

**A survey of olivine alteration products using Raman spectroscopy.** K. Kuebler, B.L. Jolliff, A. Wang, and L.A. Haskin Dept. of Earth & Planetary Sciences & the McDonnell Center for the Space Sciences, Washington University, One Brookings Drive, St. Louis, MO 63130. ([kuebler@levee.wustl.edu](mailto:kuebler@levee.wustl.edu))

**Introduction.** Identification of mineral alteration products will aid in the crucial task of interpreting past Martian environmental conditions, especially aqueous environments. Olivine has been identified at the surface of Mars [1] and is readily altered in aqueous environments. Using Raman spectroscopy, we studied three rocks with altered olivine and compared the data with mineral chemistry from electron microprobe analysis. Although the alteration in all three samples has loosely been called iddingsite their appearances and modes of occurrences differ as described. Alteration products in all three samples are likely fine-grained mixtures.

**Samples.** 1) **QBV** is a Quaternary basalt from Lunar Crater Volcanic Field, NV. It is vesicular and porphyritic, and olivines throughout are altered along their edges and fractures, presumably by reaction with magmatic waters. The alteration product has irregular boundaries and goes extinct uniformly under cross-polarized light, implying that the crystallographic structure is partly inherited from the olivine [2]. QBV also contains green olivine alteration but this was avoided in the current study. This sample was the focus of [3] where the alteration material was identified as iddingsite (by the definitions of [4-7]). 2) **16J-30** is from the upper slopes of Mauna Kea, HI. Altered olivines occur only near the exterior of the sample. In thin section, the alteration product appears similar to that of QBV in color, extinction, and morphology, differing only in mode of occurrence, likely because the alteration was done by low-T surface waters. 3) **Lafayette** is a Nakhilite, notable for post-magmatic, pre-terrestrial aqueous alteration [8]. It is a pyroxene cumulate with olivines that contain veins of alteration but in which alteration products are not confined to olivine. Similar material occurs along grain boundaries and as intergranular patches replacing olivine, pyroxene, and silicate glass [9,10]. Veins are composed of a coarse, radiating phyllosilicate that has non-uniform extinction under cross-polarized light. The veins have saw-tooth outlines (Fig. 1), in sharp contact with the olivine, and are crosscut by finer-grained smectite (whose TEM compositions and  $\sim 1$  nm lattice spacings are consistent with saponite [9]). Ferrihydrite, magnetite (or maghemite), and rare sulfate and chloride grains have also tentatively been identified [9]. Here, we focus on alteration in the olivine veins. It is hypothesized that only limited quantities of water infiltrated Lafayette, perhaps episodically [9]. The presence of ferrihydrite implies temperatures below  $100^\circ\text{C}$ ; its coexistence with magnetite (or maghemite) suggests an  $f_{\text{O}_2}$  just below the magnetite-hematite oxygen buffer [9].

**Methods.** We made tightly spaced laser Raman spectroscopic traverses (1-2  $\mu\text{m}$  steps between spectra)

across altered zones of olivine in all three samples. We use a Kaiser HoloLab 5000 with an optical configuration similar to the Mars Microbeam Raman Spectrometer [11] using a 532 nm excitation laser. Analyses on QBV and 16J-30 were made using a focused  $\sim 6$   $\mu\text{m}$  diameter beam (20x mag.) and a laser power of  $\sim 2$  mW. For Lafayette we used a  $\sim 2$   $\mu\text{m}$  beam (100x mag.) and 5 mW. Samples were analyzed under a nitrogen purge to prevent oxidation of Fe-oxides by laser heating during laboratory analysis. Peak positions and height/width ratios were determined using the curve-fitting routine of the Grams/32 software. Electron microprobe analyses were made as close to the Raman traverses as possible with a JEOL 733 using a 15 kV accelerating voltage, 30 nA beam current, and 1  $\mu\text{m}$  beam diameter.

