

A STUDY OF OLIVINE ALTERATION TO IDDINGSITE USING RAMAN SPECTROSCOPY. K. E. Kuebler, Alian Wang, L.A. Haskin and B.L. Jolliff, 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)

Introduction. A crucial task of Mars surface science is to determine past environmental conditions, especially aqueous environments and their nature. Identification of mineral alteration by water is one way to do this. Recent work interprets TES spectra as indicating altered basalt on Mars [1]. Olivine, a primary basaltic mineral, is easily altered by aqueous solutions. Alteration assemblages of olivine may be specific to deuteric, hydrothermal, surface water, or metamorphic environments. Raman spectra are produced by molecular vibrations and provide direct means for studying and identifying alteration products. Here, we present a combined study of changes in the chemical composition and Raman spectra of an olivine as it alters to iddingsite.

Iddingsite is found in some SNC meteorites and is presumably present on Mars [2-4]. The term “iddingsite” has been used as a catch-all term to describe reddish alteration products of olivine, although some authors ascribe a narrower definition [5-8]: an Å-scale intergrowth of goethite and smectite (presumably saponite) formed in an oxidizing and fluid-rich environment. Alteration conserves Fe (albeit oxidized) but requires addition of Al and H₂O and removal of Mg and Si [8]. The smectite that forms may be removed by continued alteration. Dehydration of the goethite forms hematite [8]. Our purpose is to study the mineral assemblage, determine the structural and chemical variability of the components with respect to the degree of alteration, and to find spectral indicators of alteration that will be useful during *in-situ* analyses on Mars.

Sample. QBV is a basalt cobble from a Quaternary flow at Lunar Crater Volcanic Field, NV. It is vesicular and porphyritic, and its olivine grains strongly iddingsitized along their edges and fractures [9]. Electron microprobe analyses (Fig. 1) indicate hydration of olivine and removal of Si and Mg from zones of alteration that cannot be attributed solely to igneous zonation (i.e. compositions lie on trajectories that depart from Fo-Fa mixing lines). Although olivine compositions are consistent with incipient hydration, progressive alteration to lower SiO₂ and MgO and higher FeO is not consistent with simple hydration and dilution. We ascribe the term “iddingsite” to this alteration product based on these optical and chemical characteristics but have no TEM data to demonstrate its fit with the definition above.

Methods. Three tightly spaced Raman point counts (5-8 μm between spectra) were made across altered zones of a large olivine phenocryst, followed by additional spot analyses. The Raman system used is a HoloLab5000, with a 532nm excitation laser. All analyses were made with a 20× long working distance objec-

tive, 50-second acquisition times per spectrum for traverses, and 30-100 seconds for point analyses. The laser power used was ~2 mW, and the sample placed under a nitrogen purge to prevent laser-induced oxidation during laboratory analysis. Peak positions and height/width ratios were determined using the curve-fitting routine of the Grams/32 software.

