

Moon4You: A combined Raman / LIBS instrument for lunar exploration

Erik C. Laan^{*a}, Berit Ahlers^a, Wim van Westrenen^b, Jeannette Heiligers^a, Arno Wielders^c
^aTNO Science & Industry, Space & Science, Stieltjesweg 1, 2600 AD Delft, The Netherlands;
^bVU University Amsterdam, De Boelelaan 1085, 1081 HV Amsterdam, The Netherlands;
^cSpace Horizon, Duindoornlaan 24, 2015 LB Haarlem, The Netherlands.

ABSTRACT

Moon4You is a project led by the Dutch Organisation for Applied Scientific Research TNO, with partners from industry and universities in the Netherlands that aims to provide a combined Raman / LIBS instrument as scientific payload for lunar exploration missions. It is the first time that Raman spectroscopy and LIBS (Laser Induced Breakdown Spectroscopy) are combined into one miniaturised instrument with minimum mass, volume and use of resources and can deliver data-products almost instantly. These characteristics make it the next-generation instrument for mineralogical and elemental (atomic) characterisation of lunar soil and rock samples, as well as for a host of other planetary exploration and terrestrial applications.

Keywords: Raman, LIBS, spectrometer, Moon, laser

1. INTRODUCTION

The world is at the threshold of a new age of space exploration ('Space 2.0' or 'NewSpace'). Highly regarded companies such as Virgin Galactic and SpaceX are paving the way for a more cost effective space science and exploration agenda in the coming decades. Coinciding with the transition from the institutional 'Space 1.0' to a commercial 'Space 2.0' agenda, a new phase of commercial lunar exploration ('Moon 2.0') was initiated by the announcement of the Google Lunar X PRIZE in 2007.

Participation in Moon 2.0 requires a new approach to conducting space projects. Schedules are tight, additional and non-traditional risks are involved, and new types of requirements are imposed on scientific payloads. Moon4You is a project led by the Dutch Organisation for Applied Scientific Research TNO, with partners from industry and academic planetary science research centres in the Netherlands, that aims to provide a combined Raman / LIBS instrument as scientific payload for Moon 2.0 lunar (and other planetary) exploration missions.

A first opportunity to fly the Raman / LIBS technology into space is currently pursued by TNO and partners. Within the Odyssey Moon MoonOne mission (planned for launch in 2012), this instrument "Moon4You" will participate with one of the competitors in the \$30M Google Lunar X PRIZE. This prize will be awarded to the first team which, privately funded, lands on the Moon and travels a minimum distance of 500 meter on the surface.

For Odyssey Moon, the prize is just one of the incentives to go back to the Moon. The main driver is the foreseen business with respect to lunar transport of scientific and exploration assets. A study performed by the Futron Corporation, an aerospace consultancy based in Bethesda, MD, predicts that companies such as those competing for the Google Lunar X PRIZE will be able to address a market in excess of \$1 billion over the course of the next decade.

For our Raman/LIBS instrument, the main lunar science objective is to in-situ determine the mineralogical and elemental composition of the lunar surface. Such data will (a) provide details on the geological and geochemical evolution of the Moon (b) perform detailed in-situ mapping of potential lunar resource materials and (c) demonstrate and validate the Raman/LIBS technology for future planetary exploration missions and terrestrial spin-offs.

*erik.laan@tno.nl; phone +31 15 2692723; fax +31 15 269 2111; www.tno.nl/moon4you

2. A NEW AGE OF SPACE EXPLORATION

When Burt Rutan's company, Scaled Composites, won the 2004 Ansari X PRIZE by being the first non-governmental organization to successfully send a manned vehicle into space, renowned experts stated that the world found itself in a 'new age of space exploration'.

Up until a few years ago, space exploration to most people meant NASA, ESA, astronauts, satellites and billion-dollar government projects. In this 'Space 1.0' era, focus was on discovering and exploring the universe, and seeing how successful we could be in space from a purely scientific point of view. Since then a change in people's perspective of what space exploration should be has occurred. In succession to Space 1.0, obviously indicated with Space 2.0, space is considered as a resource for commercialization and should be expanded beyond the exclusive domain of scientists and space agencies and should include the involvement of private entrepreneurship.

