DEVELOPMENT OF THE POTASSIUM-ARGON LASER EXPERIMENT (KArLE) INSTRUMENT FOR IN SITU GEOCHRONOLOGY. B. A. Cohen[1], Z.-H. Li[1,2], J. S. Miller[1,3], W. B. Brinckerhoff[4], S. M. Clegg[5], P. R. Mahaffy[4], T. D. Swindle[6], and R. C. Wiens[5]. [1]NASA Marshall Space Flight Center, Huntsville AL 35812 (Barbara.A.Cohen@nasa.gov), [2]University of Alabama Huntsville, Huntsville AL 35805; [3]Qualis Corporation, Jacobs ESTS Group, Huntsville AL 35806; [4]NASA Goddard Space Flight Center, Greenbelt MD 20771; [5]Los Alamos National Laboratory, Los Alamos NM 87545; [6]University of Arizona, Tucson AZ 85721.

Introduction: Absolute dating of planetary samples is an essential tool to establish the chronology of geological events, including crystallization history, magmatic evolution, and alteration. Traditionally, geochronology has only been accomplishable on samples from dedicated sample return missions or meteorites. The capability for *in situ* geochronology is highly desired, because it will allow one-way planetary missions to perform dating of large numbers of samples. The success of an in situ geochronology package will not only yield data on absolute ages, but can also complement sample return missions by identifying the most interesting rocks to cache and/or return to Earth. *In situ* dating instruments have been proposed, but none have yet reached TRL 6 because the required high-resolution isotopic measurements are very challenging.

Our team is now 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 uses a combination of several flight-proven components that enable accurate K-Ar isochron dating of planetary rocks. KArLE will ablate a rock sample, determine the K in the plasma state using laser-induced breakdown spectroscopy (LIBS), measure the liberated Ar using quadrupole mass spectrometry (QMS), and relate the two by the volume of the ablated pit using an optical method such as a vertical scanning interferometer (VSI). Our preliminary work indicates that the KArLE instrument will be capable of determining the age of several kinds of planetary samples to ±100 Myr, sufficient to address a wide range of geochronology problems in planetary science.

The KArLE Concept: The K-Ar isochron approach is a relatively simple, and therefore more feasible approach for in situ geochronology. K is far more abundant in typical rocks than U, Rb or Sm, so it is readily detectable. The daughter Ar has a different physical state than the parent K, so the mass spectrometer component does not need to measure isobaric species. Finally, Ar diffuses less readily than He, so is more likely to be retained for a long time within a planetary surface rock. All of these attributes enable the K-Ar system to achieve desirable measurement accuracy using currently-available flight components and techniques.

The KArLE instrument will leverage these advantages using an end-to-end concept nearly identical to the laser (U–Th)/He dating technique in use in terrestrial laboratories [2]. In this technique, U and Th are measured with conventional

