

Raman and Mössbauer characterization of a rock for potential use as an on-site calibration target for *in situ* mineralogy instruments on the Athena rover for Mars Surveyor missions. ¹B. L. Jolliff, Alian Wang, K. Kuebler, L. A. Haskin, and ²Göstar Klingelhöfer. ¹Dept. of Earth & Planetary Sciences and the McDonnell Center for the Space Sciences, Washington University, St. Louis, MO 63130. ²Institute for Nuclear Physics, Schlossgartenstrasse 9, Darmstadt University of Technology, D-64289 Darmstadt, Germany. (blj@levee.wustl.edu)

As part of the *Athena* rover payload for Mars Surveyor 2003 and 2005 lander missions [1,2], four instruments are planned for deployment by a robotic arm to do *in situ* mineralogical and chemical characterization of rocks and soil. The instruments include a Raman spectrometer for general mineralogy and detecting organic materials, a Mössbauer spectrometer for Fe-bearing mineralogy, an Alpha-Proton-X ray spectrometer (APXS) for measuring chemical compositions, and a multi-channel micro-imager for visualizing the analyzed area.

Although pre-flight calibration will be done for all instruments, to ensure the quality of the data obtained on-surface, we are planning to have an on-site calibration target carried on the rover. This is necessary because environmental conditions on the Martian surface are significantly different from what we can routinely simulate in the laboratory, and our knowledge about their influence on instrument response is limited. Ideally, we would prefer a single calibration target for all four instruments, which should have characteristics that satisfy the requirements for each instrument. A thin slab of a natural rock (3.5 cm diameter circular polished disc) is a good candidate, because it can be chosen so as to contain different mineral phases, which, together, satisfy multiple requirements. For example, the Raman spectrometer for Athena covers two separate spectral regions, one for the fundamental vibrations of silicates and other oxy-anionic minerals, and another for the region covering H₂O, OH, and organic materials. The wavenumber calibration can best be achieved in both spectral regions using a hydrous silicate existing in the calibration rock target, because it has Raman peaks in both regions. For the Mössbauer spectrometer and the Alpha-Proton-X-ray spectrometer, Fe-bearing minerals and a C-bearing mineral are needed in the calibration target. The target can easily be viewed by the micro-imager if it has an obvious morphologic (or color) variation. In addition, the rock slab should be hard and durable to withstand mechanical vibration during launch and landing.

We have selected a hydrothermally altered calc-silicate rock from the Cranberry Magnetite Mine, North Carolina [3]. Most importantly for our purposes, it contains abundant hydrous silicates that yield excellent Raman spectra (amphibole and epidote) and it contains abundant Fe-bearing minerals, including magnetite and pyroxene (ferroaugite) that yield good Mössbauer spectra. In detail, it is a banded calc-silicate rock rich in the minerals epidote (nominally

Ca₂(Al,Fe³⁺)₃OH(SiO₄)₃), pyroxene, and magnetite. It also contains abundant amphibole (ferrohastingsite) as a hydrous alteration of pyroxene; quartz; plagioclase; calcite; pyrite, and other minor sulfides; and other accessory minerals, including allanite and apatite. It contains two different assemblages (lithologies): one that is banded, with alternating green and black bands (lithology A) and one that is mostly black and massive (lithology B) (Fig. 1). Epidote, quartz, and plagioclase are the main minerals in the green bands of lithology A (and light patches in B), and amphibole, pyroxene, and magnetite, in the black bands. Pyroxene, magnetite, amphibole, and epidote are concentrated in lithology B, and individual grains, especially pyroxene, can be coarser (e.g., up to several mm). In addition to containing a useful set of minerals for Raman and Mössbauer calibration, the rock presents a strong color contrast (Fig. 1) that may be useful for calibrating the micro-imager, and it is very hard and thus durable.

For this rock to be an effective on-surface calibration target, we must be able to obtain good spectra for the required spectral regions, and we must be very sure that we will obtain those spectra anywhere on the target that we analyze. The effective sampling area of the Mössbauer spectrometer is about 15 mm diameter, thus it is expected to sense a suitable assemblage of mafic minerals nearly anywhere that the rover arm can position it relative to the disc. The laser for the Raman spectrometer, however, is only expected to illuminate about a 30 μm diameter spot in a given analysis. Our standard operating technique is to obtain a number of spectra along a linear traverse [4], so we must be sure that any such traverse will intersect epidote or amphibole, preferably several times.

