

**Analyses of IR-Stealthy and Coated Surface Materials: A Comparison of LIBS and Reflectance Spectra, and Their Application to Mars Surface Exploration** R.C. Wiens<sup>1</sup>, L.E. Kirkland<sup>2</sup>, C.P. McKay<sup>3</sup>, D.A. Cremers<sup>4</sup>, J. Thompson<sup>1</sup>, S. Maurice<sup>5</sup>, P.C. Pinet<sup>5</sup> <sup>1</sup>Space & Atmospheric Sciences, Los Alamos National Laboratory (MS D466, Los Alamos, NM 87545, [RWiens@LANL.Gov](mailto:RWiens@LANL.Gov)), <sup>2</sup>Lunar and Planetary Institute and Aerospace Corp. ([Kirkland@lpi.usra.edu](mailto:Kirkland@lpi.usra.edu)), <sup>3</sup>NASA Ames Research Center ([CMcKay@mail.arc.nasa.gov](mailto:CMcKay@mail.arc.nasa.gov)), <sup>4</sup>Chemistry Division, LANL ([Cremers\\_David@LANL.Gov](mailto:Cremers_David@LANL.Gov)), <sup>5</sup>Observatoire Midi-Pyrénées, Toulouse, France ([maurice@ast.obs-mip.fr](mailto:maurice@ast.obs-mip.fr))

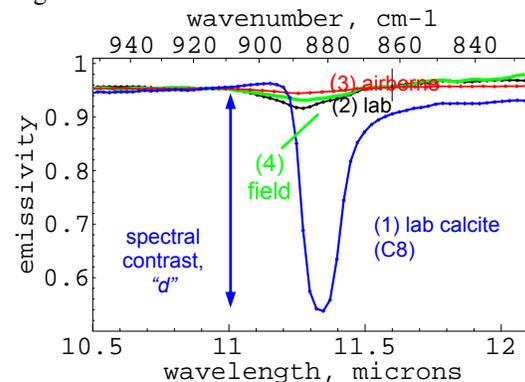
**Introduction:** Identification of non-silicate samples on Mars, such as carbonates, sulfates, nitrates, or evaporites in general, is important because of their association with aqueous processes and their potential as exobiology sites. Infrared (IR) and thermal-emission (TE) spectroscopy have been considered the primary tools for remote identification of these minerals. This includes current and future orbital assets such as TES on MGS, THEMIS on Mars Odyssey, OMEGA on Mars Express, CRISM on MRO, and now the Mini-TES on the MER rovers. While reflectance and emission spectroscopy have clearly been the method of choice for these missions, the technique is not always successful in mineral identifications due to dust, surface weathering chemistry, coatings, or surface texture. Here we describe and show IR spectra of several such samples, and then report on the relative success of LIBS analyses in determining the rock type.

**Reflectance Spectra:** Recently, attention has been paid to terrestrial carbonate samples which, because of their texture, have very low if any spectral contrast in the carbonate absorption bands, rendering them nearly invisible; hence the term “IR-stealthy” [1]. An example of this was described for samples of indurated calcite (“calcrete”) from Mormon Mesa, NV, where the calcrete constituted a distinct regional geologic unit [1,2]. The material was shown to be ~90% calcite, along with quartz crystals and possibly some clays [2]. An IR spectrum of this material is shown in Fig. 1.

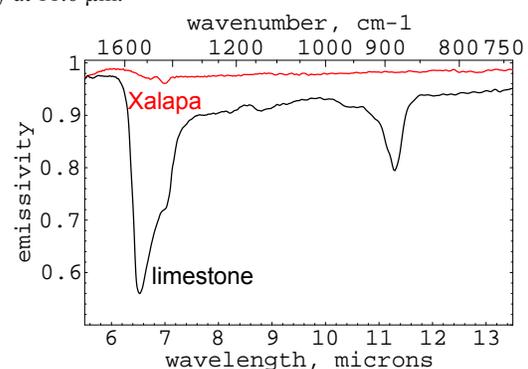
Another type of sample that is difficult to detect with infrared spectroscopy is a magnesium carbonate with unusual texture. The sample discussed here, from Xalapa, Mexico, is found on the shores of Lake Alchichica, a volcanic crater lake fed by groundwater flowing through permeable country rock composed of mafic basalts. A lowering of the lake level exposed large Mg carbonate structures. Carbonates on Mars might also be produced by groundwater flow through porous basalt. Fig. 2 shows a spectrum of this sample.