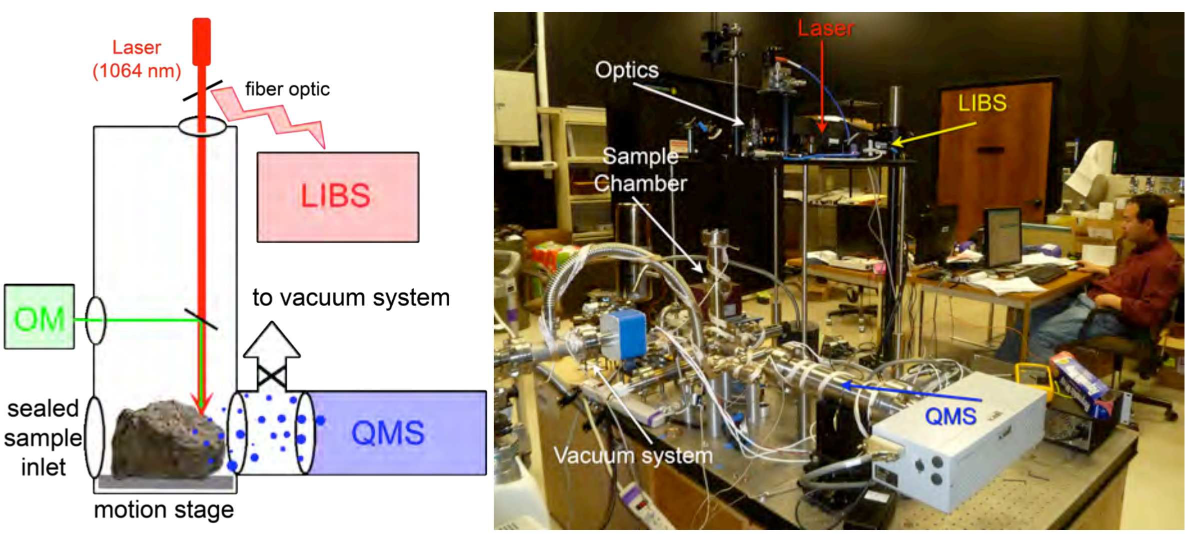

Figure 1: KArLE operational schematic and laboratory setup. LIBS = Laser-Induced Breakdown Spectroscopy; OM = Optical Method; QMS = Quadrupole Mass spectrometer. See text for more details on the specific components.

microanalytical techniques, such as electron microprobe, to determine their abundance by weight. The sample is then ablated with a laser in a UHV system to release He, whose absolute abundance is measured by magnetic-sector mass spectrometry. The relative and absolute measurements are related by precise measurement of the ablation pit using optical methods such as vertical scanning interferometry. The KArLE instrument largely follows this concept, but streamlines it by using the plasma generated by laser ablation to measure K, followed by measurement of evolved Ar by static mass spectrometry and relating the two using optical interferometry (Fig. 1). This slight change also allows both K and Ar to be measured on an identical spot on the rock, enabling an isochron to be developed to improve the age determination and revealing irregularities in the rock if they exist.

In the LIBS method, a pulsed laser beam is focused on a target to ablate a small mass of material, forming a plasma. In the high temperature of the plasma, the atoms are electronically excited to emit light. Elements in the target sample are identified by collecting, spectrally resolving, and analyzing the plasma emission, and their abundance is related to the peak height. The advantages of using LIBS for KArLE are the absence of sample preparation and the liberation of daughter Ar in the plasma. The KArLE LIBS follows advances in development of LIBS for a variety of in situ planetary applications, including the ChemCam instrument on the Mars Science Laboratory [3, 4].

Laboratory noble-gas measurements are traditionally accomplished by magnetic sector mass spectrometers. It is infeasible for flight instruments to use this magnetic sector instruments because of the large mass and power required by the high voltage and strong magnetic fields; instead, missions typically use quadrupole mass spectrometry. QMS techniques typically have lower sensitivity but their mass and power attributes are well-suited to in situ applications. Recent advances, especially improvements in resolution, have increased the performance of these instruments to the extent that they have demonstrated utility in some geochronologic applications [5]. The KArLE mass spectrometer draws on neutral mass-spectrometer instruments developed for several planetary missions (CONTOUR, MSL, LADEE) at Goddard Space Flight Center.

It is necessary to relate the absolute QMS and relative LIBS measurements to each other. Laser U-He measurements accomplish this by measuring the volume of the ablated material and converting it to mass via an assumed density, which for the majority of planetary samples is acceptable without introducing significant uncertainty. There are many possible methods to measure the pit volume pit without the physical contact of a probe, including scanning electron microscopy, phase shifting interferometry, and vertical scanning interferometry. We are evaluating the applicability of these methods to the LIBS and QMS setup to achieve the desired measurements.

