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Raman spectroscopic characterization of a highly weathered basalt: Igneous mineralogy, alteration products, and a microorganism

Alian Wang, Bradley L. Jolliff, and Larry A. Haskin

Department of Earth and Planetary Sciences and McDonnell Center for the Space Sciences, Washington University, St. Louis, Missouri

Abstract. On-surface identification of minerals on Mars is likely to depend mainly on observations of rocks and soils as found, without access to fresh surfaces or other sample preparation. Both the original mineralogy of rocks and their alteration mineralogy will be important. To determine the capability of Raman spectroscopy to provide good mineralogical characterization of an altered igneous rock such as might be encountered on Mars, we have analyzed the heavily weathered, exterior surface of a cobble of Keweenawan basalt and compared the results with those from a roughly cut, unpolished interior surface, using a Raman point-counting method. Despite ubiquitous hematite, a strong Raman scatterer, and despite considerable alteration, original igneous plagioclase and pyroxene were identified and their approximate proportions determined from point-counting traverses on the original surface of the rock. Saponite, an alteration product, was easily identified on the freshly cut surface but could only occasionally be identified on the weathered surface, where saponite-rich areas were highly photoluminescent. Amygdular fill gave strong spectra of calcite and thomsonite (a zeolite). Tiny, sparse crustose lichen gave clear spectra of their waxy organic coating. On the basis of the surface Raman spectra alone, the rock could be identified as a mafic rock, probably basaltic, that was hydrothermally altered in an oxidizing environment at a temperature between ~250 and ~350°C.

1. Introduction

Rover- or lander-based Raman spectroscopy can provide definitive, detailed, in situ mineral characterization and rock identification on planetary surfaces. Past studies [*Wang et al.*, 1995; *Haskin et al.*, 1997; *Wang et al.*, 1998a] have shown that Raman spectroscopy offers unambiguous identification of minerals that contain oxy-anion groups (silicates, carbonates, sulfates, phosphates, etc.) or that consist of oxides, hydroxides, sulfides, etc. An early application could be to Martian rocks and soils during the Mars Surveyor missions in the next 10 years.

The red color typical of Martian surface materials suggests that many of these materials have been altered to oxides or oxyhydroxides of ferric iron or have become coated with them [e.g., *Bell et al.*, 1995]. Hematite has been identified using the thermal emission spectrometer (TES) on the Mars Global Surveyor [*Lane et al.*, 1999], and spectral characteristics of rocks at the Mars Pathfinder site suggest the presence of maghemite or ferrihydrite in altered rock surfaces [*McSween et al.*, 1999]. Thus it is necessary to determine what can be learned from altered rocks or rock surfaces by using Raman spectroscopic techniques. In particular, can rock types be determined despite alteration? Can environments of alteration be determined by mineralogical analysis? Can the roles of water and atmospheric components in the formation and alteration of Martian rocks and soils be discovered by automated on-surface analysis? Is there evidence for reduced inorganic carbon and organic compounds? Answering those questions requires knowledge of the detection limit of minerals and carbonaceous materials, especially when they occur as mixtures or are rare in or on rocks. We may anticipate that modal information obtained from the surface of a coated or weathered rock will require careful interpretation.

Our past work has shown that igneous minerals can readily be identified [*Wang et al.*, 1995], and their proportions quantified [*Haskin et al.*, 1997]. This includes a sample of an actual Martian rock, the Zagami meteorite [*Wang et al.*, 1999a]. All of those analyses were done on fresh surfaces. Preliminary study of a varnish-coated basalt [*Israel et al.*, 1997] showed that minerals within the varnish coating itself could be identified and where the varnish was thin or absent, the original igneous minerals could be identified. The type of varnish coating on rocks from terrestrial desert environments is biologically derived, however, and not necessarily a good analog for Martian rocks. The results from the recent Pathfinder-Sojourner alpha proton X-ray spectrometer (APXS) major-element chemical analyses [*Reider et al.*, 1997] can be interpreted as indicating that dust partially coated the surfaces of most of the rocks analyzed. Images showed areas of rock with sand-blasted textures, indicating that some rock surfaces may be relatively free from any type of coating or to have very thin coatings [*McSween et al.*, 1999]. So, some access to fresh rock surfaces, either as dust-poor ventifacts or as spaces between dust coatings, can be expected. Nevertheless, the possibility remains that in some locations Martian rocks may have been considerably altered by hydrothermal, aqueous sedimentary, or surface weathering processes. To simulate what might be learned from an in situ Raman spectrometer examining altered Martian basalt, we have examined the weathered surface of an ancient terrestrial basalt to learn what can be determined by such an analysis

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without producing a fresh specimen. In general appearance, the rock surface is relatively smooth but with considerable fine-scale relief, and is brick-red in color with spots and amygdular fill of white to tan material. Also for this study, we configured our laboratory Raman spectrometer to operate in a point-count mode [*Haskin et al.*, 1997] with a long working distance objective, very similar to the Athena Raman system currently under development for the Mars Surveyor Program.

2. Samples and Experiment

The rock specimen examined in this study is a large (football-sized) cobble of a strongly altered basalt from the 1100 Ma Keweenawan North Shore Volcanic Group [*Brannon*, 1984], collected along the north shore of Lake Superior, northeastern Minnesota. This sample, designated AKB-1 (altered Keweenawan basalt [*Morris et al.*, 1998]) was selected for study because it was altered extensively by hydrothermal and low-temperature processes, yet it still retains evidence of its igneous mineralogy and composition. Two types of surfaces of this rock were studied. One was the heavily weathered exterior surface (Plate1a), with local surface relief of several millimeters. The second was a roughly cut, flat, unpolished surface (Plate1b). Examination of these two surfaces with the Raman spectrometer enabled a comparison of results from the weathered, unprepared surface with a freshly exposed surface.

The rock consists of a fine-grained, reddish, altered basaltic groundmass containing small (several millimeters) ovoids of a soft, grayish green clay mineral, possibly an alteration product of a primary phenocrystic phase (probably olivine), and coarse (centimeter size) light-colored amygdules filled by zeolite and calcite. The groundmass has textural domains ranging from relict subophitic to intergranular to radiate (Figure 1), consisting mainly of laths of partially to strongly altered feldspar forming a nearly complete, interconnected network, and interstitial pyroxene coated by hematite plus Ti oxide. Plagioclase (pseudomorphs) and pyroxene grains are typically elongate with long dimensions of several tens of micrometers and short dimensions of 5–10 μm or less. The texture varies from place to place on a scale of millimeters, and some glomerocrysts of (relict) plagioclase attain coarser grain sizes, but in all cases that we examined, these are strongly altered. Clay-filled ovoids occur mainly on fresh, interior surfaces; on exterior, weathered surfaces, most of the soft clay fillings appear to have been removed by abrasion. Small (d ~180 μm) crustose lichen on the exterior surface of the rock survived handling and were thus observed during Raman point counts.