One of the major advantages of the involvement of private entrepreneurship in space exploration is that it brings along commercial opportunities that allow more room for experimentation and possible breakthroughs. The making of the steam engine, the invention of the telephone, and the rapid expansion of the Internet have all been tangible outcomes flowing from private enterprise. Extending this to space technologies will provide an enormous boost to worldwide space exploration.

Current examples of endeavours in the field of commercial space exploration include Sir Richard Branson's Virgin Galactic (the first European Space Tourism Agency); SpaceX that is on the threshold of a revolution to provide cost efficient access to space for commercial application and XCOR that has developed a rocket propelled plane to serve space tourism, atmospheric research and microgravity studies needs. Even the European Space Agency ESA has taken a positive viewpoint and is studying possibilities to contribute generically to private space exploration.

3. THE GOOGLE LUNAR X PRIZE

Similar to the transition from Space 1.0 to Space 2.0, the world is witnessing the beginning of a new phase of lunar exploration indicated by the transition from Moon 1.0 to Moon 2.0.

Moon 1.0 started in the 1960s when the United States and the Soviet Union engaged in a historic superpower Moon race, which culminated in 12 men exploring the surface of the Moon. On July 20, 1969, Neil Armstrong and Buzz Aldrin became the first human beings to set foot on the Moon. The first human steps on the lunar surface were the highlight of an extended U.S. program to study and map the Moon and fulfilled the 1961 promise of President John F. Kennedy that the U.S. would land a man on the Moon 'before the end of the decade'. The scientific return from these missions was unprecedented, and remains unrivalled even today. Scientific return included nearly complete high-resolution imaging of the lunar surface, over 380 kg of lunar samples returned to Earth, topographic, seismic and gravity data, and information on the lunar surface environment.

This first era of lunar exploration, indicated with Moon 1.0, suddenly came to an end as public and political interest faded away. On December 14, 1972, Apollo 17 astronauts Captain Gene Cernan and Dr. Harrison Schmitt became the last men on the Moon and the hardware already built for Apollo 18-20 was discarded.

It is now more than thirty years ago since the last human left Earth orbit. This hiatus in space exploration is now on the verge of being overcome. A renewed strategy for progressive Moon exploration, Moon 2.0, has been agreed upon in which the efforts of governments are complemented by a growing interest from the private sector to partner in the permanent return to Earth's sister world.

Moon 2.0 was 'officially' introduced by the announcement of the \$30 million Google Lunar X PRIZE (GLXP) competition, sponsored by the world's largest internet search engine, on September 13, 2007. Like the aforementioned 2004 Ansari X PRIZE the GLXP is initiated by the X PRIZE Foundation, which aims "to bring about radical breakthroughs for the benefit of humanity". One of its stated purposes is to excite the global public by "increasing the connection that individuals around the world feel to space exploration, science, and education by taking advantage of new tools for the rapid and targeted distribution of information".

The X PRIZE Foundation believes that a key ingredient required to achieve such breakthroughs is competition. One of the best examples of the influence that competitions can have on people's drive to try the impossible is Charles Lindbergh. On May 20th, 1927 he was the first man to make a solo, non-stop flight over the Atlantic Ocean. This flight and his later achievements were the start of modern intercontinental flight. Ever since Charles Lindbergh's first flight,

this industry grew exponentially and is now part of our daily life. It can be questioned whether Charles Lindbergh would have also performed this flight without Raymond Orteig awarding a price of \$25,000 to the first man to fly non-stop over the Atlantic Ocean. This illustrates that competition can be a strong drive to realize breakthroughs, which is what the X PRIZE Foundation aims for.

Winning the GLXP requires a spacecraft to safely land on the surface of the Moon, travel 500 meters over the lunar surface and send images and data back to the Earth. Teams that are at least 90% privately funded can join this competition. The first team that lands on the Moon before December 31, 2013 and completes these mission objectives will be awarded \$20 million. After that date the prize will drop to \$15 million. The second team to do so will be awarded \$5 million. Additional prize money (totalling \$5 million) can be won by successfully completing additional mission tasks such as roving longer distances (> 5,000 meters), imaging man-made artefacts (e.g. Apollo hardware), discovering water ice and/or surviving through a frigid lunar night (approximately 15 Earth days).

