1   **Revision 2**

2   **MINERALOGY AND CHEMISTRY OF SAN CARLOS HIGH-ALKALI**

3   **BASALTS: ANALYSES OF ALTERATION WITH APPLICATION FOR MARS**

4   **EXPLORATION**

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26   **Abstract**

27   The discovery of Fe, Mg, and Al phyllosilicate clays on Mars using visible and shortwave

28   infrared (VSWIR) spectroscopy from orbit indicates aqueous alteration of basaltic rocks.

29   Analyses at Gusev Crater by the Spirit rover and Gale Crater by the Curiosity rover have

30   discovered alkaline basaltic rocks. In this work, multiple methods—VSWIR spectroscopy,

31   x-ray diffraction (XRD), and chemical analyses—were used to study a suite of alkaline

32   basalts from San Carlos, AZ, which have been altered by water in an oxidative, semi-arid

33   environment. As an analog for the weathering of alkaline basaltic rocks on Mars, a suite

34   of rocks visually identified to have different degrees of alteration were characterized to

35   understand the spectral, mineralogical and chemical trends in alteration as sensed by

36   multiple techniques. Samples with strong 1.9-μm H_2O-related absorptions in VSWIR

37   commonly exhibited absorption bands at 1.4, 2.2, and/or 2.3 μm, indicating the presence

38   of clay minerals or silica as well as features at 0.5-0.9 μm indicative of ferric iron oxides.

39   Primary mineralogy for all samples, as determined by point analyses with the microprobe

40   and XRD, consisted of olivine, plagioclase, nepheline, augite, and titanomagnetite.

41   Compositional imaging and spot analyses with the microprobe revealed distinct alteration

42   textures and phases, suggesting weathering pathways involving the oxidation of iron in

43   olivine and primary Fe(II) oxides to form Fe(III) oxides as well as the formation of

44   aluminum phyllosilicates and magnesium phyllosilicates from feldspars and olivines,

45   respectively, while pyroxene remained relatively unaltered. Bivariate plots of major

46   oxides both from bulk chemical analysis and microprobe measurements also revealed

47   trends in alkali and silica depletion and calcium enrichment, but there was little chemical

48   fractionation in most of the major oxides. The strength of the 1.9-µm H_2O absorption,

49   loss on ignition, and depletion in silica and sodium, correlated with increasing alteration.

50   The datasets provide an analog for understanding possible weathering pathways in

51   martian alkaline basalts and thresholds for the detection of aqueous alteration in multiple

52   datasets.

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54   **1.0 Introduction**

55   Orbiting visible and near-infrared spectrometers, and data from landed missions, have

56   revealed a diverse array of aqueous environments preserved in the rock record from

57   ancient Mars. The vast majority of the surface of Mars is basaltic in composition [e.g.,

58   *Rogers and Christensen* et al., 2007] but sulfates, chlorides, carbonates, and hydrated

59   silicates have been detected by orbiting spectrometers and confirmed by rover data [e.g.,

60   *Bibring* et al., 2006; *Mustard* et al., 2008; *Ehlmann & Edwards*, 2014; *Grotzinger* et

61   al.,2015]. Currently, the Mars Science Laboratory Curiosity rover is exploring Gale

62   Crater, a site that hosts a diverse array of lithologies, including suites of rocks that are

63   more alkali-rich than other martian basalts, as revealed by analyses with the ChemCam

64   Laser-Induced Breakdown Spectroscopy instrument (LIBS) [*Wiens* et al., 2012, 2013;

65   *Maurice* et al., 2012; *Cousin* et al., 2015; *Sautter* et al., 2015; *Vasavada* et al.,2014] and

66   the Alpha Particle X-ray Spectrometer (APXS) [*Gellert* et al., 2013]. Jake Matijevic, the

67   first target analyzed by both ChemCam and APXS, is interpreted to be a fine-grained

68   igneous rock with an alkaline composition similar to nepheline-normative mugearites

69   [*Stolper* et al., 2013; *Blaney* et al., 2014]. Three other rock targets, and multiple other

70   rocks and clasts measured remotely by ChemCam, were found to have alkaline basalt

71 compositions and to plot in the basanite field on a total alkali silica (TAS) diagram

72 (Figure 1), suggesting alkali-rich igneous protoliths as source material for sedimentary

73 rocks and a greater diversity of martian igneous compositions [*Schmidt* et al., 2014;

74 *Meslin* et al., 2013; *Sautter* et al., 2014]. Similarly, alkaline suites of rocks have also been

75 measured in the Columbia Hills, Gusev crater by the Spirit rover [*McSween* et al., 2006].

76 Collectively, these data suggest unique types of martian volcanism and/or aqueous

77 alteration to explain their geochemistry [*McSween* et al., 2006; *Schmidt* et al., 2014; *Udry*

78 et al., 2014].

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80 To date, most spectral libraries and analyses of aqueous alteration of igneous protoliths as

81 Mars analogs have focused on subalkaline basalts [e.g., *Golden* et al., 2005; *Hurowitz* at

82 al., 2005; 2007; *Hausrath* et al., 2008; *Ehlmann* et al., 2012; *Greenberger* et al., 2012].

83 Few analog studies of alkaline basalts exist, but these have become relevant to the

84 interpretation of returned data, given the finding of Spirit and Curiosity rovers, as

85 described above. Thus, there are two goals of this work: (1) the study of aqueous

86 alteration of specifically alkaline basalts as Mars analogs and (2) the collection of laser-

87 induced breakdown spectroscopy (LIBS) data of well-characterized and Mars-relevant

88 samples to improve the ability of ChemCam to quantify elemental composition and

89 identify signs of aqueous alteration in minerals and soils at Gale Crater. For the latter

90 objective, ChemCam uses a partial least squares (PLS) approach to determine the

91 geochemistry of martian rock samples based on a library of known standards [*Clegg* et al.,

92 2009; *Wiens* et al., 2013]. PLS works best when the library samples closely match the

93 composition of materials being observed [*Clegg* et al., 2009; 2014; in review]. Hence, the

94   rocks described and characterized here were used to supplement others to create a

95   new, >400 sample database [*Clegg* et al., 2014; in review] from the previous library size

96   of 72 [*Wiens* et al., 2013]. Here we report on (1).

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98   We used multiple laboratory techniques to characterize a suite of 2 -3 Myr basalt flows

99   from San Carlos, AZ. Waters had interacted with the samples, causing oxidative

100   weathering and some clay formation. Samples collected from the flows exhibited a range

101   in alteration extent and/or style, indicated to first order by varying amounts of reddish-

102   brown material on the rock surface, extending into the interior. The San Carlos suite was

103   chosen as an analog for alteration of alkaline basalts on Mars due to the similarities in

104   original rock lithology and the fact that alteration appeared to be minor. The semi-arid

105   environment is likely warmer than that at the Mars surface, thus speeding reaction

106   kinetics, but the relatively small degree of alteration offered the chance to study in detail

107   the early stages of chemical breakdown of an alkaline basalt. Visible and shortwave

108   infrared (VSWIR) spectra, X-ray diffraction (XRD), bulk chemistry, and electron

109   microprobe data were collected from this suite of basalts. The data was used to identify

110   all primary minerals and their compositions, estimate bulk composition and mineralogy,

111   characterize alteration by identifying various minerals and alteration reactions, and

112   provide information on past weathering processes, as well as primary compositions.

113   Following sample characterization, the San Carlos basalt suite was measured by LIBS, in

114   both whole rock and compressed pellet forms, for addition to the ChemCam library

115   [*Ehlmann* et al., 2013; Clegg et al., 2014; in review]. Here, using the suite of techniques,

116   we determine the primary and secondary mineralogy and chemical alteration pathways of

117   the San Carlos rocks.

118

119   **2.0 Geologic Setting and Samples**

120   Six of the seven samples were collected from the San Carlos ultramafic inclusion locality,

121   in Peridot Canyon, San Carlos, Arizona (Figure 2). Peridot Mesa, incised by the canyon,

122   is composed of late Tertiary or early Quarternary basalt flows. One sample was

123   purchased from the same locality in order to obtain a pristine, least weathered rock and

124   may be from a slightly different locale than the rest of the suite. Bright green ultramafic

125   xenoliths, largely olivine, are widespread throughout the locality, occurring as large

126   gravity-settled masses in the basaltic flows. The host rock is fine-grained and consists of

127   plagioclase laths with smaller grains of pyroxene, nepheline, leucite, and titanomagnetite;

128   small olivine xenocrysts are also present [*Frey and Prinz*, 1978]. All samples exhibit

129   various degrees of weathering as evidenced by differences in color and reaction

130   boundaries between the host rock and xenolith. Highly altered basalts appear rust-colored,

131   whereas less altered basalts appear gray. The rust colored texture on the exterior of the

132   rock was analyzed in thin sections and identified as a rind, which we define as an

133   alteration horizon with a gradation from altered to more pristine material. In contrast,

134   coatings are deposited from external sources, and are discontinuous with the surface of

135   the rock [*Salvatore et al.*, 2013]. Only sample F has an identifiable coating of gypsum.

136   The size of each sample varies from about a quarter of a meter to fist-sized (Figure 2).

137   For this work, we focus on the basaltic host rock, rather than the olivine-rich xenoliths.

138

139 **3.0 Methods**

140 *3.1 VSWIR Spectral Measurements*

141 The suite of basalts was labeled and photo-documented under normal lab conditions.

142 Also, written descriptions of each rock were made prior to further analysis. The suite of

143 sample rocks was then measured under ambient lab conditions using an Analytical

144 Spectral Devices (ASD) spectrometer with a contact probe attachment to obtain visible

145 and shortwave-infrared reflectance spectra from 0.4 to 2.5 μm. Spectra were calibrated to

146 reflectance using a Spectralon™ reflectance standard. Data were acquired from multiple

147 surfaces on each rock in order to assess sample heterogeneity.

148

149 The spectral continuum, i.e., overall shape, is an indicator of the style and degree of

150 alteration. Changes in overall continuum shape from flat to downward-sloping to curved

151 and concave down are related to the style and intensity of rock alteration. Negative slopes

152 between 0.75 and 1.0 μm indicate NIR "blue" slopes (decreasing reflectance with

153 increasing wavelength); positive slopes between the same range indicate NIR "red"

154 slopes (increasing reflectance with increasing wavelength) [e.g., *Farrand* et al., 2006]. In

155 terms of styles of alteration, an overall concave down slope over the 0.4-2.5 μm range,

156 i.e., initially increasing reflectance then decreasing reflectance with increasing

157 wavelength, suggests the presence of Fe(III) oxides and strong UV/visible absorptions to

158 create the initial upward continuum slope to ~1.5-2.0 μm and hydrated silicates with

159 strong 3 μm H_2O- and OH-related absorptions that create the downward sloping

160 continuum to longer wavelengths. In contrast, an overall negative slope (for basaltic

161 materials) suggests a coating or powder obscuring the surface, possibly a thin coating of

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162 silica [e.g., *Mustard* et al, 2005; *Minitti* et al., 2007; *Skok* et al., 2010], and the underlying

163 rock need not be significantly altered.

164 The spectra were also examined for absorptions due to primary and secondary minerals.

165 Broader features nearer 1.0 μm and from 1.8- 2.2 μm are due to electronic transitions of

166 Fe(II) in pyroxenes. Features centered at 1.0 μm and 2.2 μm indicate high-Ca pyroxenes,

167 whereas broad absorptions at 0.90 μm and 1.90 μm indicate low-Ca pyroxenes [*Sunshine*

168 *& Pieters*, 1993]. Iron oxides have absorptions in the UV region and near 0.9 μm. Steep

169 positive slopes at wavelengths less than 0.50 μm and from 0.6 to 0.8 μm indicate the

170 presence of ferric iron oxides, which are weathering products; long wavelength features

171 near 0.9 μm also indicate well-crystalline ferric iron oxides. Hematite is distinguished by

172 an electronic transition at 0.86 μm. Goethite has a similar feature between 0.9 and 0.93

173 μm [*Morris* et al., 2000]. Phyllosilicates and clay mineralogy are indicated by a

174 combination of OH stretching and metal-OH bending between 2 and 2.5 μm. Absorptions

175 near 2.2 μm indicate Si-OH or Al-OH in phyllosilicates and opaline silica. For Al-rich

176 clays such as montmorillonite, the Al-OH absorption occurs at 2.21 μm and is sharper

177 than the Si-OH absorption in silica. Fe-OH is indicated by absorptions near 2.29 μm, and

178 absorptions around 2.31 μm indicate Mg-OH. An absorption near 1.9 μm indicates an H-

179 O-H bend and OH stretch caused by the presence of molecular H_2O in clay interlayers

180 [*Bishop* et al., 1994]. Bands near 1.4 μm indicate the first overtone of the OH stretch and

181 H_2O combinations [*Bishop* et al., 2008; *Clark* et al., 1990; *Clark* et al., 2007a].

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183 Band depth calculations for the 0.53, 1.9, 2.2, and 2.3 micron absorptions in host basalt

184 spectra were determined using ENVI. Spectra were continuum-removed, and the

185   absorption of each identified band was measured by manually finding the band center in

186   the continuum-removed spectra. In this work, we used the CRISM defined band

187   parameters BD530, BD1900, BD2210, and BD2290 to measure continuum-removed

188   band strengths [*Pelkey* et al., 2007]. Quantification of these band depths provides

189   information on relative water content, ferric iron content, and metal-hydroxide content

190   (Table 2).

191

192   *3.2 Preparation for Geochemical Analyses*

193   After spectral measurements were taken, a subset of samples was chosen based on

194   diversity in types of aqueous alteration, weathering products, and degree of alteration, as

195   evident from both the spectral properties and visual analysis. A small portion of each

196   sample within the subset was selected for preparation of polished thin sections,

197   impregnated with epoxy, and allowed to cure overnight. The purpose of the epoxy

198   impregnation was to preserve any coatings or alteration rinds present on the rock, which

199   affect VSWIR spectral properties and would otherwise have been washed away or

200   abraded during thin section preparation. Locations of thin-section cuts were selected to

201   include a wide variety of minerals, each representing the different spectral classes of

202   materials. Ideal portions contained surfaces and interior portions of both host rock and

203   xenoliths, thought only the host rock is the focus of this study. The intent of the thin-

204   section analysis was to determine the chemical composition of mineral phases present

205   and to examine textural relationships between primary and secondary minerals.

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207   The San Carlos host rocks were also analyzed for bulk chemical composition (major,

208   minor, and trace elements). Rocks were somewhat heterogeneous from visual indicators

209   of aqueous alteration, so representative parts of the host rock of each sample that did not

210   have an alteration rind and that lacked xenoliths were chipped off using a rock hammer

211   and chisel or rock saw. The intent of the bulk rock measurement was to compare the

212   chemistry across rock samples and to test for trends corresponding to degree of alteration,

213   measuring the composition and degree of alteration of the basalts only, not xenoliths, and

214   leaving analysis of any potential rinds for microprobe work.