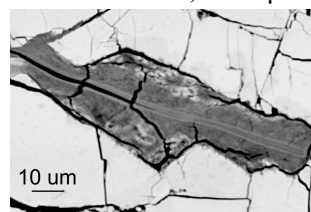
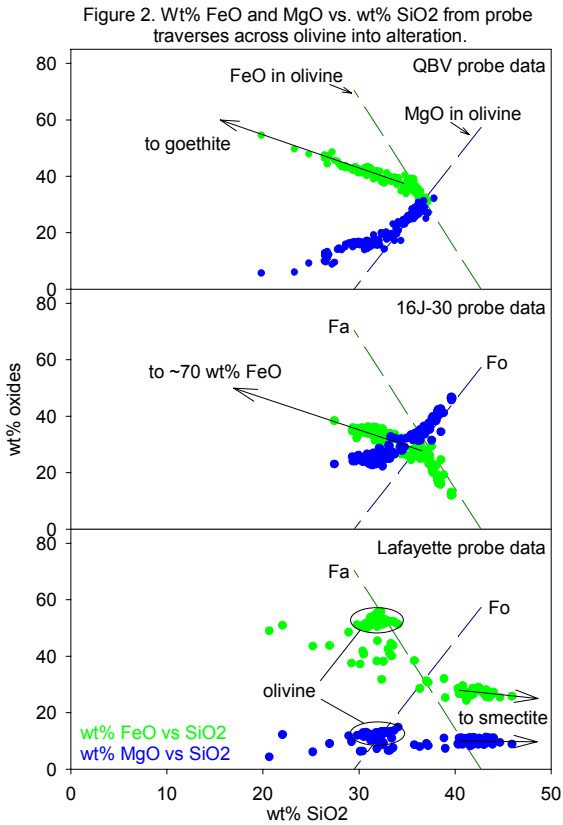


Figure 1. Alteration vein in a Lafayette olivine.

**Electron microprobe analyses.** Representative olivine and average alteration product compositions are given in Table 1. Sample 16J-30 has the most magnesian olivine and the widest compositional range (Mg# 0.63-0.88). Lafayette olivines are the most ferroan and are equilibrated (Mg# 0.25-0.34). QBV olivines have intermediate compositions and are only moderately zoned (Mg# 0.51-0.64). Alteration in QBV and 16J-30 involved progressive removal of Mg and Si, accompanied by an increase in FeO. Compositions lie on trajectories (Fig. 2) that depart from Fo-Fa mixing lines and trend toward goethite in the case of QBV (at 81 wt% FeO and 0 wt%  $\text{SiO}_2$ , Fig. 2a). The trend in 16J-30 points toward  $\sim 70$  wt% FeO, implying an additional component (Fig. 2b). In contrast, Lafayette alteration shows more complex trends (Fig. 2c): removal of FeO at constant MgO and  $\text{SiO}_2$ ; loss of  $\text{SiO}_2$  with increasing FeO, and loss of FeO with increasing  $\text{SiO}_2$  and with a slope trending towards phyllosilicate (e.g., smectite) compositions.

**Raman spectral analysis.** A detailed discussion of QBV can be found in [3]. In general, as the laser beam passes from olivine into altered material, olivine peaks diminish within 10  $\mu\text{m}$  and peaks of goethite (248, 301, 392, and  $471\text{cm}^{-1}$  in Fig. 3a) and a “polymerized” silicate phase ( $\sim 630$ , 680, and  $\sim 940\text{cm}^{-1}$  peaks) appear, then dominate. A broad, weak band that does not belong to goethite appears in the OH stretching region ( $3400$ – $3800\text{cm}^{-1}$ ) of some spectra. Hematite is present in a few spectra and may represent dehydration of goethite. Spectra of the alteration in 16J-30 contain peaks similar to the “polymerized” silicate phase in QBV but lack goethite peaks. In their place are two weak, broad fea-



