration  
688 identified on a rock clast within Gale crater, which was discovered on the “Bathurst Inlet” target  
689 by the ChemCam instrument near the Bradbury Landing site on sol 55 (Ollila et al., 2014;  
690 Mangold et al., 2015). Bathurst Inlet is a fine-grained layered sedimentary rock (fine sandstone  
691 or siltstone) with a composition comparable to hawaiiite (Schmidt et al., 2013; Mangold et al.,  
692 2015) and uniquely high Li abundances ( $> 30$  ppm) observed at the surface (Ollila et al., 2014).  
693 Li abundance, along with Rb, Na, and K, are also shown to systematically decrease with  
694 increasing ChemCam shot number, suggesting an enrichment of these elements at the uppermost  
695 surface. Ollila et al. (2014) interpreted this enrichment of alkali elements at the surface as  
696 evidence for modern aqueous alteration on the uppermost surface of the rock, potentially caused  
697 by processes like frost deposition, melting, and subsequent alteration. The preservation of these  
698 alteration signatures on Bathurst Inlet is thought to be the result of the resistant nature of the rock  
699 and the sheltering of these ChemCam analysis points by a slight overhang on the rock, which  
700 may have reduced the amount of physical erosion and removal of these alteration products  
701 (Ollila et al., 2014).

702         Lastly, while our study was able to isolate the uppermost surfaces of rocks and  
703 investigate them using XRD techniques, the XRD capabilities of the Curiosity rover are unable  
704 to sample just the uppermost millimeters of rock surfaces, precluding our ability to quantify  
705 differences between rock surface and interior mineralogies on Mars. Regardless, Salvatore et al.

706 (2013) found that oxidative weathering products, which primarily manifest themselves as  
707 chemical and not mineralogical variations, do not result in significant differences in XRD  
708 patterns between rock surfaces and interiors. Our XRD analyses on Antarctic sedimentary rocks  
709 confirm the results from Salvatore et al. (2013), showing little differences between rock surfaces  
710 and interiors where oxidative weathering is found to dominate. Instead, diffraction patterns are  
711 widely variable, from no observable changes between interiors and surfaces, to an increase in  
712 crystalline alteration phases in surfaces, to a decrease in crystalline alteration phases in surfaces.  
713 Such variability clearly demonstrates that oxidative weathering does not dominate the surfaces of  
714 sedimentary rocks throughout the TAM. Alternatively, the XRD data are consistent with each  
715 clast undergoing its own unique geologic and alteration history, thus resulting in their own  
716 alteration signatures.

717         The results of our investigation have significant implications for the weathering of  
718 sedimentary rocks in the modern martian environment. First, the diversity of alteration products  
719 found throughout the TAM, including those consistent with aqueous alteration, suggests that a  
720 diversity of alteration processes are also able to dominate rocky landscapes under hyper-arid and  
721 hypo-thermal environments on modern Mars. While liquid water is more stable and prevalent  
722 throughout the TAM than it is on the martian surface, Mars has experienced numerous  
723 significant climatic shifts in the recent geologic past as a result of variations in the planet's  
724 obliquity (Jakosky and Carr, 1985; Laskar and Robutel, 1993; Head et al., 2003; Forget et al.,  
725 2006). Second, should similar alteration processes and products be at work on Mars and  
726 generated at the surfaces of rocks, respectively, estimates of modern martian erosion rates from  
727 Gale crater indicate that the products of surface alteration may not remain preserved at the rock's  
728 surface for prolonged periods of time. For example, the rate of siliceous alteration rind

729 formation in sandstones in Arena Valley, Antarctica, is on the order of  $0.05 \text{ mm My}^{-1}$  (Weed and  
730 Ackert, 1986; Weed and Norton, 1991), which is more than four orders of magnitude slower than  
731 the measured erosion rate of  $0.74 \text{ m My}^{-1}$  in Gale crater by Farley et al. (2014). At these rates of  
732 surface alteration, it is unlikely that evidence for significant chemical alteration would survive  
733 the physical erosion that currently dominates the martian surface.

734

### 735 *Relationship to Global Oxidative Weathering Processes on Mars*

736         Oxidative weathering products were identified using VNIR and TIR spectral datasets as  
737 globally significant components of the martian surface (Salvatore et al., 2014). Considering that  
738 much of the martian surface is composed of sediments and sedimentary rocks (e.g., Grotzinger et  
739 al., 2011; Le Deit et al., 2015; Edgett, 2016), which we show are not likely to be dominated by  
740 oxidative weathering processes on their surfaces, why might oxidative weathering products be a  
741 spectrally significant component of the martian surface, as proposed by Salvatore et al. (2014)?  
742 To address this seemingly incongruent set of observations, one must consider processes at both  
743 the scale of individual rocks (as we have done in this current investigation) as well as those that  
744 dominate broader geologic landscapes.