Analysis by X-ray diffraction of the basaltic matrix reveals a mixture of plagioclase, clinopyroxene, hematite, zeolite, and a smectite (saponite). In some areas investigated with the electron microprobe, zeolite, K-feldspar, and albite pseudomorphously replace what was presumably once more calcic plagioclase. Iron oxide forms ubiquitous coatings on pyroxene grains. Saponite occurs as a fine-grained alteration mineral within the matrix as well as in larger ovoids where its identification was confirmed by X-ray diffraction (XRD). In the amygdules the zeolite thomsonite (natrolite group) was identified (optically and by XRD) along with calcite.

The amygdules in this rock are interpreted as vesicle fillings because the adjacent basaltic mesostasis shows textures that resulted from preferred nucleation and directional solidification away from vesicle boundaries (Figure 1c). On the other hand, clay-filled ovoids have Fe-oxide-rich reaction rims but do not show directional solidification textures in the surrounding basaltic mesostasis. These saponite-filled ovoids therefore may be pseudomorphs after magnesian olivine phenocrysts. Some of these ovoids contain calcite and zeolite in addition to saponite.

Electron microprobe analysis of pyroxene yields a high-Ca composition of $En_{37-38}Fs_{17-20}Wo_{43-45}$, taking all Fe as Fe^{2+}, but including a significant Al component (Al_2O_3 ~ 3–4 wt%). The identification of Mg-rich smectite (saponite) is confirmed (SiO_2 = 43 wt%, MgO = 26 %, Al_2O_3 = 9 %, FeO = 2 %, and CaO = 2.2 %). Analysis of plagioclase reveals a range from Ab 84 to Ab 97, reflecting albitization, and the Ca/Na ratio of altered more calcic parts of grains, if unchanged by alteration, suggests an original plagioclase composition of about An 50 to An 60.

Samples analyzed by Raman spectroscopy were prepared in several different ways. The original football-sized, oblong rock was sawn and slabbed using a large diamond-impregnated metal blade and tap water for lubrication and cooling. Rock fragments containing the exterior, weathered surface were rinsed ultrasonically in deionized water. Interior sections from the slab were ground gently to remove saw marks. These sections were also rinsed in deionized water prior to Raman analysis. Thin sections prepared from the slab were bonded with super glue.

Automated Raman spectral point-counting measurements were made either along linear traverses or at points on a rectangular grid on both rock surfaces. Additional Raman measurements were made on selected locations and within areas of mesostasis. The lines and rectangles shown on Plates1a and 1b indicate the locations of the linear and grid traverses along which Raman measurements were taken.

The instrument used for this study is a HoloLab 5000 (Kaiser Optical Systems, Inc.) Raman spectrometer. The excitation source is the 632.8 nm line from a He-Ne laser. The laser beam is carried by optical fiber to the sampling probe head, which directs it toward the sample surface through a microscope, which in turn, collects the backscattered radiation. A second optical fiber carries the backscattered radiation to the spectrograph. The spectrograph has an axially transmissive optical configuration that uses a HoloPlex™ volume holographic grating and a volume holographic notch filter. This spectrograph provides simultaneously wide spectral coverage (-177 to 4017 cm^{-1}), high spectral resolution (~ 4 cm^{-1}), and high light throughput (~10 times that of Czerny-Turner configuration). A two-dimensional (1024 × 256) charge-coupled device (CCD) is used as the multichannel detector. With this configuration, the Raman spectrum from an ordinary mineral can be obtained in a few seconds.

The microscope has an automated scanning stage that can reposition a sample along a pre-selected path in the X and Y plane, perpendicular to incident laser beam. Scans can be taken either at points along a line or at points on a grid, yielding a series of spectra taken at fixed intervals for a fixed measurement time. For most measurements in this study, the beam-focusing and sampling objective was a 20×, long-working distance objective with a numerical aperture of 0.4. This objective condenses the laser beam to a spot <2 μm in diameter at the focal point. The size of the sampled spot at the rock surface is substantially bigger than 2 μm, however, even when the beam is focused on the surface, for a complex set of reasons involving the characteristics of the mineral surface [e.g., *Haskin et al.*, 1997]. During each set of automated point-counting measurements in this work, the distance between the measurement points was held constant. The laser beam was focused on the first measurement point but was not adjusted subsequently. Thus, owing to the surface relief of the specimen being analyzed, the sampled spot usually was not in the focal plane of the laser beam. The quality of the Raman spectra