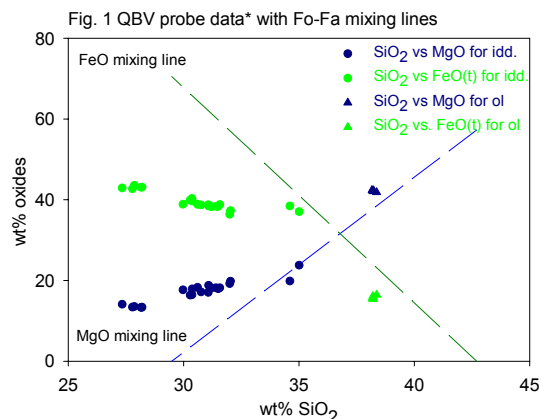


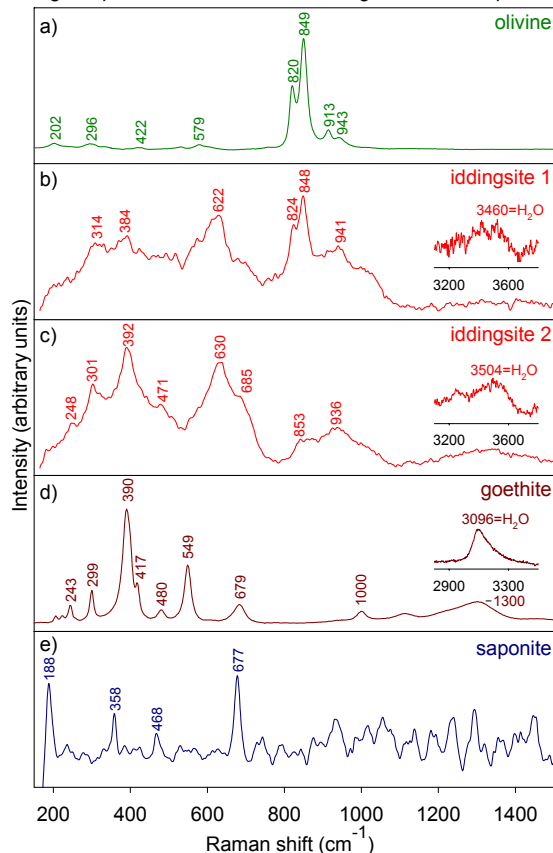
Fig. 1 QBV probe data* with Fo-Fa mixing lines
*Idd. oxide sums ave. ~90% and olivine ~97% presumably owing to incipient hydration. Sums of oxides other than those plotted are not >4 wt% in any analysis.

Spectral features of the iddingsitized area. A typical olivine spectrum and two representative iddingsite spectra from QBV are shown in Fig. 2 along with standard goethite and saponite spectra. The spectra obtained are similar throughout the iddingsite. Changes in relative peak intensities and peak shifts, however, indicate a mixture of phases and variable compositions.

Three groups of peaks can be distinguished. **1)** The only feature that can be attributed to olivine is a variably developed feature ~850 cm⁻¹. It usually appears in spectra taken at the alteration front and is considered a “remnant” of the olivine doublet at 820-850 cm⁻¹. **2)** Four peaks can be attributed to goethite (245, 302, 390 and 478 cm⁻¹), the strongest of which is the ~390 cm⁻¹ peak. **3)** A third group includes two multi-component features that cannot be attributed to olivine, goethite, saponite or any other smectite. A strong, broad feature is present in the 550-750 cm⁻¹ region, where Si-O_b-Si units (O_b= bridging oxygen) peaks occur. It is centered ~630 cm⁻¹ but has a shoulder ~690 cm⁻¹. A weaker feature is located in the 800-1000 cm⁻¹ region, where Si-O_{nb} units (O_{nb}= non-bridging oxygen) peaks occur, and is centered at ~935 cm⁻¹. The co-existence of these units suggests a partially polymerized silicate framework. The stronger 630 cm⁻¹ band suggests a degree of polymerization higher than pyroxene whereas the mid-intensity of ~935 cm⁻¹ band suggests a layered structure has not been formed. These two constraints imply a structure with a degree of polymerization between that

of a double-chain and sheet silicate. The presence of multiple peak components and large peak shifts, however, indicate variable degrees of polymerization, or a mixture of “polymerized structures.” A broad, weak band in the O-H stretching mode region ($3400\text{--}3800\text{ cm}^{-1}$) appears in a few spectra. No saponite or smectite is apparent; but smectite is presumably minor relative to the goethite in iddingsite and only a few layers thick [8].

Fig. 2 Spectra from QBV & standard goethite and saponite.

