CONSIDERATION OF LIBS FOR EXPLORATION OF CAVES. R. C. Wiens[1], A. Ollila[2], M. Spilde[2], P. Boston[3], J. Barefield[1], L. Le[1], S. Clegg[1], J. Lasue[1], H. Newsom[2], D. Vaniman[1], [1]Los Alamos National Laboratory (rwiens@lanl.gov), [2]University of New Mexico, Albuquerque, [3]New Mexico Institute of Mining and Technology, Soccoro.

Introduction: Caves represent a particularly interesting target of exploration from a habitability standpoint. They are naturally shielded from cosmic rays, their thermal variability is buffered relative to more extreme surface temperatures, and because of this, caves on Mars, for example, are more likely to have contained liquid water in the past, and may in some locations still host liquid water today. With these advantages, caves are a prime location to search for biota, either extinct or currently existing. Caves in the form of lava tubes are known to exist on the Moon and on Mars. Phenomena that occur in caves also occur in pore spaces and fractures in rocks, so the potential locations in which these phenomena are at work may be far more extensive than simply represented by known or inferred caves. A disadvantage for cave exploration is the challenge for mobility, power, and communications.

Caves on Earth represent an interesting niche for exploring unusual life forms, educating planetary scientists on what differences in organic materials one might expect on another planet. Of interest is not only the types of biota but also the geochemical artifacts they leave behind. Ferromanganese deposits (FMDs) found in some caves, including Spider and Lechuguilla Caves in southern New Mexico, are the result of biogenic activity concentrating reduced Fe and Mn. These deposits can be a few mm thick on cave ceilings and up to a few cm on walls, and contain up to > 30% Fe_2O_3 and > 15% MnO, representing concentrations of > 1000x relative to the surrounding calcite and dolostone [1].

LIBS Capabilities: Laser-induced breakdown spectroscopy (LIBS) is a robust analytical technique with potential applications in caves due to its portability and its ability to provide rapid elemental analyses without requiring any sample preparation. The LIBS technique uses a pulsed laser focused on a target to create a "spark" or plasma which is spectrally analyzed to determine the elemental composition. The analysis spot size is small, generally < 0.5 mm diameter, and LIBS can use repeated laser shots to analyze depth dependent compositional variation in a sample. Nearly all elements are analyzed simultaneously, including Fe and Mn and all of the CHNOPS elements important for exobiology.

LIBS was chosen for the compositional remote sensing instrument on the Mars Science Rover *Curiosity*, which is launching this year. This instrument, named ChemCam, can provide elemental composition analyses at a distance of up to 7 m from the rover with a goal of 10% accuracy and precision for major elements, and with capabilities to analyze many minor and trace elements, including Li, Mn, Cr, Rb, Sr, Zr, Ba, and Pb [2].

As part of a recent MSL field test, co-authors JB, LL, and SC fielded a backpack LIBS instrument to provide proxy ChemCam data during the Mars Science Laboratory's "Fast Motion Field Test" near Cameron, AZ. This unit contains a sensor head with a compact flashlamp-pumped Nd:YAG laser emitting 25 mJ pulses, which is positioned on the ground, much like the sensor head of a commercial metal detector. Optical fibers carry the plasma light to three spectrometers in the backpack. The spectrometers cover the same spectral range (~240-900 nm) as the ChemCam instrument. The laser beam is enclosed and safety interlocked so no eye protection is needed. Analyses can be done in < 5 minutes. This instrument or a similar one could be used to provide real-time elemental analyses for terrestrial cave exploration.

LIBS Targets of Interest in Caves: LIBS instruments typically have very good sensitivities for alkalis and alkali earths. Additionally, detection limits for Fe and Mn in a portable LIBS unit such as the one described above should be well under 1% oxide wt. Besides providing immediate in-situ analyses of FMDs, a portable LIBS unit can provide assays of rock types, whether calcite, dolostone, Si- or Al-rich precipitates, or sulfur-bearing materials. LIBS has also been used in the laboratory to distinguish pollens, spores, or bacterial species [e.g., 3], however, the biota associated with FMDs is likely too sparse to detect or distinguish with LIBS.