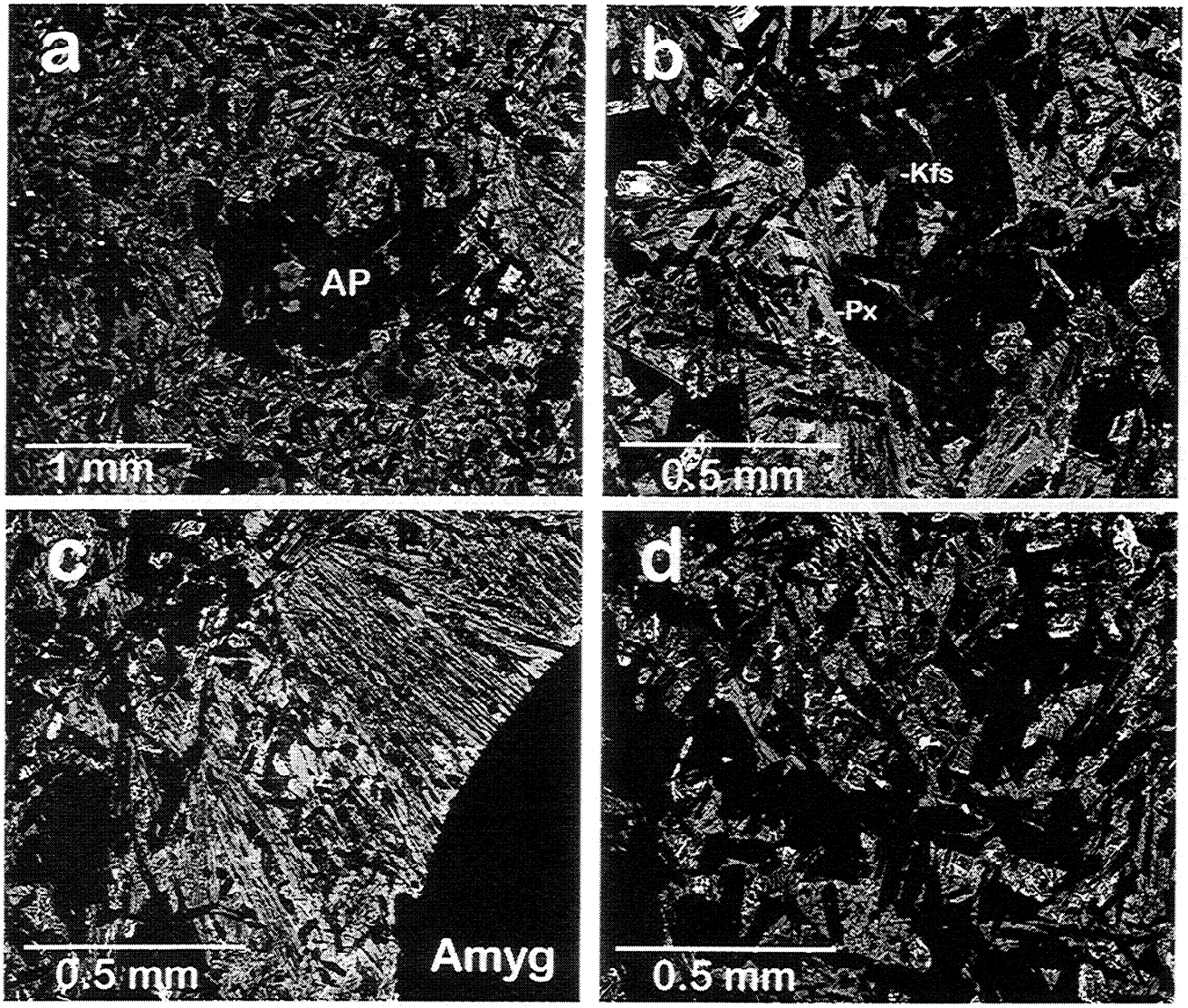

Figure 1. Backscattered electron images of typical textures found within the altered basaltic mesostasis of AKB-1. (a) Typical area of mesostasis showing plagioclase (dark), pyroxene (medium gray), and hematite (bright). In the center of the image, plagioclase was relatively coarse, perhaps formed as a glomerocryst prior to eruption and rapid cooling. Relict plagioclase in the coarse area is mostly altered to a Ca-Na zeolite plus K-feldspar. (b) Higher magnification image of an area similar to Figure 1a showing fine intergranular texture where pyroxene (Px) crystals fill in the interstices between plagioclase laths. Fine "patches" of K-feldspar (Kfs) can be seen within some of the coarse relict plagioclase crystals, which are now largely replaced by zeolite plus K-feldspar. (c) Variolitic texture adjacent to an amygdule; orientation of crystal laths suggests nucleation at what was once a large vesicle with rapid growth away from the interface. (d) Area of matrix showing very fine hematite coatings (bright) on pyroxene grains. It is these fine coatings that impart the red color to the rock (Plate 1).

obtained and the breadth of the sampled spot thus vary according to the extent of deviation from the focal plane. The effective depth of sampling field of this configuration of the Raman system is ~±5 mm from the focal plane, as determined from experiments on olivine and quartz crystals [*Wang et al.*, 1998a]. The relevant sampling depths for rocks are smaller, and change according to the nature of the rock.

In experiments such as these, when the laser beam is focused on the sample surface, the spot size at the surface is as small as 1-2 μm. The laser light penetrates into the sample and is refracted and reflected from internal surfaces (from grain boundaries, fractures, etc.), however, so the volume of the sample that is excited by the laser radiation varies unpredictably from point to point. The diameter of this excitation volume likewise varies, over a range of perhaps 10 μm to tens of microns. When the laser beam is not focused on the sample surface owing to surface relief of the rock, the laser spot size at the sample surface is larger and increases with the distance from the focal plane of the beam, so that the beam may define a spot of the order of ~100 μm. Not all the Raman-scattered light emitted from the excited volume can penetrate through the surface of the sample. Also, the numerical aperture of the objective and the diameter of the optical fiber used in these experiments can accept light from only about a 100 μm diameter area centered about the axis of the objective, so not all of the Raman photons that emerge from the sample surface can be collected and transmitted to the spectrograph for analysis. All to-

gether, this means that the sampled volumes in our Raman experiments are typically <100 μm in diameter, and likely significantly less for some of the spectra taken. These complications are described in more detail by *Haskin et al.* [1997] and by *Wang* [1999].

3. Raman Measurements and Results

3.1. Phase Identification in the Rock Matrix and Amygdules

We first identified the mineral phases exposed on both the original heavily weathered exterior surface and the roughly cut, flat, unpolished surface of the rock by examining selected mineral grains of different morphologies. Figure 2 shows typical Raman spectra of the mineral phases obtained in this way.

3.1.1. Matrix minerals. The main mineral phases found in the dark red matrix of this rock are hematite (alpha-Fe_2O_3), pyroxene, plagioclase, and saponite (Figure 2a). Minor and trace minerals observed include K-feldspar, quartz, and anatase (a polymorph of TiO_2) (Figure 2b).

The dominant matrix mineral seen in the spectra is hematite (Figure 3a), which is responsible for the reddish color of the rock matrix. Pure, well-crystallized hematite yields sharp major Raman peaks near 1322, 612, 411, 294, and 227 cm^{-1} [*Wang et al.*, 1998b]. The peak positions of hematite in this rock vary from location to location within the matrix. The most obvious variations are the position of a sharp doublet near 294 and 227 cm^{-1} and the intensity of this doublet relative to other peaks. In most hematite spectra the peak positions of this doublet varied and occurred several wavenumbers below the expected value, ranging downward to as low as 274 and 214 cm^{-1}. For some extreme cases this doublet was the only observed feature in the spectra. This suggests a considerable variation in the crystallinity and grain size of the hematite in this rock.