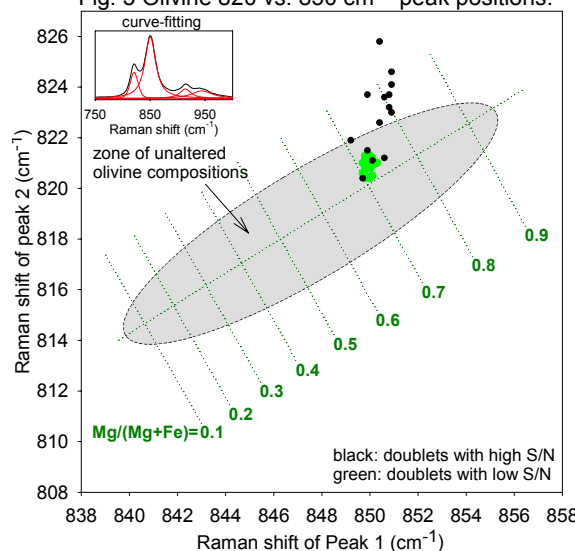


Across the alteration front and into the iddingsite. Comparing spectra along each traverse, intensities of the olivine doublet quickly degrade into the remnant feature at the alteration front (Fig. 2 a-c). The remnant rarely occurs within the iddingsite. The peaks of the goethite and “polymerized structures,” however, appear in the olivine spectra ahead of the alteration front (possibly from iddingsite at depth because olivine is relatively transparent to the laser) but only dominate in spectra from the iddingsite. The goethite peak is stronger where the iddingsite is more developed. Hematite peaks occur in six spectra and may represent goethite that has been dehydrated. Some spectra acquired inside the iddingsite but near the alteration front have high backgrounds.

Changes in olivine near the iddingsite. Each peak of the $820\text{--}850\text{ cm}^{-1}$ doublet is assigned to a mixed contribution of the symmetric (ν_1) and asymmetric (ν_3) stretching modes of Si-O_{nb} bonds in SiO_4 tetrahedra

[13]. Their peak positions shift upwards almost synchronously with increasing $\text{Mg}/(\text{Mg}+\text{Fe})$ [11, 12]. The $\text{Mg}/(\text{Mg}+\text{Fe})$ values of an olivine can be determined using a two-peak plot and fall within a narrow zone (grey region in Fig. 3) [11]. The good S/N olivine spectra from our traverses indicate $\text{Mg}/(\text{Mg}+\text{Fe})=0.7$ (green dots). Olivine peaks near the alteration front are weaker and broader (black dots) and the 820 cm^{-1} peak positions shifted to higher wavenumbers more quickly than the 850 cm^{-1} peak. This observation is consistent with the fact that the 820 cm^{-1} peak has a higher contribution from the ν_3 (asymmetric mode) than the 850 cm^{-1} peak. This mode is more easily affected by variations in the SiO_{nb} force constant, and is more affected by the breakdown of SiO_4 during polymerization [13].

Fig. 3 Olivine 820 vs. 850 cm^{-1} peak positions.



Conclusions. Several spectral features combine to indicate that the alteration of olivine to iddingsite involves the polymerization of SiO_4 tetrahedra towards that of a phyllosilicate, but has not yet been reached (none were detected) in QBV. The shift of the $\sim 820\text{ cm}^{-1}$ peak to higher wavenumbers near the alteration front is a good indicator of the start of polymerization. The coincidence of the goethite peaks with the degradation of the olivine doublet reflects concurrent oxidation of the Fe^{2+} . This work shows that Raman spectroscopy can be used to identify aqueous alteration on Mars and to constrain conditions of alteration.

Acknowledgements: This work supported in part by NASA grant NAG5-12114 & NAG5-10703.

References: [1] Wyatt and McSween (2002) *Nature*, 417, 6886, 263-266. [2] Burns (1986) *Nature*, 320, 55-56. [3] Treiman and Lindstrom (1997) *JGR*, 102, E4, 9153-9163. [4] Romanek et al. (1998) *MAPS*, 33, 775-784. [5] Delvigne (1979) *Pedologie*, 29, 3, 247-309. [6] Gay and LeMaitre (1961) *Am. Min.*, 46, 92-111. [7] Ross and Shannon (1925) *Proc. U. S. National Museum*, 67, pp.19. [8] Eggleton (1984) *Clays & Clay Minerals*, 32, 1, 1-11. [9] Israel et al. (1997) *JGR*, 102, 12, 28705-28716. [10] Wang et al. (2002) *JGR*, accepted. [11] Kuebler et al. (2000) *LPSCXXXI* #1887. [12] Chopelas (1991) *Am. Min.*, 76, 1101-1109. [13] Lam et al. (1990) *Am. Min.*, 75, 109-119.