MULTIANALYTICAL SCIENCE WITH THE CODEX IN-SITU DATING SPECTROMETER. F. S. Anderson[1], J. Levine[2], N. J. Smyth[2], M. A. Tebolt[2], and T. J. Whitaker[1], [1]Department of Space Operations, Southwest Research Institute, Boulder, Colorado 80302, USA (anderson@boulder.swri.edu), [2]Department of Physics and Astronomy, Colgate University, Hamilton, New York 13346, USA.

Introduction: The CODEX (Chemistry, Organics, and Dating EXperiment) spectrometer we have developed as a prototype in-situ dating instrument for planetary missions has proven itself by recovering the ^{87}Rb/^{87}Sr isochron ages of the Zagami meteorite [1] and a lunar analogue [2]. Here we describe additional capabilities of our instrument and how we are beginning to use them to complement Rb-Sr geochronology. Crucially, we are now able to analyze isotopes from multiple radioisotopic decay systems in the same samples, which gives a richer understanding of any specimen's geologic history than can a single isotopic system alone.

Complementary analyses: In our resonance ionization experiments, atoms ablated from the sample surface by a first laser pulse are excited by subsequent pulses of lasers tuned to electronic transitions in the elements of interest, and are finally ionized from the excited states. In a second mode of operation, we nonresonantly ionize ablated atoms and molecules directly from their ground states, and this has allowed us to sensitively detect organic molecules in the Murchison meteorite [3]. Turning the post-ablation lasers off altogether converts our instrument into a laser ablation mass spectrometer, and we have used data collected this third mode as an aid in identifying the minerals we analyze [4]. Furthermore, tuning the post-ablation lasers to resonantly excite Pb [5] rather than Rb and Sr allows us to gather geochronological data in the Pb-Pb system, which has the advantage that an age may be determined from isotopes of a single element, so that elemental fractionation in our instrument becomes irrelevant.

Pb geochronology by resonance ionization: The advantage of working with isotopes of a single element more than makes up for the fact that Pb is generally less abundant in planetary materials than are Rb and Sr (e.g., [6]). For example, when we dated the Duluth Gabbro using the Rb-Sr system [2], we obtained 200 Ma precision only by amassing >300 spot analyses into a single isochron. By contrast, we achieve the same precision in only 13 spot analyses in our analysis of Pb isotopes in Zircon 91500, a 1065 Ma single crystal [7]. Moreover, the largest source of error in our Pb measurements is often the fractional uncertainty in the very tiny abundance of ^{204}Pb; if we completely neglect the small amount of common Pb that the ^{204}Pb represents, then the correlation of ^{207}Pb to ^{206}Pb (Fig. 1) allows us to date the zircon with 50 Ma precision.

One of the inherent advantages of resonance ionization mass spectrometry is its sensitivity, which is seen in our analysis of lunar meteorite MIL 05035. This meteorite has a whole-rock concentration of Pb of only 400 ppb [8,9]. To our knowledge, the only other Pb isotopic study of this meteorite was by Zhang et al. [10], who obtained four analyses of a single zirconolite crystal. As we do for our other specimens, we examined hundreds of ~100 μm spots over the surface, and

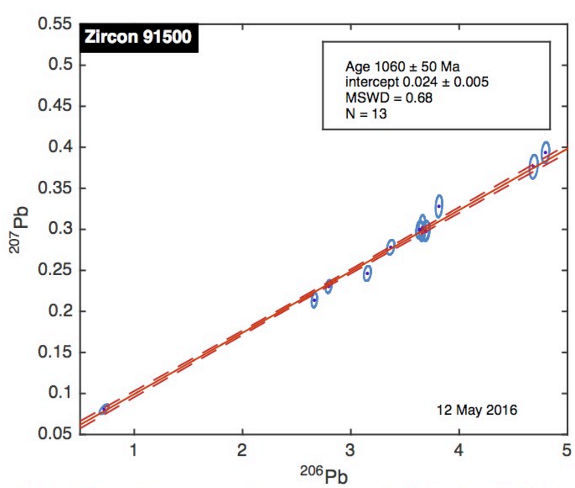

Fig. 1: ^{207}Pb vs. ^{206}Pb correlation diagram for Zircon 91500 [7] from Keuhl Lake, Ontario. In the assumed absence of common lead (we measured ^{206}Pb/^{204}Pb ~1000), this correlation is interpretable as an isochron line. Our age coincides with that reported by [7].