Two types of pyroxene spectra were observed (Figure 2a). Characteristic Raman spectra of pyroxene were obtained in a few locations but with very low signal-to-noise ratio. These spectra were obtained from the rare, relict pyroxene grains as observed in thin section. The best three of these have peak positions suggesting an Mg' [=molar $Mg^{2+}/(Mg^{2+} + Fe^{2+})$] value of ~0.4 – 0.5, a little lower than the ~0.6 obtained from the relict grains analyzed by electron microprobe (EMP). It is uncertain whether these values of Mg' represent the pre-alteration pyroxene composition (see *Wang et al.* [1999b] for information on the pyroxene calibration).

The more common type of pyroxene-like spectrum was found in conjunction with the spectrum of hematite (Figure 2a) and is presumably a consequence of the alteration of pyroxene leading to hematite. Backscattered-electron imaging shows that pyroxene grains are invariably coated (or altered on their Fe-rich rims) by hematite (Figure 1d). These pyroxene spectra showed only one clear Raman peak, a strong peak above 660 cm^{-1}, produced by the symmetrical stretching vibration of Si-O_b-Si bonding (where O_b is bridging oxygen) in $[Si_2O_6]_n$ chains in the pyroxene structure. The other major Raman peak of normal pyroxene (near 1000 cm^{-1}), which would be produced by the symmetric stretching vibration of Si-O_{nb} bonds (where O_{nb} is nonbridging oxygen) in SiO_4 tetrahedra, was rarely observed or was very weak in these spectra. In general, a reduction in the fraction of oxygens that are nonbridging (e.g., polymerization) reduces the intensity of the peak near 1000 cm^{-1} and causes a shift of the peak near 670 cm^{-1} toward higher wavenumbers [*Wang et al.*, 1994]. This reduction in the fraction of nonbridging oxygens is consistent with transmission electron microscope (TEM) studies showing that pyroxene alters to hydrous pyriboles (amphiboles and wider-chain silicates), to sheet silicates, and to pyroxenoids [*Buseck et al.*, 1982]. The observed peak position (661 to 668 cm^{-1}) is too low to suggest a sheet silicate (>680 cm^{-1}) and the lack of the peak near 1000 cm^{-1} rules out pyroxenoids. The 661 – 668 cm^{-1} peak is in the range expected for pyriboles, although no OH peak was observed that would confirm this assignment. The OH peak could be difficult to detect in this fine-grained matrix, however. For the purpose of phase identification (but not pyroxene alteration) in this study, we will use the term "pyroxene" to specify the mineral observed in both types of spectra.

Plagioclase is the second most abundant matrix mineral of this rock (Figure 2a). Almost all plagioclase spectra are mixed with peaks from hematite and commonly pyroxene, both of which are stronger Raman scatterers than plagioclase. The major Raman spectral feature of plagioclase is a doublet in the 460-520 cm^{-1} region, assigned to the vibrational mode of T-O_b-T (T = Si or Al) units by previous studies [*Sharma et al.*, 1983]. In the spectra obtained from this rock, the exact positions of these two peaks vary within a narrow range, from 503 to 510 cm^{-1} for the first peak, and from 475 to 480 cm^{-1} for the second peak. This variation, accompanied by variations in peak widths, suggests the existence of plagioclase of different albite-anorthite proportions and a decrease in the regularity of the plagioclase structure as a consequence of alteration. Based on petrographic observation and electron microprobe analysis, both are possible. Further Raman study is needed to learn the relationship between Raman features and structural and compositional characteristics of plagioclase. In several rare cases, the major peak was found near 513 cm^{-1}, and a triplet instead of a doublet appeared in that region (Figure 2b). Although the spectral pattern is still characteristic of feldspar, it is more characteristic of K-feldspar than of plagioclase.

Grayish green saponite occurs as clots and ovoids scattered throughout the fine-grained matrix. Saponite has its main Raman peaks near 3680, 3420, 680, 355, 295, and 190 cm^{-1} (Figure 2a). It shows only a weak feature in the 1000 cm^{-1} region of the spectrum. The general pattern of its spectrum is that of a sheet-silicate mineral with a ratio of O_b/Si >3. The main peak near 680 cm^{-1} is produced by the vibration of linked TO_4 (T = Si or Al) tetrahedra in $[Al_xSi_{4-x}O_{10}]_n$ tetrahedral layers. The position of that peak is characteristic of the tri-octahedral structure (in which bivalent cations fill all of the sites in the octahedral layers) and is lower than we have observed for minerals with di-octahedral structure. The sharp, intense peak near 3680 cm^{-1} could reasonably be assigned to the vibration of an OH group, and the broad band centered near 3420 cm^{-1} results from the vibrations of interlayer water molecules. In general, the structural features revealed by this Raman spectrum match very well with those of saponite $[Na_x(Mg_3(Al_xSi_{4-x}O_{10})(OH)_2 \cdot 4H_2O]$. A very similar spectrum was acquired from standard saponite sample SapCa-2 obtained from the American Clay Mineral Society.

3.1.2. Amygdule minerals. The minerals identified as amygdular fill were calcite and a zeolite (Figure 2c). The Raman spectral pattern of calcite is characterized by four major peaks at 1086, 713, 282, and 156 cm^{-1} [*Herman et al.*, 1987]. The first two peaks are produced by the symmetric stretching and bending vibrations of the CO_3^{2-} anionic group. The other two are the external vibrational modes that cause relative translations between the cations (Ca^{2+}) and the anionic groups. The exact positions of peaks in the carbonate spectra from the amygdules are characteristic of calcite ($CaCO_3$) and are readily distinguishable from those of magnesite ($MgCO_3$), siderite ($FeCO_3$), dolomite ($CaMg(CO_3)_2$), and aragonite, the other structural form of $CaCO_3$.

