Rover- or lander-based Raman spectroscopy has recently been shown to have promise as a technique for definitive, detailed in situ characterization of mineral phases on planetary surfaces. An early application could be to martian rocks and soils. The red color now recognized as typical of martian surface materials suggests that some or even most surface materials may have been altered to oxides or oxyhydroxides of Fe, or have become coated with such oxides. It is necessary to determine what can be learned from altered rocks or rock surfaces. As a first-order determination of this, we have taken Raman spectra from a highly altered Keweenawan basalt, sample AKB-2. Two surfaces of this rock were studied. One was the heavily weathered original surface, with surface relief of several mm. The other was a roughly cut, flat, unpolished surface. The rock consists of a fine-grained, reddish, altered basaltic matrix containing small (several mm) "clots" of a grayish-green clay mineral, possibly an alteration product of a primary mafic-silicate phenocrystic phase, and coarse (cm-size) light-colored amygdules filled by zeolite and calcite. Examination of a petrographic thin section and analysis by X-ray diffraction show the matrix to consist of olivine, which is partly altered to hematite plus Ti-oxide, and a smectite with the X-ray diffraction pattern of saponite. The zeolite was identified by X-ray diffraction as thomsonite.

The main part of this study is automated Raman spectral point counts along several traverses on the rock surfaces. The instrument used was a HoloLab 5000-633 (Kaiser Optical Systems, Inc.) with a 632.8 nm excitation laser (He-Ne). For the traverse part of the study, we used a 20x, 0.4 NA, long-working-distance (LWD) microscope objective and the effective depth of sampling field of the system was ±5 mm as determined separately from experiments on olivine and quartz crystals. The spectrometer is equipped with an automated X-Y scanning stage, whose movement allowed us to do point-counting [1] and to test the effects of sample surface relief on instrument response. First, we identified the mineral phases present by examining points on the roughly sawn surface. We found hematite, plagioclase, K-feldspar, pyroxene, and plagioclase, K-feldspar, pyroxene, and anatase (a zeolite), and a mineral with a Raman spectrum of a phyllosilicate and assumed for now to be that of smectite. Figure 1 shows the typical Raman spectra of these minerals.

Matrix: The dark red matrix of the altered basalt yielded spectra of (in order of relative abundance) hematite (alpha-Fe2O3), plagioclase, smectite, K-feldspar, pyroxene, and anatase (a zeolite). The positions of the hematite spectral peaks varied from location to location within the matrix. The sharp doublet did not always occur at the expected value of 294/225 cm-1, but was lower in many spectra, ranging downward to peak positions as low as 274/214 cm-1. At the lowest extreme, this doublet was the only obvious peak in the spectrum. This suggests a wide-range variation in the crystallinity and grain size of the Fe oxide. The greenish-gray mineral occurring in the fine-grained matrix and as clots scattered throughout the matrix gave the Raman spectral pattern we tentatively assign to hematite. The doublet has an OH stretching vibrational mode near 3680 cm-1 region.

Amygdules: The mineral phases inside of the large, white amygdules are mainly calcite (CaCO3) and thomsonite (NaCuAl(Si3Al)O10(OH)2). In some locations these two minerals are either mixed with a third, highly photoluminescent phase, or contain impurities that cause them to luminesce. Figure 2 shows two pie diagrams based on two 100-point sets of measurements, one on the original surface and one on the roughly-sawn slab. For these traverses, the excitation laser beam was focused on the rock surface only at the beginning of each traverse, and no additional adjustment was made during the whole set of 100 measurements. As the sample surface moved beneath the objective during the traverse, the focal plane remained fixed, but the surface rose above or fell below it because of the surface relief. The frequency of occurrence of the minerals obtained from the roughly cut, flat surface (100 spectra) is shown in the upper pie diagram in Fig. 2 and that for the weathered rock surface is shown in the lower pie diagram. The most frequently observed material was hematite (approximately mixed with other Fe oxides and oxyhydroxides). This product of weathering and alteration was encountered with greater frequency on the weathered surface than on the roughly cut surface. The second most abundant phase observed was plagioclase. The third most abundant was the smectite phase, which occurred in the same ratio to plagioclase from both surfaces. On the weathered surface, this phase has a highly photoluminescent background, which obscured the spectral peaks. Only a trace of the pyroxene that was originally the principal igneous phase of the rock was found, and none was detected on the weathered surface. Petrographic examination confirmed that little pyroxene remains within the rock. Overall, the results of the traverses were satisfactory. Out of the 100 points taken, the traverse of the roughly-sawn slab yielded 99 identifiable spectra. That of the weathered surface yielded 91 identifiable spectra; the remaining nine points were of smectite, but the spectra for them were not definitive independent of visual examination.