4. THE MOONONE MISSION BY ODYSSEY MOON

In December 2007, the first official competitor for the GLXP was unveiled: Odyssey Moon Limited (hereafter simply referred to as Odyssey Moon) that wants to participate with its 'MoonOne' spacecraft.

Odyssey Moon is a private commercial lunar enterprise that has a long term vision on lunar (transport) services and products to aid humanity's sustained return to the Moon. The management of Odyssey Moon has an impressive track record in business, finance, space technologies, Space 1.0 and Space 2.0.

Odyssey Moon plans to send a series of small robotic missions to the Moon in support of science, exploration and commerce in the coming decade. Its inaugural MoonOne mission will involve a unique small robotic lander designed to deliver scientific, exploration and commercial payloads to the surface of the Moon.

This MoonOne mission was already scheduled before the announcement of the GLXP and is therefore independent of the GLXP, meaning that the mission will be executed even if another competitor wins the GLXP.

On March 11, 2008 Odyssey Moon issued a Request For Information (RFI) for a Payload Flight Opportunity on its MoonOne Lunar Lander. The MoonOne spacecraft is currently scheduled for launch in early 2012 and has 15 to 25 kg of additional payload capacity available. Odyssey Moon therefore offered an opportunity for the international lunar community to place scientific or technology demonstration payloads onboard the MoonOne mission. Following this announcement, the Moon4You programme, aiming to place a Raman/LIBS instrument on the surface of the Moon, signed a Letter Of Intent (LOI) with Odyssey Moon on February 2, 2009.

The Lunar Lander that will be used for the MoonOne mission is based on the NASA Ames lunar lander design. NASA Ames has developed a lunar lander for low cost, short schedule and low mass lunar missions that employ low cost launch vehicles. The intention is to use this lander in a sequence of lunar missions in the upcoming years (the 'small lunar mission series') that have to be executed within a budget of \$100 million per mission. Figure 1 shows a test-model of the NASA Ames lunar lander

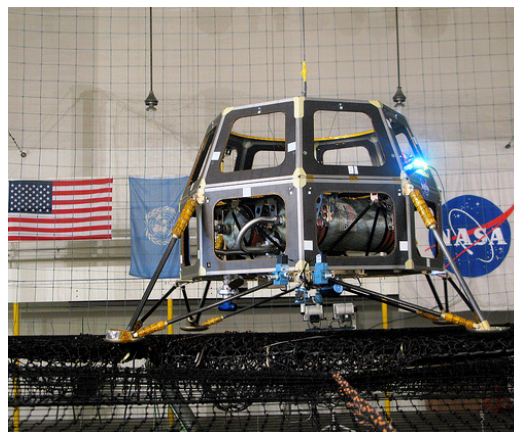


Figure 1: the NASA Ames Lunar lander on which the MoonOne lander will be based (courtesy NASA)

5. THE RAMAN/LIBS INSTRUMENT

The Moon4You Raman / LIBS instrument is a fundamental, next-generation instrument for mineralogical and elemental (atomic) characterisation of lunar soil and rock samples. It uses an Optical Head to illuminate samples with laser light that generates physical phenomena (Raman shift and plasma for the LIBS) with light emission. Emitted light is collected and relayed to a spectrometer using optical fibres to record a spectrum on a CCD for sample identification. Additional hard-ware components are a Deployment Mechanism (DPM) to accurately position the Optical Head above the sample and an Electronic Assembly for instrument support and CCD readout. It is the first time that Raman spectroscopy and LIBS are combined into one miniaturised instrument with minimum mass, volume and use of resources, a high spectral performance and rapid analysis.

An international team, under the leadership of TNO Science and Industry, has designed, built and tested an Elegant Bread Board (EBB) of this instrument under ESA contract [1, 2, 3, 4]. The EBB comprises a specifically designed, extremely compact, spectrometer with high resolution over a large wavelength range, suitable for both Raman spectroscopy and LIBS measurements. The EBB also includes lasers, illumination and imaging optics as well as fibre optics for light transfer. It weighs less than 1 kg and is robustly designed to withstand launch environmental conditions and temperature fluctuations between -70 and +70°C without hysteresis. The built instrument forms a base that can be adapted for any wanted application into a portable and highly robust instrument.