Another context in which reflectance-spectroscopy results may not reflect the composition of the samples is in the presence of rock coatings. With regard to the “Opportunity” rover site, there is disagreement as to whether the TES orbital data showing hematite might be caused by a surface coating or whether it requires coarse hematite (e.g., coarse particles or rocks) [4].

Fig. 3 shows hematite spectra that illustrate the ambiguity in spectral band shapes between a hematite coating and coarse hematite.



**Fig. 1:** Spectral contrast (i.e. detectability) varies with target texture. The spectra are: (1) a laboratory spectrum of a calcite hand sample [3]; (2) a laboratory spectrum of calcrete (sample “mm4bhr”); (3) an airborne (SEBASS) spectrum of a region covered with calcrete boulders; (4) a field spectrometer signature measured of the same target region as the airborne spectrum. The reduced spectral contrast can make even regional outcrops undetectable. The units are apparent emissivity for the airborne, C8, and field spectra; and true emissivity (one minus hemispherical reflectance) for the laboratory spectrum. For clarity the spectra are offset -0.042 (airborne) and -0.0045 (field) to match the calcrete emissivity at 11.6  $\mu\text{m}$ .



**Fig. 2** The primary cause of the varied spectral contrast in these two samples is surface roughness at the grain scale. Carbonates frequently exhibit rough surface textures at the grain scale from formation or weathering processes. The samples (“xalapawehr” and limestone sample “mmlssep00”) are shown in true emissivity (1-hemispherical reflectance). Spectra measured by Paul Adams (The Aerospace Corp.).

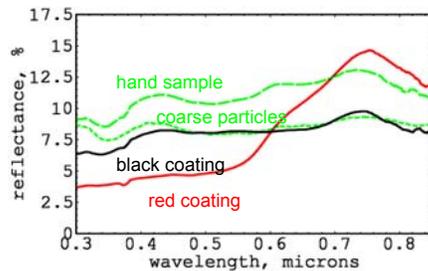


Fig. 3 Reflectance spectra measured of a hematite hand sample, hematite red and black coatings, and coarse hematite particles (150–250  $\mu\text{m}$ ). The samples are: hand sample (“gry\_hem”), black coating (“bhm3”), and red coating (“bhm1”), all measured at The Aerospace Corporation by Paul Adams. The coarse particles are from [5], sample “gds\_69\_a150-250u”.

**LIBS Spectra:** Laser-induced breakdown spectroscopy (LIBS) is very complementary to reflection spectroscopy on landed missions in that it provides qualitative elemental identification of samples at distances up to  $\sim 20$  m [6]. The fact that active laser ablation is used means that depth profiling below surface coatings can be done remotely. LIBS has been under development by the Mars program, including limited rover field testing [7]. Here we discuss lab analyses of samples using spectral ranges, resolutions, and laser powers appropriate to remote analyses on planetary surfaces.

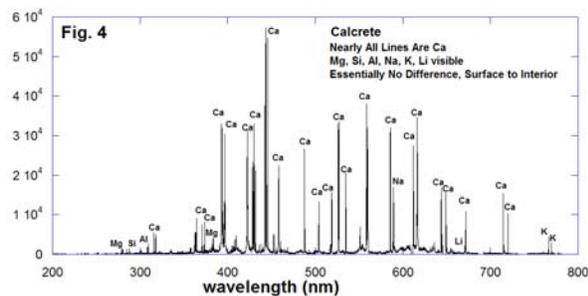


Fig. 4 shows a LIBS spectrum of the Mormon Mesa Calcrete. It is immediately obvious that the material is nearly pure calcite. A large number of calcium lines are present, with only slight hints of other major elements, except for the very strong line of sodium, representing a few ppm Na. Carbon lines (248 and 193 nm) were attenuated by the optical system, which will not be the case in a flight instrument, allowing clear identification of the carbon content.