![Figure 1. Typical Raman spectra of mineral phases in AKB-2.](image-url)
Organic surprise: Four sharp, multipeaked spectra indicating organic compounds were obtained on the traverse of the weathered surface. The spectra are dominated by peaks from an ester of a tertiary aliphatic acid. Examination under the binocular microscope showed that surface was dotted with small, white, round organisms (still unidentified). Spectra of the type observed are typical of the waxy protective coatings exuded by some organisms.

Additional weathered surface traverses: A second pair of 60-point traverses was done, both along the same track on the weathered surface, to evaluate the extent of loss of information from measurements taken off-focus on the uneven, weathered surface of the rock. One set was taken by focusing the beam on the surface at each point, the other by setting the focus only at the beginning of the traverse. Another purpose of these traverses was to observe the transition from matrix to amygdular fill. The results for the two traverses were similar. The same minerals were identified at the same locations along the traverse, except that on the automated traverse using a fixed focal point for the laser beam, nine points gave no spectra because the surface was too deeply indented at the position of an amygdule for collection of Raman signal. The weathered surface is also strongly photoluminescent in the fill of a large amygdule, which obscured the Raman signal of the zeolite (2 traverse points) but signal was readily seen from calcite in the same amygdule because calcite is a stronger Raman scatterer than zeolite.

Implications: Suppose these spectra had been obtained from a rock on the surface of Mars. The frequent occurrence of hematite and other Fe\(^{3+}\) oxides would indicate that the rock had experienced an oxidizing environment at some point of its formation. The presence of smectite could result from surface weathering or hydrothermal alteration. However, the presence of hematite rather than Fe-oxhydroxides as part of an oxidative alteration assemblage including phyllosilicates, in this case smectite, suggests that alteration took place above 250–300\(^\circ\)C, but the stability of smectite implies temperatures no greater than about 500\(^\circ\)C [2]. If we were able to analyze a fresh portion of the rock, (broken surface or drill core) to know the alteration is pervasive, that would further indicate a hydrothermal setting as opposed to surface weathering. The identification of specific zeolites should help to distinguish hydrothermal alteration, such as might have occurred at depth in the martian crust, from acid-sulfate weathering as might have been associated with volcanic activity at the surface [3]. Only a few zeolites are stable in acid-sulfate environment, but zeolites are commonly deposited from hydrothermal solutions.

The occurrence of calcite along with the zeolite as breaks in a matrix consisting mainly of Fe oxide and plagioclase would suggest deposition of those minerals from aqueous fluids rather than an igneous origin. The only obviously igneous mineral encountered on the traverse of the weathered surface was plagioclase. It might at first be tempting to presume the parental igneous rock was a fragment of an ancient crustal anorthosite. An anorthosite, however, would not alter to Fe oxide, and the Fe oxide is unlikely to be dust or a coating given the large size of the patches of calcite-zeolite amygdule fillings. Also, the plagioclase spectra were not clustered along the traverse, but were scattered among the Fe oxide spectra. Thus, it would be more plausible to conclude that the Fe oxides represented the weathering product of a mineral intimately mixed with plagioclase, most likely pyroxene, but perhaps olivine or both mafic minerals. The appearance of the organic Raman spectra would surely excite outrageous speculation by some and suspicion about pre-mission decontamination in others.

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