DATING ZAGAMI WITH 20 Ma PRECISION USING A PROTOTYPE IN-SITU DATING INSTRUMENT.

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Introduction: Through continued development of the Chemistry, Organics, and Dating EXperiment (CODEX), a portable instrument for in-situ elemental, organics, and dating analysis, we have improved our Rb-Sr dating precision of the Zagami meteorite from ±100-200 Ma to ±20 Ma (**Figure 1**). We have achieved this improvement by 1) reducing the contribution of ablation-derived plasma to the noise in our measurements, and 2) decreasing fractionation and matrix effects by using higher ablation intensities.

Our previous ±200-Ma precision was sufficient to address billion-year uncertainties in the crater-count chronology of the inner solar system [1]. Specifically, the chronology is unconstrained during the interval between 3000-1000 Ma [2-5] because none of the samples of known provenance collected on the Moon have been dated to this period. Crater counts derived from Lunar Reconnaissance Orbiter images suggest that Apollo-era chronologies might be miscalibrated by up to 1100 Ma during this interval [1].

Our improved precision of ±20 Ma is sufficient to resolve the timing of events during the era of giant basin formation on the Moon. Specifically, there are at least 11 basins that are stratigraphically assigned to the Nectarian Period [6], but the duration of the period is disputed. The difference between the ages of Nectaris and Imbrium has been variously reported as 100 Ma [7] or 300 Ma [8]. The difference is not merely academic; the favored dynamical model of Solar System evolution [9] has been tuned to permit a renewed era of exceptionally high meteoroid bombardment of the inner Solar System, which may never have occurred [10]. Understanding when the basin-forming impacts occurred, and whether or not the impactors represented a new influx of large projectiles in the inner Solar System, will require well-provenanced samples from widely spaced basins on the Moon, and dating precision of approximately ±50 Ma.

CODEX: CODEX uses pulsed laser ablation to vaporize atoms from ~80-μm spots on a target rock held under vacuum. The plume of vapor from each pulse consists of a mixture of electronically cold neutral atoms, electronically excited neutrals, ions, and even polyatomic "grains." By removing the ions from the plume, then resonantly ionizing neutral Sr atoms and, after a short delay, neutral Rb, we can inject separate pulses of Sr and Rb atoms into a time-of-flight mass spectrometer. We use 460.86 nm and 554.49 nm radiation to excite ground-state Sr atoms to a high-lying bound electronic state from which we ionize them with 1064-nm light from a Nd:YAG laser. A microsecond or so later, we illuminate the vapor plume with 780.24 nm and 775.98 nm radiation to excite ground-state Rb atoms to a state from which we ionize them with 1064 nm light from a second Nd:YAG laser. The ~1 μs delay offsets the arrival time of Sr and Rb at the detector of our time-of-flight mass spectrometer, lifting their mass-87 isobaric interference [11, 12].

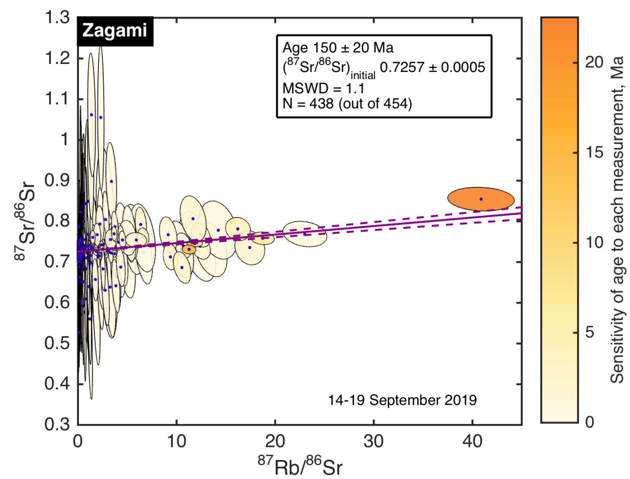

Figure 1: Isochron diagram for Zagami. With our improved noise suppression, we detected both ^{87}Sr and ^{87}Rb at the >2σ level in 438 of the 454 spot analyses we attempted. The color shading represents the sensitivity of the age to each measurement; one indication of the robustness of this result is that, having acquired 438 points, we no see none that alone affect the age by more than 25 Ma.

Several additional modes of analysis are also possible. For example, the CODEX can analyze organics in two-step laser mass spectrometry mode, and it can examine the ions from the ablation plume in laser-ablation mass spectrometry mode, without using the resonance ionization lasers. Because a CODEX analysis interrogates many spots on the sample, it is possible to map elemental abundances at microscopic scales. Such data can complement and contextualize our geochronological measurements by tentatively identifying mineral phases and secondary alteration products [13, 14]. Finally, CODEX has demonstrated the ability to produce Pb-Pb dates with precision of ±50 Ma [15, 16].

