THE LOST LUNAR ZIRCONS: HOW SAMPLE PROCESSING HAS BIASED THE APOLLO ZIRCON RECORD. J. R. Davis[1], C. A. Crow[1], R. Economos[2], K. Lehman Franco[2], T. Erickson[3] [1]Department of Geological Sciences, University of Colorado Boulder, Boulder, CO 80309 (jennifer.davis-4@colorado.edu) (carolyn.crow@colorado.edu), [2]Department of Earth Sciences, Southern Methodist University, Dallas, TX 75275, [3]Jacobs-JETS, NASA Johnson Space Center, Houston, TX 77058

Introduction: The lunar surface hosts a variety of minerals that are important for understanding the chemical and physical history of the Moon [1]. One of the most important phases is the accessory mineral zircon. Zircon is a durable mineral and quite resistant to destruction so, it is able record and retain U-Pb crystallization ages through subsequent geologic processing [2]. Zircons also incorporate trace elements (e.g. REEs, Ti) that are a function of oxidation state and temperature yielding valuable information about formation conditions [3]. Lastly, the zircon crystal structure records microtextures indicative of impact shock P-T conditions [4]. When these conditions result in the mobilization of Pb, it is also possible to constrain the timing of the impact or metamorphic event [e.g. 5, 6, 7, 8]. As such, zircon is a valuable tool for investigating the crustal history of the Moon.

Ideally, zircons are analyzed in petrologic sections in order to retain context. Multiple studies have successfully found and analyzed zircons samples in Apollo sections [e.g. 6, 9]; however, they are relatively rare in most samples. To obtain better statistics on some samples and to perform bulk grain analyses, previous studies have extracted zircons from samples using standard mineral separation techniques [e.g. 6, 10]. The separation was done by crushing, heavy liquid density separation, and hand-picking aided by UV fluorescence. In this study we have re-evaluated the samples from [11] and have found that over 80% of zircons were missed in some samples during previous separations. We have reported preliminary results of an investigation into (1) the ways in which separation methods have biased our geochronologic datasets, and (2) the reason why extraction methods for terrestrial samples are not successful on lunar samples. Ultimately, our goal is to provide a summary of best practices based on our findings.

Summary of Previous Methods: Extraction methods vary depending on the mineral being isolated and employ a variety of different techniques. Previous studies have isolated lunar zircons using a simple three-step method of crushing (this was skipped for soil samples), density separations via Methylene Iodide (MI or MEI), and UV light picking. MI was chosen as a heavy liquid because it does not require prior magnetic separation, which must be done using a hand magnet for lunar samples, which is very time intensive. MI also has a density of ~3.3 g/cm^3, which should produce a clean separate with zircons (density of ~4.6-4.7 g/cm^3) sinking to the bottom of the liquid and major phases (e.g. olivine, plagioclase, phosphates) floating. Since most lunar zircons are not euhedral (typically shards) and clear, it is difficult to distinguish using an optical microscope. Terrestrial zircons commonly fluoresce with UV light; thus, this method was also used for picking lunar zircons. [Note: Hopkins and Mojzsis 2015 did not use UV fluorescence, but instead mounted the heavy separate in epoxy and used the scanning electron microscope (SEM) to identify zircons.]

The different steps used to isolate zircons rely on the grains of interest in these samples having the expected chemical and physical properties (e.g. density of ~4.6-4.7 g/cm^3 and sufficient trace elements to cause fluorescence under UV light) [12]. However, as we will show here, this is not always true for lunar zircons.

Methods: In this study we have re-processed previous MI floats (i.e. the material that is less dense than ~3.3 g/cm^3), which should have no zircons since the MI is a full ¼ less dense than zircon. Our initial investigation focuses on Apollo 14 impact melt breccia 14311 since this sample has zircons that have been well characterized both in section and via mineral extraction [e.g. 6, 13]. Additionally, multiple subsplits of 14311 were allocated for zircon extraction, allowing us to investigate sample heterogeneity.

The initial goal for this work was to do a second processing of the MI floats to separate phosphates (~3.1-3.2 g/cm^3) using magnetic separation. This produced a very clean separate with nearly 99% of material being removed with a neodymium hand magnet. The remaining non-magnetic materials were sprinkled onto double-sided sticky tape and mapped on the SEM via backscattered electrons (BSE) and energy dispersive spectroscopy (EDS) to identify phosphates (which have as intense UV fluorescence). Surprisingly, 249 zircons were also identified in the re-processed MI float. There were only 48 zircons found in the MI sink, so over 80% of the zircons were missed using traditional sample processing techniques.

Results and Discussion: We have conducted a reassessment of our processing methods and begun a detailed geochronologic and microtextural study of these zircons.