The instrument was previously pre-selected as part of the ExoMars rover's Pasteur payload and its end-to-end functional performance has been demonstrated with the EBB using natural samples under Mars-mission representative conditions. Subsequently a Development Model (DM) (see Figure 2) of the spectrometer was built, which is intended to be adapted (interfaces, temperature, atmospheric pressure, radiation, dust environment) for accommodation on lunar missions. As a result, parts of the Raman/LIBS instrument have a high Technology Readiness Level (TRL), while other subsystems (e.g. the DPM) have a low TRL, which is expected to rise rapidly depending on specific mission boundary conditions.



Figure 2: Combined Raman / LIBS Development Model (DM) spectrometer unit together with system engineer Berit Ahlers.

6. THE LUNAR SCIENCE CASE FOR RAMAN/LIBS

As mentioned in the Introduction section, the main science objective of the Moon4You instrument onboard a lunar mission would be to determine the mineralogical and elemental composition of the lunar surface, to (1) provide details on the geological and geochemical evolution of the Moon (2) perform detailed in-situ mapping of lunar material of interest for lunar exploitation means and the realization of a future lunar base (3) demonstrate and validate technology for future planetary exploration missions and terrestrial spin-offs. In this section we provide a short background to the importance of lunar science in general, followed by a discussion of these objectives.

(a) Importance of lunar science: some background

The Moon, our celestial nearest neighbour, is very different from Earth in many respects. It has virtually no atmosphere, its interior is essentially water-free, its oxygen fugacity is extremely low, and compositionally it is thought to be significantly depleted in iron and volatile elements [5]. Yet, measurements of lunar rocks returned with the Apollo missions demonstrated that the isotope ratios of oxygen, the most abundant element on both planetary bodies, require a very strong genetic link between the material that formed the Earth and the Moon [6]. Similar precise isotopic matches have been found for other elements such as magnesium [7], silicon [8], potassium [9], and tungsten [10], reinforcing the genetic link between the Earth and the Moon.

Three competing hypotheses for the Moon's origin (i.e. coeval formation in a common orbit, formation of the Moon elsewhere in the solar system followed by gravitational capture, and rotationally induced fissure of the Earth) were largely abandoned on the basis of this chemical evidence and observations of the angular momentum of the Earth-Moon system. It is now widely accepted that our Moon formed as a result of the most dramatic event in Earth's early history: a giant collision between the nearly fully accreted young Earth and a Mars-sized impactor [11,12]. Debris from this violent impact coalesced in an orbit around the Earth to form our Moon [13].

This event had enormous and far-reaching effects on the constitution of our planet. Some of these effects are felt on the Earth's surface to this day, as the Moon is the only satellite in the solar system capable of influencing planetary climate. Its relatively large mass and close proximity, resulting from its impact origin, have had a stabilising effect on the orientation of Earth's rotation axis, which was essential for the evolution of climate and life on Earth [14]. The bulk chemical compositions of the Earth and the Moon were also affected to a significant extent by mixing material from the young Earth and the impactor. The impact's huge energy caused extensive melting of both the Earth and the newly forming Moon, leading to the formation of global magma oceans hundreds to thousands of kilometres deep on both bodies. Recent geochemical studies strongly suggest that the crystallization of these magma oceans was a key event in the early differentiation of the silicate Earth and the Moon [15].

On Earth, the thermal effects associated with the Moon-forming impact may be responsible for the persistence of a magnetic field on the Earth's surface until today, without which life would be exposed to harmful solar radiation.

Constraining both the origin and differentiation of the Early Earth, its present-day chemical composition, and models of planetary-scale magma oceans thus require detailed knowledge of the giant Moon-forming impact. Given their coupled formation and evolution, Early Earth models must be linked intimately to models for the composition, origin and