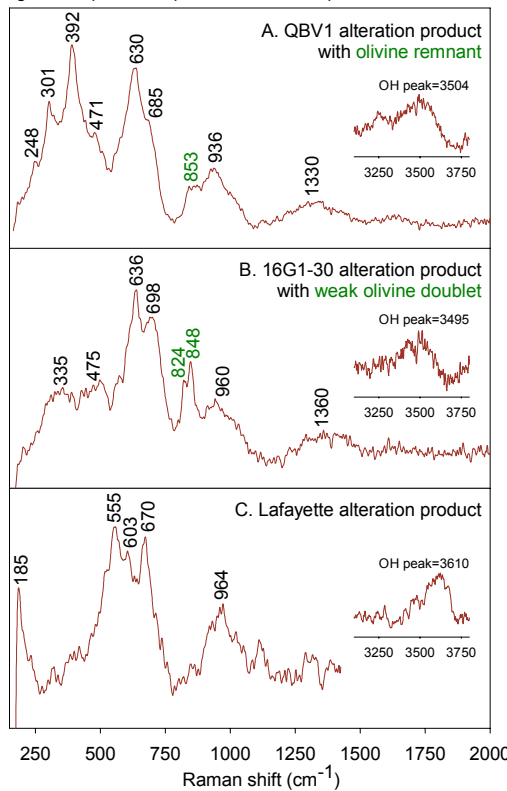
tures centered ~335 and ~475 cm<sup>-1</sup> (Fig. 3b), possible secondary peaks of Fe-oxides whose primary peak (~670 cm<sup>-1</sup>) is obscured by those of the polymerized silicate. Peak positions in 16J-30 occur at higher Raman shifts, reflecting more magnesian compositions. A broad peak whose center varies from 1300 to 1360 cm<sup>-1</sup> is common and suggests hematite. Major hematite peaks were not observed, however, so the hematite is presumably poorly crystalline. Hematite is present as grain coatings near the altered surface of this sample as seen in thin section. The major Raman peaks (670 & 555 cm<sup>-1</sup>) from the fine-grained phyllosilicate in the Lafayette olivine veins (Fig. 3c) imply a trioctahedral phyllosilicate structure (similar to that of vermiculite), and the peak at ~555 cm<sup>-1</sup> indicates an Fe-rich composition [12]. Peaks at 964 cm<sup>-1</sup> and ~603 cm<sup>-1</sup> indicate the presence of a second “polymerized” silicate phase, as well. No sulfate or iron oxide was encountered. Broad OH peaks are also present in a few spectra from 16J-30 and Lafayette. The OH peak shifts are variable in 16-30, implying

Table 1. Representative olivine and average alteration compositions.

	QBV				16J-30				Lafayette			
	olivine core	olivine rim	alteration n=80	sdev	olivine core	olivine rim	alteration n=50	sdev	olivine core	olivine rim	alteration* n=29	sdev
SiO <sub>2</sub>	36.2	35.4	30.9	3.13	38.8	36.4	32.1	1.79	32.3	31.9	42.2	1.21
TiO <sub>2</sub>	0.03	0.07	0.08	0.05	0.00	0.04	0.45	1.42	0.09	0.10	0.04	0.06
Al <sub>2</sub> O <sub>3</sub>	0.00	0.03	1.04	1.04	0.01	0.03	1.04	0.66	0.00	0.02	4.55	1.26
Cr <sub>2</sub> O <sub>3</sub>	0.00	0.00	0.01	0.01	0.09	0.01	0.01	0.02	0.00	0.00	0.02	0.02
FeO(t)	34.1	35.3	41.0	4.20	19.2	30.5	32.5	3.54	55.8	54.1	27.2	1.08
MnO	0.57	0.64	0.68	0.14	0.34	0.72	0.64	0.13	0.94	1.00	0.48	0.10
MgO	29.0	26.5	17.0	4.41	41.1	32.0	25.9	5.09	10.8	11.6	9.9	0.97
CaO	0.30	0.49	0.95	0.26	0.15	0.34	0.26	0.07	0.12	0.12	1.18	0.32
ZnO	0.09	0.01	0.05	0.05	0.02	0.00	0.04	0.04	0.00	0.06	0.05	0.05
Na <sub>2</sub> O	n.d.	n.d.	n.d.	---	n.d.	n.d.	n.d.	---	0.01	0.00	0.22	0.07
K <sub>2</sub> O	n.d.	n.d.	n.d.	---	n.d.	n.d.	n.d.	---	0.00	0.00	0.60	0.18
Sum	100.3	98.4	91.7		99.8	100.0	92.9		100.0	98.8	86.4	

\*SO<sub>3</sub>, Cl also present according to [9].

Figure 3. Spectra acquired from altered portions of the olivine.



poor crystallinity.

**Conclusions.** All of the alteration products imply aqueous alteration. Raman and EMP data indicate that “polymerized” silicates and Fe-oxides or Fe-hydroxides are the olivine alteration products in the two terrestrial samples, QBV and 16J-30. Goethite and hematite imply oxidation of the Fe<sup>2+</sup>. Data from Lafayette suggest a different alteration process involving the formation of a trioctahedral phyllosilicate and perhaps more limited mobility of SiO<sub>2</sub> (lower water/rock ratio?).

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