THE CASE FOR IN-SITU DATING IN GEOLOGIC CONTEXT FOR THE MOON AND MARS USING THE CHEMISTRY, ORGANICS, AND DATING EXPERIMENT (CODEX). F. S. Anderson[1], T. J. Whitaker[1], and J. L. Levine[2], [1]Southwest Research Institute, 1050 Walnut St, Boulder CO; anderson@boulder.swri.edu, [2]Colgate University, Hamilton, NY 13346.

Introduction: The Chemistry, Organics, and Dating EXperiment (CODEX) addresses two of the most important goals of planetary science, specifically for Mars and the Moon: identifying evidence of non-terrestrial organics, and understanding the history and duration of events in the solar system, in order to place the evolution of life, and humanity, in context [1].

The first goal, focussing on potential biosignatures and habitable environments, is key to understanding our place in the solar system, the galaxy, and the universe. The second goal, dating, may appear to be relatively low priority; after all, the geologic history of solar system builds on an extensive record of impact flux models, crater counts, and ~270 kg of lunar samples analyzed and dated in terrestrial labs. However, the impactor flux estimates may be biased by fact that the Apollo samples were mostly collected out of their original geological contexts, or were tenuously connected to an assumed context. Moreover, it is difficult in many cases to relate a "terrain age" defined by crater counts to any particular geologic event. For example, if the "North Ray" sampled by the Apollo 16 astronauts is not ejecta from the Nectaris impact as proposed by Stöffler et al. [2], the existence of the Late Heavy Bombardment (LHB) throughout the inner Solar System becomes uncertain [3, 4]. Furthermore, these uncertainties are significant enough to lead to estimated errors in lunar age exceeding 1 Ga [5]; specifically, ~3.5 Ga terrains may be 1.1 Ga younger. For other solar system bodies such as Mars, the main uncertainty "...is the ratio of Mars to moon impact rates", which results in "...absolute ages on Mars [that] are only good to a factor of 2 to 4" [6]. For example, the range in estimated terrain age for the Amazonian period varies by nearly 700 Ma, not including the potential uncertainty of 1.1 Ga from the Moon [7-11]. The need for cratering rates as much as 4X higher than previously modeled is consistent with recent modern cratering rates observed on Mars by the High Resolution Imaging Science Experiment (HiRISE) instrument [12]. Finally, recent studies show that different crater counting methods can lead to significant biases [13].

Importance: These issues can lead to important changes in our understanding of the history of the solar system, and and hence the environment within which life evolved. For example, if new lunar crater counts based on better high resolution imaging derived from the Lunar Reconnaissance Orbiter Camera (LROC) are accurate, then numerous consequences arise, including (1) the extension of the era of volcanism on the Moon and Mars by up to 1.1 Ga, (2) extending the end of the era of water on Mars by up to ~500 Ma, and (3) that life arose on Earth not during a period of impact rate diminution, but instead during a period of active bombardment. Following previous work, refinements in cratering flux will furthermore be propagated to Mercury [e.g., 14, 15], Venus [e.g., 16, 17, 18], Earth (where the record of ancient impacts has been erased by erosion and plate tectonics [19]), and models of early solar system dynamics [20].

Approaches: There are two complimentary approaches to improving our current understanding of solar system history. The first is the return of samples for in-/organic analysis and dating on Earth using the exquisite precision and range of current and future laboratory instruments. However, a key problem is the need to sample a wide range of terrains, requiring many sample returns. After all, Apollo will likely remain the best sample return mission ever, yet the most important decadal survey goals for the Moon focus on the obtaining more samples for dating [1]. Given the great cost of sample return missions, combined with the ongoing need to sample multiple terrains, the Decadal Survey explicitly supports in-situ dating [1], with a capability goal of ±200 Ma for the NASA Technology Roadmap [21].

New constraints on impactor flux are sought for two eras of solar system history. Specifically, dates from the most ancient parts of Moon may provide a test for the existence and intensity of the LHB. The second possibility is the era between 1-3.5 Ga, for mission to Mars or the Moon, which collaterally will address the high priority science described under ***Importance***, above. For Mars missions that are follow-ons to the Mars 2020 rover, CODEX will: (1) produce measurements of fine-scale elemental chemistry and organic detection/characterization; (2) acquire the information needed to select the best samples to cache, (3) provide in-situ dates, allowing us to establish the temporal context of habitability and potential biosignatures, (4) provide unprecedented information about surface samples of great import to the broader planetary science community before the cache is returned to the Earth, and (5) provide compelling science results needed to make the case for actually returning this cache to Earth. For the Moon, the organics capability will be exchanged for a dual dating approach, combined with fine-scale chemistry measurements allowing CODEX to be used to understand the evolution and age of the anomalously young flows of the 1-3 Ga crater counted surfaces found near the Aristarchus plateau.