Both first-principle analysis and model isochrons [6] show that a 10% measurement uncertainty coupled with a factor of 2 spread in K content among samples will be sufficient to achieve meaningful dates on lunar and Martian rocks. In most natural rocks, radiogenic isotopes are found in higher amounts in accessory minerals such as K-feldspar and phosphates, compared with the bulk silicates (olivine, pyroxene, feldspar). Therefore, analyzing tens of individual points on the whole rock will ensure that varying amounts of these accessory minerals are measured. Using published uncertainties for the measurement components (10% relative for the LIBS and QMS, and 2% for VSI), we believe that an accurate age with a precision of ±100 Myr is achievable with this method.

Applications: The geochronology instrument must be integrated into a suite of other instruments and measurements to give the rock context. Appropriate measurements include remote sensing for geologic setting, imaging and microscopic imaging for petrology, and microanalytical techniques for chemical

Table 1. KArLE measurement requirements and component performance.

Measurement Requirement		Breadboard Component Performance	Flight Component Performance
K		Ocean Optics LIBS	MSL LIBS (ChemCam, without telescope optics)
Spectral range (nm)	760-780	725-820	240-800
Spectral Resolution (nm)	1	0.1	0.09-0.3
Ar		Hiden RGA	MSL QMS (SAM component)
Mass Range (Da)	2-40	1-50	2-535
Mass Resolution (Da)	1	1	<1
Sensitivity (cps/mol)		6.03E+17	1E+18
Pit volume		Keyence VK-X200 Laser Confocal Microscope	Phoenix Atomic Force Microscope (MECA component)
Field of view (μm)	1000x1000	3308×2506	2000x1000
Depth of view (μm)	1000	10,000	50
Resolution (μm)	TBD	0.5-3.67	0.25

and mineralogic composition and variation. The instruments for making these measurements are expected to be present on any lander or rover as part of a standard measurement suite. However, the KArLE components themselves achieve many of these common analyses as well (e.g. full elemental characterization via LIBS, microscopic imaging via the optical component).

Secondly, measurements must be made with as much contextual information about the sample's location, composition, and properties as possible to ensure that the fundamental dating assumptions are valid, namely that the samples forming the isochron are cogenetic and that the system is closed.

Finally, the measurement must generate an age that enables a geologic interpretation that clearly improves upon current knowledge. Many problems in geochronology require the resolution and sensitivity of a terrestrial laboratory and therefore cannot be solved by in situ instrumentation. However, many fundamentally important objectives on the Moon, Mars, and other rocky bodies could be met with an approach that yields ages with ± 100 Myr precision.

Lunar volcanism. The relationship between basalt composition, location and age is crucial in understanding the nature of lunar magmatism. In the absence of sample return, our only way of understanding the ages of these rocks is via crater-counting techniques on orbital images. Recent missions have enabled discovery of basaltic units with crater-count ages as young as 1.2 Ga, including those in Oceanus Procellarum, the Aristarchus Plateau and Mare Moscoviense on the lunar far side [7, 8]. These young basalts are unknown in the returned sample collection but may be a clue to the origin of some lunar basaltic meteorites such as Kalahari 009 and NEA 003 [9]. Obtaining the age and composition of a young basalt flow and tying this information to the crater count and composition is therefore a desirable measurement.

Lunar impact history. The lunar crater record provides the baseline with which we calibrate the absolute ages of all cratered surfaces in the inner solar system. While the lunar crater curve is well-bounded between ~1 and ~4 Ga, the curve on the older and younger ends is poorly constrained. The most important candidate on the Moon for absolute dating is the South Pole-Aitken (SPA) basin. It is the largest, deepest, and stratigraphically oldest impact basin on any terrestrial planet. Though determining the SPA basin age from gardened regolith may require very highly precise dates on hundreds of samples [10, 11], in situ dating of younger basins within SPA, such as Apollo and Ingenii, with an uncertainty of ±100 Ma would be useful bounds on SPA itself and on the subsequent impact history of the far side.