215

216   *3.3 Bulk Chemical Analysis*

217   Bulk chemical analysis was performed by Activation Labs, Ltd. in Ontario, Canada. Bulk

218   rock chips were powdered and mixed with Li metaborate and Li tetraborate flux in

219   graphite crucibles. The mixture was fused in a furnace at 1150° C and the resulting fused

220   material was dissolved in a mixture with 5 % nitric acid. Fused samples were then diluted

221   and analyzed with Perkin Elmer Sciex ELAN 6000, 6100 or 9000 ICP/MS. For every

222   group of samples, three blanks, three controls before the sample group, and two blanks

223   after the sample group were run. Duplicates were analyzed after every 15 samples and the

224   instrument was calibrated every 40 samples. Total Fe is reported as Fe_2O_{3T} for these data

225   because of oxidation during the fusion process.

226

227   *3.4 Electron Microprobe*

228   The thin sections were first observed using a petrographic microscope to survey rock

229   textures and alteration and to identify areas of interest. The host rock (basanite) is

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230   composed mainly of fine-grained pyroxene, plagioclase, and olivine. Xenoliths are

231   almost entirely composed of coarse-grained olivine with some pyroxene and opaque

232   minerals. Samples were then placed in a vacuum carbon evaporator and coated with a

233   thin layer of conductive carbon. Electron microprobe measurements were done with the

234   JEOL JXA-8200 at Washington University in St. Louis. Measurements were made using

235   a 15 KV accelerating potential, 25 nA beam current, and a range of beam sizes from 1 to

236   10 micrometers, depending on the grain size and the susceptibility of a grain to

237   volatilization. Both reflected light and back-scattered electron imaging were used to

238   search for textures caused by alteration and to focus the beam for analyses of elemental

239   abundances. Energy-dispersive spectrometry (EDS) was used to identify mineral phases

240   and to guide subsequent quantitative analyses.

241

242   Quantitative analyses were done using the five wavelength-dispersive spectrometers and

243   a combination of diffracting crystals for two to four elements, as follows: Na, Mg, Al,

244   and Si were analyzed using the TAP crystal; Mn, Fe, and Si were analyzed using the LIF

245   crystal; Ti and Cr were analyzed using LIFH; and S, K, and Ca were analyzed using PET.

246   Elemental standards used were Amelia Albite P-103 (Na), Shankland synthetic Forsterite

247   P-658 (Mg), Alaska Anorthite NMNH 137041 (Al), Gates Wollastonite (Si and Ca),

248   Madagascar Orthoclase GRR78 (K), Mn Olivine RDS P-1087 (Mn), Fe_2O_3 Elba

249   Hematite P-238 (Fe), TiO_2 GRR (Ti), and Cr_2O_3 P-585 (Cr). Quantitative analyses were

250   done using Probe for EPMA software and x-ray corrections were done using the CITZAF

251   correction software ($\Phi(\rho z)$ algorithm; *Armstrong* et al., 1995).

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253   Because the microprobe does not distinguish Fe^{2+} and Fe^{3+}, total Fe concentrations are

254   reported in terms of FeO. These values were converted to Fe_2O_3 for comparison with

255   bulk chemical analyses, for which total Fe was reported as Fe_2O_3. For magnetite and

256   spinels, Fe_2O_3 values were adjusted for contributions from ferric oxide (Fe^{3+}) using

257   stoichiometry. The fraction of Fe^{3+} to total iron was calculated by adjusting the fraction

258   of Fe^{2+} to total iron until the sum of total cations was 3.00.

259

260   *3.5 X-ray Diffraction*

261   Bulk rock powders were placed into 3.8 cm by 5 cm fixed sample mounts and tamped

262   down using a metal spatula in order to form a flat surface. X-ray diffraction (XRD)

263   measurements were taken using the Bruker d8 X-ray powder diffractometer at

264   Washington University in St. Louis using Cu-Kα radiation at a maximum power of 100W

265   operating at 40 kV and 40 mA, with a 0.5 per second per step count time. Data was

266   analyzed using the DIFFRAC.EVA and DIFFRAC.SUITE TOPAS software for Rietveld

267   refinement. Rietveld refinements were performed automatically, using a peak fitting

268   algorithm with a library of standard minerals, and manually by selecting peaks of interest

269   and identifying potential mineral candidates based on bulk geochemical data.

270

271   **4.0 Results**

272   *4.1 VSWIR spectral Analysis*

273   Diversity in spectral properties both among samples and within samples indicates

274   differences in both weathering extent and the nature of weathering chemical processes

275   affecting the rocks. For the host rock, key features were the variation in overall slope and

276   continuum shape, the depth of absorption features related to ferric iron, and the depth or

277   narrowness of vibrational absorption features at longer wavelengths (1.4 to 2.5 μm),

278   indicating the presence of metal-OH and H_2O (Table 1; Figure 3).

279   *4.1.1 Continuum shape and slope*

280   Overall continuum shape and slopes at longer wavelengths are indicators of the degree

281   of alteration, as well as the style of alteration. Less altered samples have an overall flat

282   slope with few prominent absorption features. This pattern is typical for a relatively

283   pristine basalt, which has an overall low albedo and shallow, broad features related to

284   pyroxene around 1.0 μm and 2.0 μm. With increasing alteration, the overall continuum

285   shape changes from flat to downward sloping (blue-sloped spectrum), e.g., samples B and

286   F. Blue-sloped spectra can indicate surface coatings on basalts, and a gypsum coating

287   was identified for sample F [*Skok* et al., 2010]. As alteration progresses, the overall

288   continuum shape becomes more curved and has a concave-down shape, common for

289   spectra of altered materials due to ferric oxide absorption at shorter wavelengths and the

290   leftward shoulder of the strong OH and H_2O absorptions from 2.7 to 3 μm. The samples I

291   and A have the most curved, concave-down overall continuum shape. Based on overall

292   continuum shape and slope, samples are ordered, in terms of increasing alteration, from J,

293   K, B, F, C, I, to A (Table 3).

294

295   *4.1.2 Fe-related absorptions*

296   Indicators of ferric iron are absorption features at 0.53 and ~0.9 μm, as well as slopes

297   between 0.6 and 0.8 μm. Relatively pristine basalts have shallow bands at 0.53 μm and

298   broad, shallow bands at ~0.9 μm, related to Fe(III) electronic transitions in crystalline Fe-

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299   oxides. The depths of both of these bands are related to ferric iron content, and increase

300   with increasing alteration; sample A has a strong absorption feature at 0.53 μm and a

301   sharp band at 0.91 μm. Slopes between 0.6 and 0.8 μm also indicate the presence of Fe-

302   oxides. Samples J and K have a negative slope between 0.6 and 0.8 μm, suggesting little

303   to no ferric iron content, whereas samples I and A have steep positive slopes in this same

304   region, suggesting greater ferric iron content with increasing alteration. On the basis of

305   the band depth at 0.53 μm (BD530), samples are ordered in terms of increasing ferric iron

306   content from J, K, B, F, I, C, to A.

307

308   *4.1.3 H_2O and metal-OH absorptions*

309   Absorption features at 1.9 μm are an indicator of H_2O in clay interlayers, hydrated silica,

310   or other hydrous phases and should increase with alteration and sample weathering. In the

311   San Carlos samples, increasing BD1900 is correlated with BD530, suggesting a

312   relationship between water and ferric iron content (Figure 4). All samples contain bands

313   at 1.4 μm of varying depths, related to hydroxyls in hydrated silicates and molecular

314   water; these features are small and shallow in J and K samples, and increase in depth for

315   C, I, A samples.

316   Absorption features at longer wavelengths indicate the presence of hydrated silicates. The

317   depth and position of absorption features at longer wavelengths varies significantly

318   between samples, indicating changes in Al-OH and Fe,Mg-OH content (Table 2). Less

319   altered samples (J and K) have broad, shallow absorption features near 2.2 μm, indicating

320   Si-OH possibly due to the presence amorphous silica or poorly crystalline silicate

321   weathering products. More altered samples have sharper absorption features at 2.2 μm,

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322   indicating Al-OH and/or weak, broad features at 2.29 μm or 2.3 μm, indicating Fe or Mg-

323   OH. Sample B has a both a broad absorption feature at 2.2 μm due to Si-OH and a sharp

324   feature at 2.3 μm, indicating greater Fe/Mg-OH-bearing phase content compared to other

325   samples. Samples A and I have strong, sharp absorption features at 2.2 μm and weaker

326   bands at 2.3 μm, suggesting more crystalline Al clays, or greater Al-OH content

327   compared to Mg-OH content. BD2210 (Al-OH or Si-OH) increases with BD1900 (water

328   content) and BD530 (ferric iron content) for all samples, suggesting a trend in alteration

329   with increasing and correlated Si-OH/Al-OH and ferric iron as alteration progresses.

330   BD2290 (Fe-OH) varies little with other spectral parameters and only one sample (B) has

331   a BD2290 value above 0.03 (Table 3; Figure 4).

332

333   From the initial suite of 7 rocks, 4 spectral endmembers were identified on the basis of

334   these three classes of spectral parameters. J appears to be the least altered sample with an

335   overall flat continuum shape, weak ferric absorption features, and broad features at 2.2

336   μm. B is an intermediately altered basalt, and has a blue-sloped spectrum, a weak band at

337   0.53 μm, broad features at 2.2 μm, and a sharp feature at 2.3 μm. C is also an

338   intermediately altered basalt but with a slightly curved, concave-down continuum shape

339   and small, sharp features at 0.53 and 2.2 μm. Sample A is the most altered sample with a

340   curved, concave down overall shape and very sharp absorption features at 0.53 and 2.2

341   μm. These 4 samples represent a different extent and/or style of weathering, and their thin

342   sections were analyzed in detail with the electron microprobe.

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345   *4.2 Bulk Chemical Analysis*

346   Results from bulk chemical analysis are given in weight percent oxide for all 7 samples,

347   along with calculated normative mineralogy (Table 4). Totals range from 95.2% to 99.1%

348   with differences due to loss on ignition and slight variations in Fe^{2+}/Fe^{3+}. Variations in

349   weight percents for individual oxides are minimal, with the most variation in Na_2O

350   (3.34% to 5.27%). Bulk rock compositions fall within the basanite field on a TAS

351   diagram (Figure 1). Sample J has a slightly higher alkali content (7.46 %) compared to all

352   other samples. In contrast, sample Sample A, has a slightly lower alkali content (5.61 %)

353   relative to other samples. From bulk chemical data, normative mineralogy for each

354   sample was calculated by the CIPW normative method. The San Carlos samples have less

355   silica and alkalis than the Jake M rock at Gale crater (Stolper et al., 2013) and are most

356   comparable to the Wishstone class at Gusev crater (McSween et al., 2006), albeit slightly

357   lower in magnesium and iron.

358

359   *4.3 Electron Microprobe Analysis*

360   The four spectral endmembers were analyzed using backscattered electron imaging and

361   spot analyses to look for primary and alteration textures, and determine mineral

362   compositions. Key findings were distinct textures for olivine, titanomagnetite, and

363   plagioclase laths, compositional ranges for various minerals, and evidence for alteration

364   on the micron scale.

365

366   *4.3.1 Overall textures and mineral assemblages*

367   All samples have an overall porphyritic texture with larger olivine phenocrysts set in an

368   intergranular matrix of plagioclase laths with interstitial pyroxene, titanomagnetite, and

369   nepheline. Small amounts of glass might be present between grains, but were not detected

370   in petrographic microscope images or verified by electron microprobe analyses. For

371   sample J, most grains are euhedral and grain boundaries are well-defined, and throughout

372   the sample, the texture remains consistent (Figure 5a). The mineral assemblage consists

373   of plagioclase, high-Ca pyroxene (augite), nepheline, and titanomagnetite, with zoned

374   olivine phenocrysts. Samples B and C consist of the same mineral assemblage, with the

375   exception of zoned titanomagnetite in B, which is not present in C (Figure 5b and c). For

376   sample A, the overall texture in the interior of the section was similar to that for the

377   pristine sample; towards the rock exterior, most of the grains are subhedral, while the

378   grain boundaries are poorly defined and appear frayed or ragged (Figure 5d,e, and f). In

379   Sample B, grain boundaries at the rock exterior also appeared frayed (Figure 5g). The

380   mineral assemblage for the Sample A consists of mottled plagioclase, high-Ca pyroxene

381   (augite), nepheline, leucite, and titanomagnetite intergrown with an ulvöspinel phase,

382   with olivine phenocrysts, some of which have been partially altered to poorly crystalline

383   hematite or other iron-enriched phases (Figure 5h).

384

385   *4.3.2 Compositions by mineral*

386   Olivine phenocrysts have compositions between Fo_{90} and Fo_{60} (Figure 6). For sample (J)

387   olivine compositions cluster around Fo_{90} with only a little zoning with higher Fe near the

388   rim. More altered samples contain mixtures of olivine and hematite or another iron oxide

389   from olivine alteration/oxidation. Possibly, olivine dissolution with removal of Mg^{2+} and

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390   oxidation of FeO to Fe_2O_3 is responsible for the variably high iron olivines in more

391   altered rocks. Pyroxene is mostly high Ca pyroxene (Figure 7). Most compositions plot in

392   the augite field, with several compositions falling in the pigeonite and enstatite fields.

393

394   Opaque mineral compositions plot between Ti-hematite (ilmenohematite) and

395   titanomagnetite in solid solution with ulvöspinel (Figure 8). Sample J contains only

396   titanomagnetite with no ulvöspinel phase. Sample A contains a wormy intergrowth of

397   ulvöspinel and titanomagnetite partially oxidized to ilmenohematite. Sample C contains

398   pristine titanomagnetite or titanomagnetite with distinct zones of exsolved ulvöspinel.

399

400   Feldspar compositions mostly lie in the plagioclase field between An_{30} and An_{70} (Figure

401   9). Sample J, has an average plagioclase composition of $An_{56.5}Ab_{42}Or_{1.5}$. Samples B and

402   C have average compositions of $An_{50}Ab_{48}Or_2$ and $An_{49}Ab_{49}Or_2$, respectively. Sample A

403   has an average plagioclase composition of $An_{54}Ab_{44}Or_2$. A few compositions fall within

404   the alkali feldspar field (compositions on average are $\sim An_{21}Ab_{63}Or_{16}$). These

405   compositions are alkali-rich edges from zoning of plagioclase in the primary melt. Both

406   samples B and C contained zoned feldspars, with the average alkali-rich rim composition

407   of $An_2Ab_{46}Or_{52}$ in B and $An_5Ab_{47}Or_{48}$ and $An_5Ab_{75}Or_{20}$ in C. Feldspathoids fall into two

408   groups, nepheline or leucite, and occur as distinct grains between plagioclase laths or as

409   individual grains near clusters of plagioclase laths. Nepheline is present in all samples,

410   whereas leucite only occurs in samples C and A. Leucite compositions approach

411   endmember $KAlSi_2O_6$, while nepheline compositions vary between samples. J has an

412   average nepheline composition of $Ne_{71}Ks_6An_1Qz_{21}$; Samples A, B, and C have average

18

413   nepheline compositions of $Ne_{68}Ks_6An_2Qz_{23}$, $Ne_{71.5}Ks_{6.5}An_{1.1}Qz_{20.6}$, and $Ne_{68}Ks_6An_{11}Qz_{14}$,

414   respectively.