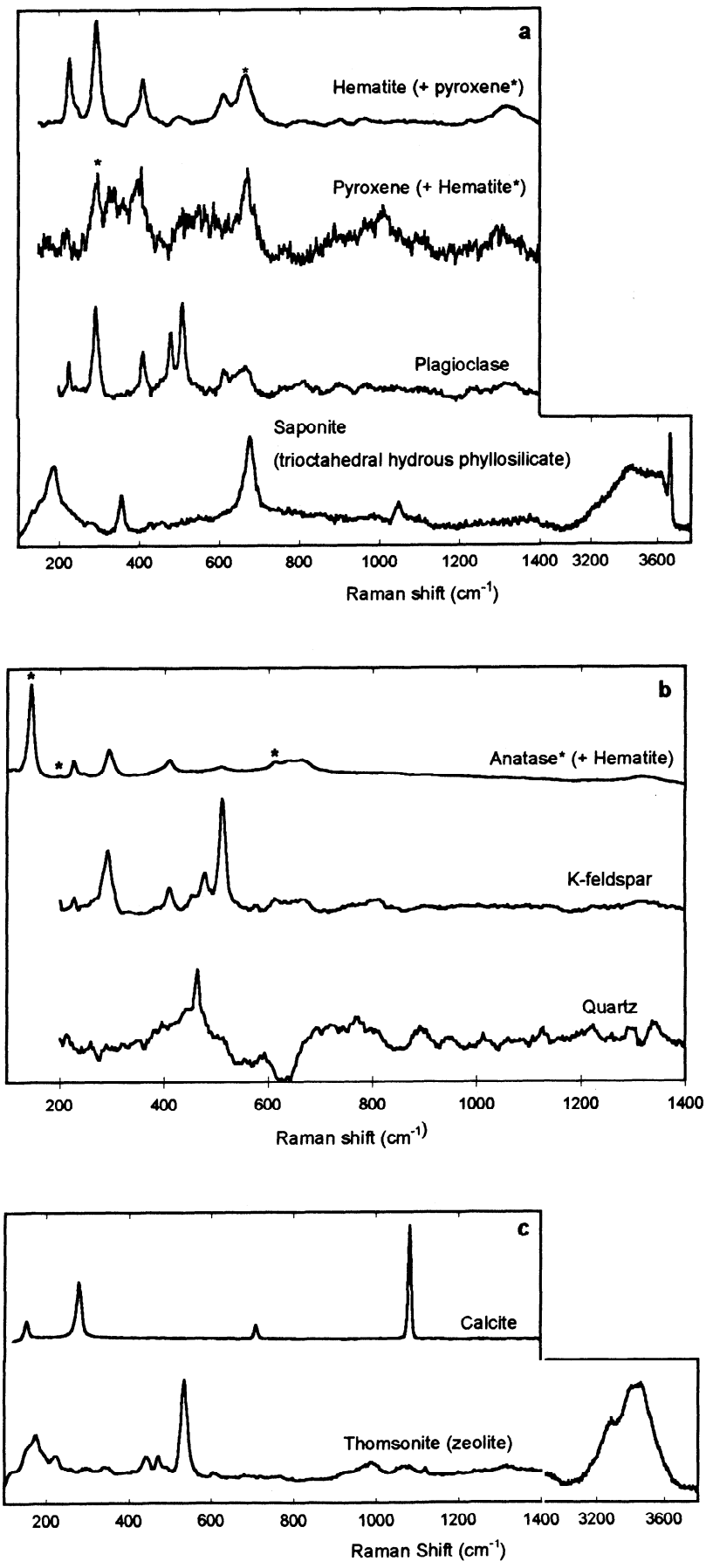

Figure 2. Typical Raman spectra of mineral phases found in rock AKB-1: (a) major mineral phases of the rock matrix, (b) minor mineral phases of the rock matrix, and (c) mineral phases of the amygdular fill.

The zeolite mineral is a thomsonite-gonnardite solid solution of the fibrous zeolite group and has a Raman spectrum very similar to that of the pure end-member thomsonite [*Wopenka et al.*, 1998] (ideal chemical formula $NaCa_2[(Al,Si)_5O_{10}]_2 \cdot 6H_2O$ [*Gottardi,* 1978]). Fibrous zeolites have a framework structure consisting of weakly cross-linked aluminosilicate chains along the *c* axis. The chain elements are rings of SiO_4 and AlO_4 tetrahedra. Elliptical cages or channels are present among the connected chains, within which H_2O molecules and large-diameter cations (e.g., Na^+, Ca^{++}) are located. Analysis by EMP yields formula proportions as follows: $Na_{1.0}Ca_{1.9}Al_{4.8}Si_{5.2}$ to $Na_{1.4}Ca_{1.4}Al_{4.2}Si_{5.8}$ (cf. ideal formula above). The Raman spectrum of thomsonite is characterized by peaks arising from the fundamental vibrational modes of the coupled TO_4 (T = Si or Al) tetrahedra and by peaks from the stretching and bending modes of H_2O molecules [*Wopenka et al.*, 1998]. These two groups of Raman peaks appear in the regions below 1200 cm^{-1} and between 3000–3800 cm^{-1}, respectively. The strongest Raman peak of thomsonite observed from the amygdule zeolite is located near 538 cm^{-1}, assigned in several previous studies [*Pechar and Rykl*, 1983; *Dutta and Del Braco*, 1985; *Dutta and Shieh*, 1986; *Dutta and Puri*, 1987] to the bending vibrational mode of the coupled T-O_b-T (T = Si or Al) units. The symmetrical and asymmetrical stretching modes of those units produce rather weak peaks near 700 cm^{-1} and 1040 cm^{-1}, and these could not be observed in most of the thomsonite spectra from this rock sample. The broad doublet near 3430 and 3280 cm^{-1} is from the stretching vibrations of OH bonds in water molecules. The number of peaks, the peak positions, and the peak widths depend on the local environmental symmetry of the water molecules, which is determined by the specific interconnections between the aluminosilicate chains in thomsonite. The spectral pattern of this region (as well as that of fundamental mode region) allowed us to distinguish thomsonite from the other fibrous zeolites, e.g., natrolite, mesolite, scolecite, gonnardite, and edingtonite [*Wopenka et al.*, 1998].

In many locations inside amygdules, thomsonite is either mixed with a third, highly photoluminescent phase (detected using a Raman imaging microscope, ChemIcon™ company), or it contains impurities that cause it to luminesce strongly. This photoluminescent background overwhelms the Raman peaks of thomsonite in these locations.

