COMPACT REMOTE RAMAN-LIBS INSTRUMENT FOR MARS OR TITAN

R. C. Wiens[1], S. Maurice[2], S. Clegg[1], S. Sharma[3], A. Misra[3], S. Bender[1], R. Newell[1], N. Dallmann[1], N. Lanza[1] O. Forni[2], J. Lasue[1,2], F. Rull[4] [1]Los Alamos National Laboratory, USA (rwiens@lanl.gov), [2]Institut de Recherche en Astrophysique et Planetologie, Toulouse, France; [3]Hawaii Institute for Geophysics and Planetology, U. Hawaii, Manoa, USA; [4]Centro de Astrobiologia, CSIC-UVA, Madrid, Spain

Introduction: The ChemCam instrument [1,2] on board the Mars Science Laboratory (MSL) mission [3] will demonstrate the utility of remote laser-induced breakdown spectroscopy (LIBS) for planetary reconnaissance when the Curiosity rover lands at Gale Crater [e.g., 4] on Mars later this year. The LIBS technique will permit rapid active remote interrogation through dust layers and up to 1 mm into rocks (far deeper in soils) using an analysis spot size in the range of 300-600 µm. In addition to the typical elements analyzable by other techniques (Na, Mg, Al, Si, S, Cl, K, Ca, Ti, Mn, Cr, Fe, Ni, Zn) LIBS adds the capability for the light elements, H, Li, Be, B, C, N, and O, which are critical for understanding habitable soils, organic material, and ices. ChemCam's analysis range is 7 m, and the team expects to provide elemental compositions with ±10% relative accuracies.

Beginning with PIDDP funding in 2002 and an R&D100 award in 2003 this team has developed a combined Raman-LIBS instrument concept. Raman spectroscopy has long been viewed as highly useful for planetary science [e.g., 5], as it provides information on mineralogy and organic molecule structure that is highly complementary to elemental compositions provided by LIBS. For remote analyses a combined instrument is feasible because both techniques require a pulsed laser, telescope, and spectrometer [6-10]. A further advantage of a combined Raman-LIBS instrument is that using the LIBS mode, the laser can remove dust and profile into the sample, providing access to the subsurface that would not be possible with only the Raman technique [6]. Co-authors SS and AM have demonstrated remote Raman spectroscopy analyses to distances of 100 m using prototype instrumentation [11].

Compact Remote Raman-LIBS Concept for Mars or Titan. Recently a rugged Raman-LIBS (RLS) concept was developed through a New Frontiers Phase A mission study for the SAGE Venus Lander mission [12,13]. Designed to make the first measurements of the Venusian surface in over three decades, the RLS instrument was designed to be very rugged and completely autonomous in operation due to the unforgiving nature of the Venus surface and short survival duration.

For future Mars or Titan missions we are exploring instrument concepts for which the mass would be reduced well below that of ChemCam. This is feasible using a single laser as with ChemCam. In that instrument the Nd:KGW laser output is 35 mJ at 1067 nm, but the energy reaching the target is only 15 mJ due to inefficiencies associated with a telescope design required for imaging. By removing the Remote Micro-Imager (RMI) from ChemCam, designing an off-axis telescope and assuming there are other imaging assets, the laser energy on target could be increased by 80% at the same wavelength. With this design the telescope aperture can be reduced below the 110 mm used for ChemCam, decreasing the associated mass.

Significant additional mass can be saved with the spectrometers. Thermal mismatching of the interior of the rover, where the ChemCam spectrometers reside, resulted in the need to retrofit the detectors with thermo-electric coolers at a late stage in the project, doubling the original 2.4 kg mass of ChemCam's Body Unit comprising the spectrometers, electronics, and DPU. Cooling of the detector is unlikely to be needed on future Mars or Titan missions, given appropriate accommodation. ChemCam uses three spectrometers of a very simple Czerny-Turner design. A single spectrometer can suffice to cover LIBS emission lines of nearly all of the elements, and at the same time observe Raman spectra. Given the transmission requirements of Raman spectroscopy, a high-efficiency transmission spectrometer has been developed jointly by U. HI and LANL for SAGE which uses an intensified detector with a dynamic range more than adequate for both techniques. With the design features described here it appears feasible to perform both remote LIBS and Raman spectroscopy with an instrument mass of 6 kg, compared to the ChemCam mass of slightly under 10 kg, with which it performs LIBS plus imaging.