Preliminary Work: We made preliminary LIBS analyses on two apparently unaltered limestone wall rocks and three FMDs from Lechuguilla Cave, collected for the Spilde et al. study [1]. Analyses were made with the portable backpack LIBS unit used for the ChemCam team's Fast Motion Field Test.

Fig. 1 shows portions of ten averaged spectra of one FMD and one limestone sample. Within this spectral range Mn, Fe, Al, Ca, and Sr peaks are clearly visible in the FMD (sample L050608-3). Other portions of the spectrum, not shown here, contain H, Li, C, O, Na, Mg, Ba emission peaks. Independent analyses of the FMD sample gave 21.9% CaO, 16.7% Al_2O_5, 7.5%

P_2O_5, 6.1% MnO, 6.0% Fe_2O_3T, 4.5% Sr, 3.6% SiO_2, 3600 ppm Ti, 1750 ppm Zn, 760 ppm Li, and 470 ppm Ba, with a high loss on ignition. Of these, the LIBS analysis would be expected to observe Si, Ti, P, and Zn at these levels, but did not do so in the small (< 0.5 mm) analysis spot, suggesting heterogeneity in these deposits. By comparison, in the limestone sample (L060316A4), Mn and most other minor and trace elements were below the detection limits of both LIBS (Fig. 1) and the independent analysis. Strontium, at 65 ppm, was just above the detection limit of LIBS at 407.7 nm.

Speleological environments on Earth are typically moist, and such surfaces tend not to couple with the laser beam as well as dry rocks. As a precursor to taking a LIBS unit into a cave, we wetted the above samples and re-analyzed them. Samples with visible or pooled water on the surface did not couple well enough with the laser to produce spectra. There are several options to resolve this potential problem. We demonstrated, for example, that drying the surface with an absorbant towel removed water well enough to provide useful spectra. Another option is to increase the laser energy. The LANL team has an 80 mJ laser that could be substituted for the 25 mJ one to overcome the poorer coupling of wet samples.

References: [1] Spilde M.N., et al. (2005) Geomicrobiology of cave ferromanganese deposits: A field and laboratory investigation. Geomicrobio. J. 22, 99-116. [2] Wiens R.C., Maurice S., and the ChemCam team (2011) The ChemCam instrument suite on the Mars science Laboratory Rover curiosity: remote sensing by laser-induced plasmas. Geochemistry News, 145, http://www.geochemsoc.org/publications/geochemicalnews/gn145jun11/chemcaminstrumentsuite.htm. [3] Multari R.A., et al. (2010) The use of laser-induced breakdown spectroscopy for distinguishing between bacterial pathogen species and strains. Appl. Spectrosc. 64, 750-759.

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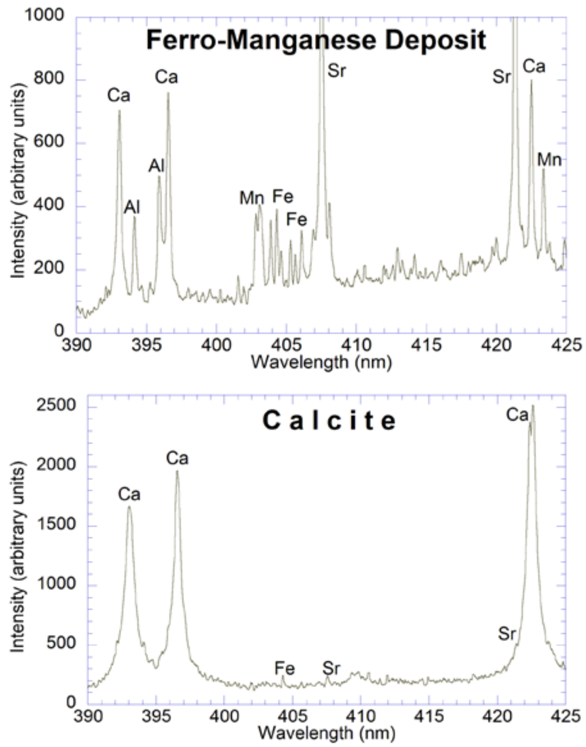

Fig. 1. A small portion of the portable LIBS spectrum of a Lechuguilla Cave FMD (top) and calcite-rich wall rock (bottom).