3.1.3. A Micro organism. Figure 3a shows a tiny crustose lichen, several of which are found on the original weathered rock surface. These lichens are ~180 μm in diameter, whitish yellow in color, and semi spherical in shape. Raman spectroscopic measurements on several of them yielded a consistent spectral pattern (Figure 3b). The most intense peaks are located near 2931, 839, 433, and 1727 cm^{-1}. The group of four sharp, intense Raman peaks near 2900 cm^{-1} is characteristic of vibrations of saturated C-H bonding (symmetric and anti symmetric stretching vibrations of CH_3 and CH_2). The sharp peak near 1727 cm^{-1} is from the C=O stretching vibration of a saturated aliphatic ester, which also

a

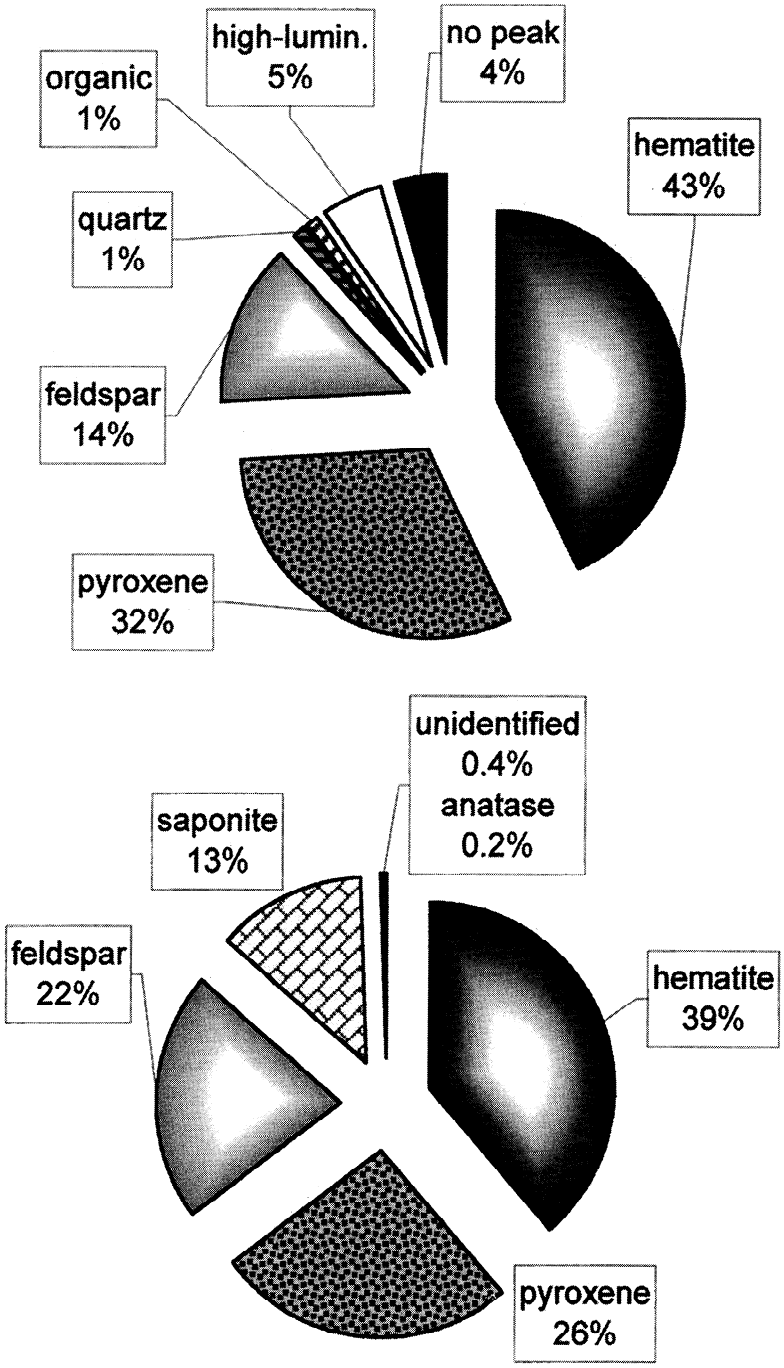

Figure 4. Mineral modes of the rock matrix obtained from the point-counting measurements on the rectangular grid areas (a) on the heavily weathered exterior surface of the rock and (b) on the roughly cut, flat, unpolished interior surface of the rock.

1.2). This confirms that mineral modes obtained on altered rock surfaces require careful interpretation.

Because we have the specimen of weathered basalt in hand and we know where it came from, we know that it was originally a basalt. We can speculate reasonably on petrologic grounds that the saponite is an alteration product of olivine, although no residual olivine was found by petrographic examination of a thin section of the rock. We can estimate the mineral proportions only roughly from the Raman spectra because the hematite is so ubiquitous and, being a strong Raman scatterer, dominates so many of the spectra. We can estimate the pyroxene to plagioclase ratio only very roughly (given the state of alteration or original pyroxene and plagioclase), as about 1.2 to 2.3. Much of what used to be plagioclase is now a mixture of zeolite and alkali feldspar, and much of the pyroxene is oxidized and coated by hematite, and possibly altered in such a way as to no longer give pyroxene spectra useful for determining Mg'.

Although we have reported the results as modes in Figure 4, these results are not the modes that one would obtain by petrographic point counting. Obviously, given the small number of points, the statistical uncertainty would be relatively high, and we do not offer a statistical treatment (as is routinely done, using the

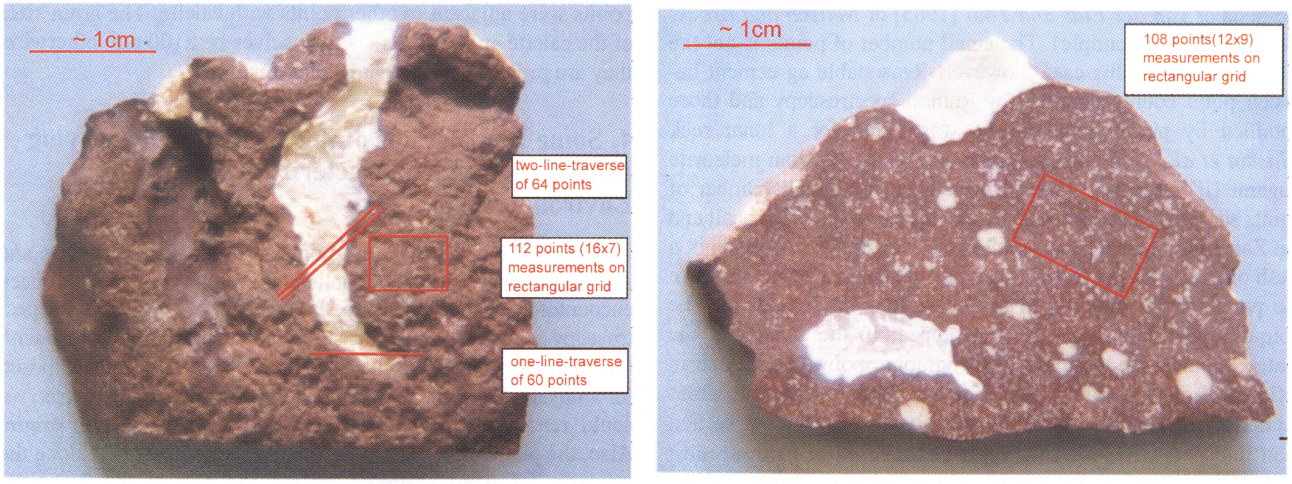

Plate 1. Samples of altered Keweenawan basalt AKB-1: (a) the sample of the weathered rock surface and (b) the roughly sawn flat surface.