First, we address the quality of the Raman spectra. Typical Raman spectra for the main minerals and several minor minerals, those most useful for calibration, are shown in Fig. 2. Among these, amphibole and epidote are both suitable for wavenumber calibration of the Raman spectrometer across both regions of interest. Epidote has many strong fundamental vibration peaks in 200–1200 cm⁻¹ region, and an OH stretching vibrational peak near 3378 cm⁻¹. The main amphibole in lithology A of this rock has four OH peaks in the 3600–3700 cm⁻¹ region. These peaks have much narrower peak widths than that of the epidote 3377 cm⁻¹ peak, thus they are the most suitable for wavenumber calibration; however, the epidote OH peak is very strong and will also suffice for that calibration. The amphiboles also have fairly strong peaks in the funda-

mental vibrational region. Calcite was identified in several locations in this rock. It is a good calibration mineral for the APXS, but its abundance is minor.

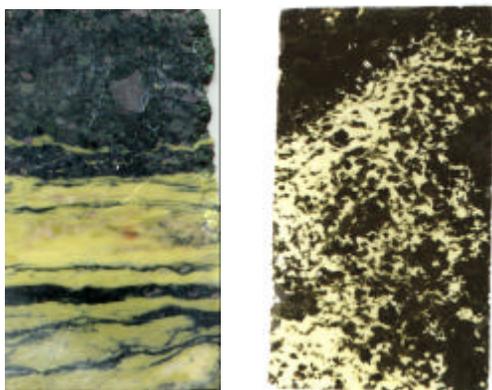


Figure 1. Images (approximately to scale) of rock slabs banded lithology A (left slab, lower part) and massive, Fe-rich lithology B (left slab, upper part, and right slab).

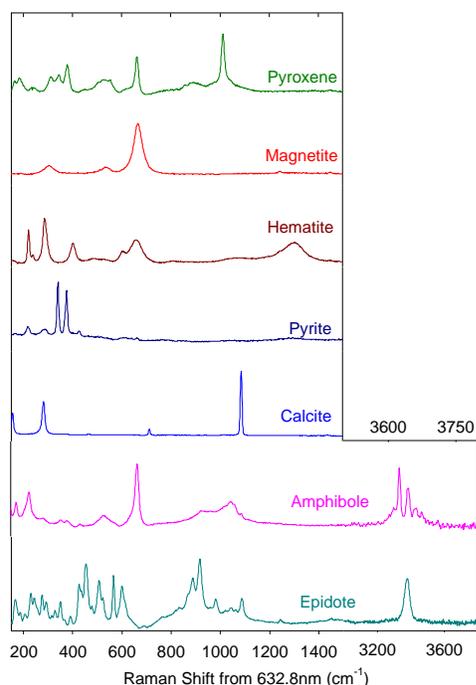
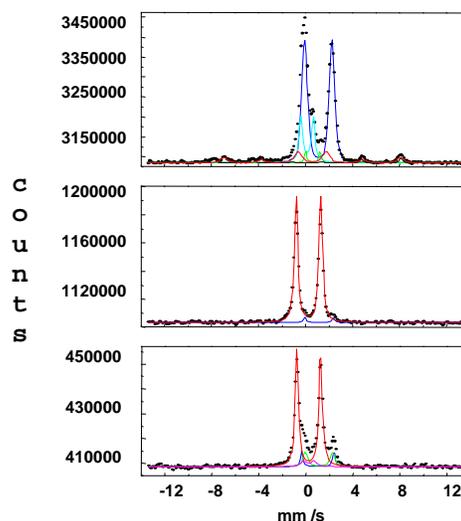


Figure 2. Raman spectra of the mineral phases useful for instrument calibrations

Among the Fe-bearing minerals, magnetite, which is concentrated in the dark lithology, is the most useful phase for calibration of the Mössbauer spectrometer. In addition to magnetite, epidote, amphibole, and pyroxene in this rock are all Fe-rich minerals and have characteristic peaks in Mössbauer spectra. Figure 3 shows Mössbauer spectra along with the spectral curve fitting results, taken from lithology B (upper spectrum, upper

part of left-side slab, Fig. 1), and two spectra taken in lithology A (banded lower part of Fig.1, left slab). The sextet component in the upper spectrum corresponds to magnetite, and one of the three doublets in same spectrum is from pyroxene (augite type). The other two doublets are Fe^{3+} and Fe^{2+} components, probably a superposition of different minerals such as amphibole and epidote. A more accurate data analysis is currently under way to improve the mineral assignments.



left, banded lithology; lower two spectra).

To test the frequency with which we can expect to encounter mineral grains having suitable Raman spectra for calibration, we made several multi-point linear traverses of Raman spot measurements on two flat, cut surfaces of slabs of lithology A and B. The distribution of minerals in both lithologies is heterogeneous, and the grain sizes variable. However, we found from 3 traverses in lithology A that we can expect to encounter amphibole ~12% of the time, and epidote ~36% of the time. In lithology B, we encounter amphibole ~44% of the time, and epidote ~31% of the time.

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