

# Field and routine laboratory use of Raman spectroscopy for mineral identification: applications to rocks

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In the geosciences, Raman spectroscopic analysis has traditionally been a laboratory tool for structural analysis of minerals. Recent developments in instrumentation, however, make possible the use of Raman spectroscopy as a tool for routine identification of minerals and other substances in field situations – geologic, environmental, and forensic. Such analyses have generally been done by other methods, usually involving sample collection and subsequent laboratory analysis of the samples. In a companion abstract, we describe a miniaturized Raman spectrometer we are developing in collaboration with an engineering team at the Jet Propulsion Laboratory that can be deployed robotically on Mars for mineralogical analysis of rocks and soils, which represents an extreme type of field use. Here, we describe the value and need for such analysis, using as examples some studies done in our laboratory. These applications are related to the studies of extraterrestrial materials, but they illustrate how Raman spectroscopic analysis can be used in non-traditional ways.

1. Definitive mineralogy: Is there really andesite on Mars, and why do we care? The Sojourner rover on the 1997 Pathfinder mission to Mars carried an alpha-proton-X-ray spectrometer that analyzed rocks and soils for their principal chemical elements. The rock compositions were found to be consistent with a terrestrial rock called andesite. Andesite is relatively rich in SiO<sub>2</sub> and as such, may contain the silicate minerals quartz, Na-plagioclase, and amphibole, a potential water-bearing mineral. On Earth, andesite is produced where an oceanic crustal plate plunges beneath another tectonic plate, carrying sedimentary rocks that contain water. Remelting results in andesitic lava. Andesite on Mars would indicate similar crustal recycling and an extensive role for water. In contrast, the Moon has no tectonic plates, no water, and no andesite.

Water is essential to the origin and evolution of life. If Mars really produced rocks such as andesite, then water and hydrothermal activity were significant, as on the Earth. But is the crust of Mars somewhat like that of the Earth? We don't know. We need a distinctive signal from quartz or amphibole, and to quantify the proportions of the minerals in the rocks, to identify the minor minerals, and to characterize the Fe/Mg/Ca ratios of minerals containing those elements to know whether andesite was truly present. A Raman spectrometer can determine these quantities.

2. Determining past environments. Rock AKB-1 is a cobble from a basaltic lava that formed 1.1 billion years ago. It was collected in Minnesota from a stream that feeds Lake Superior. It is weathering away. Its surface is dark red. It had vesicles, but these are now filled with materials that are white to tawny in color. Is this what low-temperature weathering and exposure does to a fresh basalt?

Raman spectral scans were done at regular intervals across the surface. All spectra from the rock matrix (red surface) contained peaks of hematite. Many contained peaks of feldspar and some contained peaks of pyroxene. The latter two minerals indicate that the rock was once a basalt. The pyroxene grains showed altered structures. Iron from obliterated pyroxene is the source of the hematite. Similarly, grains of olivine gave way to blebs of saponite, a clay mineral; this required the action of water. Formation of the hematite required an oxidizing environment and temperatures above 250–300°C. The vesicles gave spectra of calcite and thomsonite (a zeolite). Thomsonite can form at temperatures as low as 70-110°C but it disintegrates at ~350°C. Saponite undergoes progressive loss of water above ~250°C. The alteration mineral assemblage in AKB-1 is consistent with moderate-temperature (~300°C) hydrothermal alteration. That is, the rock did not attain its altered character in the stream, but at depth in a location where hot, salt-bearing water was circulating. The spectra for this analysis could easily have been obtained in the field.

A bonus of the Raman scans of the surface of this rock was a beautiful spectrum of a waxy substance. The traverse path at one point landed the beam on a tiny crustose lichen.

3. Routine laboratory characterization. The standard procedure for characterizing a rock begins with sawing the rock, then slicing off a small block, gluing that block to a microscope slide, and grinding it down to make a transparent thin section. The thin section is then examined using the petrographic microscope, the minerals under each of about 1,000 points on a grid are identified, and the mineral proportions are thus determined. The electron microprobe is then used to determine chemical composition and obtain ratios such as Mg/Fe/Ca in the minerals that contain them. Alternatively, one might simply place a sample under the objective of a Raman spectrometer, turn on the laser, and let the beam traverse the surface, taking spectra at chosen intervals. Mineral identification and quantification would be done to first cut by computer analysis, and the geoscientists would need only to look at spectra flagged by the computer as not consistent with standard spectra from the catalog. This procedure would not eliminate the need for more detailed analysis in a general sense, but it would suffice for many studies.

Such an analysis is non-destructive with respect to most other uses of the sample. Raman spectroscopic analysis can be just one step in a series of measurements to be done on a sample. This can be an advantage if the sample is small or precious. Consider lunar rocklet no. 115273,7039, a particle from the 2 – 4 mm sieve fraction of a soil. By doing a Raman scan along one surface of the particle, we were able to identify the rocklet as a KREEP basalt (relatively rich in potassium, rare-earth elements, and phosphorus).

4. A small, portable Raman spectrometer would be useful in standard geologic exploration. Raman spectrometer could aid in the identification of minerals and determine properties such as Mg/Fe ratios and indicators of metamorphic grade. Some of this can be done in the field without instruments by an experienced field geologist, but typically it requires iteration between the field and the petrographic lab that might be avoided. Such an application would be especially useful where field work is restricted by location or weather, e.g., cold regions such as Antarctica. To fulfill the promise of Raman spectroscopy as a routine tool for mineralogy, much needs to be done, however. In addition to further instrument development, we need to produce software to operate the instrument and to compile and analyze the data. We need a database that is broad and versatile. We must develop algorithms that identify minerals from spectra and give a confidence estimate of the accuracy of each identification.

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