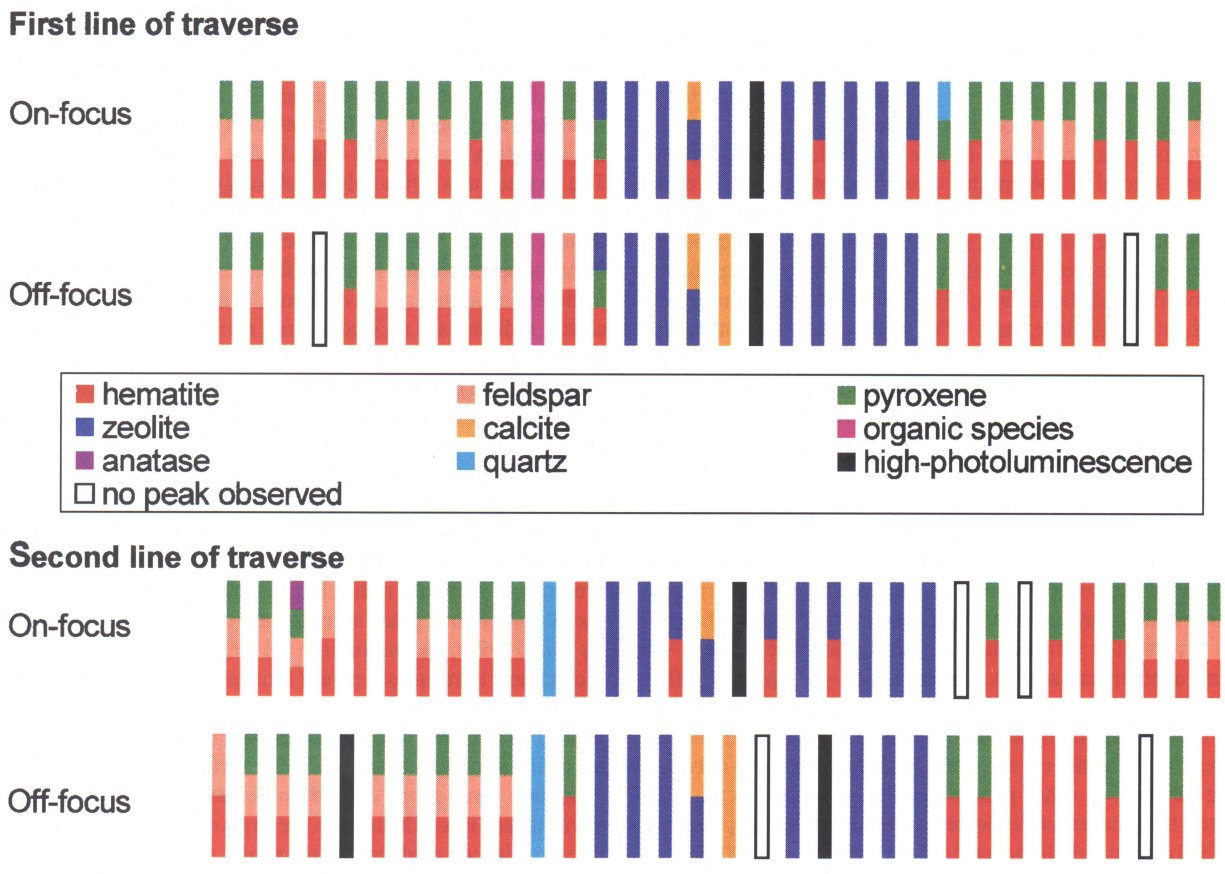

Plate 2. Mineral phase distributions along a two-line traverse on the weathered exterior surface of the AKB-1 (see Plate 1a). The results obtained by on-focus and off-focus (using the automated stage) point-count measurements at the same spots are compared.

methods of *van der Plas and Tobi* [1965] or *Neilson and Brockman* [1977], for example). The small number of points is not the main problem in this case, however. Reasonable agreement between point counts obtained by Raman spectroscopy and those obtained by petrographic means was found for a lunar rock [*Haskin et al.*, 1997] and for a sample of the Martian meteorite Zagami [*Wang et al.*, 1999a], even given the small number of points sampled in those cases. Unlike the lunar KREEP basalt and the Zagami meteorite, the sample of Keweenawan basalt is not a fresh or nearly fresh igneous rock. The matrix has been altered to the point that hematite is nearly ubiquitous in the spectra. The ubiquitous hematite coatings that appear in the spectra of the matrix would not dominate a petrographic point count done in reflected light. Hematite has a higher Raman scattering cross section than pyroxene, which in turn, has a higher cross section than feldspar. Given that the laser beam is out of focus at most points, producing an excitation volume with a diameter of the order of ~100 μm, hematite appears in the spectra even when that mineral occupies a minor part of the laser excitation volume. Also, the farther out of focus the laser beam is, the more likely it is that hematite will dominate the spectrum and the less likely it is that the less sensitive pyroxene and, especially, feldspar will appear. The igneous minerals of the rock were identified readily and unambiguously by this experiment, but their relative proportions could not be obtained accurately. It will be necessary to study rocks at different stages of alteration to learn how to interpret their spectra and determine how best to do quantitative mineralogy and how well igneous mineralogy can be reconstructed. In contrast to the matrix, hematite is absent from the spectra of amygdular fill and most spectra of saponite.