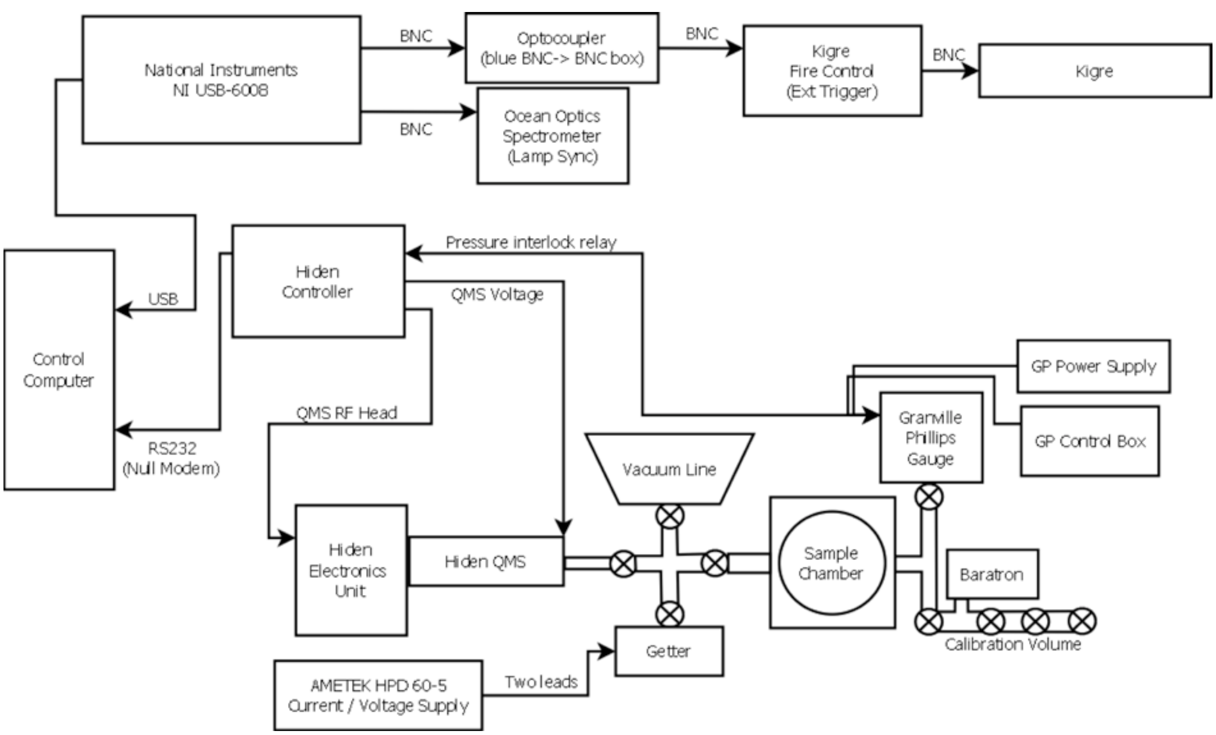

Figure 2. KArLE QMS/LIBS breadboard schematic (see Fig. 1 and Table 1 for component definitions).

Martian terrains. The absolute ages of Mars's geological events, and thus the time history of the planet's evolution, will not be fully understood until the relative Martian chronology derived from stratigraphy is tied to an absolute chronology via radiometric dating of Martian rocks. Absolute ages of Martian surface units are uncertain by as much as a factor of two on older surfaces [12] and disagreements can be an order of magnitude or more on younger, lightly-cratered surfaces [13]. In situ age dating with an uncertainty of ±100 Ma would be a significant improvement, especially for sites in middle Mars history (late Hesperian through mid-Amazonian).

Development: 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 parts (Table 1). These COTS parts 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).

