LEAD-LEAD AND RUBIDIUM-STRONTIUM IN SITU DATING USING THE CHEMISTRY, ORGANICS, AND DATING EXPERIMENT (CODEX)

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Introduction: We have continued to develop the Chemistry, Organics, and Dating EXperiment (CODEX) instrument, improving the TRL of the instrument subsystems, and extended previously published Rb-Sr dating [1, 2] to Pb-Pb dating. Our instrument uses laser-ablation (LA) to remove atoms at each of hundreds of analytical spots on a ~1 cm^2 sample, and resonance ionization (RI) to selectively ionize atoms of Pb, Rb, and Sr, thereby mitigating isobaric interferences, followed by mass spectrometry (MS) to determine the abundance of individual isotopes [1]. From our measured isotopic abundances, we are able to construct Pb-Pb and ^{87}Rb-^{87}Sr isochron for the specimen. In addition, we have previously demonstrated that we can measure elemental and organic abundance, using simpler CODEX modes of laser ablation and two-step laser mass spectrometry, respectively [e.g., 3].

Importance: Understanding the relative timing of geologic events using crater counting is the keystone to unraveling the history recorded on the surfaces of rocky bodies. Crater counts, in conjunction with radiometrically-dated Apollo and Luna samples, have been used to estimate the absolute ages of events on the Moon [4]. The resulting cratering flux has been extrapolated to Mars [5], Mercury [6, 7], Venus [8], Vesta [9-11], and used in models of early solar system dynamics [12].

However, recent analysis [13] indicates three major complications to the crater chronology picture: a) crater-counted terrains may not be the sources of dated samples, b) there is a need to extrapolate crater count relationships to very young and old terrains, and c) there is a two-billion year gap of samples with well-known provenance suitable for crater counting from 1 to 3 Ga (**Fig. 1**).

These problems result in billion-year uncertainties for the history of the Moon [13] and solar system. For example, the era of bombardment of the inner solar system, as recorded by lunar impacts, may have effectively ended ~3.7 Ga ago or at some younger time. Because life on Earth is thought to have arisen between ~3.7 and ~3.0 Ga ago, the model improvement could reveal new insights about the habitability of the early Earth. Similarly, the era of liquid water on the Martian

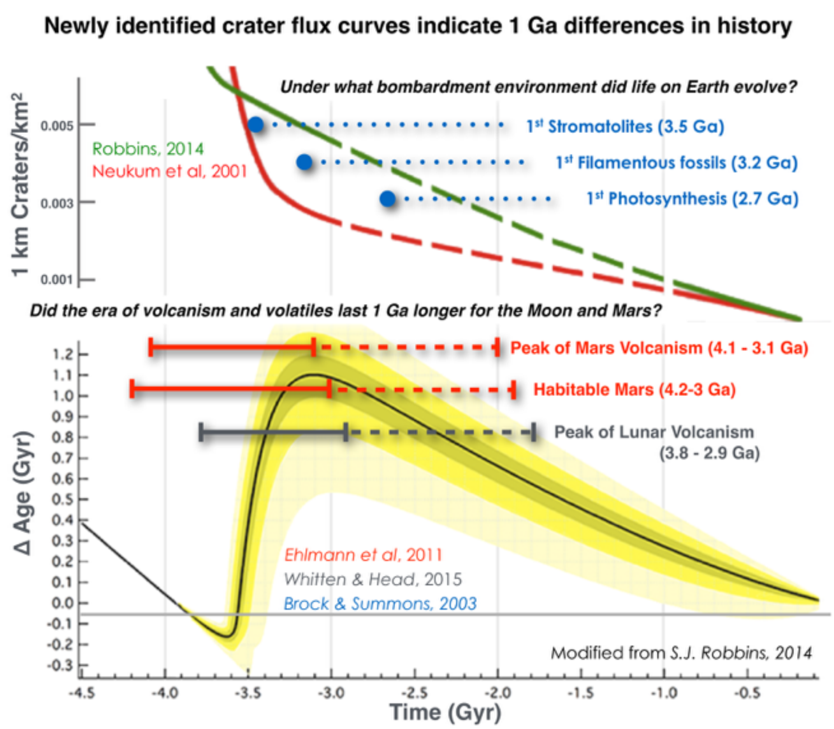

Fig. 1: Illustration of how poorly constrained lunar chronology functions, with up to 1 Ga of uncertainty, influence interpretation of key geologic events for the Moon, Mars, and even Earth.

surface, which is intimately related to possible life on Mars, as well as the eras of voluminous volcanism on the Moon and Mars, might have ended ~3 Ga ago or extended to as recently as ~1.7 Ga ago.