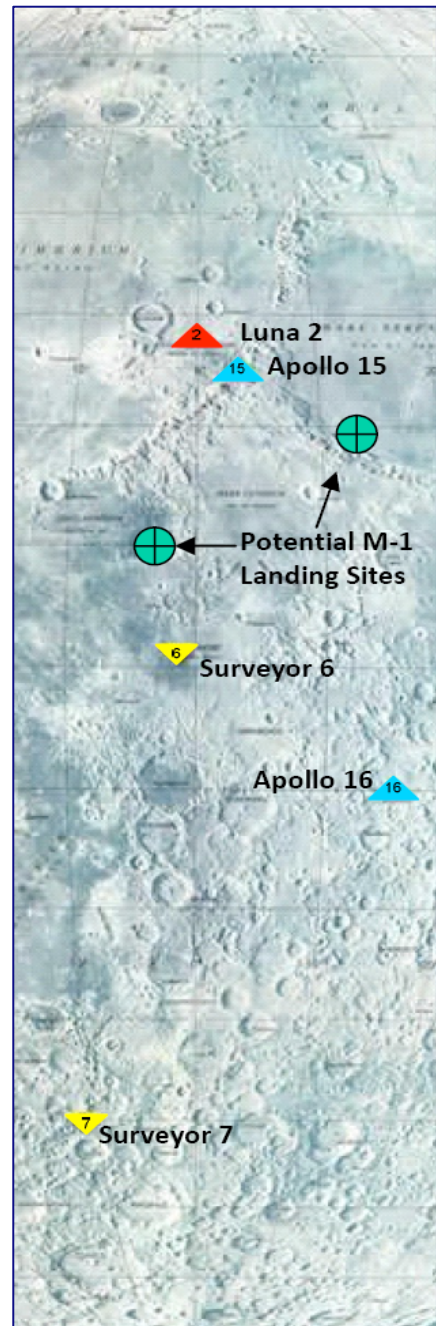


Figure 3: the prospective landing sites for the MoonOne mission

evolution of the Moon itself. On Earth, most of the geological and chemical evidence of the giant impact, which took place at least 60 million years after the birth of the solar system, was erased by subsequent continuous geological activity (plate tectonics and erosion). This inhibits us from putting firmer constraints on this defining moment in Earth's history. In contrast, the Moon has not experienced significant geological activity over the past ~3 billion years. The implication of this observation is that the Moon is unique in potentially retaining substantial information about the processes responsible for the differentiation of the Early Earth: *to understand how the current Earth has evolved we need to understand the Moon.*

(b) Lunar science with Raman/LIBS

Two current prospective landing sites for the MoonOne Lunar Lander are shown in Figure 3. Both are on the lunar near side, relatively close to the equator. High-resolution camera images, obtained from lunar orbit, show the landing sites are covered by so-called dark mantle deposits. The discovery of these unique, but not widely known deposits constitutes one of the major scientific discoveries of the Apollo-era missions. Dark mantle deposits consist of very fine-grained (40 micrometer diameter), rounded volcanic material scattered across parts of the lunar surface, recognizable by their very low reflectivity (hence their dark appearance). These deposits cover the underlying surface, comparable to the way snow covers landscapes on Earth.

By investigating these deposits, first recognized in the Apollo 17 samples returned to Earth in 1972, it was concluded that they were produced by fire-fountaining during volcanic eruptions – a process that is well known from volcanic eruptions on Earth. Most of the deposits consist (Figure 4) of glassy beads, formed during rapid cooling of magma during eruption into the thin lunar atmosphere. The deposits also contain small rounded grains of the mineral ilmenite (an iron-titanium oxide that plays an important role in the evolution of the interior of the Moon).

These deposits are unique in two complementary areas at the heart of both fundamental and applied lunar science:

(1) The volcanic glasses are the most so-called 'primitive' materials identified in the complete lunar sample collection. Their compositions therefore provide lunar scientists with their best estimates of the composition of the lunar deep interior. Uncertainty about the lunar interior composition is currently the primary problem hampering the development of improved models of the formation of the Earth-Moon system.

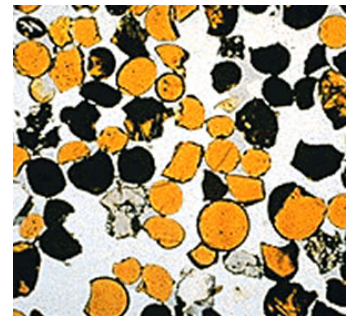


Figure 4: Microscope image of orange glassy beads and black ilmenite grains from a Apollo 17 soil sample.