Method: CODEX is uniquely able to analyze the microscopic chemical and organic makeup of a sample, while simultaneously determining its age and spatial context. CODEX analyzes drill cores provided by the rover coring system, which are transferred into the CODEX analysis chamber. Prior to analysis, locations on the sample are laser-ablated to remove surface contaminants. CODEX then interrogates hundreds of locations on the cylindrical surface of the core in a 2D grid using three modes: A) laser ablation mass spectrometry (LAMS) to measure chemistry, B) two-step laser desorption/ionization mass spectrometry (L2MS) to measure organics, and C) laser desorption resonance ionization mass spectrometry (LDRIMS) to measure rubidium-strontium geochronology (**Fig. 1**). CODEX produces images of the spatial distribution of chemical elements, compounds, and organics, and determines the isochron age of the sample. The images allow us to decipher the spatial relationships and geochemical setting of any detected potential biosignatures. This information is crucial to identification and prioritization of samples for caching and ultimate return to Earth.

Prototype Results:

Chemistry. CODEX produces chemical maps of a sample core, revealing indicators of geologic context, history, and habitability. Importantly, because CODEX can place these observations in spatial context with organic signatures, and temporal context using its LDRIMS capability, the complex history of habitability can be determined and used to target the most important geologic localities in the search for life. CODEX uses LAMS to assess elemental, and molecular chemistry. LAMS utilizes laser ablation to directly create ions and survey elements and compounds. An image of the chemistry of the core surface is generated, without requiring a separate imager (**Fig. 2**), which enable several key geological observations, from the primary composition of the rocks to the secondary alteration processes and the record of habitability.

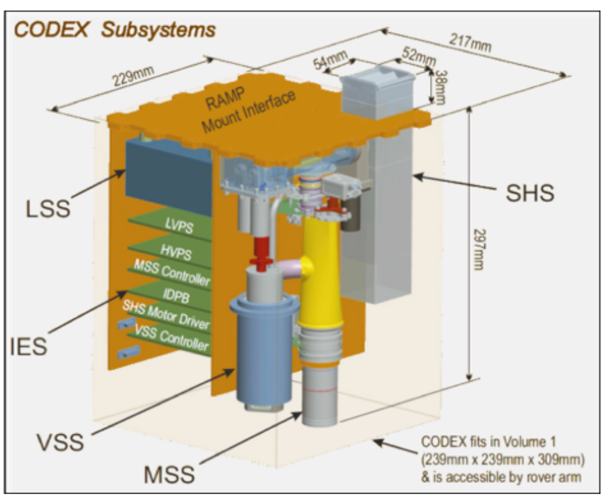

Figure 1. CODEX Instrument. SHS = Sample Handling Subsystem; MSS = Mass Spectrometry Subsystem; VSS = Vacumn Subsystem; IES = Instrument Electronics Subsystem; LSS = Laser Subsystem.

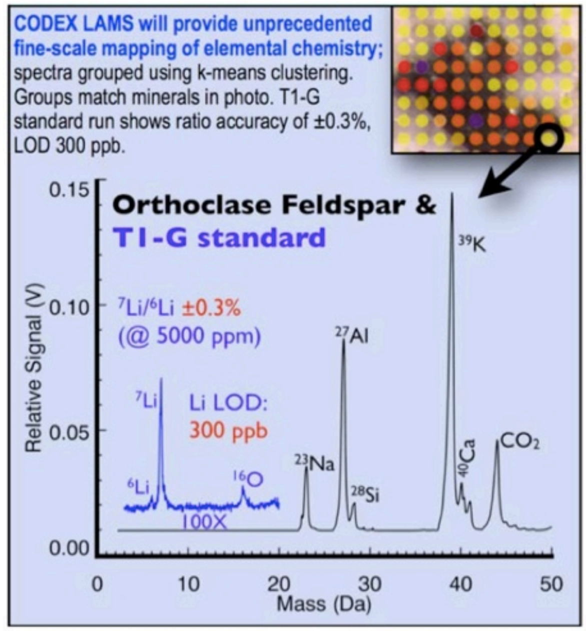

Figure 2: Example of a CODEX chemistry measurement.

Organics. CODEX addresses whether organics are a potential biosignature or are abiotic. The abiotic organic chemistry of the exogenous carbonaceous chondrite meteorites, like Murchison, consists of over 10,000 separate organic molecules present in almost every conceivable isomer; extant life, however, has a tendency to concentrate only a few possible compounds, usually monomers (i.e. the 20 proteinaceous amino acids). CODEX uses L2MS to produce high sensitivity measurements of organic compounds at microscopic scales. In L2MS, atoms and molecules are gently removed from a sample surface by IR laser desorption, then photoionized using a UV laser. Using the portable CODEX prototype in L2MS mode, we have demonstrated the ability to determine organic parent masses and characteristic fragments in test samples such as organic dyes and meteorites like the carbonaceous chondrite Murchison (**Fig. 3**). Previous analyses have shown that the aromatic organics are present in Murchison at ~15-30 ppm, suggesting that

