**PLANETARY RAMAN SPECTROSCOPY FOR SURFACE EXPLORATION AND *IN SITU* RESOURCE UTILIZATION ON THE MOON** Alian Wang[1], Zongcheng Ling[1,2], and Bradley L. Jolliff[1], [1]Department of Earth & Planetary Sciences and the McDonnell Center for the Space Sciences, Washington University, St. Louis, MO, 63130 (alianw@levee.wustl.edu), [2]Department of Space Science and Applied Physics, Shandong University, Weihai, People's Republic of China.

Study of lunar rocks and soils – igneous mineralogy: We have published a series of papers (Wang et al., 1995, Haskin et al, 1997, Korotev et al., 1997) that demonstrate the capability of planetary Raman spectroscopy for definitive mineral identification and characterization of lunar materials (rocks and soils), as well as to obtain information on mineral proportions and rock textures. During the development of the Mars Microbeam Raman Spectrometer, we conducted another series of application studies to evaluate the feasibility of extracting compositional information from stand-alone Raman measurements, which have been proven to be very successful. Examples include obtaining Mg/(Mg+Fe) ratios from olivine (Kuebler et al., 2006); determining Mg/(Mg+Fe+Ca) and Ca/(Mg+Fe+Ca) in pyroxene (Wang et al., 2000); classifying the variety of feldspar (Or, Ab, An, and solid solutions thereof) (Freeman et al., 2001); obtaining information on Fe, Cr, Ti, Al, and Mg contents in Fe-Ti-Cr-oxides (Wang et al., 2004); and distinguishing the variety of phosphate minerals (Jolliff et al., 2006). Recently, we used the accumulated knowledge through these studies to investigate two typical lunar soils, 67513 and 71501. Figure 1 a, b shows the compositional distributions of olivine and pyroxene grains in these two lunar samples. Results demonstrate that with a few tens to a hundred Raman point measurements, which could be made by a robotic Raman system on the lunar surface, a lunar soil sample (with grain size ~50 +/-20 μm) can be well characterized in terms of its mineralogy and the compositional features of major minerals.
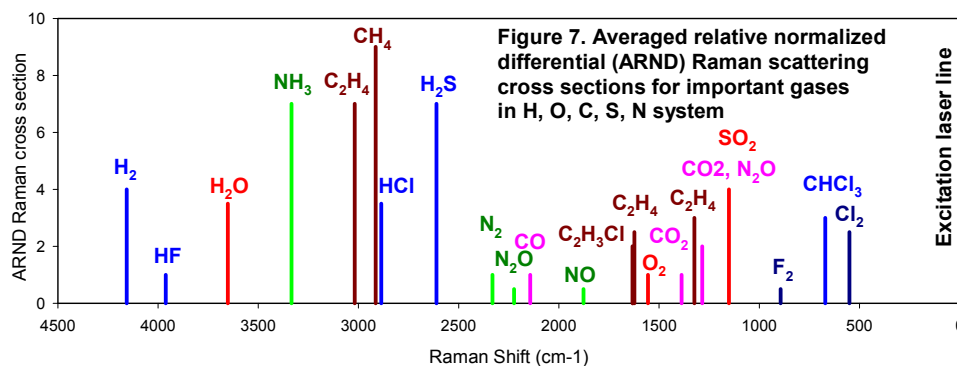
Figure 1. *Compositional distribution of olivine (blue) and pyroxene (magenta) grains in lunar soils 67513 & 7150*1
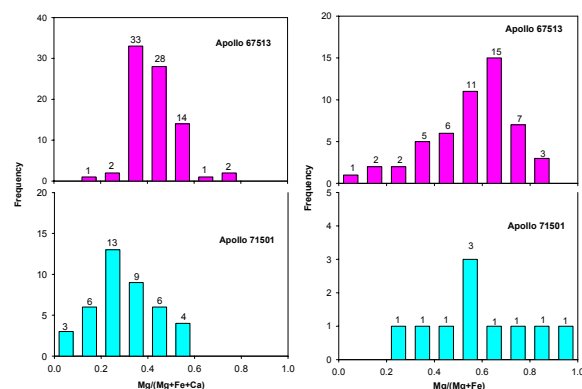
Detection of ice and hydrous minerals in polar deposits: The neutron spectrometer on the Lunar Prospector orbiter found increased concentrations of H in lunar polar regions, possibly associated with permanently shaded craters [*Feldman et al.*, 2001]. The questions posed for the next landed mission to the Moon are as follows: (1) In what form is the H? Is it as solar-wind-implanted H^+, water-ice left by cometary impacts, or as H_2O/OH structurally bonded to minerals? (2) How can we effectively extract the hydrogen for ISRU purposes? Raman spectroscopy can address the first question by detecting the characteristic Raman peaks of H_2 (after heating the surface soils), water-ice, and H_2O/OH-bearing minerals. Raman spectroscopy can address the second question using a process-control Raman sensor on ISRU platforms (see next section below). Our current view of Raman spectroscopic applications for ISRU is based on ISRU processes discussed extensively in the 1980s -1990s *[Lewis and Lewis, 1987; Lewis et al., 1993; Mendell, 1984]*. Further Raman applications will emerge following new ISRU designs in the current phase of return-to-the-Moon mission-concept development.