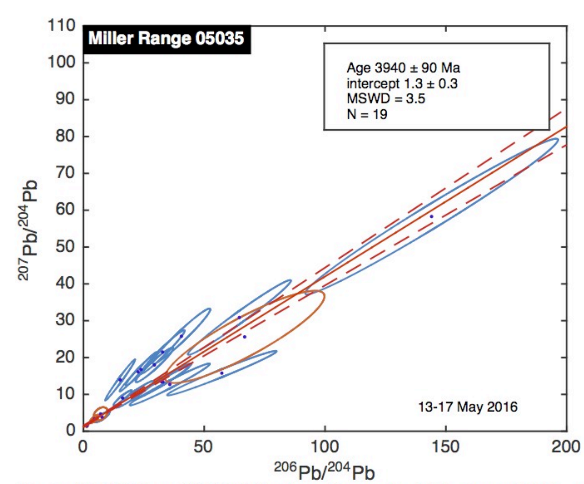

Fig. 2: ^{207}Pb/^{204}Pb vs. ^{206}Pb/^{204}Pb isochron diagram for Miller Range 05035, a lunar meteorite with only 400 ppb Pb [8,9]. Our age coincides with determinations in [10, 11].

found 19 in which $^{204,206,207,208}Pb$ were all detected at the >2σ level. The $^{207}Pb/^{206}Pb$ isochron age we obtained (Fig. 2) is 3940 ± 90 Ma, consistent with the Pb age determined by Zhang et al. [10], and also with the age of this meteorite as determined using the Sm-Nd and Rb-Sr systems [11].

Synthesis of ages from multiple isotopic systems: From the concordance of its age as determined using multiple isotopic systems, MIL 05035 appears to have had a simple geologic history, with crystallization around 3900 Ma and no significant events recorded thereafter until the sample was ejected from the Moon. For many planetary specimens, however, different isotopic systems yield different age estimates [e.g., 12], and each isotopic system provides necessary clues to help interpret the complex geologic history of the specimen.

Multi-isotopic examination of the Martian meteorite Zagami illustrates this point. Like others, (e.g., [6]) we found a young apparent age in the Rb-Sr system [1], but our new data (Fig. 3) imply a much older Pb-Pb age (consistent with [13]). Similar discrepancies between very old Pb-Pb ages and very young ages from other radioisotopic systems have been observed for many Shergottites [e.g., 14], and the proposed interpretations have planetary-scale implications for our understanding of Mars's geologic history. For example, Borg et al. [6] argue that the young Rb-Sr and Sm-Nd ages imply crystallization of Zagami only 166 Ma ago, which implies that Mars has been geologically active for at least 96% of its history, and they believe that the U-Pb isotopes in Shergottites has been disturbed. Disputing this, Bouvier et al. [14] argue that the 4048 Ma Pb-Pb age represents the crystallization of Zagami (and similarly for the other Shergottites), and that the other isotopic systems have been reset by the ejection of the meteorites from Mars. This interpretation obviates the need for Mars to have remained geologically active for most of its history. Recently, Bellucci et al. [15] proposed an elegant interpretation of Pb isotopic data for Chassigny by postulating a reservoir of extremely radiogenic Pb, globally distributed on the surface of Mars, perhaps from an ancient impact event. The persistence of such a reservoir is plausible only if Mars has had no tectonic recycling for nearly all of its history [15]. In short, conclusively determining a quantity as fundamental as the global cooling rate of Mars will rely on geochronological data from multiple isotopic systems. To this end, we have also begun experiments to measure Sm and Nd isotopes with our instrument.

In the model proposed by Bellucci et al. [15], the "unsupported" radiogenic Pb becomes incorporated into Martian meteorites during their ejection from Mars. Alternatively, in the understanding of Bouvier et al. [14], ejection resets the other isotopic systems. Either way, multi-isotopic in-situ dating of extraterrestrial rocks collected directly from their geologic contexts, such as we propose to do, would avoid all of the chronological complications associated with ejection, and therefore offer much clearer views of Solar System history. Its complementary modes of analysis give CODEX the versatility needed to decipher complex geologic histories of planetary samples.

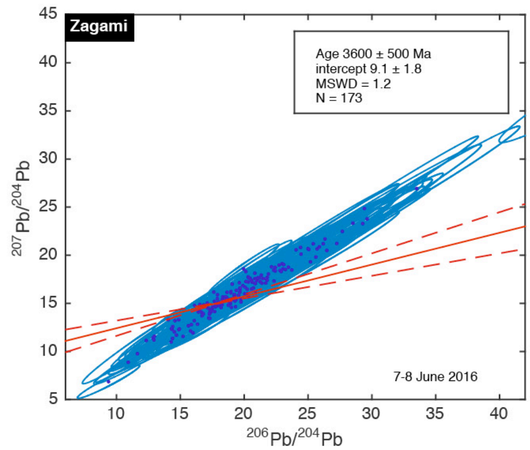

Fig 3: $^{207}Pb/^{204}Pb$ vs. $^{206}Pb/^{204}Pb$ isochron diagram for Zagami. The extremely old age evinced here is consistent with the Pb age of [14] but inconsistent with ages determined by other radioisotopic systems (e.g., [1, 6]). Note that the best fit line (red) need not align with the uncertainty ellipses (blue) of most data points, which are tilted toward the origin because of the scarcity of ^{204}Pb.

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