415

416   Evidence of phyllosilicates is found in samples A and B (Figure 10). Phyllosilicates in

417   sample A occur between plagioclase laths, along the rims of altered olivine grains, and

418   between plagioclase and augite crystals. Most of these materials analyzed with the

419   electron microprobe have weight percent oxide totals between 80% and 89% suggesting

420   that they contain a significant amount of OH or H_2O. For sample A, the most

421   phyllosilicate-like compositions were found between plagioclase laths. In the sample B,

422   most phyllosilicate-like compositions were found around altered olivine rims or between

423   altered olivine rims and plagioclase laths. Spot analyses between plagioclase laths

424   revealed more montmorillonite-like compositions. Analyses between altered mafic

425   minerals revealed compositions similar to saponite, other Fe/Mg smectites, and chlorite

426   (Figure 10).

427

428   *4.3.3 Primary and secondary textures*

429   Primary textures for olivine phenocrysts are euhedral crystals with angular boundaries,

430   best seen in sample J. There is some zoning but compositions are overall Mg-rich (Figure

431   5a). In samples A, B, and C, olivine grains are zoned and many have a veiny texture

432   along the edges or through the grain, representing olivine altered to hematite or another

433   Fe(III) oxide (Figure 5b-h). Primary plagioclase and alkali feldspars, identified from

434   sample J, are elongated laths with well-defined grain boundaries (Figure 5a). Feldspar

435   laths in A, B, and C have a range of textures from mottled or wormy on the rock exterior

436 to fairly pristine in the rock interior (Figure 5b, c, and e). Highly irregular, wormy

437 feldspar laths are present in sample A only (Figure 5e and f). Primary augite is euhedral

438 with angular boundaries for all samples, and no alteration textures for pyroxene were

439 found. Titanomagnetite in sample J occurs as bright, distinct grains with well-defined

440 grain crystal boundaries (Figure 5a). Other samples contain pristine titanomagnetite

441 textures (C) and intergrown titanomagnetite and ulvöspinel (possibly exsolved; B)

442 (Figure 5b and c). Secondary alteration textures for titanomagnetite occur only in the

443 sample A, where titanomagnetite crystals have a mottled, wormy texture with some

444 irregularly shaped, distinct spinel zones (Figure 5e and f).

445

446 *4.4 XRD Analysis*

447 Using both an automated peak fitting algorithm and manually selected peaks for inclusion

448 in the Rietveld refinement model, we identified mineral assemblages and the percentages

449 of each mineral for every sample. The resultant mineral suites are in agreement with the

450 assemblages identified by our normative mineralogy analysis of the bulk chemical data

451 (Figure 11a-b, Table 4). Phyllosilicate peaks were not directly detected at low-2θ but

452 phyllosilicates identified in VSWIR spectra and microprobe images were also included in

453 Rietveld refinements.

454

455 *4.4.1 Forward Modeling*

456 We combined the percentages of minerals identified by Rietveld refinement with the

457 average mineral compositions obtained from electron microprobe point analyses in order

458 to obtain total oxide abundances. All of the phases identified by Rietveld refinement were

20

459   listed, and, when available, the average composition (in terms of oxide weight

460   percentages) from electron microprobe spot analyses was assigned as the 'true'

461   composition for each mineral. Each oxide weight percent was weighted by the percentage

462   determined through the Rietveld refinement analysis. These percentages were then

463   adjusted in order to closely match the bulk oxide weight percentages with the bulk

464   chemical analysis data, minimizing residuals (Tables 3, 4). Most of the minerals detected

465   in the XRD data set were also identified in electron microprobe images and analyzed by

466   direct spot analyses. Also, the relative order of the most abundant primary minerals in

467   XRD (arranged from most to least abundant) is in agreement with the normative

468   mineralogy calculations and visual analysis of petrographic microscope images. For the

469   primary minerals, the order from most to least abundant is: plagioclase, augite, olivine,

470   nepheline, and ulvöspinel/titanomagnetite (Table 4).

471

472   **5.0 Discussion**

473   Results from VSWIR spectra suggest multiple weathering products and evidence for the

474   formation of ferric oxides, crystalline to poorly-crystalline phyllosilicates, and

475   amorphous silica coatings or weathering products in varying amounts for all samples.

476   Results from bulk chemical analysis indicate weathering is modest and largely

477   isochemical with little changes in oxide weight percent totals between individual samples,

478   except for 1-2% alkali and silica (Figure 12a-g). Electron microprobe analysis found little

479   evidence for pervasive phyllosilicate or ferric oxide alteration, but rather distinct

480   alteration textures and relatively similar compositions for the primary minerals (feldspars,

481   pyroxene, olivine, and opaques).

21

482

5.1 VSWIR Spectra Weathering Trends

Overall shape varies from relatively flat (relatively pristine basalt with minor coatings

and phyllosilicates; J) to downward sloping (presence of coatings and small amounts of

phyllosilicates; B) to concave down (clay-like; C and A) as alteration increases. This

suggests an overall trend from relatively pristine basalt to thin coatings to well-ordered

phyllosilicates. The band depth at 0.53 μm (BD530) and the slope between 0.6 and 0.8

μm increase with increasing alteration (as determined by changes in continuum shape,

petrographic textures, and chemistry of discrete mineral phases). This suggests an overall

trend in increasing ferric iron and oxidation as alteration progresses. BD1900 increases

with increasing sample alteration based on visual analysis (amount of red material on

surface) and overall continuum shape. BD1900 also correlates with both BD530 and

BD2210 suggesting a continuous alteration trend of increasing hydration (BD1900), iron

oxidation (BD530), and Si/Al-OH bearing phases (BD2210; Figure 4a, b, and c). A

similar overall trend is reflected in the correlation between BD2210 and BD530,

suggesting a trend of increasing Si/Al-OH bonds and oxidation as alteration progresses

(Figure 4d and e). Band depths at longer wavelengths (BD2210 and BD2290) show little

correlation, indicating that Fe/Mg-OH and Si/Al-OH for well-crystalline hydrated

silicates are not strongly related (Figure 4a). BD2290 and BD530 are also not correlated,

possibly indicating iron oxide formation is not closely related to the processes that create

Fe-OH and Mg-OH bearing phases in these samples.

5.2 Bulk Chemistry Weathering Trends

22

505   The bulk rock samples all plot in the basanite field and have little variation in bulk

506   composition (Figure 1; Table 2). The CIA (chemical index of alteration) values for all

507   samples range from 0.526 (sample A) to 0.505 (sample J). On a classic diagram used in

508   studies of terrestrial and martian weathering (e.g., *Nesbitt & Wilson*, 1992; *Nesbitt &*

509   *Young*, 1989), there is little evidence for mobility of cations and chemical alteration.

510   Despite the similarity in bulk composition, some trends between silica and other oxides

511   or sums of oxides arise (Figure 12a-g). Silica and alkalis are positively correlated (Figure

512   12a), with high-alkali, high-silica compositions corresponding to the less altered samples

513   (J, K, and F) and lower-alkali, lower-silica compositions corresponding to more highly

514   altered samples (B, A, and I). A similar correlation occurs for silica and Na_2O (Figure

515   12b). CaO and silica are negatively correlated (Figure 12c); higher silica (less altered)

516   samples are lower in CaO compared to lower silica (more altered) samples ($R^2 = 0.43$).

517   This trend may be caused by preferential retention of CaO during weathering or by Ca-

518   rich fluids. The former seems favored by the lack of evidence for salts in most samples

519   (except the surface of F) and the pristine pyroxene grains observed in altered rocks.

520   Al_2O_3 and Fe_2O_{3T} are not correlated with Si (Figure 12d and e). MgO remains relatively

521   constant for all values of silica (Figure 12f). In general, for common basaltic minerals and

522   glass, glass is the first to weather, followed by olivine, pyroxene, and then plagioclase

523   [*Eggleton* et al., 1987]. The typical ion mobility relationship is Na > K > Ca > Si > Mg >

524   Al > Ti > Fe for basaltic weathering [*Gislasson* et al., 1996]. Na and K are assumed to be

525   mainly released from the weathering of plagioclase. Na_2O and K_2O contents typically

526   decrease with increasing alteration, and this trend is found for these samples (Figure 12a).

527   Mg and Ca, released by weathering of olivine and pyroxene, respectively, typically

23

528   decrease with increasing alteration, but that is not the case for these samples. Both

529   elements are retained, along with Fe, while Si does appear to have been transported in a

530   similar manner to the alkalis. Plots of oxides vs. loss on ignition (LOI) show interesting

531   trends relating to changes in chemistry with hydration and/or oxidation (Figure 13a-c).

532   LOI is strongly inversely correlated with silica content (Figure 13a); lower LOI values

533   correspond to higher silica values (less altered samples ($R^2 = 0.76$). A similar inverse

534   correlation occurs between LOI and alkali content (Figure 13b), suggesting that more

535   altered samples (A, B, and I) have higher LOI values and lower alkali content compared

536   to less altered samples ($R^2 = 0.58$). CaO and LOI are positively correlated (Figure 13c),

537   with more altered samples having high LOI and high CaO compared to less altered

538   samples ($R^2 = 0.61$). In these samples, we infer that the most mobile cations were (in

539   order of decreasing mobility) Na, K, Si, Fe, Mg, Ca, and Al. The lack of weathering of

540   pyroxene appears essential for these trends.

541

542   Comparison of oxides to spectral parameters shows similar trends as oxide-oxide plots.

543   BD1900 negatively correlates with alkali content, suggesting a relationship between

544   increasing hydrous alteration and decreasing alkali content due to cation mobility (Figure

545   14a-d). However, BD1900 is not correlated with Fe_2O_{3T} ($R^2 = 0.03$). Some more altered

546   (higher BD1900) samples are preferentially enriched in Fe_2O_{3T}, potentially due to the

547   formation of Fe(III) oxides observed in Samples A, B, and C. Sample C is anomalous in

548   that it has relatively high Fe_2O_{3T}, but BD1900 is low compared to all samples (Figure

549   14d). Similar trends found in silica and BD1900 plots are seen in comparisons of BD530

550   with alkalis (Figure 15a). Alkali content generally decreases with increasing BD530; this

551   trend is controlled by the strong negative correlation between BD530 and Na_2O, due to

552   the mobility of Na in basaltic weathering pathways. BD530 shows a strong positive

553   correlation with Fe_2O_{3T}, and band depth increases with increasing Fe_2O_{3T} content (Figure

554   15c). Both BD1900 and BD530 show a positive correlation with CaO, possibly due to the

555   lack of weathering of Ca-rich pyroxenes (Figures 14b and 15d).

556

557   *5.3 Electron Microprobe Mineralogical Analyses of Alteration*

558   On the basis of point analyses and traverses of individual grains, alteration processes

559   were found to affect individual minerals differently, adding context to the general

560   weathering patterns given by VSWIR spectra and bulk chemistry. Most minerals

561   identified by VSWIR spectra were verified by microprobe data; hematite, Al smectite,

562   Fe/Mg phyllosilicates, olivine, and high-Ca pyroxene were all identified through BSE

563   imaging and spot analyses.

564

565   For olivine grains, edges were altered to 'veiny' textures composed of hematite or

566   another Fe(III) oxide like goethite or ferrihydrite. Highly altered olivine grains were

567   transformed into a 'mesh' of hematite (or other Fe(III) oxide) veins, with only small areas

568   of Fe(II)-rich olivine remaining. Primary olivine grains are unzoned in the least altered

569   sample (J), and olivine phenocrysts in altered samples (A, B, and C) have magnesian

570   cores. Olivine grains in altered samples have rims that are higher in Fe owing to primary

571   compositional zoning or oxidation to hematite; hematite alteration is indicated by a

572   vermicular texture on the olivine grain rim. Analyses show both compositional zoning

573   (Fe-rich rims vs. Mg-rich cores) and mixing of olivine with altered hematite veins (Figure

25

574   6). There is no silica directly (spatially) related with this alteration, thus it appears that

575   silica was mobile and lost from the grain, as was Mg, thought these elements were not

576   always clearly lost from the bulk sample. Two traverses across larger olivine grains in J

577   and C also found olivine-pyroxene intergrowths. Pyroxene was found to vary little; most

578   compositions plot in the augite field (average composition of $Wo_{39}En_{48}Fs_{13}$) and

579   alteration textures similar to those for olivine were not observed, indicating this phase

580   was not susceptible to alteration [as also observed by *Eggleton* et al., 1987].

581

582   Typical feldspar compositions for J, A, and C fall within a plagioclase composition

583   (between An_{30} and An_{70}). Analyses in sample B found alkali-rich rims (average

584   composition $An_2Ab_{46}Or_{52}$) along the edges of plagioclase laths reflecting overgrowth of

585   plagioclase grains by material precipitated from evolved residual melt (Figure 9). Mottled

586   textures were found for many feldspar laths in A, B, and C, and alkali-rich feldspars

587   (average compositions $An_5Ab_{47}Or_{48}$ and $An_5Ab_{75}Or_{20}$) were detected on lath edges in

588   sample C (Figure 5). More pristine feldspar samples have higher anorthite components,

589   and overall higher amounts of Ca, while more altered samples have more alkali-rich

590   compositions. All samples contain dark, unaltered phases between plagioclase laths,

591   consistent with nepheline compositions. Smaller laths of leucite are also present in A and

592   C.

593

594   Opaque phases were found as discrete grains of titanomagnetite and intergrowths of both

595   titanomagnetite and ulvöspinel. This latter occurrence may be the result of exsolution of

596   ulvöspinel as samples are altered [*Price*, 1980]. Alternatively, the ulvöspinel and

597   titanomagnetite intergrowth could be a primary texture from cooling or changes in

598   oxygen fugacity of the original lava. For example, ulvöspinel and titanomagnetite exist as

599   one phase at high temperatures; as temperature decreases, ulvöspinel exsolves out as a

600   separate phase. Textures of the zoning are irregular and amoeboid-like for the most

601   altered sample (A), and angular/well-defined for less altered samples (B and C). No

602   zoning was observed in the least altered sample (J), all opaques were titanomagnetite. In

603   addition to zoning, titanomagnetite altered to ilmenohematite, indicating increased

604   oxidation (Figure 8). Phyllosilicate clay alteration was not pervasive, and most

605   measurements of potential clay minerals were limited to a few micrometers distance from

606   the edges of the plagioclase laths or altered olivine. Highly altered phases with frayed

607   edges in the interstices between feldspar laths, around olivine edges, and in vesicles are

608   likely poorly ordered phyllosilicates. Weight percent totals for most of the inferred

609   phyllosilicates were low, between 80 and 90 %, consistent with 10 to 20 percent water

610   contents, typical for many smectites. Ternary diagrams of Al, Fe, and Mg, common

611   cations in smectite octahedral sites, show most phyllosilicate-like materials in sample A

612   plotting near the Al vertex, near montmorillonite. Phyllosilicate-like compositions in

613   sample B fall between Mg and Fe, suggesting trioctahedral smectites (Figure 10).