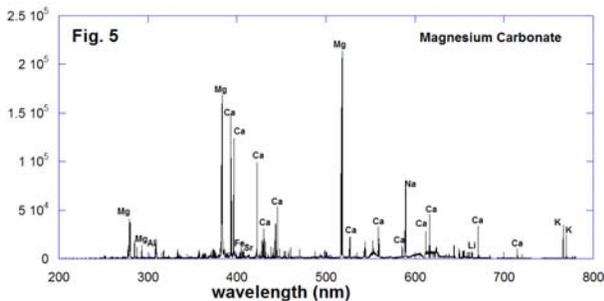


Fig. 5 shows the spectrum of Xalapa, the IR-stealthy carbonate sample from Fig. 2. This sample is clearly a magnesium-calcium carbonate. X-ray fluorescence data indicated very little calcium in the upper portion. The calcium lines are more sensitive than Mg, but even so, the LIBS spectrum shows a sizeable fraction of Ca.

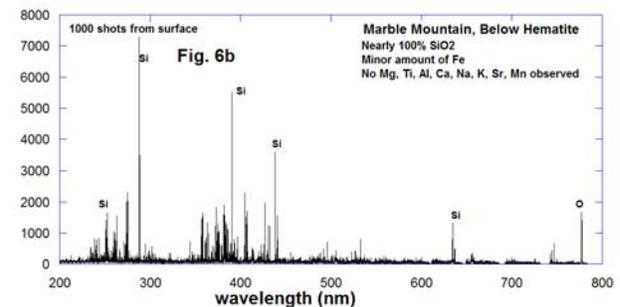
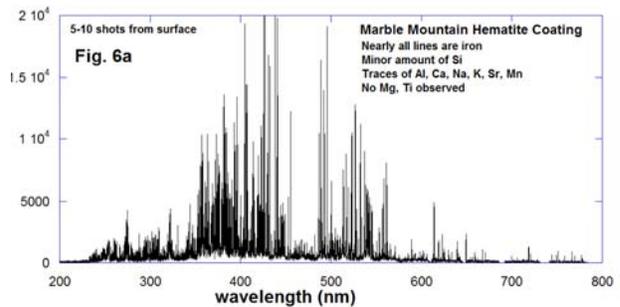


Fig. 6 shows the ability of LIBS to clearly distinguish rock coatings from the underlying composition, as well as to determine the hematite is a coating rather than massive. The Marble Mountain sample in Fig. 6 was collected by Paul Adams from the Saline Valley, Inyo County, CA. It is clearly seen by the LIBS analysis to be quartz underlying the hematite coating, as shown by the Fig. 6b profile 1000 shots below the surface. A flight instrument would take about 20 minutes to remotely profile the 1000 shots ( $\sim 1$  mm) through the coating. The Si lines are relatively insensitive, so that a sample such as this one with prominent Si lines is known, without calibration, to be essentially pure  $\text{SiO}_2$ . If Mars samples have similar coatings, only LIBS will be able to remotely distinguish underlying compositions from coatings.

**Conclusions:** We have shown that in cases where identification by reflectance spectroscopy is difficult or impossible, LIBS can provide unambiguous, rapid remote identification. The two techniques should be viewed as complementary to one another.

**References:** [1] Kirkland L.E. et al. (2004) *J. Geophys. Res.*, 10.1029/2003JE002105. [2] Kirkland L. et al. (2002) *Remote. Sens. Env.* 80, 447-459. [3] Christensen P.R. et al. (2000) *J. Geophys. Res.* 105, 9735-9739. [4] Kirkland L.E. et al. (2003) *Lunar Planet. Sci. XXXIV*, abstract 1944. [5] Clark R.N. (1993) The U. S. Geological Survey Digital Spectral Library: Version 1: 0.2 to 3.0 microns, U.S. Geological Survey Open File Report 93-592, 1340 pages. [6] Cremers D.A. et al. (2002) “Laser-Induced Breakdown Spectroscopy”, *Encycl. Of Analy. Chem.*, Wiley, Chichester. [7] Wiens R.C. et al. (2002) *J. Geophys. Res.*, 10.1029/2000JE001439.