Information on grain size is also available from the point-count data. A total of 306 spectra were taken on the matrix of the two AKB-1 samples (not including the saponite-containing points, which are within the matrix, or the amygdular points, which are separate from the matrix). Of these, 49% yielded hematite, pyroxene, and plagioclase; 29% yielded hematite plus pyroxene without plagioclase; and 17% yielded only hematite, and most of these had a low signal-to-noise ratio. Only 5% of the matrix points yielded hematite plus plagioclase without pyroxene, and only 1 point yielded plagioclase plus pyroxene without hematite. This indicates that the matrix is fine-grained enough that the sampling volumes in our Raman experiments, which have diameters ≤100 μm consistently intercepted several grains and usually intercepted grains of both plagioclase and pyroxene plus hematite alteration products (whether the beam was in focus or out of focus, Plate 2). We thus conclude that the grain size of the principal igneous minerals, pyroxene and feldspar, is small relative to ~100 μm. If a particular mineral had a typical grain size of, say, ~10 μm, and another had a typical grain size of ~50 μm, this difference would not have been detected by this experiment. Also, of the 16 spectra containing saponite peaks (all were within the matrix area of the freshly cut sample), 11 showed saponite only, and 5 were adjacent to other points yielding saponite spectra. This indicates that the saponite occurs as relatively large grains or, more likely, relatively large aggregations of grains (≥100 μm).

Most of the 52 points taken on amygdular material showed peaks for only a single mineral. Forty of these points yielded zeolite spectra, and of these, 29 were of zeolite only. Fifteen of these zeolite spectra were adjacent to another point yielding a zeolite spectrum, indicating that the amygdules are relatively large (hundreds of μm; see also Plate 2). Only four points that yielded zeolite also yielded calcite. Twelve points yielded calcite spectra, six of these yielded calcite spectra only, and three of the points were adjacent to other points with calcite. The grain sizes of the calcite and zeolite may themselves be ≥100 μm; otherwise, they are present as aggregates of grains.

4. Some Implications of this Study for Identifying Rock Types and Characterizing Past Environments on Mars

We now return to the questions asked in the introduction and determine what we could conclude about this rock if it had been encountered on the surface of Mars and analyzed by Raman spectroscopy as a stand-alone measurement technique. We begin with the weathered surface only, as if no fresh surface were exposed for analysis. From the pyroxene and plagioclase of the matrix, we could reasonably conclude that the rock is igneous in origin. Also, the plagioclase-bearing spectra were not clustered along the traverse but were scattered among the rest of the Fe-oxide-dominated spectra, most of which also included a peak for pyroxene. Thus it would be plausible to conclude that the Fe oxides represented the weathering product of pyroxene intimately mixed with plagioclase. From the roughly subequal proportions of those minerals, we could conclude that the igneous rock was mafic. Knowing that plagioclase is a weaker Raman scatterer than either pyroxene or hematite, and that most measurement points were not in good optical focus so that the exciting laser beam was spread onto an area perhaps 100 μm in diameter, we would suspect that the observed proportion of plagioclase was less than the true rock mode. Given that and the relatively small grain size, we would conclude that the rock is volcanic. The absence of primary undersaturated minerals (e.g., feldspathoids) and the calcic nature of the alteration assemblage suggest that the lava was not alkalic. The absence of a silica polymorph suggests the lava was mafic or perhaps intermediate. Thus, in answer to the first question, although the rock type in this case cannot be determined precisely from the spectra taken on its surface, its identity can be limited to a tholeiitic basalt, an olivine basalt, an andesite, or possibly a clastic sedimentary rock consisting mainly of those igneous minerals. We would tentatively rule out a clastic sediment on the basis that the proportions of pyroxene and plagioclase appear to be roughly cotectic, once their relative sensitivities of detection are taken into account.

Because virtually all of the pyroxene spectra occurred in multimineral spectra dominated by hematite, we would infer that the hematite was a derivative of the pyroxene and had been produced by weathering or alteration in an oxidizing environment. The presence of hematite rather than Fe-oxyhydroxides suggests that the alteration took place at temperatures above 250–300°C [*Morris et al.*, 1995], a lower limit to the temperature of alteration. The second and third questions are thus answered: The environment was hydrothermal and probably subsurface, and it was oxidizing as well as aqueous, and this information was obtained from spectra obtained on the unprepared rock surface.

In fact, even more detailed information about the alteration environment is available. The presence of the calcite and thomsonite are further evidence of extensive alteration. The extensive concentration of calcite and zeolite in a single location as observed on a linear traverse would indicate filling of a vein or an amygdule. (The Raman experiment on Mars could presumably be targeted to cross such a macroscopic feature through prior observation by the imaging camera required to guide a rover or a lander arm to a sample for analysis. In a sophisticated mission with a close-up microscopic imager, such targeting should be routine.) Generally speaking, calcite could be low-temperature sedimen-

tary, higher-temperature hydrothermal, or even igneous in origin. Thomsonite, containing waters of hydration, may be stable to relatively high temperatures for a zeolite but not to greater than about 350 °C [*Miyashiro and Shido*, 1970], providing an upper limit to the temperature of alteration. The presence of the specific zeolite thomsonite would enable us to distinguish hydrothermal alteration that might have occurred at depth in the Martian crust, from acid-sulfate weathering that might have been associated with volcanic activity at the surface. *Ming and Gooding* [1988] indicate that only the most siliceous zeolites (Si>>Al atomic) are expected to be stable in an acid-sulfate environment.

Suppose we were fortunate enough to identify the saponite. This might be possible because of a different regime of surface alteration on Mars in which the saponite was not all photoluminescent, perhaps because sandblasting refreshed weathered surfaces without scouring the soft clays or because there were drill cores or cuttings available for Raman analysis. The presence of saponite could result from surface weathering or from hydrothermal alteration. The stability of saponite implies temperatures no greater than ~ 500°C [*Morris et al.*, 1995], although we would expect loss of interlayer water in the interval of 100–250°C and progressive loss of OH beyond 300°C. The identification of large grains or aggregates of pure saponite, a highly magnesian clay mineral, would be consistent with alteration of olivine phenocrysts. (Olivine is expected to be the least stable of the original igneous minerals under alteration conditions.)

In answer to the final question, in this case, organic carbon was clearly present and it still carried definitive evidence about organic functional groups. The appearance of such an organic Raman spectra obtained during a rover traverse on Mars would surely excite outrageous speculation by some scientists and cause deep suspicion about premission decontamination in others.

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L. A. Haskin, B. L. Jolliff, and A. Wang, Department of Earth and Planetary Sciences, Campus Box 1169, Washington University, One Brooking Drive, St. Louis, MO 63130-4899. (alianw@levee.wustl.edu)

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