(2) The surfaces of the small glassy beads are covered by thin layers that are enriched in economically interesting elements, including gallium, lead, potassium, sodium, and zinc. Because dark mantle deposits are fine-grained and well-sorted they would be relatively easy to mine, with elements relatively easily extractable through heating. Ilmenite-rich lunar dark mantle deposits like the ones sampled by Apollo 17 are currently being considered as a source of iron and titanium metal as well as oxygen, which could be used as building material, life support or rocket fuel for a future lunar base. Another resource that could be extracted from dark mantle deposits in the future include Helium-3 (a promising fuel for nuclear fusion reactors on Earth).

Since their initial discovery, minor amounts of dark mantle deposits have been identified in lunar soil samples from all Apollo missions, and over 20 compositional types have now been identified. However, despite 37 years of research, it is still not known how representative these samples are for the Moon as a whole. Several fundamental questions remain unanswered: How variable are the glassy bead compositions, and what does this tell us about the composition and evolution of the lunar interior? Do other mantle deposits contain even higher concentrations of economically important elements? How does the glass-to-mineral ratio vary from deposit to deposit, and which minerals besides ilmenite are present?

As the MoonOne mission plans to land in the vicinity of dark mantle deposits, the combined Raman/LIBS instrument could provide unprecedented information about the chemical and mineralogical composition of the local mantle deposits, and by comparison with existing Apollo 17 samples, about the regional variability of these key resources. As volcanic material is formed by melting in the subsurface, constraining the composition of these dark mantle deposits has the potential to significantly advance our understanding of the composition and the evolution of the lunar interior. In summary, Extending the compositional and mineralogical database of dark mantle deposits and their immediate surroundings is therefore of great interest to both fundamental lunar science and applied lunar resource science.

A second major advantage of the proposed landing sites shown in Figure 3 can be found in the fact that the landing site will be near to several past landing sites. This allows for a unique validation of the Raman/LIBS instrument by comparing the Raman/LIBS measurements with mineralogical and compositional knowledge from samples returned to Earth by the Apollo 15 and 16 missions.

By comparing spectra obtained with Raman/LIBS with spectra obtained from measurements performed on the lunar samples that were brought to the Earth by the Apollo programme, Moon4You can provide an important contribution to the validation of the instrument on a planetary scale. Notably, such a validation has not been performed before for any micro-analytical space exploration instrument.

The validation experiment will increase confidence in the Raman/LIBS instrument for other future planetary missions as well as for terrestrial spin-offs of the instrument (see following section). A small disadvantage is that an equatorial landing site does not allow for the detection of water ice as a polar landing site is needed for this. However, Odyssey Moon's second lunar mission ('MoonTwo') is foreseen to go to the poles. By also accommodating the Raman/LIBS instrument on MoonTwo, information regarding the types and concentrations of water-containing minerals can eventually be provided.

7. COMMERCIAL APPLICATIONS OF RAMAN-LIBS MOON DATA

One of the interesting elements of the new Moon 2.0 programme is that the data from the instrument could be commercially exploited. We have defined two kinds of datasets which could be commercially interesting for third parties. The science data return from the instrument is one category. The second category is the engineering data from the instrument. The science data will be used by the science team to study the lunar regolith from a scientific point of view and they will provide level 2 data products. It is these data products which we intend to sell commercially to potentially interested parties such as: national science institutes, space agencies, commercial aerospace companies focusing on delivering hardware for future moon exploration and mining and building companies. Secondly, as the Raman-LIBS instrument is not only valuable for lunar research, but also for any other celestial body with a solid surface, the engineering data of the instrument can be used by space agencies to prepare for future spacecraft missions to the planets and moons of our solar system. Furthermore with this engineering data, the Technology Readiness Level of 9 can be proved and as such create a more reliable Raman/LIBS instrument for future planetary missions. With each new planetary mission we intend to sell the science and engineering data to interested parties and create a new business model in planetary exploration based on the commercialisation of scientific and engineering data.