Figures 1 and 2 show combined Raman-LIBS spectra of gypsum ($CaSO_4 \cdot 2H_2O$) and olivine ($Mg_{2-x}Fe_xSiO_4$) measured in air in the 534-699 nm wavelength range. The Raman spectrum (Fig. 1a) of the target at 9 m was excited with 9 mJ/pulse of the 532 nm laser focused to 529 µm diameter and signal accumulated for 1 sec in the gated mode with a 2-µs gate width. In the Raman spectrum of gypsum, the strongest Raman peaks observed at 1006 cm^{-1} originate from the symmetric stretching vibrations of the SO_4^{2-} ion, $n_1(SO_4)$, and its position depends on degree of hydration. The other internal modes of vibration of sulfate ions appear at 1136 (n_3), 415 and 495 (n_2), and 621 and 671 (n_4) cm^{-1} are clearly visible. In the high-frequency region, the two bands at 3406 and 3498 cm^{-1} clearly represent the presence of chemically bounded water molecules in the gypsum [e.g.,7]. In the combined LIBS and Raman spectra of gypsum the laser power was increased to 35mJ/pulse. The Raman lines in Fig. 1(b) are marked with letter "R". In Fig. 1 (c), LIBS spectra were obtained by removing the broad white light background and the Raman lines, which have shorter (10^{-13} s) lifetime, by delaying the detector gate by an additional two micro-seconds. the LIBS lines in Figs. 1(c) originate from Ca (I) excited states, a major cation in gypsum. In the combined LIBS Raman spectra of gypsum the LIBS lines at 588.99 and 589.59 nm indicate the presence of a trace amount of Na in the sample.

Figure 2(a) shows the Raman spectra of olivine $(Mg,Fe)_2SiO_4$ with fingerprint Raman doublet lines at 821 and 852 cm^{-1} above the fluorescence background. The oli-

vine Raman doublet originates from the stretching modes of Si-O_{nb} bonds of tetrahedral silicate, where O_{nb}=non-bridging oxygen [e.g., 7]. The remote LIBS spectrum of olivine shows strong emission lines at 552.8 nm and a weak line at 571.1 nm of Mg; and strong emission lines of Si II at 634.7 and 637.1 nm (Fig. 2b). The emission lines of Na, H and Ca in the LIBS spectrum of olivine indicate the presence of these elements in trace amounts. The Fe emission lines are observed only weakly in the LIBS spectrum of olivine indicating that this sample is indeed Mg-rich olivine (Fo 92) containing ~8% of iron [7].

Operations Concept. The single laser powering the compact Mars/Titan Raman-LIBS spectrometer would be based on, if not identical to, the ChemCam unit. Using a frequency doubler it could operate either at 534 nm or at a combination of 534 and 1067 nm. In a frequency-doubled diode-pumped laser the longer wavelength is naturally output unless it is blocked within the instrument. The combination of the two wavelengths was demonstrated with a laboratory prototype Raman-LIBS instrument as described in [14]. Direct 534 nm laser light is prevented from entering the spectrometer, as its shortest wavelength is just longer than that of the laser beam. The laser is defocused slightly for Raman spectra, which can be obtained over a larger area than the≤ 600 µm LIBS spot size. Alternately the laser energy can be reduced for analyses over the same spot size as LIBS, in order to take full advantage of its depth profiling.

Analysis Capabilities. With an expected laser output of 12 mJ at 534 nm, the compact Mars/Titan Raman-LIBS spectrometer is expected to provide LIBS elemental composition measurements to 7 m similar to ChemCam, for emission lines over a spectral range of 535-810 nm. Essentially all of the elements with emission lines at shorter wavelengths also have emission lines in this spectral range. A partial exception is carbon, for which the 248 nm emission line is stronger than those in the visible and near-infrared (VNIR) range covered. However, given an intensifier, it is likely that these other emission lines will be better detected than the 248 nm line is on ChemCam. In addition, the Raman capability on this instrument identifies carbon-bearing samples.

Raman spectra covering up to 4,000 cm^{-1} are obtained with a resolution of 10 cm^{-1}. It has been demonstrated that low (1 to 3 vol %) concentrations of minerals in basaltic glass matrix can be detected with stand-off Raman system to 9 m distance [15].