Reassessment of Methods: Our re-processing has clearly demonstrated that MI is not a suitable method for lunar zircon extraction and has the potential to create significant biases in geochronologic and geochemical datasets. We further investigated the effectiveness of UV fluorescence on identification of lunar zircons. Of the 249 zircons that floated in MI, 119 fluoresced, meaning that ~50% of zircons would be missed using this separation method. Since MI density separations and UV light picking miss a significant portion of zircons, we strongly recommend these processing techniques are not used during future lunar sample processing. Our preferred separation methods include crushing, magnetic separation, making of sprinkle or epoxy mounts, and identification via EDS.

Potential Biases in Datasets: Missing significant fractions of zircons during traditional separation methods could potentially skew geochronology and other trace element data. We have begun measuring the ages of the 14311,58 zircons. So far, ^{207}Pb-^{206}Pb and U-Pb ages have been obtained using secondary ion mass spectrometry (SIMS) for the 81 zircons separated as part of the processing for [11] and 41 of the largest zircons that floated in MI that were discovered during reprocessing. These are shown in Figure 1. For comparison, we have also plotted the 14311,20; 14311,50; and 14311,60 Pb-Pb ages from zircons from [6], which were also separated using MI. The two age distributions between Figure 1 and Figure 2 are dramatically different. 14311 subsample 58 has an abundance of ages at ~3.9 Ga, while 14311 subsamples 20, 50, and 60 do not. While the dataset for the former is not yet complete, it does suggest that either (1) 14311 is heterogeneous and samples sizes of a few grams are not sufficient to capture a representative suite of zircons, or (2) the density of the zircons are correlated with age.

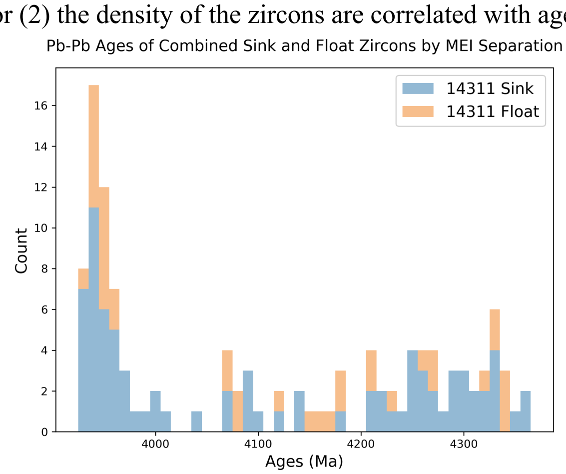

Figure 1: A stacked histogram showing the combined Pb-Pb ages determined from zircons in 14311,58 that sank in MEI (from [11]) and zircons that floated in MEI. This represents how datasets from lunar material could be missing data if not all zircons are isolated from the bulk material for further analysis. Bin sizes are 10 Ma.

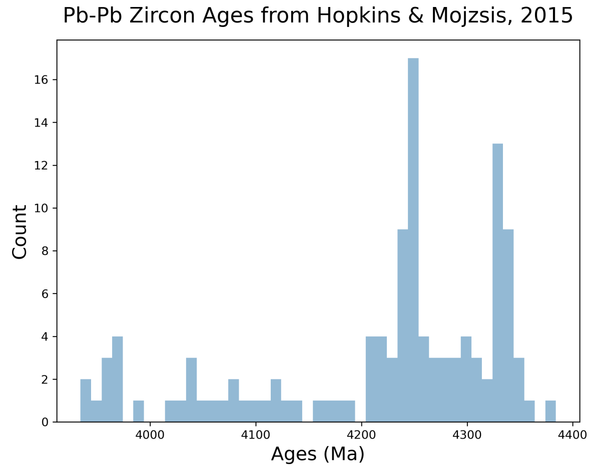

Figure 2: A histogram of the Pb-Pb ages determined from zircons separated from 14311 subsample 20, 50, and 60 from Hopkins and Mojzsis 2015. These ages are from zircons that sank in MEI. This graph compares the heterogeneity between subsamples and how this may affect age distributions. Bin sizes are 10 Ma

Future Work: We will collect SIMS U-Pb ages for the remaining 14311,58 zircons prior to this meeting, so we will be able to present the full datasets and comment on the potential biases due to separation methods. We will also begin an electron backscatter diffraction (EBSD) study of the zircons that did not sink in MI to understand why these zircons have drastically lower densities. Lunar zircons have long histories (up to ~4.4 Ga) and many have evidence of shock deformation from meteorite impacts [e.g. 5. This is likely the source of the density difference, but we are interested to understand which mechanisms are responsible (e.g. trapped melt, crystal lattice damage).

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