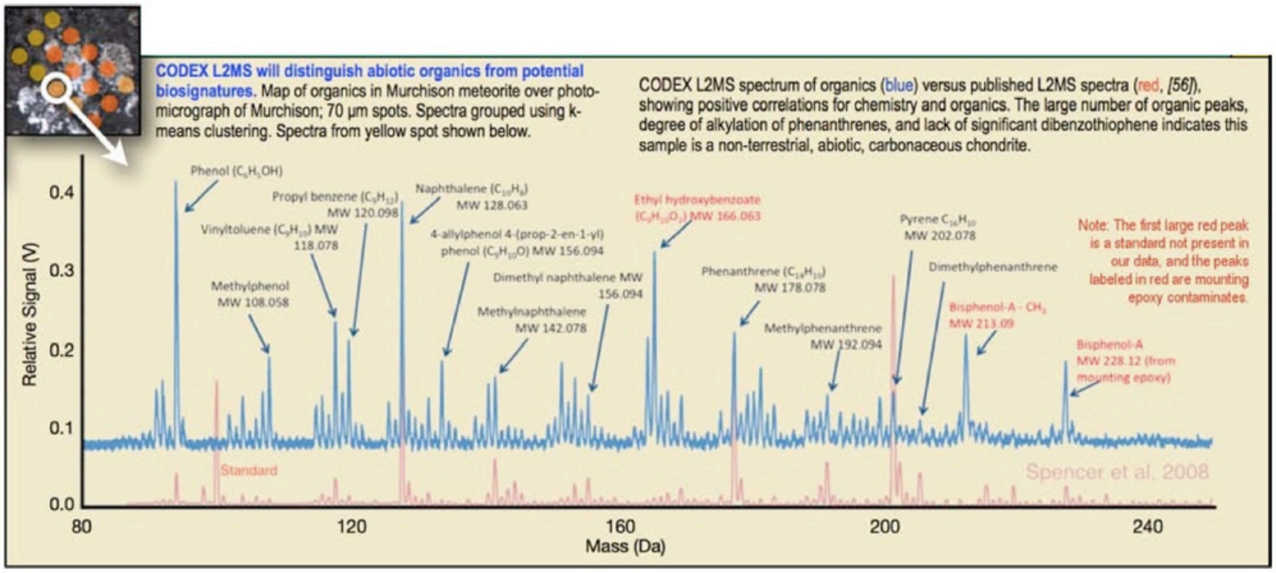

Figure 3: Example of a CODEX organics measurement.

our current sensitivity is ~0.6 ppm. L2MS can also provide additional constraints on elemental chemistry, by providing additional insight into elemental peaks and molecular fragments in the mass spectrum.

Dating. Understanding the rates of change for planetary processes (such as the history of water, climate, and potential biology) requires absolute ages. CODEX provides high-quality dates, establishing a local stratigraphic context, identifying the best locations for seeking biosignatures, and providing a foundation for understanding the history of Mars. CODEX uses LDRIMS-based Rb-Sr isotope analysis to determine isochron ages for samples. As a demonstration of the technique, the CODEX LDRIMS approach has been tested on the Martian meteorite Zagami [3], a basaltic shergottite composed of pyroxenes, maskelynite, and oxides with a Rb-Sr isochron age of 166±6 Ma [4]. In each analysis, we measured over 100 spots with a ~200 µm spacing and 70 µm diameter; the spots which yielded sufficient Rb and Sr for analysis are shown in an isochron diagram (**Fig. 4**), which implies an age 230 ± 170 Ma. This is consistent with the previously published age and with other analyses we have performed, and has precision exceeding NASA requirements (±200 Ma).

For the Moon, for which alteration by water and heat will be unlikely, a second dating approach based on Pb-Pb may be possible. Recent models based on our successes with resonance ionization of Rb-Sr suggest that we could significantly improve the precision of our measurement using a single isotope radiometric approach such as Pb-Pb. Furthermore, the overall confidence in lunar dates will be strengthened by using both measurements for the Moon.

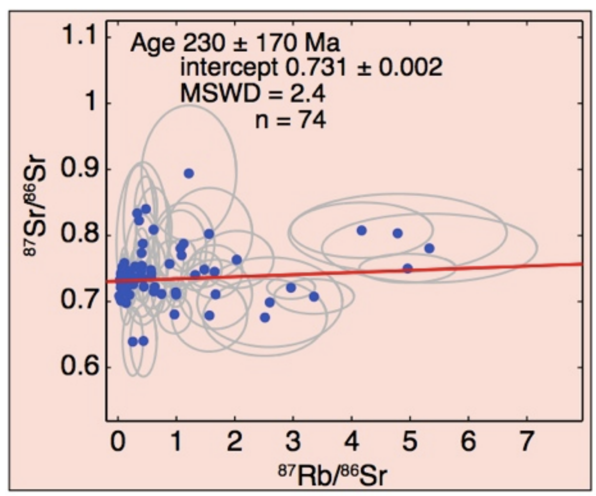

Figure 4: Example of a CODEX dating measurement, on Martian meteorite Zagami.

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