Development of the Potassium-Argon Laser Experiment (KArLE) for In Situ Geochronology. B. A. Cohen, NASA Marshall Space Flight Center, Huntsville AL 35812

Introduction: Absolute dating of planetary samples is an essential tool to establish the chronology of geological events, including crystallization history, magmatic evolution, and alteration. Thus far, radiometric geochemistry of planetary samples has only been accomplishable in terrestrial laboratories on samples from dedicated sample return missions and meteorites. In situ instruments to measure rock ages have been proposed, but none have yet reached TRL 6, because isotopic measurements with sufficient resolution are challenging.

We have begun work under the NASA Planetary Instrument Definition and Development Program (PIDDP) to develop the Potassium (K) – Argon Laser Experiment (KArLE), a novel combination of several flight-proven components that will enable accurate K-Ar isochron dating of planetary rocks. KArLE will ablate a rock sample, measure 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 measuring the volume of the ablated pit using a optical methods 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 geochemistry problems in planetary science. Additional benefits derive from the fact that each KArLE component achieves analyses common to most planetary surface missions.

The KArLE Concept: The K-Ar isochron approach is an extremely promising one for in situ geochronology. K is far more abundant in typical rocks than U, Rb or Sm so is readily detectable. The daughter Ar has a different physical state than parent K, so the mass spectrometer component does not need to measure isobaric species. Finally, Ar is less readily diffused than He. 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 [1]. In this technique, U and Th are measured with conventional 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 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. 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 reveals irregularities in the rock if they exist.

In the LIBS method, a laser pulse is focused on a target to ablate a small mass of material and to form a microplasma above the surface. 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 light, and their abundance is related to the peak height. The advantages of using LIBS for KArLE is the absence of sample preparation and the liberation of daughter Ar in the plasma pulse. The KArLE LIBS follows advances in development for a variety of uses by collaborators Roger Wiens and Sam Clegg at Los Alamos National Laboratory (LANL), including in the ChemCam instrument on the Mars Science Laboratory [2, 3].

Laboratory noble-gas measurements are traditionally accomplished by magnetic sector mass spectrometers. However, flight instruments cannot use this technique because of the large mass and power required by the high voltage and magnetic field involved, and instead typically use quadrupole mass spectrometry. QMS techniques typically have lower sensitivities 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 [4]. The KArLE mass spectrometer draws on neutral mass-spectrometer instruments developed for several planetary missions (CONTOUR, MSL, LADEE) at Goddard Space Flight Center under collaborators Paul Mahaffy and Will Brinckerhoff.

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 ability of these methods to work with the LIBS and QMS setup to achieve the desired measurements.

Both first-principle analysis and model isochrons [5] 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 and mineralogic composition and variation. These 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. Furthermore, 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 [6, 7]. 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 [8]. 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 [9, 10], 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.

**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 [11] and disagreements can be an order of magnitude or more on younger, lightly-cratered surfaces [12]. 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).