CHARACTERIZATION OF MINERAL PRODUCTS OF OXIDATION AND HYDRATION BY LASER RAMAN SPECTROSCOPY – IMPLICATIONS FOR IN SITU PETROLOGIC INVESTIGATION ON THE SURFACE OF MARS. Alian Wang, L. A. Haskin, and B. L. Jolliff, Dept. Earth & Planetary Sciences and the McDonnell Center for Space Sciences, Washington University, St. Louis, MO 63130. (alianw@levee.wustl.edu)

We have proposed laser Raman spectroscopy for in situ mineral characterization on planetary surfaces [1]. A Raman spectrometer on a planetary rover should provide straightforward, unambiguous identification of mineral phases, including major rock-forming minerals (e.g., silicates, carbonates), accessory minerals (e.g., phosphates, oxides, sulfides), secondary minerals produced by environmental alteration (e.g., sulfates, carbonates, zeolites, Fe oxides, clays), and reduced inorganic carbon and organic compounds. Mars presently has an oxidizing (mainly CO$_2$ atmosphere and may have had considerable surface and atmospheric water in the past. Therefore, sedimentary rocks, hydrothermal deposits, and mineral products of oxidation and aqueous alteration of originally igneous rocks may be common on the martian surface. Using a red laser as the excitation source and a spectrograph with high throughput (HoloLab 5000-633), we have examined types of minerals that may represent typical products of oxidation and hydration. We present here some spectra of oxides and clays obtained as a demonstration of the ability of Raman spectroscopy to identify minerals of those types.

**Fe-oxides and Fe-oxyhydroxides:** Figure 1 shows Raman spectra from six minerals of this group. Among them, hematite (alpha-Fe$_2$O$_3$), goethite (alpha-FeOOH), and lepidocrocite (gamma-FeOOH) are strong Raman scatterers, whereas magnetite (Fe$_3$O$_4$) and, especially, maghemite (gamma-Fe$_3$O$_4$, which has magnetic and superparamagnetic forms) are relatively weak Raman scatterers. The Raman spectral peaks of hematite vary somewhat in position because of variation in crystallinity or grain size. In extreme cases, the characteristic doublet at 294/225 cm$^{-1}$ shifts downward in wave number to 274/214 cm$^{-1}$, and can become the only obvious peak in spectrum. Because of the structural difference between the alpha-Fe$_2$O$_3$ (Trigonal R3C) and gamma-Fe$_2$O$_3$ (Cubic P2$_1$3) phases, the Raman spectrum of hematite is easily distinguished from that of maghemite. Goethite and lepidocrocite both have orthorhombic symmetry, but differ in space group (Pbmm & Amam). Their Raman spectra are thus very different from each other. The main peak of goethite occurs at 386 cm$^{-1}$, and that of lepidocrocite at 252 cm$^{-1}$. Magnetite has its main Raman peak near 667 cm$^{-1}$, and is distinguishable from other Fe-oxides of spinel (or inverse-spinel) structure, such as chromite (FeCr$_2$O$_4$) at ~680 cm$^{-1}$ and ~550 cm$^{-1}$, spinel (MgAl$_2$O$_4$) at ~770 cm$^{-1}$ and ~408 cm$^{-1}$, gahnite (ZnAl$_2$O$_4$) at ~660 cm$^{-1}$ and ~419 cm$^{-1}$ and franklinite (ZnFe$_2$O$_4$) at ~620 cm$^{-1}$ and ~334 cm$^{-1}$. Ilmenite (FeTi$_2$O$_3$) is a very weak Raman scatterer, but its magnesium analog geikielite (MgTiO$_3$) has a distinctive Raman spectrum with main peaks at ~720 cm$^{-1}$ and ~490 cm$^{-1}$.

**Phyllosilicates:** Individual flakes of clay minerals give very characteristic Raman spectra [2]. Raman spectral quality depends heavily on mineral grain size [e.g., 3], which for clays typically ranges from ~5 to ~20 µm in common terrestrial settings. The clay minerals studied here are all fine powders. They were analyzed as piles of loosely stacked grains, by using a broad (slightly unfocused) excitation laser beam (20x objective, 0.4 NA, beam diameter ~5 µm). They are difficult to study in this open form. The intrinsically weak Raman signals from the individual tiny flakes are diffused by multiple reflections and scattering at grain boundaries and are further obscured by a high photoluminescence background deriving from impurities. For kaolinite (not shown), two sharp and characteristic Raman peaks (3621 and 3697 cm$^{-1}$) were observed in the OH-stretching vibrational region, but the principal kaolinite aluminosilicate vibrational modes were swamped by a high background. The montmorillonite sample gave a peak near 705 cm$^{-1}$ (not shown); this peak can be assigned to an Si-O-Si vibration. Illite has a mica-like structure; the quality of its Raman spectrum depends on its degree of hydration. A good illite spectrum was obtained from a different sample [4], but the two illite samples analyzed as part of this work (not shown) yielded strong peaks only of anatase (TiO$_2$), apparently present as an impurity. Better success was obtained with an iron-rich chlorite (ripidolite) and two smectites (hectorite and nontronite). Figure 2 shows the Raman spectra obtained from samples of these. Both fundamental aluminosilicate vibrational modes and OH stretching modes were observed. One sulfatic tephra sample gave spectra for jarosite, a sulfate-bearing product of weathering.

**Conclusions:** From these preliminary experiments we conclude that Raman spectroscopy should provide considerable information about the nature of weathering products produced under conditions of oxidation and hydration, for example, oxides and oxyhydroxides of Fe, clay minerals, and sulfates. The identification and characterization of clay minerals by
Raman spectroscopy, especially as they may be encountered under planetary surface conditions, obviously requires further study. A better database of peak locations for oxides and clay minerals and knowledge of the effects of cation substitutions in clay minerals are needed.

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