UPDATE ON DEVELOPMENT OF THE POTASSIUM-ARGON LASER EXPERIMENT (KARLE) INSTRUMENT FOR IN SITU GEOCHRONOLOGY.

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Introduction: Absolute dating of planetary samples is an essential tool to establish the chronology of geological events, including crystallization history, magmatic evolution, and alteration. We are addressing this challenge by developing the Potassium (K) – Argon Laser Experiment (KArLE) under the NASA Planetary Instrument Definition and Development Program (PIDDP), building on previous work to develop a K-Ar in situ instrument [1]. KArLE ablates a rock sample, determines the K in the plasma state using laser-induced breakdown spectroscopy (LIBS), measures the liberated Ar using quadrupole mass spectrometry (QMS), and relates the two by the volume of the ablated pit using laser confocal microscopy (LCM). Our goal is for the KArLE instrument to be capable of determining the age of several kinds of planetary samples to address a wide range of geochronology prolems in planetary science.

Under the current PIDDP funding cycle (through 2014), we have constructed a full breadboard of the KArLE concept. This prototype is intended to verify the measurement capabilities and performance, and to conduct trades in implementation, to bring the concept to TRL 4. For this breadboard, we are using commercial off-the-shelf parts with performance similar to flight instruments (MSL ChemCam and SAM [2, 3]). The same COTS components are currently used in our collaborators' laboratories for low-cost testing for their flight instruments (Ocean Optics LIBS in the LANL LIBS laboratory; Hiden RGA in the GSFC mass spectrometer laboratory).

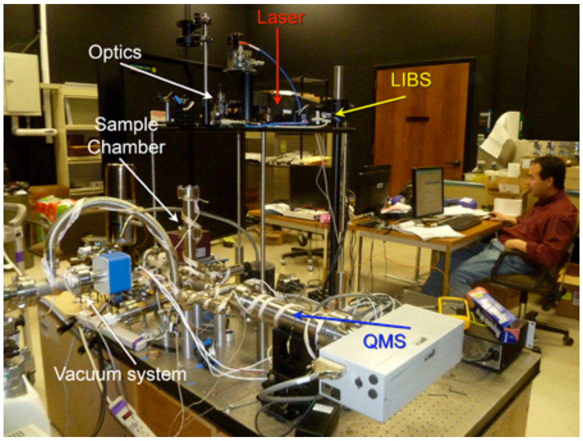

Fig. 1 KArLE breadboard, with integrated QMS and LIBS.

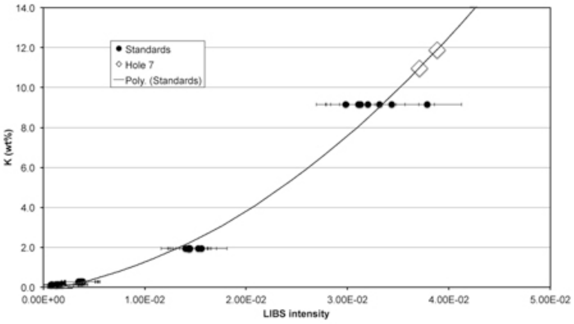

Fig. 2. Initial LIBS calibration curve for KArLE and preliminary analyses of the Fish Canyon Tuff standard (Hole 7).

KArLE Progress: The LIBS and QMS are currently integrated into a single test chamber (Fig. 1) and we have defined an operational procedure. We are calibrating both the LIBS and QMS using samples of established composition and noble gas content. We have also acquired LIBS and QMS measurements on microcline and rhyolite samples to verify the testbed instruments' performance in the breadboard configuration.

The relationship between the LIBS emission and the elemental abundance is specific to the laboratory setup and depends on viewing geometry, depth of the ablated pit, material properties, ambient pressure, etc. [5]. We calibrated our LIBS K abundance curve at pressures between 10^{-7} and 10^{-9} torr using Brammer pressed powdered standards spanning a range of K_2O content (Fig. 2). Unfortunately, the calibration curve at K abundances greater than 1-2% is underconstrained due to the lack of standards available; we are currently pursuing alternative standards.

The performance of quadrupole mass spectrometers has improved over the last two decades to the extent that they have demonstrated utility in some geochronologic applications [6]. By having a low-volume, bakeable test chamber (~1L), we have been able to achieve mass spectrometer backgrounds in the 10^{-11} torr region that enable us to measure small amounts of gas evolved by LIBS ablation using either the Faraday cup or the electron multiplier on the QMS (Fig. 3). We have calibrated our Faraday response function using known aliquots of Ar dispensed through a calibrated Dorflinger pipette.