614

615   *5.4 Possible Alteration Pathways*

616   Overall alteration trends, as opposed to distinct weathering pathways, are suggested by

617   bulk chemical data and comparison of oxides with spectral parameters (Figure 16; Figure

618   17a). Comparisons of BD1900 and BD2210 suggest an alteration pathway from J to C

619   and A, characterized by a change from amorphous silica to Al-smectites with greater

27

620   hydration of feldspars and accompanying formation of Fe-oxides from olivine, ulvospinel,

621   and titanomagnetite. Comparison of BD2210 and BD530 suggests an overall alteration

622   trend related to increasing amorphous silica and/or well-ordered Al-phyllosilicates, as

623   well as oxidation.

624   BD2290 shows no correlation with BD1900 ($R^2=0.0054$) when considering all samples,

625   however, Sample B has a large BD2290 value compared to all other samples. This

626   indicates that Sample B might represent the early stages of alteration, where only the

627   most susceptible mineral, olivine, is dissolved to form Fe/Mg-phyllosilicates. Alteration

628   may not have been pervasive enough in Sample B to also form Al-phyllosilicates, like

629   those present in Samples A and C. Thus, Sample B, compared to Samples A and C, might

630   be a less weathered example of the same alteration pathway that formed Samples A and

631   C. Alternatively, Sample B might represent an alternate weathering regime where Fe

632   from dissolved olivine is preferentially incorporated into phyllosilicates, and Fe is not

633   oxidized to form hematite or other Fe(III) oxides (Figure 12d).

634

635   The trend of decreasing alkalis with decreasing silica in feldspars emphasizes the direct

636   relationship in bulk chemical compositions, and suggests something about cation

637   mobility as these samples are altered. It is possible that decreasing alkali content in the

638   bulk composition is related to the weathering of plagioclase grains as alteration

639   progresses (Figure 17b). Increasing Ca with increasing silica content in the bulk

640   composition may be caused by retention of Ca due to the lack of pyroxene alteration, as

641   other primary phases are weathered. LOI (as a measure of sample hydration) is negatively

642   correlated with alkali and SiO_2 content, and confirms the trend of increasing hydration (as

28

643   measured by B1900) with decreasing alkali and SiO_2, related to the loss of alkalis due to

644   the weathering of feldspars as alteration progresses.

645   Data from the electron microprobe indicates increasing oxidation, loss of alkalis (Na and

646   K), and the formation of Al-OH and/or Fe/Mg-OH phyllosilicates as samples are altered

647   (Figure 17c). The wormy intergrowths of titanomagnetite and ulvöspinel in the most

648   altered sample (A) contain ilmenohematite from the oxidation of titanomagnetite. Further

649   evidence for persistent iron oxidation is indicated by Fe(III) oxide rims or a 'mesh' of

650   Fe(III) oxide veins in olivine grains for altered samples (A, B, and C). Fe^{2+}, concentrated

651   in the rims of zoned olivine grains, is oxidized to Fe^{3+} as alteration progresses. Olivine

652   grain rims, then, are preferentially altered to poorly crystalline hematite (or other Fe(III)

653   oxide), as evidenced by the veiny 'mats' of poorly crystalline Fe(III) oxide on olivine

654   rims in B and A. As alteration progresses, the Fe-rich rims of olivine grains are

655   completely altered to a pseudo-hematite phase and orange-colored veins pervade through

656   the Mg-rich olivine core. Mottled plagioclase laths in altered samples indicate some

657   alteration of plagioclase, which may relate to decreasing alkali content trends seen in the

658   bulk chemical data. Frayed grains along the edges of plagioclase laths may represent

659   phyllosilicates formed from plagioclase alteration (Figure 10). Weathering of plagioclase

660   releases alkalis (Na and K), Ca, Al, and Si. Most of the alkalis are lost, resulting in the

661   general trend of decreasing alkali content relative to Si; however, it is possible that some

662   K is incorporated with Al into leucite ($KAlSi_2O_6$), as leucite is only present in altered

663   samples A, B, and C. Al and Si are retained, and likely incorporated into phyllosilicates

664   along the edges of mottled plagioclase laths, resulting in the relative immobility of Al

665   compared to Si seen in bulk chemical data. Compositions for these grains plot near the Al

666   vertex of the Al-Fe-Mg diagram, verifying the Al-rich phyllosilicate signatures seen in

667   VSWIR spectra for two of the altered samples (A and C). Si and Mg are lost as the more

668   Mg-rich olivine is dissolved, and incorporated into the Fe/Mg phyllosilicates found along

669   the edges of altered olivine grains in B. Analyses for frayed grains along the edge of

670   altered olivine grains plot along the Mg-Fe join, verifying spectral data of saponite or

671   other Fe/Mg phyllosilicates. Thus, Al clays are likely created by the alteration of

672   plagioclase laths, while Fe/Mg phyllosilicates are formed from altered Mg-rich olivine

673   [as also seen by *Velde & Nicot*, 1985]. The Fe-rich rims of the zoned olivine are oxidized

674   to form pervasive pseudo-hematite veins, and titanomagnetite is also oxidized to form

675   ilmenohematite, causing ulvöspinel to exsolve out as a secondary phase. Pyroxene and

676   nepheline, both present in unaltered sample, J, and persistent in all altered samples,

677   remain pristine and show no signs of alteration (Figure 17d).

678

679   **6.0 Implications**

680   In the context of recent discoveries on Mars by MER and MSL, it is evident that alkaline

681   basaltic rocks are present on Mars, and their primary mineralogy, as well as any alteration

682   products, needs to be further studied [*McSween* et al., 2006*; Stolper* et al., 2013]. The San

683   Carlos suite of high-alkali basalts (basanites), studied here, with moderately high alkali

684   percentages and feldspathoid phases is particularly relevant as an analog. VSWIR

685   spectral analyses detected metal-OH absorptions and Fe(III) electronic transitions of

686   secondary minerals formed by hydrous alteration and oxidation. Signs of hydration and

687   oxidation are also seen in bulk chemical data in the San Carlos suite as trends of various

688   oxides versus LOI or silica; however, both bulk chemistry and electron microprobe

689   analyses show that samples have undergone mainly isochemical alteration, with only

690   subtle compositional variations accompanying alteration in Na, K, and Si (Figure 16).

691   XRD analyses provide identification and structural information on the primary phases

692   within samples. They are sometimes sensitive to the presence of clays and other

693   amorphous substances, but did not identify the small amounts of clays observed here with

694   the other techniques. Electron microprobe microanalysis reveals the effects of oxidation

695   and also that the development of phyllosilicate clay minerals is subtle. BSE images of

696   alteration textures showed altered mineral phases indicated by VSWIR data, and spot

697   analyses also revealed the effects and extent of oxidation. Areas around the edges of

698   wormy plagioclase laths and oxidized olivine grains were found to contain phyllosilicate-

699   like compositions, corresponding to the phyllosilicate identifications from the spectral

700   data. Evidence for the oxidation of iron (Fe^{2+} to Fe^{3+}) is also evident in analyses of

701   mottled titanomagnetite and ulvöspinel intergrowths in the most altered sample (A).

702   Alteration was most prevalent within a few millimeters of the sample's surface. The

703   samples still contain mostly primary mineralogy with some incipient alteration.

704

705   The nature of alteration observed here over the last 2-3 Ma for the San Carlos alkaline

706   basalts is similar to results from some studies of subalkaline basalts. Salvatore et al.

707   [2013] found limited formation of crystalline products in oxidative weathering rinds of

708   basalts from Antarctica, and Ehlmann et al. [2012] found evidence for mostly closed-

709   system alteration in basalts in contact with Icelandic groundwater systems. In contrast,

710   Greenberger et al. [2012] found mostly open system weathering in Deccan traps basalts.

711   The main controls on alteration style and secondary mineralogy appear to be time,

31

712 temperature, and the activity of H_2O. In this way, San Carlos is intermediate in alteration

713 extent between the Antarctica samples analyzed by Salvatore and the Icelandic samples

714 analyzed by Ehlmann. San Carlos samples show less evidence for well-crystalline

715 alteration products, but have similar spectral signatures to the Icelandic samples analyzed

716 by Ehlmann. The presence of additional alkalis does not appear to appreciably change the

717 secondary mineralogy. As expected from prior work [e.g. *Nesbitt and Wilson*, 1992], the

718 alkalis are most readily mobilized. They are one of the few elements with measurable

719 chemical trends here. Aiuppa et al. [2000] inferred the dissolution susceptibility of

720 primary minerals to be olivine > clinopyroxene > plagioclase in alkaline basalts altered

721 by CO_2-rich groundwater, though here we found olivine > plagioclase > pyroxenes.

722

723 Formation of Fe(III)-bearing oxides, silica, and/or Al/Fe/Mg phyllosilicates is similar to

724 mineral assemblages observed on Mars at multiple locations. Al smectites, Fe/Mg

725 smectites, Fe oxides, and hydrated silica have been identified in multiple locations [e.g.,

726 *Ehlmann & Edwards*, 2014]. Nearly isochemical alteration during oxidation and

727 hydration, as observed in San Carlos samples, seems to be typical of several formations

728 on Mars showing evidence of alteration [e.g., *Ming* et al., 2008; *Ehlmann* et al., 2011;

729 *McLennan* et al., 2014] – albeit with several notable exceptions for particular rock

730 formations where leaching is more extensive [e.g. *Clark* et al., 2007b; *Arvidson* et al.,

731 2014; *Hurowitz* et al., 2016]. There are some differences between the primary chemistry

732 and mineralogy of our samples versus martian ones. For example, our samples have less

733 magnesium and iron than some martian alkaline basalts, and nepheline and leucite have

734 not yet been identified on Mars. Perhaps most significantly, the altered San Carlos rocks

735 have fewer amorphous phases than reported by CheMin for all rock and sand samples at

736   Gale crater so far [e.g. *Treiman* et al., 2014; *Bish* et al., 2014]. If the amorphous phase(s)

737   are secondary products of alteration (rather than primary volcanic or impact glass), this

738   may be a result of the faster reaction kinetics at warmer San Carlos, Arizona, facilitating

739   the formation of Fe oxides and phyllosilicates. Yet, these Fe oxides and phyllosilicates

740   products in the San Carlos rocks were apparently undetectable with XRD, instead being

741   revealed by a combination of VSWIR spectroscopy and electron microprobe chemical

742   analyses. This is likely because they are not yet well-crystalline on the scales being

743   probed by x-rays, and they are relatively low in abundance. One possibility is that

744   martian sedimentary rocks at Gale crater are actually more altered (bulk percent alteration

745   products) but to alteration products equally or less well-crystalline than those in our San

746   Carlos rocks. Further sampling of materials at the Gale crater site and investigations with

747   future, different payload suites are required to investigate this hypothesis.

748

749   The use of a variety of techniques elucidates the sensitivity of each method to alteration

750   products (clays and Fe oxides), primary mineralogy, and alteration styles/extent.

751   VSWIR's sensitivity to hydrated silicates is apparent in this study, where the most altered

752   sample showed sharp, deep absorptions beyond 2.2 μm, indicating the presence of silica

753   and/or montmorillonite, even in relatively "pristine" samples. Analysis with the electron

754   microprobe suggests that alteration was most pervasive on the outer surface, but evidence

755   of weathering and dissolution was visibly apparent throughout the sample. For the XRD

756   data, primary minerals (plagioclase, alkali feldspars, nepheline, augite, and

757   titanomagnetite) were easily detected and the relative abundances reflected those

758   determined from visual analysis in petrographic microscopes and backscattered electron

759   microprobe images. Secondary minerals, such as phyllosilicates and ferric oxides, were

760   identified in all samples in the spectra, but low abundances meant precise amounts were

761   difficult to determine with microprobe or XRD. Combined with VSWIR data from orbit

762   or ChemCam analyses from the first few microns of a sample, XRD provides primary

763   mineralogy and detection of well-crystalline alteration minerals and abundant amorphous

764   phases. VSWIR's sensitivity to alteration products, including the ability to identify iron

765   oxides and the major cation in phyllosilicates, even when poorly crystalline, is a useful

766   complement to primary mineralogy abundances determined from more intensive

767   geochemical methods.

768

769   Thus this study demonstrates that the existence of evidence of aqueous alteration, its

770   extent/style, and weathering pathways can be better understood using multiple techniques.

771   Bulk geochemistry was useful, in this work, for determining that alteration was mainly

772   isochemical and that cation exchanges occurred in a closed system, with the exception of

773   alkali and silica loss. This finding has important implications for Alpha Particle X-ray

774   Spectroscopy (APXS) on MER, as bulk chemistry plots provide insight on the mobility of

775   cations compared to typically immobile cations, and aid in understanding alteration styles.

776   The presence of iron oxides is an important indicator of alteration style and oxidation

777   extent, and the MER instruments had this capability with Mössbauer spectrometers,

778   though MSL does not. For the Mars-2020 rover mission with SuperCam (Raman, LIBS,

779   VSWIR), Scanning Habitable Environments with Raman & Luminescence for Organics

780   and Chemicals (SHERLOC), Planetary Instrument for X-ray Lithochemistry (PIXL),

781   combined spectroscopy and geochemistry techniques will be critical [*Maurice* et al., 2015;

782   *Allwood* et al., 2015; *Beegle* et al., 2014]. PIXL and SHERLOC will not be able to

783   replace the capabilities of microprobe spot analyses of individual grains, but for sand-

784   sized and larger grains, it might be possible to determine differences in weathering

785   textures and primary and secondary mineral assemblages even within phases. The

786   detection of phyllosilicates and ferric iron may be challenging, depending on specific

787   instrument sensitivities at the sub-pixel level. SuperCam SWIR spectroscopy (1.3 to 2.6

788   um) combined with SuperCam passive VNIR spectroscopy and Mastcam-Z (0.4-1.0 um)

789   multispectral imaging will be crucial for recognizing slightly aqueously altered rock

790   outcrops and mapping subtle trends, as demonstrated here.

791

792   Given the identification of primary mineralogy and alkaline composition in many rocks at

793   Gale crater by MSL, the San Carlos suite constitutes a useful terrestrial analog in terms of

794   both primary and secondary alteration mineralogy. The use, in this work, of combined

795   spectroscopy and geochemistry methods serves as a proof of concept for the importance

796   of complementary methods in both current and future missions. The implications of this

797   work have special relevance for Mars2020, and will motivate the use of instruments on

798   MER and MSL to better understand aqueous alteration on Mars.

799

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843   **References**

844   Aiuppa, A., Allard, P., D'Alessandro, W., Michel, A., Parello, F., Treuil, M., and

845   Valenza, M. (2000), Mobility and fluxes of major, minor and trace metals during basalt

846   weathering and groundwater transport at Mt. Etna volcano (Sicily), Geochimica et

847   Cosmochimica Acta, 64(11), 1827-1841.

848

849   Allwood, A., et al. (2015), Texture-specific elemental analysis of rocks and soils with

850   PIXL: The Planetary Instrument for X-ray Lithochemistry on Mars 2020, Aerospace

851   Conference, 2015 IEEE, 1-13.

852

853   Armstrong, J. T. (1995), CITZAF: A package of correction programs for the quantitative

854   electron microbeam x-ray analysis of thick polished materials, thin films, and particles.

