

IDENTIFICATION OF MINERALS IN SEVERAL MARTIAN SURFACE ANALOG MATERIALS BY RAMAN SPECTROSCOPY. BRADLEY L. JOLLIFF, ALIAN WANG, AND LARRY A. HASKIN, Department of Earth and Planetary Sciences and McDonnell Center for the Space Sciences, Washington University, One Brookings Drive, St. Louis, MO 63130. (blj@levee.wustl.edu)

Characteristic Raman spectra can be obtained for oxy-anionic minerals and for some oxide, sulfide, and other minerals of interest for planetary remote sensing. Because peak widths are intrinsically narrow, peaks from one mineral seldom overlap those of others. Raman spectra are thus potentially useful for characterization of rocks and soils by planetary on-surface remote sensing. Raman spectroscopy can operate in the visible range of the spectrum, convenient for instrumentation. Small, robust Raman spectrometers for this use can be constructed. We have shown the potential value of Raman spectroscopy for characterization of lunar rocks, including most of their major, minor, and accessory minerals [1-3]. Here, we show preliminary results for mineral identification in a very limited suite of martian-surface analog materials.

Mars is a mainly silicate planet, and the results already demonstrated for lunar rocks indicate what we may expect for igneous rock analysis on Mars. On Mars, however, part of the iron will be present in the Fe(III) oxidation state. Also, on Mars we can expect sedimentary minerals and minerals produced or altered by hydrothermal interactions. There may be abiotic or biotic organic materials; Raman spectroscopy can also identify and quantify such materials.

More specifically, we may expect the following from Raman spectra: Peaks for different minerals that contain the same oxy-anionic species (e.g., different silicates, different carbonates, etc.) are sharp and mostly non-overlapping, enabling mineral identification almost by inspection [4]. Different spectral patterns occur for different silicate structures (monomers, chains, layers, frameworks) and different crystal structures (e.g., monoclinic versus orthorhombic pyroxene [1]). Peaks for other oxy-anionic groups are easily distinguishable from those of the silicates, which is important for identifying sedimentary minerals (e.g., carbonates, sulfates, clays). Some peak frequencies within a given oxy-anion group depend on cation proportions (e.g., Fe^{2+} and Mg^{2+} in olivine, and Fe^{2+} , Mg^{2+} , and Ca^{2+} in carbonates and pyroxenes [e.g., 5,6,7]). Spectral patterns also reflect the extent of hydration, providing information on water and on surface and sedimentary conditions. The laser excites fluorescence of rare-earth ions in minor minerals such as phosphates; the resulting lines lie near silicate lines in Raman spectra and can be readily observed. Peaks produced by rock varnish or dust may

appear in the spectrum or even dominate it [8], but major minerals of the host rock can still be identified provided the layer of varnish or dust is thin enough. The Raman method can in principle detect and characterize organic components that might be found in the martian regolith. These properties combine to make Raman spectroscopy the most convenient, definitive mineralogical tool available for on-surface remote sensing.

Because the exciting laser spot is small ($\leq 20 \mu\text{m}$) and the dwell time per sample point is short (~ 1 -2 minutes), quantitative analyses can be done by point counting [2]. Spectra of a hundred different points on a rock or soil can be taken, and the proportion of each mineral is related to the frequency of appearance of its signal in the spectra. This is sufficient for identification of a rock type as well as characterization of the principal minerals.

As a very preliminary test of the quality of Raman spectra we might expect from sedimentary minerals, hydrothermal minerals, and altered silicates, we took spectra from fragments of five geologic materials: a travertine, a palagonitic Hawaiian basaltic tephra, a Hawaiian basaltic tephra containing a sulfate alteration product, an iron-carbonate-bearing ore, and a hydrothermally altered basalt containing phyllosilicates and amygdular calcite and zeolites. Spectra from each are shown in Figure 1.

TRATIVI. This is a microcrystalline calcite-variety travertine, crystallized from a hydrothermal spring in Italy. Despite its fine-grained texture, which causes diffusive scattering of both the laser beam and the backscattered Raman radiation, thus decreasing the signal strength, we readily obtained definitive spectra of calcite from each of several rock fragments tested and from a powdered sample.

HWMK600. This is a sample of palagonitic basaltic tephra, strongly altered Hawaiian volcanic ejecta [e.g., 9]. Fe-bearing alteration products dominate surfaces of mineral grains both on the rock surface and within. The broad, double band of hematite was readily identified in spectra from several points. Readily identifiable spectra for plagioclase and mafic silicates (pyroxene, and pyroxene-olivine mixtures) were obtained at some spots, although they are somewhat degraded in comparison to those of the same minerals in coarse-grained or less altered basalts.

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HWMK24. This sample is a jarositic basaltic tephra, also from Hawaii. It contains jarosite, a hydrated iron-bearing sulfate mineral $[(K,Na,H_3O)-Fe_3(OH)_6(SO_4)_2]$. Several definitive spectra of jarosite were obtained among the spectra taken on a small fragment of this sample.

BCS-301. This is a crushed and magnetically concentrated Lincolnshire iron ore rich in Ca and Fe carbonate and Fe oxides. In siderite, the Fe carbonate, the influence of the Fe^{2+} appears greatest in the lowest energy peak ($\sim 200\text{ cm}^{-1}$). Spectra of calcite and a

hydrated Fe(III) oxide were also obtained from this sample.

AKB-1. Amygdular fill and fine-grained groundmass were examined in this hydrothermally altered Keweenaw basalt, which we selected for its secondary minerals. Within coarse amygdules, we obtained spectra of calcite and thomsonite (a zeolite: $NaCa_2[(Al,Si)_5O_{10}]_2 \cdot 6H_2O$). Reddish areas of matrix gave spectra of pyroxene and hematite. Small, light-colored grains within the basaltic matrix gave the spectrum of a phyllosilicate, probably a smectite, a clay alteration product of a primary mafic silicate. The bands in the higher wavenumber region of the spectra of the zeolite and the clay are those of water (OH stretching modes); the sharp peak in the phyllosilicate indicates a muscovite-like OH in a specific structural site [10]. The broader H_2O bands result from hydration of less specific sites [e.g., 11].

This preliminary experiment demonstrates the ability of Raman spectroscopy to identify important minerals in surface materials (besides unaltered igneous rocks) of the general types we may expect to find at the martian surface. Used in the point-counting mode [2], these and other minerals (oxy-anionic minerals, plus some oxides and sulfides) can be detected and characterized, whether present as major, minor, or trace components of rocks and soils.

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Figure 1. Raman spectra of minerals from five martian analog samples.