To relate the absolute QMS and relative LIBS measurements to each other, KArLE measures the volume of the ablated material and converts it to mass via an assumed density, which for the majority of planetary samples is acceptable without introducing signifi-

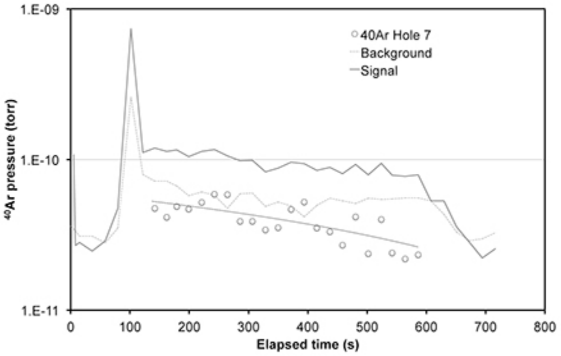

Fig. 3. QMS response at mass 40 to liberated gas from LIBS ablation. 300 LIBS shots were fired over 30 s at t=100s, causing the transient pressure spike. The data were extrapolated back to the abundance at t=100.

cant uncertainty. There are many possible methods to measure the pit volume pit without the physical contact of a probe; after evaluating scanning electron microscopy, phase shifting interferometry, and vertical scanning interferometry, we are currently using confocal laser microscopy with a long-working-distance objective (Fig. 4).

We recently began work on the Fish Canyon Tuff, a well-characterized Ar dating standard [4], to verify we are on track to meet KArLE goals. For this natural sample, we polished one face to provide a reference surface for the microscopy work, then inserted the sample into the test chamber and collected simultaneous LIBS and QMS measurements. We then removed the sample to the laser confocal microscope for pit volume analysis. Our preliminary results yield a K concentration of 8-10 wt% and a ^{40}Ar yield of 5×10^{15} mol for 500-μm diameter pits (200 laser shots). These measurements yield ages within 25% of the accepted Fish Canyon Tuff age of 28 Ma. The largest sources of uncertainty at this point are related to procedural blanks and calibration curves, which are sparse. We expect to greatly improve on this value in the next year in three ways: a) eliminating procedural uncertainties by better characterizing and standardizing our workflow, backgrounds, and blanks; b) reducing the measurement uncertainties by improving our calibration curves and finding the “sweet spots” for simultaneous measurements, and c) collecting multiple measurements per rock to construct isochrons [7].

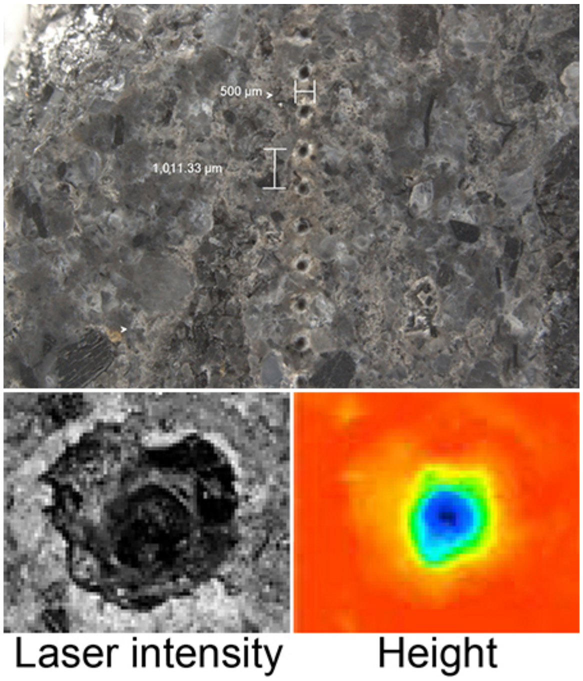

Fig. 4. (top) Optical image of a series of 10 LIBS ablation pits in Fish Canyon Tuff. (bottom) Concurrently measured laser return and depth profile (red=shallow; blue=deep) of Hole 7 (field of view ~500μm).

Upcoming work: In the next year of KArLE development, we intend to explore an extensive matrix of testing conditions to understand the complex effects of pressure, temperature, composition, sample preparation sample alignment, etc. on the KArLE measurements. We plan to integrate the laser confocal microscope into the LIBS-QMS test rig to be able to take all measurements on the same in situ spot with before-and-after imaging capability. Finally, we will create a flightlike design for the KArLE instrument that we will be able to propose for further development.

Summary: The KArLE instrument concept uses flight-heritage components combined in a novel way to make in situ noble-gas geochronology measurements. Additional benefits derive from the fact that each KArLE component achieves analyses common to most planetary surface missions. The dual-use components make KArLE a highly attractive way to integrate geochronology into a payload capability. The flight heritage and breadboard measurements already suggest that the finished instrument will be able to fit on landers and rovers to Mars, the Moon, asteroids, Mercury, outer planet satellites – indeed, any rocky surface. Flight opportunities in planetary science for the KArLE instrument include Curiosity 2020, Discovery, New Frontiers, and Flagship missions.

References: [1] Swindle, T. D., et al. (2003) *LPSC* **34**, #1488. [2] Wiens R.C. et al. (2012) *Space Sci. Rev.* **170**, 167–227. [3] Mahaffy et al. (2012) *Space Sci. Rev.* **170**, 401–478. [4] Lasue, J., et al. (2012), *JGR* **117**, doi:10.1029/2011JE003898. [5] Renne et al. (2010) *Geochim. Cosmochim. Acta* **74**, 5349–5367. [6] Schneider, B., et al. (2009) *Quaternary Geochronology* **4**, 508-516. [7] Bogard, D.D. (2009) *MAPS* **44**, 3-14.