745         For example, our investigation here suggests that oxidative weathering processes, while  
746 almost certainly occurring in the modern Antarctic environment, are either being overprinted by  
747 more mature alteration phases or are undergoing physical erosion at a rate that outpaces  
748 oxidative weathering processes. While our investigation only considered weathering that  
749 occurred on rock surfaces, chemical weathering processes continue to alter rock fragments and  
750 sediments after they are separated from their host rock. Campbell and Claridge (1987) showed  
751 how the age of soils and sediments throughout the Transantarctic Mountains could be readily

752 distinguished based largely on the extent of oxidation, and how soil oxidation does not  
753 necessarily correspond to the weathering patterns of surface clasts. This is an important  
754 observation when relating the weathering of individual rocks to spectral signatures identified  
755 from orbit.

756         Sediments on the martian surface are derived from a range of parental materials,  
757 including igneous rocks, impact ejecta, and sedimentary rocks. Unlike the Earth, where  
758 sediments undergo a wide range of physical and chemical sorting during their formation and  
759 evolution, martian rovers and landers have shown that sediments are both physically and  
760 chemically immature (e.g., Grotzinger et al., 2011; McLennan, 2012). Considering the cold, dry,  
761 and stable modern environment on Mars, as well as the recognized physical and chemical  
762 immaturity of these sediments, it is likely that the dominant form of chemical alteration capable  
763 of acting upon martian sediments is oxidative weathering. It is no wonder, therefore, that  
764 oxidative weathering products are identified from orbit across the martian surface. While  
765 physical erosion may outpace the weathering of rock surfaces in the modern martian  
766 environment, the initial oxidation of rock surfaces prior to physical erosion, the accumulation of  
767 immature sediments on the surface, and their constant exposure to the oxidizing martian  
768 environment would promote oxidative weathering in the modern martian environment on the  
769 scale of geologic landscapes.

770

## 771 **Summary & Conclusions**

772         In this study, we tested the hypothesis that anhydrous oxidative weathering (caused by  
773 the long-term exposure of iron-bearing rocks to the cold, dry, stable, and oxidizing Antarctic  
774 environment) dominates the surfaces of sedimentary rocks exposed throughout the TAM, as it



775 does to doleritic lithologies in the MDV. Samples were prepared and analyzed using a suite of  
776 analytical techniques to determine the effects of subaerial weathering on the surfaces of rocks  
777 obtained from the Polar Rock Repository. The sedimentary rocks investigated here show a  
778 diverse range of surface mineralogy and chemistry relative to their interiors. While some rock  
779 surfaces do exhibit geochemical, mineralogical, and spectral signatures that are consistent with  
780 oxidative weathering, others show evidence for more traditional aqueous alteration like that  
781 observed in warmer and wetter environments. A subset of samples also shows evidence for  
782 alteration mineral coatings on the surfaces of the rocks, suggesting that these mineral phases  
783 either precipitated out of solution or altered *in situ* at the rock surfaces as a result of frequent and  
784 repeated exposure to liquid water. Unlike the doleritic rocks studied in Salvatore et al. (2013),  
785 these observations are instead more consistent with a wide variety of alteration processes  
786 influencing these rock surfaces and not a single process dominating the surfaces of sedimentary  
787 rocks throughout the TAM.

788         The results of our laboratory investigation also have significant implications for the  
789 chemical weathering of sedimentary lithologies on the martian surface. First, with few  
790 exceptions, the magnitude of surface weathering observed in sedimentary rocks throughout the  
791 TAM is relatively small compared to that of more temperate or tropical environments on Earth.  
792 In fact, with the exception of some of our samples shown to have significant coatings, it is  
793 unlikely that the bulk composition and extent of weathering of any of the samples analyzed in  
794 this study would be misinterpreted if only the surface were measured and not the less altered  
795 rock interior. Additionally, LIBS measurements show that coatings of the compositions and  
796 thicknesses found in this study would be easily identified on Mars using the ChemCam  
797 instrument onboard Curiosity or the SuperCam instrument to fly on the Mars 2020 rover mission

798 (Wiens et al., 2014). Second, previously reported rates of surface weathering in the Antarctic  
799 compared to modern estimates of erosion rates in Gale crater suggest that physical erosion on  
800 Mars may substantially outpace the rate of chemical weathering of rock surfaces in Gale crater.  
801 If so, it is possible that the products of surface weathering may never be identified on martian  
802 sedimentary rocks due to the dominance of physical erosion at the surface, although they may be  
803 present in martian soils where they can accumulate over geologic timescales.

804 In conclusion, our results suggest that “modern” (i.e., Amazonian) chemical weathering  
805 of sedimentary rocks on Mars is unlikely to be a significant geological process that would inhibit  
806 the investigation of rock compositions in Gale crater. While previous studies have shown that  
807 oxidative weathering products are spectrally dominant components at the regional and global  
808 scales of orbital investigations (Bibring et al., 2006; Salvatore et al., 2014), the results presented  
809 here demonstrate how differences in bulk composition, friability, porosity/permeability, and  
810 geologic histories of individual sedimentary rocks can lead to differing extents and types of  
811 geochemical alteration preserved at the surfaces of these rocks even in the coldest and driest of  
812 terrestrial environments.

813

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