855   Microbeam Analysis, 4, 177-200.

856

857   Arvidson, R. E., et al. (2014), Ancient aqueous environments at Endeavour crater, Mars,

858   Science, 343(6169), 1248097.

859

860   Beegle, L. W., et al. (2014), SHERLOC: Scanning habitable environments with raman &

861   luminescence for organics & chemicals, an investigation for 2020, AGU Fall Meeting

862   Abstracts, 1, 6.

863

864   Bibring, J.P., et al. (2006), Global mineralogical and aqueous Mars history derived from

865   OMEGA/Mars Express data, Science, 312(5772), 400-404.

866   Bish, D., et al. (2014), The first X-ray diffraction measurements on Mars, IUCrJ, 1(6),

867   514-522.

868

869   Bishop, J. L., Pieters, C.M., and Edwards, J.O. (1994), Infrared spectroscopic analyses on

870   the nature of water in Montmorillonite, Clays and Clay Minerals, 42(6), 702-714.

871

872   Bishop, J.L.,Lane, M.D., Dyar, M.D., and Brown, A.J. (2008), Reflectance and emission

873   spectroscopy study of four groups of phyllosilicates: smectites, kaolinite-serpentines,

874   chlorites, and micas, Clay Minerals, 43, 35-54.

875

876   Blaney, D. L., Wiens, R. C., Maurice, S., Clegg, S. M., Anderson, R. B., Kah, L. C., &

877   Madsen, M. B. (2014), Chemistry and texture of the rocks at Rocknest, Gale Crater:

878   Evidence for sedimentary origin and diagenetic alteration. Journal of Geophysical

879   Research: Planets, 119(9), 2109-2131.

880

881   Clark, R. N., King, T.V.V., Klejwa, M. and Swayze, G.A. (1990), High spectral

882   resolution reflectance spectroscopy of minerals, Journal of Geophysical Research, 95(B8),

883   12, 653-12, 680.

884

885   Clark, R.N., Swayze, G.A., Wise, R., Livo, E., Hoefen, T., Kokaly, R., Sutley, S.J.

886   (2007a), USGS digital spectral library splib06a: U.S. Geological Survey, Digital Data

887   Series 231, http://speclab.cr.usgs.gov/spectral.lib06.

888   Clark, B. C., et al. (2007b), Evidence for montmorillonite or its compositional equivalent

889   in Columbia Hills, Mars, Journal of Geophysical Research: Planets, 112(E6).

890

891   Clegg, SM, Wiens, R.C., Barefield, J.E., Sklute, E. and Dyar. M.D. (2009), Quantitative

892   remote laser induced breakdown spectroscopy by multivariate analysis, Spectrochimica

893   Acta Part B, 64, 79–88.

894

895   Clegg S.M., Anderson R.B., Forni O., Lasue J., Dyar M.D., Morris R.V., Ehlmann B.L.,

896   McLennan S.M., Bender S., Cousin A., Gasnault O., Martinez R., McInroy R., Melikechi

897   N., Meslin P.-Y., Ollila A., Tokar R.L., Maurice S., and Wiens R.C. (2014), Expansion of

898   the ChemCam calibration database. Lunar Planetary Science XLV, 2378.

899

900   Clegg S.M., Wiens R.C., Anderson R.B., Forni O., Frydenvang J., Lasue J., Pilleri A.,

901   Payre V., Boucher T., Dyar M.D., McLennan S.M., Morris R.V., Graff T.G., Mertzman

902   S.A., Ehlmann B.L., Bender S.C., Tokar R.L., Belgacem I., Newsom H., McInroy R.E.,

903   Martinez R., Gasda P., Gasnault O., and Maurice S. (2016) Recalibration of the Mars

904   Science Laboratory ChemCam instrument with an expanded geochemical database.

905   Spectrochim. Acta B, in review.

906

907   Cousin, A. et al (2015), Igneous Rock Classification at Gale (Sols 13–800). Lunar

908   Planetary Science Conference, Abstract 2452.

909

910   Eggleton, Richard A., Foudoulis, Chris, and Varkevisser, Dane (1987), Weathering of

911   basalt: changes in rock chemistry and mineralogy, Clays and Clay Minerals, 35.3,161-

912   169.

913

914   Ehlmann, B.L. and Edwards, C.S. (2014), Mineralogy of the martian surface. Annual

915   Reviews of Earth and Planetary Science 42, 291–315.

916

917   Ehlmann, B.L., Bish, D.L., Ruff, S. and Mustard, J.F. (2012), Mineralogy and chemistry

918   of altered Iceland basalts: application to clay mineral detection and understanding

919   aqueous environments on Mars, Journal of Geophysical Research, 117(E11).

920

921   Ehlmann, B.L., et al. (2013), An expanded training set for processing MSL ChemCam

922   LIBS data: spectral library samples added and effects on elemental compositional results

923   from Mars, Lunar and Planetary Science XXXXIV.

924

925   Farrand, W.H., Bell III, J.F., Johnson, J.R., Squyres, S.W., Soderblom, J. and Ming, D.W.

926   (2006), Spectral variability among rocks in visible and near-infrared multispectral

927   Pancam data collected at Gusev crater: examinations using spectral mixture analysis and

928   related techniques, Journal of Geophysical Research, 111, EO2S15.

929

930   Frey, Frederick A. and Prinz, Martin (1978), Ultramafic inclusions from San Carlos,

931   Arizona: Petrologic and geochemical data bearing on their petrogenesis, Earth and

932   Planetary Science Letters, 38(1), 129-176.

933   Gellert, R., et al. (2013), Initial MSL APXS activities and observations at Gale Crater,

934   Mars, Lunar and Planetary Science XXXXIV.

935

936   Gislasson, SR, Arnorsson, S, and Armannsson, S. (1996), Chemical weathering of basalt

937   in Southwest Iceland: Effects of runoff, age of rocks, and vegetation/glacial cover.

938   American Journal of Science, 296, 837-907.

939

940   Golden, D. C., Ming, D. W., Morris, R. V. and Mertzman, S.A. (2005), Laboratory-

941   simulated acid-sulfate weathering of basaltic materials: Implications for formation of

942   sulfates at Meridiani Planum and Gusev crater, Mars, Journal of Geophysical Research,

943   110, E12S07,

944

945   Greenberger, R. N., Mustard, J. F., Kumar, P. S., Dyar, M. D., Breves, E. A. and Sklute,

946   E.C. (2012), Low temperature aqueous alteration of basalt: Mineral assemblages of

947   Deccan basalts and implications for Mars, Journal of Geophysical Research, 117, E00J12.

948

949   Grotzinger, J. P., Crisp, J. A., & Vasavada, A. R. (2015). Curiosity's Mission of

950   Exploration at Gale Crater, Mars. Elements, 11(1), 19-26.

951

952   Hausrath, E. M., Navarre-Sitchler, A. K. , Sak, P. B. , Steefel, C. I. and Brantley, S. L.

953   (2008), Basalt weathering rates on Earth and the duration of liquid water on the plains of

954   Gusev Crater, Mars, Geology, 36(1), 67–70.

955

956   Hurowitz, J. A., McLennan, S.M., Lindsley, D. H.,and Schoonen, M. A. A. (2005),

957   Experimental epithermal alteration of synthetic Los Angeles meteorite: Implications for

958   the origin of martian soils and identification of hydrothermal sites on Mars, Journal of

959   Geophysical Research, 110, E07002.

960

961   Hurowitz, J. A. and McLennan, S. M. (2007), A~ 3.5 Ga record of water-limited, acidic

962   weathering conditions on Mars, Earth and Planetary Science Letters, 260(3), 432-443.

963

964   Hurowitz, J. A., et al. (2016), Dynamic geochemical conditions recorded by lakebed

965   mudstones in Gale Crater, Mars, Lunar and Planetary Science XXXXVII.

966

967   Maurice, S. et al. (2012), The ChemCam instruments on the Mars Science Laboratory

968   (MSL) rover: science objectives and mast unit, Space Science Reviews, 170 95–166.

969

970   Maurice, S., et al. (2015), The SuperCam Instrument for the Mars2020 Rover, European

971   Planetary Science Congress 2015, 10,185.

972   McLennan, S. M., et al. (2014), Elemental geochemistry of sedimentary rocks at

973   Yellowknife Bay, Gale crater, Mars, Science, 343(6169), 1244734.

974

975   McSween, H. Y., et al. (2006), Alkaline volcanic rocks from the Columbia Hills, Gusev

976   crater, Mars, Journal of Geophysical Research, 111, E09S91.

977

978   Meslin, P.-Y. et al. (2013), Soil diversity and hydration as observed by ChemCam at Gale

979   Crater, Mars. Science, 341.

980

981   Milliken, R.E. and Mustard, J.F. (2005), Quantifying absolute water content of minerals

982   using near-infrared reflectance spectroscopy, Journal of Geophysical Research, 110,

983   E12001.

984

985   Ming, D. W., et al. (2008), Geochemical properties of rocks and soils in Gusev crater,

986   Mars: Results of the Alpha Particle X-ray Spectrometer from Cumberland Ridge to Home

987   Plate, Journal of Geophysical Research: Planets, 113(E12).

988

989   Minitti, M. E., Weitz, C. M., Lane, M. D., & Bishop, J. L. (2007), Morphology,

990   chemistry, and spectral properties of Hawaiian rock coatings and implications for Mars,

991   Journal of Geophysical Research: Planets, 112(E5).

992

993   Morris, R. (2000), Mineralogy, composition, and alteration of Mars Pathfinder rocks and

994   soils: Evidence from multispectral, elemental, and magnetic data on terrestrial analogue,

995   SNC meteorites, and Pathfinder samples, Journal of Geophysical Research, 105(E1),

996   1757-1817.

997

998   Mustard, J. F., et al. (2005), Olivine and pyroxene diversity in the crust of Mars, Science,

999   307, 1594–1597.

1000

43

1001   Mustard, J.F., Murchie, S. L. Murchie, Pelkey, S.M., Ehlmann, B.L., Milliken, R.E.,

1002   Grant, J.A., Bibring, J.P., Poulet, F., Bishop, J.,   Dobrea, E. Noe, Roach, L., Seelos, F.,

1003   Arvidson, R.E., Wiseman, S., Green, R., Hash, C., Humm, D., Malaret, E., McGovern,

1004   J.A., Seelos,K., Clancy,T., Clark, R., Des Marais, D., Izenberg, N., Knudson, A. (2008),

1005   Hydrated silicate minerals on Mars observed by the Mars Reconnaissance Orbiter

1006   CRISM instrument, Nature, 454,305-309.

1007

1008   Nesbitt, H. W., & Wilson, R. E. (1992), Recent chemical weathering of basalts, American

1009   Journal of Science, 292(10), 740-777.

1010

1011   Nesbitt, H.W. and Young, G.M. (1989), Formation and diagenesis of weathering profiles,

1012   The Journal of Geology, 97(2), 129-147.

1013

1014   Pelkey, S. M., et al. (2007), CRISM multispectral summary products: Parameterizing

1015   mineral diversity on Mars from reflectance, Journal of Geophysical Research: Planets,

1016   112(E8).

1017

1018   Price, G.D. (1980), Exsolution microstructures in titanomagnetites and their magnetic

1019   significance, Physics of the Earth and Planetary Interiors, 23,2-12.

1020

1021   Rogers, A. D. and Christensen, P.R. (2007), Surface mineralogy of martian low-albedo

1022   regions from MGS-TES data: Implications for upper crustal evolution and surface

1023   alteration, Journal of Geophysical Research, 112, E01003.

1024

1025   Salvatore, M.R. et al. (2013), Development of alteration rinds by oxidative weathering

1026   processes in Beacon Valley, Antarctica, and implications for Mars, Geochimica et

1027   Cosmochimica Acta, 115 137–161.

1028

1029   Sautter, V., et al. (2014), Igneous mineralogy at Bradbury Rise: The first ChemCam

1030   campaign at Gale crater, Journal of Geophysical Research: Planets, 119.

1031

1032   Sautter, V., et al. (2015), In situ evidence for continental crust on early Mars. Nature

1033   Geoscience, *8*(8), 605-609.

1034

1035   Schmidt, M. E., et al. (2014), Geochemical diversity in first rocks examined by the

1036   Curiosity Rover in Gale Crater: Evidence for and significance of an alkali and

1037   volatile-rich igneous source, Journal of Geophysical Research: Planets, 119(1), 64-81.

1038

1039   Skok, J. R., Mustard, J. F., Ehlmann, B. L., Milliken, R. E., & Murchie, S. L. (2010),

1040   Silica deposits in the Nili Patera caldera on the Syrtis Major volcanic complex on Mars,

1041   Nature Geoscience, 3(12), 838-841.

1042

1043   Stolper, E. M., et al. (2013), The petrochemistry of Jake_M: A martian mugearite,

1044   Science, 341(6153), 1239463 .

1045

1046   Sunshine, J.M. and Pieters, C.M. (1993), Estimating modal abundances from the spectra

1047   of natural and laboratory pyroxene mixtures using the Modified Gaussian Model, Journal

1048   of Geophysical Research, 98, E5.

1049

1050   Treiman, A. H., et al. (2014), Ferrian saponite from the Santa Monica Mountains

1051   (California, USA, Earth): Characterization as an analog for clay minerals on Mars with

1052   application to Yellowknife Bay in Gale Crater, American Mineralogist, 99(11-12), 2234-

1053   2250.

1054

1055   Udry, A., Balta, J. B., & McSween, H. Y. (2014), Exploring fractionation models for

1056   martian magmas, *Journal of Geophysical Research: Planets*, *119*(1), 1-18.

1057

1058   Vasavada, A. R., Grotzinger, J. P., Arvidson, R. E., Calef, F. J., Crisp, J. A., Gupta, S., ...

1059   & Yingst, R. A. (2014), Overview of the Mars Science Laboratory mission: Bradbury

1060   landing to Yellowknife Bay and beyond, Journal of Geophysical Research: Planets,

1061   119(6), 1134-1161.

1062

1063   Velde, B. and Nicot, E. (1985), Diagenetic clay mineral compositions as a function of

1064   pressure, temperature, and chemical activity, Journal of Sedimentary Petrology, 55(4),

1065   541-547.

1066

1067   Wiens, R. C., et al. (2012), The ChemCam instruments in the Mars Science Laboratory

1068   (MSL) Rover: Body unit and combined system performance, Space Science Reviews,

1069   170, 167–227.

1070

1071   Wiens, RC et al. (2013), Pre-flight calibration and initial data processing for the

1072   ChemCam laser-induced breakdown spectroscopy instrument on the Mars Science

1073   Laboratory rover, Spectrochimica Acta Part B, 82, 1–27.

1074

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1089   **Tables**

1090 **Table 1.** VNIR determined mineralogy of all of the bulk rock samples in order of increasing

1091 alteration determined by visual analysis (amount of red material on surface) and overall

1092 continuum shape; underlined entries are subset used for further study. Note that all samples

1093 have 1.9-um vibrational absorptions, so these are not listed.

