AQUEOUS ALTERATION IN NAKLITE MIL 03346: LA-ICPMS AND RAMAN SPECTROSCOPY. J. D. Stopar¹, G. J. Taylor¹, and M. D. Norman², ¹SOEST/HIGP, University of Hawai‘i at Manoa, 1680 East-West Rd., Honolulu, HI, 96822 (jstopar@higp.hawaii.edu), ²Research School of Earth Sciences, Australian National University, Canberra ACT 0200, Australia.

Introduction: The secondary aqueous alteration products found in the nakhlites are important because some of them were formed on Mars while in contact with liquid water [e.g., 1-2]. The nakhlite MIL 03346 contains many alteration products similar to those identified as “Martian” in other meteorites including olivine alteration products and Ca-sulfates.

The chemistry of secondary mineral phases is a function of: 1.) the concentration of an element in solution, which depends on the source material and mobility of the element; 2.) the ability of an element to be incorporated into the precipitate; and 3.) the chemistry of the weathering environment, particularly pH and Eh of the solution and the rock/water ratio. Therefore, characterization of the mineralogy and chemistry of secondary products found in MIL 03346 can lead to a better understanding of aqueous processes and weathering environments on Mars.

In a previous abstract [3], we presented major element and rare earth element abundances for MIL 03346. Here, we continue this theme by adding minor elements and other trace element abundances acquired by the same LA-ICPMS technique. In order to better characterize the mineralogy of the secondary products, we also present a preliminary survey of MIL 03346 by confocal Raman microscopy.

Methods: Major and minor element abundances and distributions were determined by electron microprobe ( Cameca SX50, University of Hawaii) and scanning electron microscope (JOEL 5900LV with EDS, University of Hawaii).

Trace element abundances were determined using a 193 nm excimer laser ablation (LA)-ICPMS at the Australian National University. A laser spot diameter of 70 μm, repetition rate 4Hz, was used for the larger phases: olivine, augite, and bulk mesostasis. A smaller spot diameter of 19 μm and a lower repetition rate of 3Hz were used for the alteration products. The NIST 612 glass was used to calibrate instrument sensitivity, and each analysis was normalized to either CaO or SiO₂ to correct for variations in ablation efficiency among different materials. The CaO and SiO₂ abundances used in the internal calibration were determined by electron microprobe point analyses (EMPA). Trace element abundances were normalized to whole rock abundances for MIL 03346 from [4].

The confocal Raman microscope (WiTec alpha300 R, University of Hawaii) uses a green 532 nm excitation laser (370 μW) with spatial resolution better than 0.5 μm. The spectral resolution of the Raman spectra presented here is approximately ±2.5 cm⁻¹ and varies with wavelength. Raman signal was collected from the laser wavelength 532 nm up to a Raman shift of 3863 cm⁻¹.

Results: LA-ICPMS trace element abundances and Raman spectra were acquired from a variety of alteration products in MIL 03346. When possible, we combined these results with electron microprobe analyses and SEM element maps.

Olivine Alteration. Fig. 1 compares the Raman spectra of a patchy area of incipiently-altered olivine to unaltered olivine in MIL 03346. Olivine doublets for the ν₁ + ν₂ combinations are positioned at ~819 and 845 cm⁻¹. The ν₂ stretch is positioned at ~532 cm⁻¹, the ν₂ stretch at ~405 cm⁻¹, the M2-site translation at ~331 cm⁻¹, and the ν₃ stretch at ~945 cm⁻¹. These positions are generally consistent with published modes for olivine [5-8]. The lack of change (at the resolution of this spectrum) in the Raman shift peak positions with incipient alteration of olivine, suggests that these patchy areas have only experienced the initial stages of stoichiometric dissolution and that significant structural changes have not yet occurred.

![Raman spectra comparison](image)

Figure 1: Raman spectra of unaltered olivine (~Fo₄₃) and incipiently-altered olivine in MIL 03346. Total integration time is 5 s.

Fig. 2 shows an altered area within an olivine phenocryst. This area has a diamond-shaped morphology that is typical of iddingsite in its initial stages of formation. Iddingsite is typically a mixture of goethite and phyllosilicate “clays” such as saponite [9]. Fig. 3 shows that “iddingsite” veins in MIL 03346 are Si-rich and are surrounded by S-rich materials. However, not all olivine veins have iddingsite morphology.
Figure 2: SEM backscattered image of alteration in an olivine phenocryst. The diamond-shaped pattern is typical of olivine alteration and probably represents the initial stages of iddingsite formation [9-10].

Figure 3: SEM backscattered image of “iddingsite” alteration in an olivine phenocryst and corresponding color overlay (red = S, green = Fe, blue = Ca). The interior of the vein is Si-rich and Fe-Mg-poor. The edges of the vein are S-rich (red).