We have integrated LIBS and mass spectrometry into a single test chamber (Fig. 1, Fig. 2) and have defined an operational procedure. We acquired LIBS and QMS measurements on microcline and rhyolite samples to verify the testbed instruments' performance, showing that they meet our initial estimations (Fig. 3, Fig. 4). We are currently calibrating both the LIBS and QMS on samples of

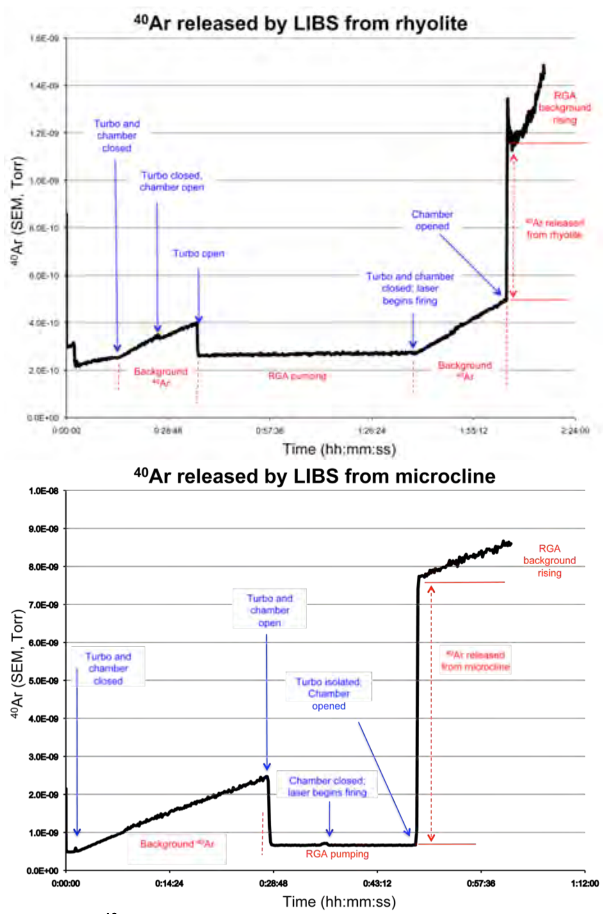

Figure 2. ^{40}Ar abundance in microcline and rhyolite test samples. The QMS was set in multiple ion detection mode using the secondary electron multiplier and continuous measurements were collected during the LIBS measurements. ^{40}Ar buildup from background is small compared to the amount released from the sample. The microcline measurement is the total release from 200 laser shots and the rhyolite from 370 laser shots.

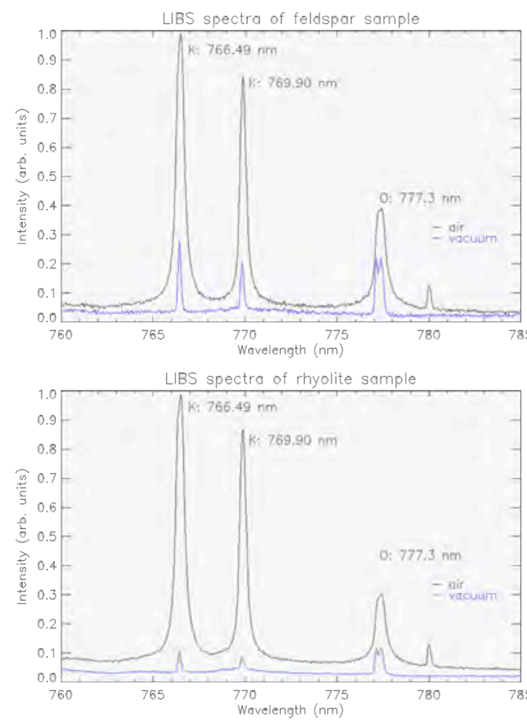

Figure 4. LIBS spectra of microcline and rhyolite test samples showing K and O peaks (the oxygen peak is a triplet with a maximum intensity at 777.3 nm). Sample spectra in air were acquired with 100 shots each. The feldspar spectrum in vacuum (1.7E-07 torr) was acquired with 200 shots, and the rhyolilte spectra in vacuum with 370 shots. Each spectrum was acquired individually and averaged during postprocessing. Backgrounds were taken each day consisting of at least 100 blank runs and averaged, then subtracted from the averaged sample spectra. LIBS signal intensity varies with confining pressure; at Mars pressure, the intensity is greater than in terrestrial atmosphere, but as pressure decreases further the signal intensity diminishes. However, even under the high vacuum conditions of the Moon, the signal is clearly differentiated from background and measurements can be made with confidence [14].