Sample	Description	Overall continuum	Ferric absorptions (μm)	Vibrational Absorptions (μm)	VNIR-determined mineralogy
<u>SanC-J</u>	large dark grey basalt	flat, constant slope	-	small 1.41; small, broad 2.21; small 2.31	hydrous Si + Fe/Mg clay
SanC-K	large mottled grey/light grey basalt	flat, constant slope	-	small 1.41; broad 2.21	hydrous Si
SanC-F	small grey basalt, white coating	downward slope	-	1.50; doublet at 1.95 and 2.04; 2.21	gypsum coating
<u>SanC-C</u>	large dark brown/rust basalt	curved, concave down	0.5, 0.53, pos. UV-Vis slope, 0.89-0.99	1.41; sharp and broad 2.21	hydrous Si + Al-smectite + Fe(III)-ox.
<u>SanC-B</u>	massive grey/brown basalt	downward slope	0.5, pos. UV-Vis slope, 0.97	sharp 1.42, broad 2.21, 2.29-2.32	hydrous Si + Mg clay + Fe(III) oxide
SanC-I	large grey/rust colored basalt	downward slope	Sharp 0.53 band	1.41; 2.21 bands	Al-smectite + Fe(III) oxide
<u>SanC-A</u>	large basaltic rock, rust colored	curved, concave down	0.5, 0.53, pos. UV-Vis slope, 0.91	sharp 1.41 and 2.21 bands	Al-smectite + Fe(III) oxide

Table 2. Band depth calculations and corresponding wavelength for all samples in order of increasing alteration determined by visual analysis and overall continuum shape; underlined entries are subset used for further study. The 1.9 μm band depth is an indicator of water content, and band depths at 2.2 and 2.3 μm indicate Al-OH and Fe,Mg-OH content [e.g., *Milliken* et al., 2005].

Sample	SanC-J	SanC-K	SanC-F	SanC-C	SanC-B	SanC-I	SanC-A
Avg wavelength	1.915	1.912	1.914	1.918	1.9132	1.914	1.917
Avg BD1900	0.072	0.113	0.101	0.068	0.128	0.166	0.155
Avg wavelength	n/a	n/a	n/a	0.529	0.526	0.526	0.532
Avg BD530	n/a	n/a	n/a	0.127	0.096	0.169	0.273
Avg wavelength	2.299	2.312	2.316	2.315	2.312	2.309	2.312
Avg BD2300	0.029	0.005	0.003	0.003	0.163	0.002	0.005
Avg wavelength	2.208	2.214	2.214	2.207	2.207	2.206	2.204
Avg BD2200	0.0285	0.039	0.024	0.043	0.020	0.070	0.099

1103 **Table 3.** Bulk chemical analysis (weight percentages) for all samples in order of increasing
1104 alteration; samples selected for further analysis are underlined.

Oxides	SanC-A	SanC-B	SanC-C	SanC-F	SanC-I	SanC-J	SanC-K
SiO_2	44.0	43.6	44.8	45.3	44.1	45.0	45.5
TiO_2	2.79	2.67	2.73	2.72	2.68	2.66	2.70
Al_2O_3	15.0	14.7	14.6	14.8	14.7	15.1	14.6
Cr_2O_3	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Fe_2O_3	13.5	12.5	13.4	13.1	13.1	13.3	12.9
MnO	0.20	0.19	0.20	0.20	0.20	0.20	0.20
MgO	8.03	7.80	9.04	8.35	7.79	7.40	8.08
CaO	7.90	7.74	7.66	7.64	7.73	7.38	7.58
Na_2O	3.34	4.86	3.92	5.27	4.30	4.62	5.27
K_2O	2.27	1.16	2.55	1.48	1.28	2.84	1.28
P_2O_5	0.75	0.73	0.77	0.79	0.85	0.86	0.85
TOTAL	97.0	95.2	98.9	98.8	95.8	98.4	98.1
Loss	3.0	4.8	1.1	1.2	4.2	1.6	1.9
$CaO+Na_2O+K_2O$	55.25	56.21	56.4	58.16	56.16	56.97	58.32
$Na_2O + K_2O$	5.61	6.02	6.47	6.75	5.58	7.46	6.55

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1106 *All Fe is reported as $Fe_2O_{3(T)}$

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1113 **Table 4.** Normative mineralogy calculated using the CIPW method from bulk chemical analysis.

1114 Modal mineralogy (italicized in parentheses) calculated by combining averages of measured

1115 mineral compositions from microprobe spot analyses and phase proportions from Rietveld

1116 refinement of bulk compositional XRD data.

Mineral	SanC-A	SanC-B	SanC-C	SanC-F	SanC-I	SanC-J	SanC-K
Feldspar	38.92	36.99	29.01	33.29	41.92	26.29	36.31
	(32)	*(24)*	*(29)*			*(31)*	
Orthoclase	14.25	7.50	15.55	9.10	8.22	17.38	8.05
			(3.5)				
	(0)	*(8.5)*				*(0)*	
Nepheline	5.24	11.69	10.28	12.85	7.06	13.53	11.47
		(12)	*(12)*			*(23)*	
	(12)						
Leucite	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	(10)	*(10)*	*(7)*			*(0)*	
Hi-Ca Pyroxene	10.50	16.19	14.81	16.43	13.46	15.46	16.24
	(19)	*(18)*	*(22)*			*(21)*	
Olivine	17.17	14.61	17.06	15.11	15.77	14.00	14.72
	(12)	*(10)*	*(11)*			*(13)*	
Ilmenite	5.47	5.32	5.22	5.22	5.30	5.11	5.22
	(0)	*(1.5)*	*(0)*			*(0)*	
Magnetite	6.08	5.70	5.86	5.76	5.92	5.84	5.70
	(7)	*(7.5)*	*(10)*			*(13)*	
Hematite	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	(4)	*(5)*	*(5)*			*(2)*	
Total	99.55	99.82	99.73	99.76	99.82	99.77	99.81

1 **Revision 2**

2 **Figure Captions**

3 Figure 1. TAS diagram showing the composition of the 7 San Carlos rocks with varying
4 degrees of aqueous alteration examined in this study. All samples plot in the basanite
5 field with SiO_2 weight percentages between 44 and 44.5 % and total alkali percentages
6 between 5.6 and 7.4 %. Dark gray circles show the composition of Jake Matijevic,
7 Bathlet Inlet, Rocknest, and Et-Then from APXS analyses at Gale crater on Mars (Stolper
8 et al., 2013). Smaller light gray circles show the compositions of all ChemCam analyses
9 at Gale crater (up to August 9, 015). Plotted ChemCam analyses were not filtered for
10 igneous samples, and the distribution of points exhibits the compositional diversity of
11 igneous float rocks and the igneous protoliths sampled by sedimentary rocks.

12
13 Figure 2. (a) Location of the San Carlos Peridot Mesa in San Carlos, AZ and an outcrop
14 of basalt with olivine xenoliths. (b) basalts ordered from least to most altered based on
15 visual appearance. Sample J; least altered basalt with bright green olivine xenoliths.
16 Sample K; relatively pristine basalt. Sample F; relatively pristine basalt with gypsum
17 coating. Sample B; intermediately altered basalt with friable olivine xenoliths (f) Sample
18 C; intermediately altered basalt with red-brown olivine xenoliths. Sample I; highly
19 altered red-brown basalt with friable olivine. Sample A; most altered red-brown basalt
20 with reddish olivine xenoliths.

21
22 Figure 3. (a) Average spectra for all 7 samples; features at 0.53, 1.0, 1.4, 1.9, 2.2, and 2.3
23 μm were used to identify primary and secondary mineralogy in each sample. (b)
24 Continuum removed endmember spectra of the 4 endmembers-J,B,C, and A- between
25 0.35 and 1.35 μm. This region was used to identify ferric iron features near 0.5 μm, as
26 well as ferrous iron features near 1.0 μm. (c) Reference spectra of iron oxides from the
27 USGS Spectral Library [Clark et al., 2007a] between 0.5 and 1.3 μm. (d) Continuum
28 removed endmember spectra of the 4 endmembers - J, B, C, and A - between 2.0 and 2.5
29 μm. This region was used to identify metal-OH absorption features that are indicative of
30 phyllosilicates; absorption bands at 2.2 and 2.3 μm are indicative of Si-OH or Al-OH and
31 Fe-OH of Mg-OH, respectively. (e) Reference spectra of phyllosilicates from the USGS
32 Spectral Library [Clark et al., 2007a] between 2.0 and 2.5 μm. (f) Spectral variability in
33 Sample J; key absorptions are at 1.9, 2.2, and 2.29-2.30 μm. (g) Spectral variability in
34 Sample B; key absorptions are at 1.9 and 2.31 μm. (h) Spectral variability in Sample C;
35 key absorptions are at 1.9 and 2.2 μm. (i) Spectral variability in Sample A; strong
36 absorptions are at 1.9 and 2.2 μm.

37
38 Figure 4. Examination of the correlation of absorption band depths for (a) 0.53 μm vs 1.9
39 μm, (b) 2.2 μm vs. 1.9 μm, (c) 2.3 μm vs. 1.9 μm, (d) 0.53 μm vs. 2.2 μm and (e) 2.3 μm
40 vs. 2.2 μm. Band depths tracking hydration (BD1900), iron oxidation (BD530), and Si-
41 OH/Al-OH content (BD2200) are directly correlated; no trend is apparent for band depths
42 tracking Fe-OH/Mg-OH content.

43
44 Figure 5. Back-scattered electron images of alteration textures. (a) Unaltered primary
45 minerals in SanC-J; lath-shaped grains are feldspar, dark interstitial phases are nepheline.

46   (b) Wormy olivine textures from replacement by hematite veins in SanC-B; mottled,
47   plagioclase dissolution texture in upper left and lower right. (c) Unaltered minerals on
48   SanC-C near the sample edge. (d) Low magnification image of SanC-A edge; white
49   square is (e). (e) Olivine altered to contain hematite veins, mottled titanomagnetite, and
50   mottled feldspar laths. (f) Different edge in SanC-A showing similar textures to (d). (g)
51   Area around altered olivine rim in SanC-B. (h) BSE image in SanC-A interior showing
52   an overall texture similar to that in SanC-C (b).
53
54
55   Figure 6. (a) Mg# (Mg over the sum of MgO, MnO, and FeO) vs Na,K,Al, Ca, and Ti
56   oxides for olivine (in weight percent) calculated on the basis of four oxygen atoms from
57   microprobe analyses. As described in the text, the observed compositional variation is
58   partly primary and partly an effect of alteration. (b)-(d) Weight percent oxide plots from
59   microprobe analyses of olivine grains (hem = hematite). (b) MgO vs. SiO_2 wt.%;
60   deviations from the Fo-Fa line represent alteration, primarily in the formation of veinlets
61   of hematite. (c) FeO vs. SiO_2 wt.%; variation along the Fo-Fa line indicates changes in
62   composition from olivine grain Mg-rich cores to more Fe-rich rims, a primary
63   compositional variation. (d) Primary variance in MgO and FeO from magnesian cores to
64   ferroan rims; deviations from the Fo-Fa line and FeO enrichment indicate the occurrence
65   of hematite veining in more Fe-rich rims.
66
67   Figure 7. Composition of pyroxene (in mole percent) calculated on the basis of six
68   oxygen atoms, as determined by electron microprobe analyses of thin sections; most
69   pyroxenes plot in the augite and pigeonite fields.
70
71   Figure 8. Weight percent oxide plots from microprobe analyses of opaques (ulvosp=
72   ulvöspinel $TiFe^{2+}_2O_4$; mag=magnetite $Fe^{2+}Fe^{3+}_2O_4$; hem=hematite $Fe^{3+}_2O_3$, ilm=ilmenite
73   $Fe^{2+}TiO_3$) calculated on the basis of four oxygen atoms (a) Composition of Fe-Ti oxides
74   from electron microprobe analyses (b) most of the oxide compositions fall along a join
75   between ulvöspinel and Ti-rich magnetite (c) more altered samples also trend towards
76   hematite as titanomagnetite is oxidized.
77
78   Figure 9. (a) Composition of feldspars (in mole percent) calculated on the basis of eight
79   oxygen atoms, as determined by electron microprobe analyses; most feldspars plot in the
80   plagioclase field with the exception of a few analyses of alkali feldspar rims in SanC-B
81   and C.
82
83   Figure 10. (a) Composition of potential clay minerals (in mole percent) calculated on the
84   basis of eleven oxygen atoms, as determined by electron microprobe analyses; most clay-
85   like minerals in SanC-A plot near montmorillonite (Mont), consistent with spectral data.
86   Clay-like compositions in SanC-B plot along the Fe-Mg axis, indicating the presence of
87   more Fe,Mg rich phyllosilicates. The single SanC-B analysis near the Al-vertex was
88   taken from altered material between plagioclase laths; most phyllosilicate-like
89   compositions for B were found near altered olivine grains, and few phyllosilicates were
90   found near plagioclase laths. No clays were found with microprobe in SanC-J or SanC-C.
91   Labeled points on ternary are shown in BSE images for (b) SanC-A and (c) SanC-B.
92