Fig. 4 presents the Raman spectrum of a typical olivine vein. Olivine alteration in Lafayette and a terrestrial basalt were studied by [11-12], and the Raman spectra of iddingsite in those two rocks are not unlike Fig. 4. In MIL 03346, olivine alteration exhibits broad peaks around 982 cm$^{-1}$ and 1135 cm$^{-1}$, which are consistent with the stretching region of non-bridging oxygen in phyllosilicate “clays”. See [13] for one of the few studies of the Raman features of phyllosilicates. There is also a small peak ~692 cm$^{-1}$ that is consistent with Si-O-Si vibrations in phyllosilicate “clays”. In addition, MIL 03346 olivine alteration has a complex series of Raman shifts and interactions in the region <600 cm$^{-1}$, with most around 600 cm$^{-1}$ and between 300-441 cm$^{-1}$, which suggest Fe,Mg phyllosilicate “clay” translational modes. However, goethite as well as a number of other minerals also have Raman shifts in the region <600 cm$^{-1}$, making this a difficult spectrum to interpret. Not shown in Fig. 4 is the broad Raman shift around 3570 cm$^{-1}$, suggesting the presence of a hydrated phase.

Figure 4: Raman spectrum of an alteration vein in olivine. Total integration time 60 s. The series of broad peaks is suggestive of phyllosilicate “clays” possibly mixed with goethite or other minerals. There is also a broad Raman peak around 3570 cm$^{-1}$ (not shown) in the OH-stretching region, consistent with a hydrated product.

LA-ICPMS data for olivine alteration veins show that the veins are enriched in mobile elements (Fig. 5). The abundances of immobile elements in the olivine veins are generally low and only slightly enriched over unaltered to incipiently-altered olivine. Phosphorous has a very high ionic potential and appears to be mobile in MIL 03346. Phosphorous in the olivine veins is significantly elevated above the unaltered olivine, while the areas of incipient alteration appear slightly depleted. Possible sources for phosphorous in the olivine veins are dissolved phosphates or glass from the mesostasis. Augite is probably not a significant contributor to the phosphorous in solution because unaltered augite has very low abundances of P.

Whole rock Cs, Rb, Ba, and Pb are concentrated in mesostasis phases. Sr is found in both the bulk mesostasis and clinopyroxene. These mobile elements are enriched in the olivine alteration veins. Cs, Rb, Ba, and Pb are below detection limits in unaltered olivine. The high abundances of these elements in both the mesostasis and olivine alteration products and low abundance in olivine suggests that these elements have been mobilized from the mesostasis (perhaps due to the dissolution of glassy phases) during aqueous alteration and are being deposited from solution in the olivine alteration veins.
Figure 5: Element mobility plot for important phases in MIL 03346. LA-ICPMS abundances have been normalized to whole rock abundances from [4] in order to remove the effects of Cs, Rb, Pb, and Zn volatility and the potential loss of elements such as Co during core formation. The elements with the lowest ionic potential are on the left, and the ionic potential increases toward the right of the plot. Phosphorous has a very high ionic potential and appears to be mobile in MIL 03346.

Figure 6: Raman spectra of unaltered augite in MIL 03346 compared to a vein within the augite. Total integration time is 25 s for the unaltered augite and 50 s for the alteration vein. The alteration vein has some Raman features in common with the augite, but the vein also has a number of additional peaks (bold numbers) not observed in the clinopyroxene.

Figure 7: Raman spectrum of unaltered titanomagnetite in the mesostasis (total integration time 60 s), and a spectrum of an unusual Fe-oxide that may represent alteration of titanomagnetite (total integration time 30 s). In the “altered” Fe-oxide, the titanomagnetite fundamental Raman shifts at ~674 and ~545 cm\(^{-1}\) are found at lower wavenumbers ~670 and ~523 cm\(^{-1}\), and the broad peak centered around 336 cm\(^{-1}\) is stronger in the “altered” Fe-oxide, which may result from oxidation (see [14]).
Other Alteration. Evidence for aqueous alteration is found in many other phases besides olivine. Fig. 6 compares the Raman spectra of unaltered augite to a vein found within augite. Fig. 7 shows the Raman spectrum of an “altered” titanomagnetite found in the mesostasis of MIL 03346. Ca-sulfates are also found throughout the meteorite. Fig. 8 shows the Raman spectrum of a Ca-sulfate in olivine. Due to fluorescence, the Raman spectrum cannot be used to determine the level of hydration in this sulfate. However, electron microprobe totals for this mineral are most consistent with anhydrite.

Summary: Major, minor, and trace element abundances are consistent with the mobilization of elements from phases in the mesostasis that can be readily dissolved when in contact with liquid water (e.g., phosphates and glass). Phosphates or glass in the mesostasis would be a good source of trace elements and P. Under favorable conditions, these phases can be more readily dissolved than pyroxenes, plagioclase, and even olivine at low pH (Fig. 9). Low sodium and potassium abundances (by electron microprobe) in the olivine veins are consistent with a limited amount (to none) of plagioclase dissolution from the mesostasis. Such limited plagioclase dissolution may be common on Mars [23].

The dissolved elements from readily dissolved minerals can then be incorporated into alteration products and veins. We have only presented a preliminary survey of alteration products in MIL 03346 using Raman spectroscopy. Further study of MIL 03346 and mineral standards for (sometimes poorly crystalline) low-temperature alteration products and mineral mixtures is needed to fully characterize the alteration products in MIL 03346.

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Figure 9: Dissolution constants for important minerals. Augite from [15], olivine from [16-17], albite from [18], fluorapatite from [19], silica glass from [20], pyrrhotite from [21], and magnetite and ilmenite from [22]. Minerals most resistant to dissolution have smaller dissolution constants (log R) and are at the bottom of the plot.