Process control for in-situ Resources Utilization (ISRU): Robots, and eventually humans will go back to the Moon, this time perhaps to explore the polar regions. Part of this effort will be to develop the technologies needed to use lunar resources as a basis for further missions to Mars and beyond. A substantial body of work has accumulated since the Apollo missions regarding ISRU concepts on the Moon [*Lewis and Lewis*, 1987; *Lewis et al.*, 1993; *Mendell*, 1984]. Planetary Raman spectroscopy can make significant contributions for ISRU on the Moon.

The first-order demand in lunar ISRU is to obtain propellants, free metals, and bulk shielding for protection against radiation. The most abundant and most readily available material for these uses is unprocessed lunar regolith. Among the procedures proposed to extract hydrogen and oxygen from lunar regolith, extracting H_2 as solar-wind-implanted elements (SWIE, including H, He, C, N, Ne, Ar, Kr, and Xe) by thermal release of gases is one of the most promising methods, because the available quantities of entrapped solar wind are sufficiently high and the economics of complete propellant production on the Moon are appealing *[Carter, 1984; Lewis and Lewis, 1987, Duke et al., 2006]*. Some indigenous and relatively volatile elements (S and Cl) will also be extracted during the heat-

Figure 7. Averaged relative normalized differential (ARND) Raman scattering cross sections for important gases in H, O, C, S, N system

ing process. The products of this process will include H_2O, H_2S, CO, CO_2, NH_3, and HCN. All of these have characteristic Raman spectra (Figure 2, Raman cross sections of some gaseous phases). A procedure for extracting O_2 that has received much consideration is "ilmenite reduction," a two-step procedure first by using H_2 to breakdown $FeTiO_3$ and produce H_2O, then by electrolysis of H_2O to produce O_2 and reusable H_2 [*Gibson and Knudsen, 1984*]. A one-step O_2 extraction procedure is the electrolysis of molten silicates. It requires only sunlight for heat and electricity, and lunar regolith as feedstock. O_2 gas will be released at the anode, and iron metal simultaneously formed at the cathode [*Colson and Haskin, 1993*]. In order to produce metals (Fe, Ni, Co) from lunar regolith, the first step is to concentrate them by the use of strong magnets, then to purify the metal using "carbonyl processing," in which CO and CO_2 are the reagent and product, but H_2S is needed for catalysis [*Culter and Krag, 1984*]. Ca, Al, and alkali metals can be extracted as oxides from "destructive distillation" of lunar silicates at high temperature [*Agosto and King, 1983*]. In addition, microbial extraction of H_2 from lunar dust has also been proposed, with CO_2, H_2S, CH_4, O_2, NH_3, H_2 as the intermediate and final products [*White and Hirsch, 1984*].

In a chemical reaction process, in-situ, automatic, and non-interruptive detection of critical species is essential for process control. A useful sensor for process control in lunar resource production will be the detection of gaseous species, either as reagents, as products, or as catalysts. Evidence for the generation and the partial pressures of these gases will provide information on the direction and effectiveness of the chemical reactions. Laser Raman spectroscopy is ideal for this type of process control, not only because all of these gaseous species are strong Raman scatterers (Figure 2, note that O_2 and H_2 are not detectable by IR spectroscopy), but also because a laser beam is used in Raman spectroscopy for excitation and the Raman scattering from the gases (NOT gas molecules as for a mass spectrometer) can be collected through a transparent window material. Therefore Raman measure-

ments can be made automatically and non-invasively, with high detection sensitivity, for gaseous species in an *as-is* status, that is, without need of any further chemical reaction as part of a detection scheme.

We anticipate that various planetary Raman sensors can be installed on an ISRU platform, at critical locations to monitor the generation and concentration of certain gaseous species, through small windows of 5-10 mm diameter on reaction vessels or on input/output tubing.

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