8. THE RAMAN/LIBS ON-EARTH SPIN-OFFS

In literature many examples can be found using either Raman spectroscopy or LIBS for; e.g. the use for explosives detection, with residue detection of up to 45 metres [16], medical applications [17], as example disease recognition by Raman spectroscopy [18] and cancer diagnosis with LIBS [19]; for gas and oil exploration [20] and drug identification [21]. However, in non-laboratory conditions measurements are hassled by non-optimal conditions, e.g. background, dust, contamination and other external influences. Therefore, a supplementary experiment is leading to better results. In addition: for a given experiment, one of the two techniques is usually sufficient. Looking at an area of application, both experimental methods may be necessary, in order to get the complete picture. As an example: while explosives are generally identifiable by Raman spectroscopy, biological, chemical and nuclear samples are better classified with LIBS. Or on the other hand carbon hydrates are distinguishable by Raman experiments, while sulphur and/or lead are better recognised with LIBS.

9. CONCLUSIONS

The ongoing new Space revolution opens up possibilities for our combined Raman/LIBS instrument to support future exploitation of material resources from celestial bodies such as our Moon and nearby asteroids. A Letter Of Intent (LOI) for a launch opportunity early 2012 on-board Google Lunar X PRIZE competitor and leading Lunar transport business Odyssey Moon has been signed, and will yield both interesting science and space qualification of our instrument. In parallel, we pursue a wide range of applications for compact combined Raman/LIBS instrumentation. Typical applications are: explosives detection, medicine quality and forensic research.

REFERENCES

- [1] Bazalgette Courrèges-Lacoste, G., B. Ahlers and F. Rull Pérez, *Spectrochimica Acta Part A*, 68, 1023-1028 (2007).
- [2] Escudero Sanz, I., B. Ahlers and G. Bazalgette Courrèges-Lacoste, *Optical Engineering*, 47(3), 033001, (2008).
- [3] Bazalgette-Courrèges Lacoste, G., B. Ahlers, E. Boslooper, F. Rull Pérez, S. Maurice, 6th Int. Conf. on Space Optics, ESA-ESTEC, Noordwijk (2006).
- [4] Ahlers, B., I. Hutchinson, R. Ingley, 7th Int. Conf. on Space Optics, CNES, Toulouse (2008)
- [5] Warren PH (2003) *Treatise on Geochemistry* 1, 559-599.
- [6] Wiechert U, Halliday AN, Lee D-C, Snyder GA, Taylor LA, Rumble D (2001) *Science* 294, 345-348.
- [7] Esat TM, Taylor SR (1999) *Int. Geol. Rev.* 41, 31.
- [8] R.B. Georg, A.N. Halliday, E.A. Schauble, B.C. Reynolds, *Nature* 447, 1102 (2007)
- [9] M. Humayun, R.N. Clayton, *Geochim. Cosmochim. Acta* 59, 2131 (1995)
- [10] M. Touboul, T. Kleine, B. Bourdon, H. Palme, R. Wieler, *Nature* 450, 1206 (2007)
- [11] Hartmann WK, Davis DR (1975) *Icarus* 24, 504-515.
- [12] Cameron AGW, Ward WR (1976) *Lunar Sci.* 7, 120-122.
- [13] Canup RM (2004) *Icarus* 168, 433-456.
- [14] Williams DM, Pollard D (2000) In *Origin of the Earth and Moon* (Eds. R. M. Canup and K. Righter), pp. 513-525, Univ. Arizona Press, Tucson.
- [15] Boyet M, Carlson RW (2005) *Science* 309, 576-581.
- [16] López-Moreno, C., et al, *J. Anal. At. Spectrom.*, 21, 55-60 (2006).
- [17] Ellis, E.I. and R. Goodacre, *Analyst*, 131, 875-885 (2006).
- [18] Krafft, C., G. Steiner, C. Beileites, and R. Salzer, *J. Biophoton.* 2, 1-2, 13-28 (2009).
- [19] Kumar, A., F-Y. Yueh, J. Singh, S. Burgess, *Applied Optics*, 43, 28, 5399-5403 (2004).
- [20] Shoute, L. C. T, K. J. Schmidt, R. H. Hall, M. A. Webb, S. Rifai, P. Abel, P. H. Arboleda, A. Savage, J. T. Bulmer, and G. R. Loppnow, *Applied Spectroscopy*, 56, 10, 1308-1313 (2002).
- [21] Hargreaves, M.D., K. Page, T. Munshi, R. Tomsett, G.L. and H. G. M. Edwards, *J. Raman Spectrosc.* 39: 873-880 (2008).