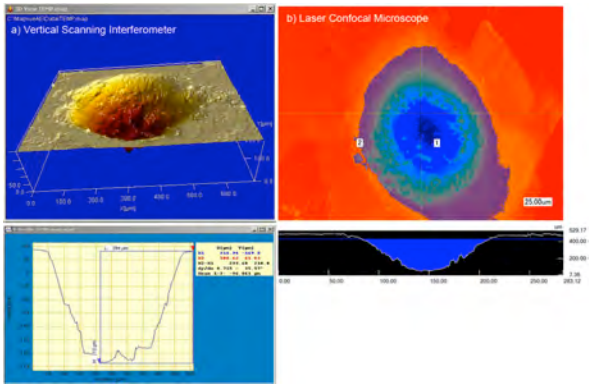

Figure 5. Volume of ablation pits using vertical scanning interferometry (left) and laser confocal microscopy (right). These measurements were acquired using two different optical methods on samples different from the LIBS/MS samples so are not directly comparable. However, they show the suitability of both methods for measuring pit volume.

established composition and noble-gas content.

Our PIDDP proposal envisioned Vertical Scanning Interferometry as the optical solution for KArLE, based on laboratory experience. However, examination of competing instrument requirements and eventual flight needs rule out VSI, particularly the need for vibration isolation and extremely close proximity to the sample surface (2-3 mm). Therefore, we are conducting trades on existing optical methods to evaluate their accuracy and precision as possible solutions, with a long-working-distance laser confocal microscope having good potential (Fig. 5). Development of this component also needs to include software development to co-register images and calculate volume via optical methods as well as experimental design to integrate the chosen method integration into the LIBS/QMS testbed.

Later this calendar year, we expect to have completed an end-to-end test of all components on a sample of known age and composition and proceed to exploring an extensive matrix of testing conditions to understand the complex effects of pressure, temperature, composition, sample preparation sample alignment, etc. on the KArLE measurements. Finally, we will use the experience to design a flight system that we will propose for further development.

Summary: The potassium (K) – argon (Ar) Laser Experiment (KArLE) instrument concept uses flight-heritage components combined in a novel way to make in situ noble-gas geochronology measurements. The KArLE instrument is currently at TRL 2. Our PIDDP funding is expected to bring the instrument to TRL 4 by 2014, demonstrating the ability of our concept to make measurements with sufficient precision and accuracy to meet scientific goals. Additional benefits derive from the fact that each KArLE component achieves analyses common to most planetary surface missions. For example, the surface textures of the rock may be of interest, or additional optics could be added to the VSI to make it a true microimager. LIBS provides a complete elemental analysis of the rock, which is a fundamental analysis. The QMS could also be used for volatile-element analysis if plumbed to other sample inlets. The dual-use components make KArLE a highly attractive way to integrate geochronology into a payload capability rather than dedicated isotopic instruments. The flight heritage of the KArLE components strongly suggests that the finished instrument will be able to fit on rovers as well as landers and the operational concept is applicable to Mars, the Moon, asteroids, Mercury, outer planet satellites – indeed, any rocky surface. Flight opportunities in planetary science for the KArLE instrument include Discovery, New Frontiers, and Flagship missions, as well as any future directed mission such as Mars sample return or human precursor missions, and additional opportunities may arise as Missions of Opportunity on international missions to these destinations.

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