93   Figure 11. (a) XRD spectra offset along the y-axis arranged from most altered (A) to least
94   altered (J) showing sharp peaks from primary mineralogy, and broader features due to the
95   presence of amorphous phases. The primary hematite peak is labeled in Sample A to
96   show the change due to alteration from the Sample J to A (b) Calculated mineral
97   abundances (in weight percent) from XRD Rietveld analyses with endmember
98   compositional information determined from microprobe analyses.
99
100   Figure 12. Bulk chemical data in weight percent vs. silica for all samples; samples
101   selected for further study from spectra are shown in bold text, (a) alkalis vs. SiO_2, (b)
102   Na2O vs. SiO_2, (c) CaO vs. SiO_2, (d) Fe_2O_{3T} vs. SiO_2, (e) Al_2O_3 vs. SiO_2, (f) MgO vs.
103   SiO_2, (g) TiO2 vs. SiO_2. Trends are enrichment in Fe(III) and depletion of Si and Na due
104   to alteration. The trend in Ca may be due to primary compositional variation and/or its
105   relative enrichment as other elements are depleted (see Figure 12c). Variation in Ti and
106   Mg are due to differences in petrogenesis.
107
108   Figure 13. Loss on ignition (LOI) versus various oxides in weight percent (a) SiO_2, (b)
109   alkalis, and (c) CaO track alteration with depletion in alkalis and silica, and slight
110   enrichment in Ca with increasing LOI, which is interpreted to represent hydration of the
111   sample upon alteration.
112
113   Figure 14. Weight percent oxides versus band depth at 1.9 μm (BD1900; tracks H_2O) for
114   all samples; bold types indicate sample subset used for further analyses (a) general
115   weathering trend of depletion in alkalis with increasing alteration (water content) due to
116   weathering of plagioclase, (b) slight trend in CaO with water content perhaps caused by
117   persistence of plagioclase and Ca-rich pyroxene as samples are weathered; no evidence of
118   Ca-salt precipitation was observed within the rock though exterior surfaces of Sample F
119   had acquired precipitated gypsum, (c) MgO, and (d) Fe_2O_{3T} shows no consistent trends
120   with BD1900, possibly because of different alteration styles observed in particular
121   samples.
122
123   Figure 15. Weight percent oxide versus band depth at 0.53 microns (BD530; tracks
124   Fe(III)-oxides) for (a) alkalis vs. BD530 which shows a trend in depletion of alkalis
125   (controlled by Na) with increasig BD530, (b) Na2O vs. BD530 which shows the trend in
126   alkali depletion is dominated by loss of Na, (c) Fe_2O_{3T} vs. BD530 shows increasing
127   oxidation ferric iron content, and (d) CaO vs. BD530 shows a small enrichment in Ca.
128   SanC-B is an outlier (as in Figure 14d) for iron.
129
130   Figure 16. Ternary diagram of Al, Ca/Na/K, and Fe/Mg for bulk compositions (in mole
131   percent) of all samples (labeled with sample letters); red circles show the fields for
132   feldpsars/feldspathoids, pyroxenes, and olivine. The arrow shows the general open-
133   system weathering trend for basalts after Nesbitt and Wilson, 1992. Closed symbols
134   represent primary minerals, while open symbols show altered minerals.
135
136   Figure 17. Overall weathering trends from (a) spectral and bulk chemical data, (b)
137   spectral data at longer wavelengths, (c) secondary textures and point analyses from the
138   microprobe, and (d) primary and secondary mineralogy. Arrows indicate the direction
139   from least to most altered.
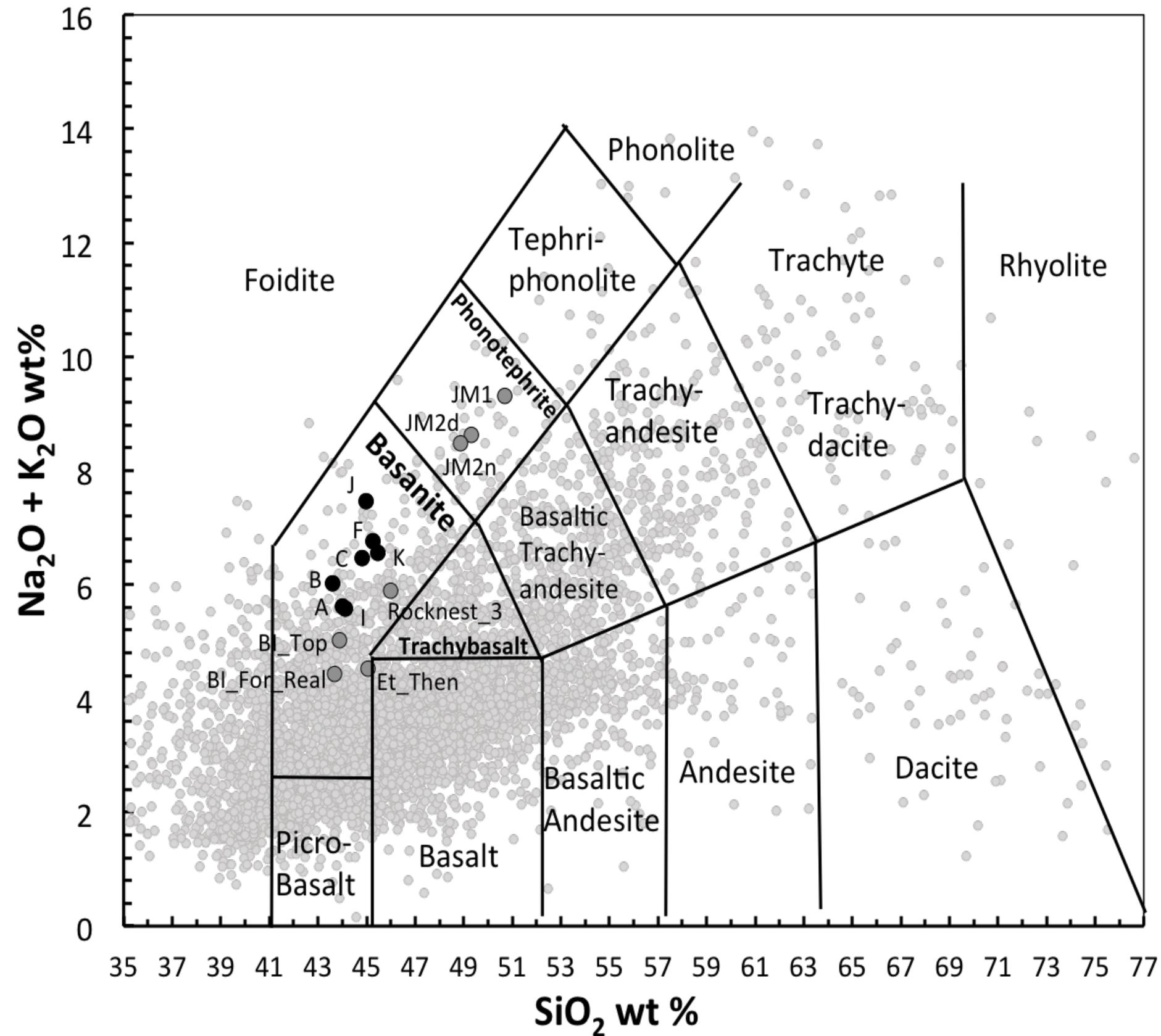
San Carlos, AZ
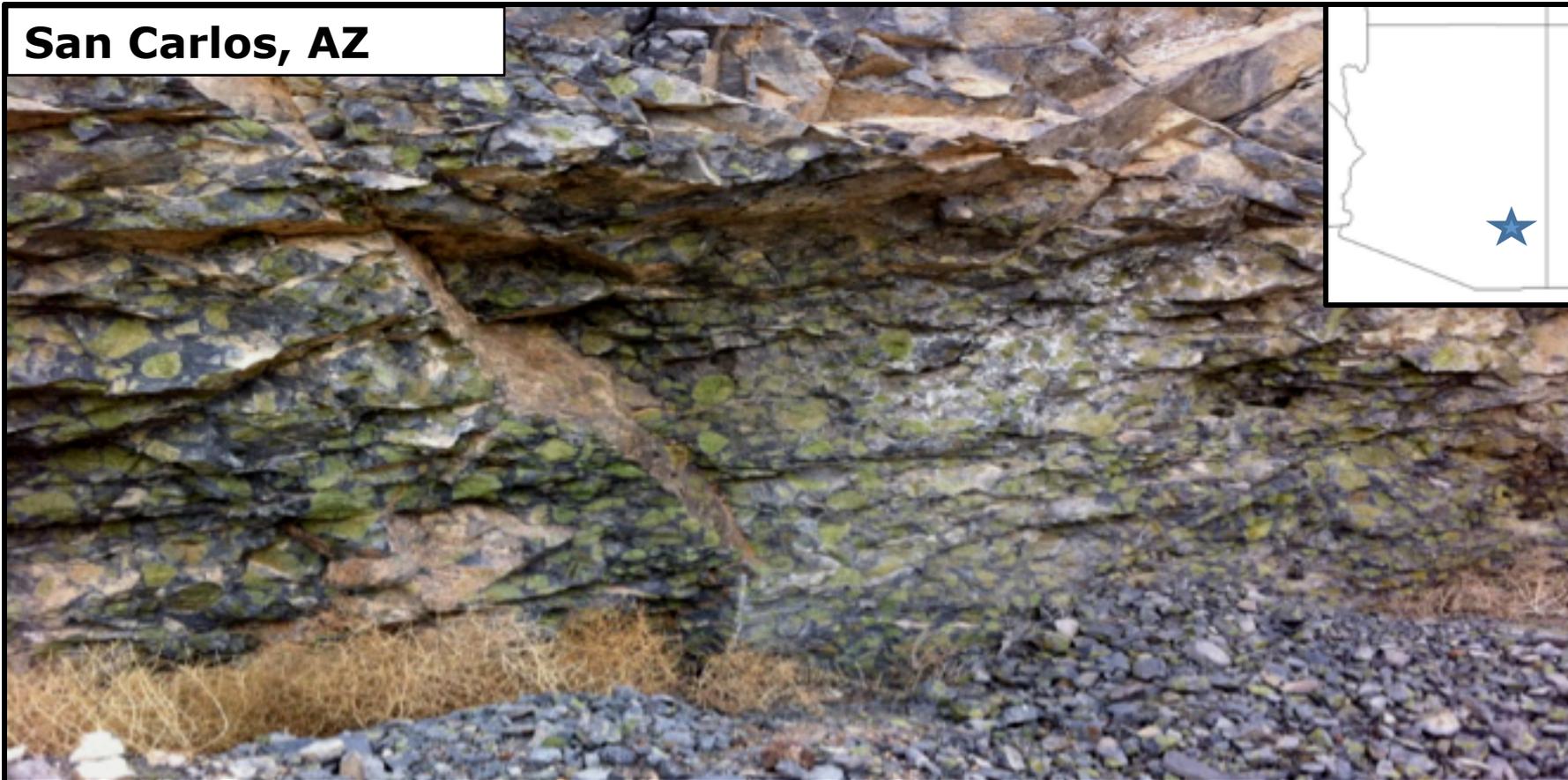
Sample J

Sample K

Sample F
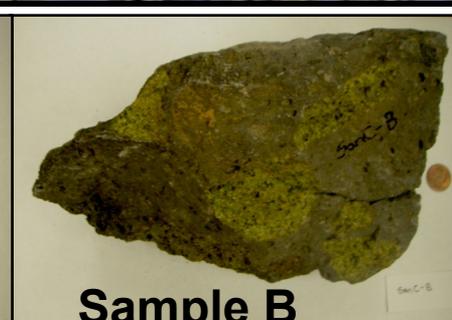
Sample B

Sample C

Sample I

Sample A

F   Sample J

G   Sample B

H   Sample C

I   Sample A

A. SanC-J — mag, olv, cpyx, neph, plag. WUSTL COMP 15.0kV ×110 100µm WD11mm

B. SanC-B — plag, neph, zoned mag, alt olv, cpyx. WUSTL COMP 15.0kV ×100 100µm WD11mm

C. SanC-C — olv, feldspar, cpyx. WUSTL COMP 15.0kV ×100 100µm WD11mm

D. SanC-A. WUSTL COMP 15.0kV ×45 100µm WD11mm

E. SanC-A; inset of D — altd olv, plag, altd mag. WUSTL COMP 15.0kV ×400 10µm WD11mm

F. SanC-A — alt olv, altd mag, wormy plag. WUSTL COMP 15.0kV ×500 10µm WD11mm

G. SanC-B — mag, zoned olv, alt to hematite, altd olv rim. WUSTL COMP 15.0kV ×100 100µm WD11mm

H. SanC-A — zoned olv, cpyx-olv intergrowth, plag. WUSTL COMP 15.0kV ×65 100µm WD11mm

Legend:
- ◆ SanC-A olv
- ● SanC-B olv
- ◇ SanC-A olv and hem
- △ SanC-C olv and hem
- ■ SanC-J olv
- ▲ SanC-C olv
- ○ SanC-B olv and hem