Improved Method: Plasma from laser ablation interferes with our ability to selectively photoionize, extract, and detect Sr and Rb. Therefore, we focused our efforts on excluding plasma, so that we could detect smaller Sr signals standing up above the noise. Spots with especially low Sr can have high Rb/Sr ratios, and therefore are especially important for precise dating. Ultimately, the solution we identified was elegant in its simplicity: whereas we had previously held the sample as close as possible to the sample electrode (which has a small hole through which the ablation laser passes, and through which the ablated plume emerges), we now re-positioned the sample 2.5 mm behind the electrode and collared the hole with a 1.5 mm long cylinder to narrow the solid angle it subtended at the ablation point. Most of the ablation plume emerges as a narrow jet normal to the surface [cf. 17], but the aperture in our sample electrode is 15° away from the surface normal, so only a small fraction of the plasma reaches the aperture. With less plasma in the mass spectrometer, our ion optics effectively suppressed background counts and focused Sr and Rb photoions to the detector.

In this work, we also present our first results using 800-nm femtosecond-laser ablation. We experimented with pulse duration and intensity, and found stable high yields of ground-state neutral Rb and Sr at pulse widths around 150 fs and energies near 0.3 mJ, with the beam focused to an ~80 μm spot on the sample (i.e., the laser intensity was about 3×10^{13} W/cm^2).

Results: With no sample preparation except a few minutes of hand-polishing, we have dated the Martian meteorite Zagami to 150 ± 20 Ma (**Figure 1**), a result which is both accurate and five times more precise than our previous best-reported measurement.

It is interesting to ask how the dating precision would scale to a sample older than Zagami. We can make a simple model in which we assume that we could employ our present measurement capabilities at any time after the formation of Zagami. Knowing the ^{87}Rb/^{86}Sr and ^{87}Sr/^{86}Sr ratios that we observed, we can calculate what these ratios would have been at any other time, assuming only the steady decay of ^{87}Rb into ^{87}Sr. Supposing that we achieve the same fractional errors on each spot analysis as we found in reality, and the same correlation between the two isotope ratios, we re-fit the isochron line and calculate the statistical uncertainty in the age. The result is shown in **Figure 2**, where we see that our age uncertainty grows more slowly than age. Our dating precision is more sensitive to, for example, the highest ^{87}Rb/^{86}Sr ratios that we observe, and the precision we achieve on ^{87}Sr/^{86}Sr ratio measurements. **Figure 2** shows that, even if a Zagami-like sample were 4500 Ma old, our present measurement would have determined its age to within 80 Ma. Such precision would provide meaningful constraints on the timing of events even in the basin-forming epoch of Solar System history.

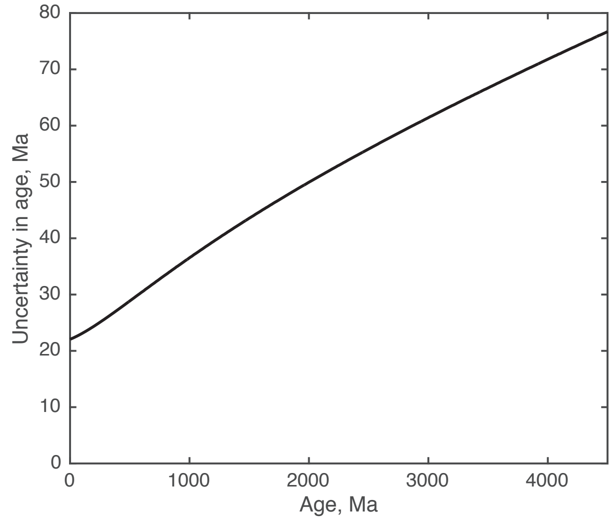

Figure 2: Scaling of dating precision with age. This curve shows how the uncertainty in the isochron age would grow as a function of the elapsed time between the crystallization of Zagami and the time at which we analyze it, assuming the isotopic abundances we observed at 150 Ma. For other times, we simply calculated how much more or less ^{87}Rb would have decayed to ^{87}Sr, and assumed that we could analyze each of our spots with the fractional errors and correlations that we observed in reality.

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References: [1] Robbins, S.J. (2014) *EPSL 403*, 188-198. [2] Hartmann, W.K. (1970) *Sci. Amer. 236 (1)* 60-276. [3] Hartmann, W.K., et al., Origin of the Earth and Moon, 2000. **1**: p. 493-512. [4] Neukum, G. et al, (2001) *SSR 96 (1)* 55-86. [5] Stöffler, D. and Ryder., G. (2001) *SSR 96* 9-54. [6] Fassett, C.I., et al. (2012) *JGR: Planets, 117 (E12)* E00H06. [7] Maurer, P., et al. (1978) *GCA 42 (11)* 1687-1720. [8] Schaeffer, O. and L. Husain (1974) *LPSC Proceedings*. [9] Gomes, R., et al., (2005) *Nature 435 (7041)* 466. [10] Zellner, N.E. (2017) *Origins of Life and Evolution of Biospheres 47 (3)*. [11] Anderson, F.S. et al (2015) *RCM 29* 1-8. [12] Anderson, F.S. et al (2015) *RCM 29 (2)* 191-204. [13] Anderson, F.S. et al (2014) *8th Int. Conf. on Mars*. [14] Foster, S. et al. (2016) *LPSC 2070*. [15] Anderson, F.S. et al. (2017) *LPSC 1246*. [16] Anderson, F.S. et al (2017) *LEAG 5082*. [17] Schou, J., et al (2007) in *Laser ablation and its applications,* 67-95.