Thus, obtaining new dates from the surfaces of Mars or the Moon are crucial to revealing which of these models of solar system history is correct. To understand the range of terranes and history on another planet will require obtaining samples with a wide geographic distribution. This likely means multiple missions, which due to cost constraints, will need to be comprised of both sample return and in-situ measurements. Fortunately, CODEX provides two chronometry systems, and maps of elemental abundance, enabling us to place measurements in mineralogical and petrological context. Previously published results show that we can readily obtain precision and accuracy better than 200 Ma for the Martian meteorite Zagami [2], and the lunar analog Duluth Gabbro [1]. Our new measurements described below illustrate how CODEX can measure a second independent geochronometer.

New Pb measurements: By adding two lasers to the CODEX system, we can use the LARIMS approach to obtain ~10 ppb sensitivity in isobar-free measurements of ^{204}Pb, ^{206}Pb, ^{207}Pb, and ^{208}Pb. We used wavelengths of 283.3 nm and 600.2 nm for resonance excitation, followed by IR photoionization. These in turn can be used to assess the isochron age of samples. We tested our approach on the Kuehl Lake 91500 Zircon and MIL 05035. The results were in excellent agreement with the known ages, being within 80 Ma of previous measurements **(Fig. 2-3)**.

Progress on instrument development: Under MatISSE 2014 funding, we are currently miniaturizing the Sr and ablation laser subsystem using an all-fiber approach, and are actively working to reduce the overall instrument. In addition, we are in preliminary design and development for the mass spectrometer and sample handling.

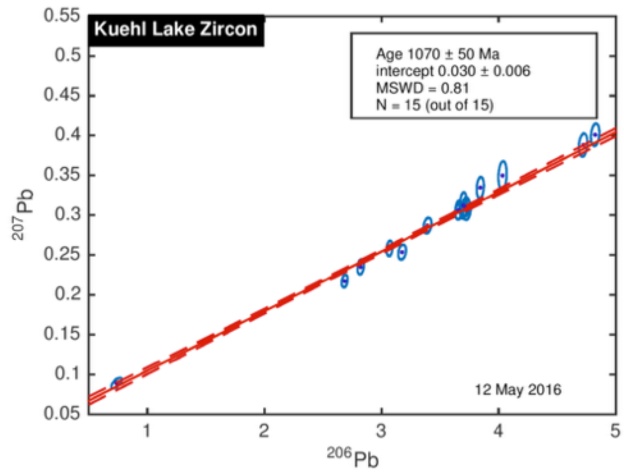

Fig. 2: LARIMS isochron of Zircon Sample. Actual age is 1.067 Ga.

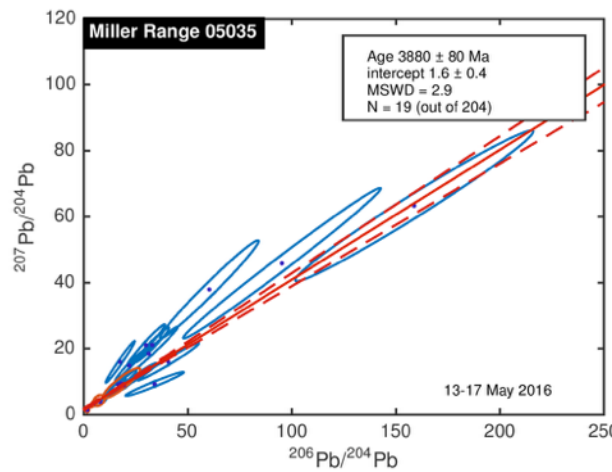

Fig. 3: LARIMS isochron for MIL-05035. Because of the low concentration of Pb in this sample (0.405 ppm) only 19 points out of 204 that we analyzed had adequate signal-to-noise to be used in the isochron. The actual age is between 3.8 and 3.9 billion years.

References:

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