Y-axis: $Na_2O+K_2O+CaO+Al_2O_3+TiO_2$

X-axis: $MgO/(MgO+FeO+MnO)$

A

altered

unaltered
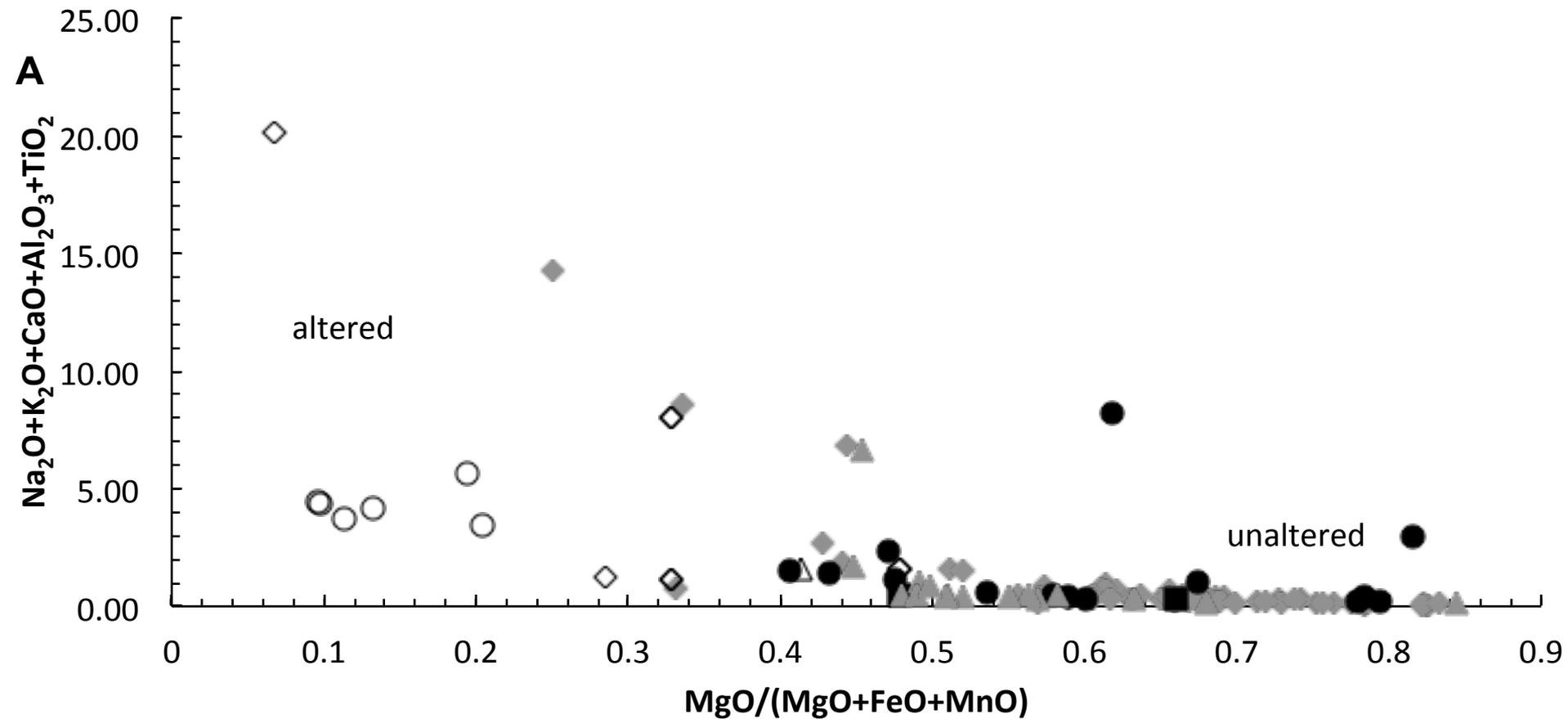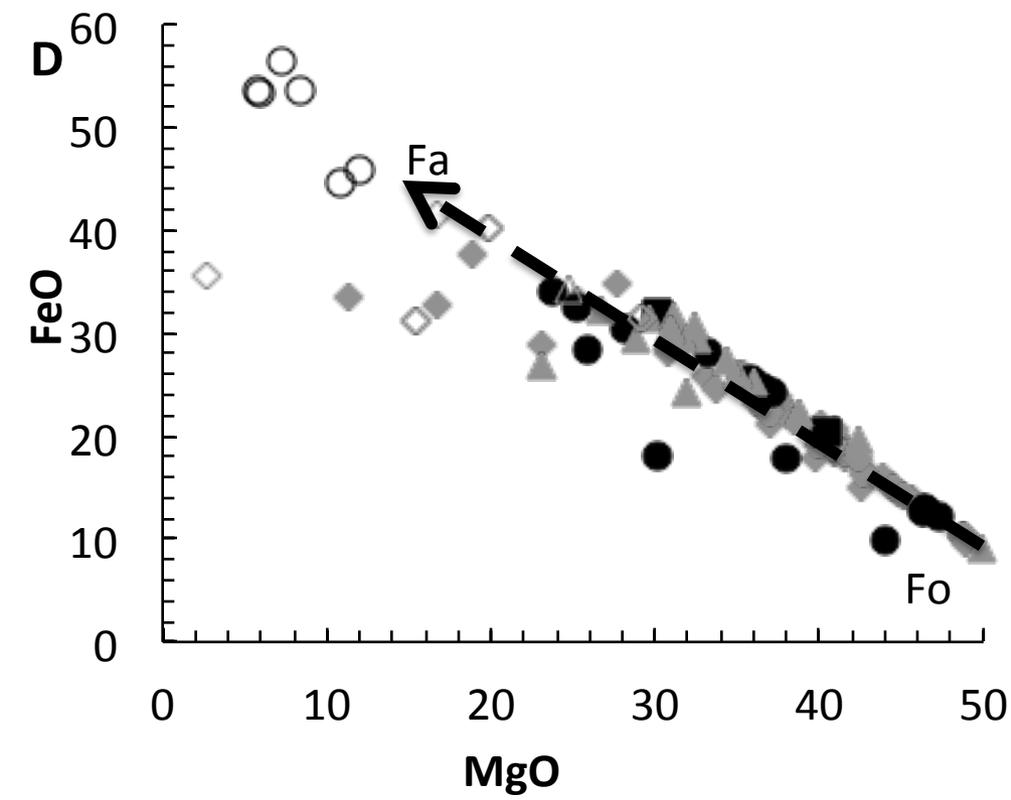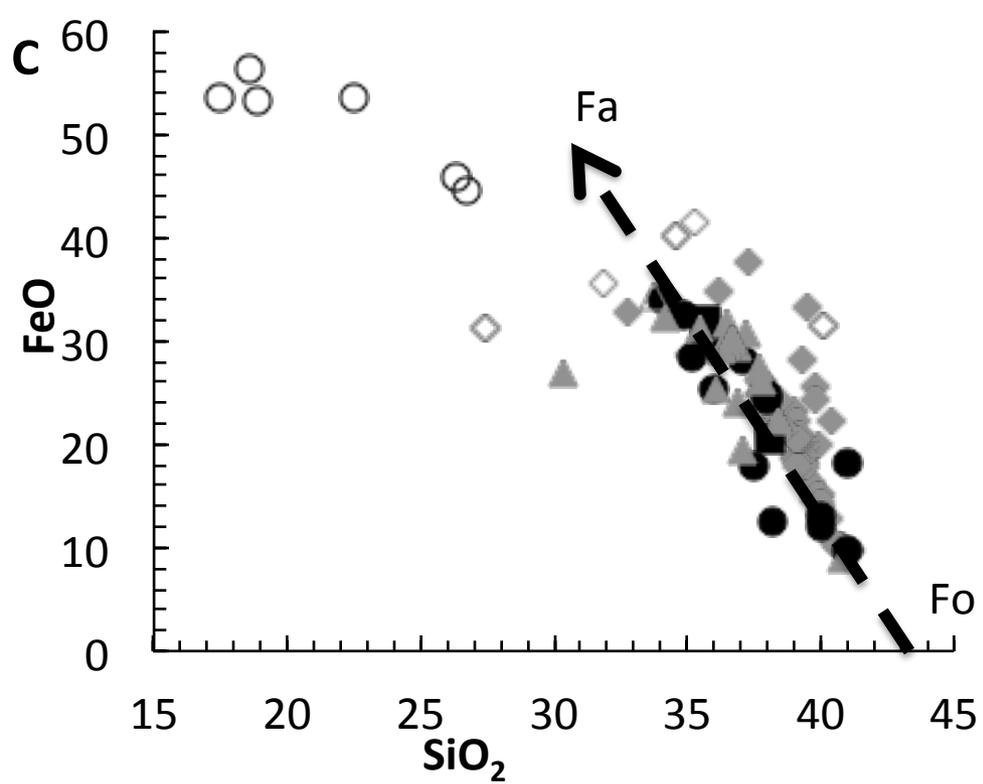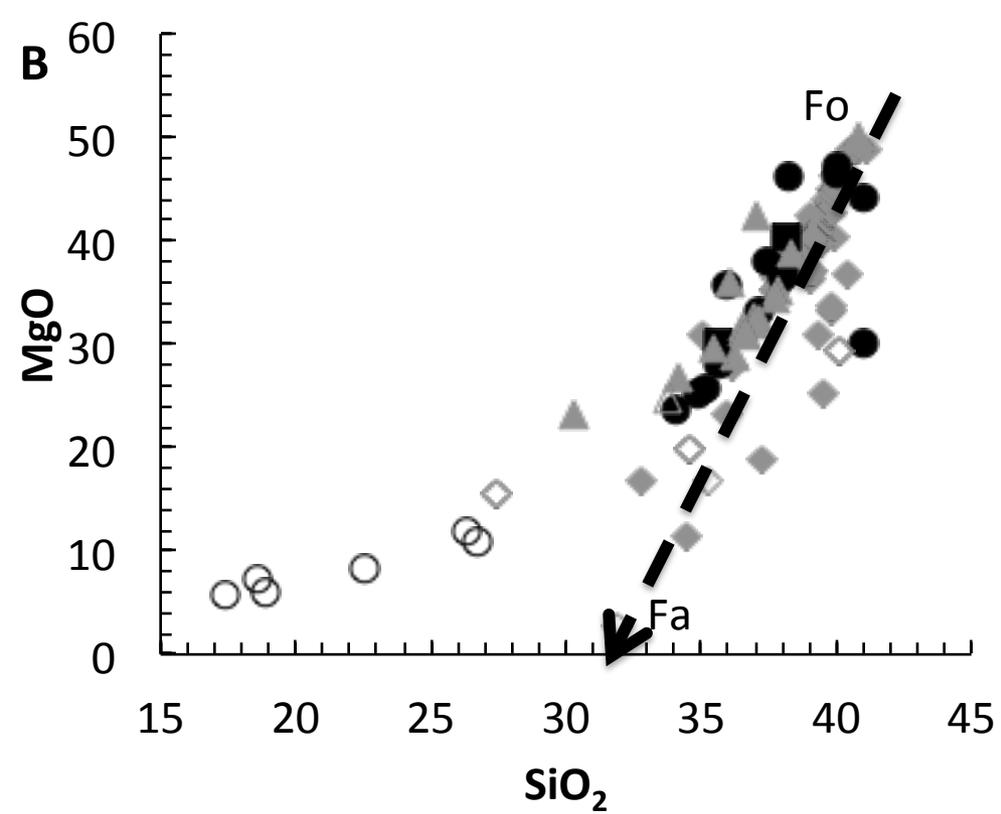
Legend:
- ◆ SanC-A pyx
- ■ SanC-J pristine pyx
- ● SanC-B pyx
- ▲ SanC-C pyx

Pyroxene quadrilateral diagram with end-members: $MgCaSi_2O_6$ (top left), $FeCaSi_2O_6$ (top right), $Mg_2Si_2O_6$ (bottom left), $Fe_2Si_2O_6$ (bottom right). Axis labels: 20, 5, 50, 45 along the left side; 50 along the bottom.

A

KAlSi$_3$O$_8$

Microcline

Sanidine

Alkali Feldspars

Anorthoclase

Albite

Oligoclase

Andesine

Bytownite

Labradorite

Anorthite

NaAlSi$_3$O$_8$

Plagioclase Feldspars

CaAl$_2$Si$_2$O$_8$

● SanC-B feldspar

▲ SanC-C feldspars

◆ SanC-A feldspar

■ SanC-J feldspar

A

B. SanC-A

1. Mg phyllosilicate

2. Al phyllosilicate

3. Al phyllosilicate

4. Al phyllosilicate

altd olv

plag lathe

WUSTL COMP 15.0kV ×400 10μm WD11mm

C. SanC-B

5. Mg-phyllosilicate

altd olv

cpyx

altd olv

WUSTL COMP 15.0kV ×100 100μm WD11mm

B

Legend:
- Plagioclase
- Forsterite
- Fe/Ti Oxide
- Augite
- Nepheline
- Leucite
- Hematite
- Sanidine
- Albite
- Analcime
- Illite/Mica

A

R² = 0.76

SiO₂ vs LOI:
- SanC-K
- SanC-F
- SanC-J
- SanC-C
- SanC-I
- SanC-A
- SanC-B

B

R² = 0.58

Na₂O + K₂O vs LOI:
- SanC-J
- SanC-F
- SanC-K
- SanC-C
- SanC-B
- SanC-I
- SanC-A

**C**

R² = 0.61

CaO vs LOI:
- SanC-A
- SanC-C
- SanC-I
- SanC-B
- SanC-F
- SanC-K
- SanC-J

A — Plot of Na₂O + K₂O versus Avg Band Depth 0.53 μm. $R^2 = 0.59$. Data points: SanC-J, SanC-F, SanC-K, SanC-C, SanC-B, SanC-I, SanC-A.

B — Plot of Na₂O versus Avg Band Depth 0.53 μm. $R^2 = 0.86$. Data points: SanC-F, SanC-K, SanC-B, SanC-J, SanC-I, SanC-C, SanC-A.

C — Plot of Fe₂O₃T versus Avg Band Depth 0.53 μm. $R^2 = 0.21$. Data points: SanC-A, SanC-C, SanC-J, SanC-F, SanC-I, SanC-K, SanC-B.

D — Plot of CaO versus Avg Band Depth 0.53 μm. $R^2 = 0.62$. Data points: SanC-A, SanC-B, SanC-I, SanC-C, SanC-F, SanC-K, SanC-J.

Al$_2$O$_3$ Kaolinite, Gibbsite

Feldpsars, Feldpsathoids

Weathering

Olivine, Fe oxides

BIA
J C
F K

CaO+ Na$_2$O +K$_2$O

MgO +FeO

Pyroxenes

0   0.2   0.4   0.6   0.8   1

increasing BD1900
(hydration)

increasing BD530
(oxidation)

alkali depletion

B

increasing BD2210

SanC-A
Sharp 2.2 μm (Al-OH)
Sharp 0.53 μm (Fe^{3+})

SanC-C
Sharp and broad 2.2 μm (Al/Si-OH)
Sharp 0.53 μm (Fe^{3+})

SanC-J
Broad 2.2 μm (Si-OH)

increasing BD2290
increasing BD530

SanC-B
Broad 2.2 μm (Si-OH)
Weak 2.31 μm (Mg-OH)
Small 0.53 μm (Fe^{3+})
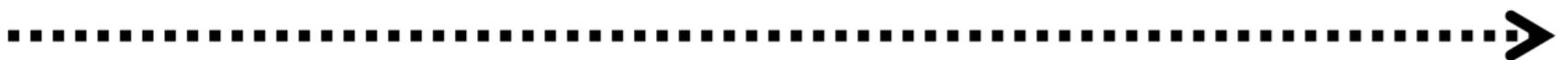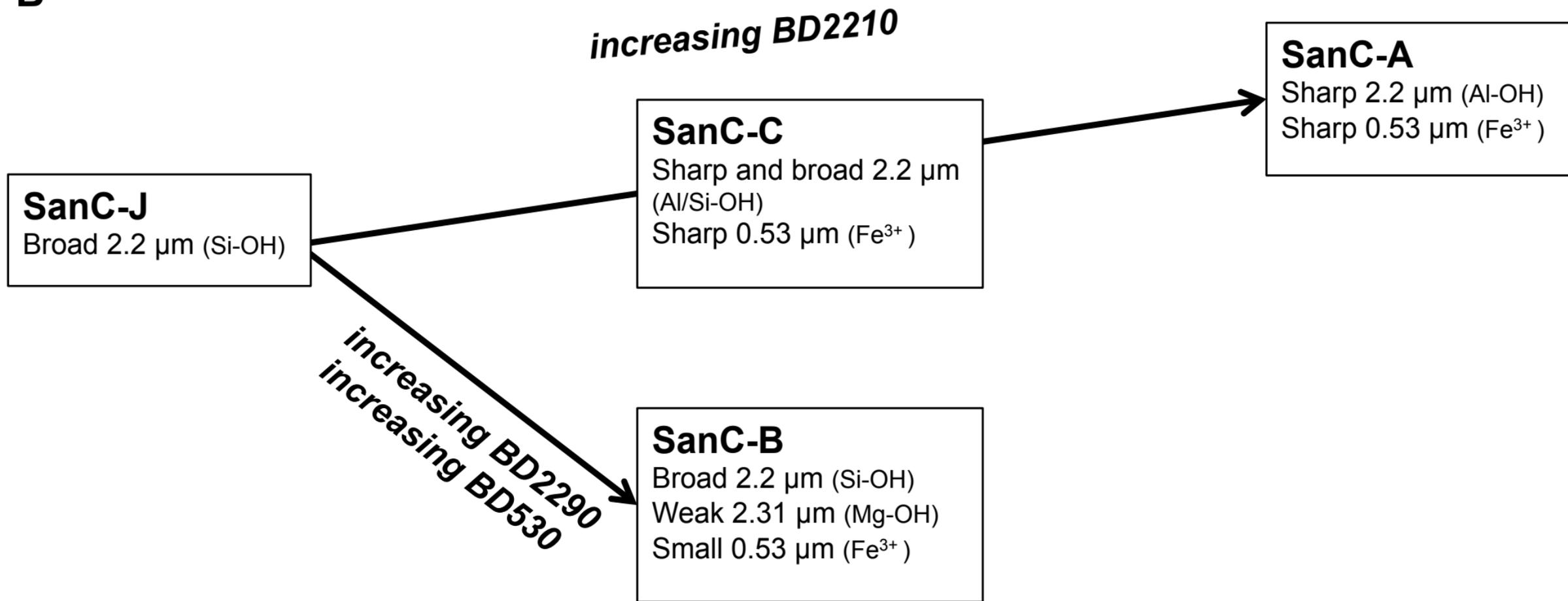
C

SanC-J
pristine plag lathes
zoned olv
pristine Ti-mag

SanC-C
mottled plag
olv altd to hem veins
pristine Ti-mag

SanC-A
wormy plag
olv altd to hem veins
mottled intergrowth Ti-mag w/ ulvöspinel
Ti-mag oxidized to Ti-hem

SanC-B
mottled plag
olv altd to hem veins
zoned Ti-mag w/ ulvöspinel

D

| Feldspar | *Dissolution of Na,K,Si* → | Al phyllosilicates |

| Mg-rich olivine cores
Ferroan rims | *Dissolution of Mg, Si*
Oxidation of Fe rims → | Fe, Mg-rich phyllosilicates
Fe,Si-rich 'mats' and veins |

| Titano-magnetite | *Oxidation of primary Fe-oxides* → | Ilmenohematite intergrown
with ulvöspinel |