Applications. As mentioned in the introduction, the combination of Raman spectroscopy and LIBS is extremely powerful, particularly in the role of reconnaissance. Beyond characterizing minerals and elemental compositions, this combined instrument can fulfill the goals of a 2018 Mars rover in terms of searching for organic materials. This instrument is highly desirable for outer solar system exploration given its unique capabilities for characterizing carbon- and nitrogen-based ices as well as water ice, both in terms of Raman spectroscopy and LIBS.

References: [1] Maurice S. et al (2012) The ChemCam Instruments on the Mars Science Laboratory (MSL) Rover: Science Objectives and Mast Unit, Spa. Sci. Rev., subm. [2] Wiens R.C. et al. (2012) The ChemCam Instruments on the Mars Science Laboratory (MSL) Rover: Body Unit and Combined System Performance. Spa. Sci. Rev., subm. [3] Grotzinger G., et al. (2012) Mars Science Laboratory Mission and Science Investigation. Spa. Sci. Rev., subm. [4] Golombek M., et al. (2012) Spa. Sci. Rev., subm. [5] Wang A., Jolliff B.L., and Haskin L.A. (1995) J. Geophys. Res. 100, 21189-21199. [6] Sharma S.K., et al. (2007) Spectrochim. Acta A68, 1036-1045. [7] Sharma, S.K. et al. (2009) Spectrochim. Acta, A73, 468-476. [8] Moros, J. et al. (2010) Anal. Chem. 82, 1389-1400. [9] Misra, A.K. et al.(2011) Proc. SPIE, 8032, 80320Q/1-12. [10] Rull F., Vegas A., Barreiro F (2011) Lunar Planet Sci. XLII, 2275. [11] Sharma S.K. (2007) Spectrochim. Acta A68, 1008-1022. [12] Clegg S.M. et al. (2011) Lunar Planet. Sci. XLII, 1568. [13] Clegg S.M. et al. (2012) Laser-induced breakdown spectroscopy of geological samples under Venus surface pressures. In preparation for submission. [14] Wiens R.C. et al. (2005) Spectrochim. Acta A61, 2324-2334. [15] Sharma, S.K. et al. (2011) Lunar Planet. Sci. XLII, 1250.
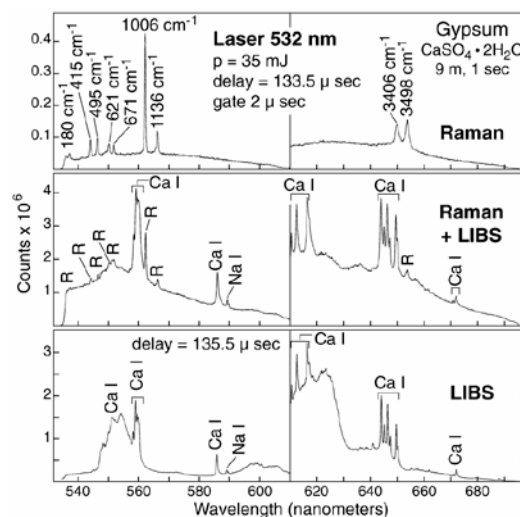

Fig. 1. Remote Raman spectrum (a), combined Raman + LIBS spectra (b) and LIBS spectrum (c) of gypsum at 9 m excited with 532 nm pulse laser.
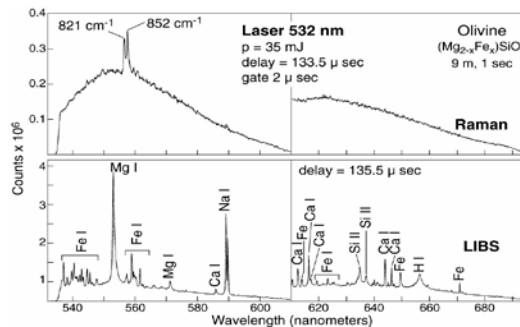

Fig. 2.Stand-off Raman spectrum (a) of olivine excited with 12 mJ/pulse, and LIBS spectrum (b) of olivine at 9 m excited with 532 nm pulse laser of p=35mJ/pulse. Spectra were recorded with 2 µs gate.