Probing the Cogeneticity of Minerals and Glasses in Lunar Breccias Using Aluminum in Zircon and Glass. E. Needham¹ (eneedha1@asu.edu), M. Barboni², D. Trail², E. Bell³, School of Earth and Space Exploration, Arizona State University, Tempe, AZ, 85287 ²Department of Earth and Environmental Sciences, University of Rochester, Rochester, NY 14627, ³Earth, Planetary, and Space Sciences, University of California – Los Angeles, Los Angeles, CA, 90095.

Introduction: Apollo lunar breccias uniquely record processes of planetary accretion, lunar magma ocean evolution, and early inner solar system bombardment [1]. In contrast to terrestrial samples, obscured by geologic activity, lunar specimens retain vital chemical and isotopic information on our solar system’s earliest history. However, these materials are not pristine - all experienced extensive impact processing and thermal disturbances, obscuring primary signals [2].

To extract petrogenetic relationships from such profoundly altered samples, researchers designate putative cogenetic clasts within breccias, hypothesizing they represent coherent igneous sequences[3]. Bulk glass compositions from such clasts are interpreted alongside accessory mineral data like zircon, assuming chemical cogeneticity between disparate phases - an assumption based solely on textural evidence. Recent work shows aluminum incorporation in zircon covaries with that in coexisting melt [4]. We leverage this new Al-in-zircon tool to directly assess melt-mineral equilibration via coupled aluminum abundance analyses in zircons and proximal glass across multiple Apollo sections. Our data facilitate an overdue interrogation of foundational assumptions underpinning interpretations of these unique extraterrestrial archives.

Methods: Recent experimental determinations conducted on terrestrial specimens have quantified the extent of aluminum (Al$^{3+}$) substitution into the zirconium silicate lattice as varying directly with the aluminum abundance in coexisting silicate melt [4-5]. This correlation is expressed via the aluminum glass index (AGI), defined as:

\[
\text{AGI} = \log(\sqrt{[\text{Al}_2\text{O}_3]/[\text{SiO}_2]}) \text{ (molar basis)}
\]

After verifying such coupled aluminum systematics for meteoritic and terrestrial systems crystallized under hydrous, oxidizing conditions, we have further calibrated this relationship for extraterrestrial materials synthesized under anhydrous, reduced conditions approximating lunar genesis. Leveraging these experimental developments, we conducted in-situ quantitative analyses targeting aluminum abundance in accessory zircon crystals alongside measurements of proximal glass major element compositions. Initial petrographic screening and compositional characterization of target crystals was facilitated via scanning electron microscopy with energy-dispersive X-ray spectroscopy (SEM-EDS). Of the 195 zircon crystals identified across 11 Apollo mission thin sections via SEM-EDS analyses, we selected candidates for detailed study based on crystallite size and proximity to glass domains.

Definitive aluminum abundance data for 38 zircon domains and adjacent glass were obtained using the UCLA Cameca ims-1290 secondary ion mass spectrometer (SIMS). U-Pb geochronology determinations were simultaneously acquired, alongside additional trace element abundance data. Supplementary textural and crystallographic information was collected using cathodoluminescence and electron backscatter diffraction (EBSD) techniques, in tandem with major element quantification of glass specimens via electron probe microanalysis (EPMA). Together, these complementary datasets enable direct testing of the hypothesized chemical cogeneticity between zircon crystals and proximal glass veins in lunar samples.

**Results:**

**Behemoth Zircon:** An extensive analytical suite was conducted on the a (>1000 µm) zircon crystal (herein...
“Behemoth”; Fig. 1a) to robustly evaluate hypothesized cogenetic relationships between the zircon host and associated silicate glass inclusions and exterior domains. Quantitative datasets obtained from the “Behemoth” include: 1) 13 distinct analyses of aluminum abundance in zircon; 2) 16 analyses of glass major element compositions; and 3) 12 U-Pb isotopic analyses to determine crystallization ages.

Multiple lines of evidence negate genetic links between the disparate materials analyzed: 1) Crystallization Ages: The zircon core yields a statistically coherent U-Pb age population of 4323 ± 10 Ma (MSWD = 0.83), based on multiple concordant analyses. However, discordant analyses conducted <100 μm from exterior boundary surfaces exhibit scatter to younger ages from 4000–4100 Ma, indicating disturbance of the rim domains. 2) Textural Evidence: Cathodoluminescence imaging reveals the outermost zircon margins to be heterogeneous and brecciated, whereas the interior domains preserve vestiges of original igneous zoning patterns. Pervasive fracturing is evident throughout the zircon in both optical and electron imaging. Rapid penetration rates and sample loss during SIMS analyses further indicate such fracturing persists through the third dimension. 3) Aluminum Abundance: Aluminum concentrations in the zircon core (35–45 ppm) are analogous to the disturbed exterior domains. However, melt inclusions in the core contain far higher Al$_2$O$_3$ (28–32 wt%) than the younger, proximal glass (16–20 wt% Al$_2$O$_3$). This decoupling in aluminum systematics argues against shared parental melts for the disparate materials analyzed.

All Analyzed Zircons: In supplement to the "Behemoth" crystal, additional zircon specimens spanning a crystallization age range from 4.00–4.405 Ga were interrogated for comparative aluminum systematics between the accessory phases and associated silicate glass (total n=15). Electron microprobe (EPMA) and SIMS methodologies enabled quantification of major element (e.g. Al$_2$O$_3$) abundances in the glass specimens and aluminum contents in the crystalline zircon domains, respectively. No demonstrable correlation exists between the aluminum abundance in zircon crystals (commonly 35–45 ppm) and the calculated aluminum glass index for coexisting glass (variable between different samples). These data are summarized in Figure 2. The absence of coherent relationships for the aluminum systematics argues against melt-mineral equilibration and hence genetic links between the crystal phases and quenched melts.

![Fig. 2. Plot of Aluminum in Zircon vs the Aluminum Glass Index value of the adjacent proximal glass, for all analyzed zircons in this study. Note the lack of positive correlation between the zircon and glass compositional terms.](https://example.com/figure2.png)

Conclusions: We conclude the extensive brecciation and chemical modification incurred by lunar samples has likely destroyed original igneous relationships on the mineral scale. Moving forward, the common assumption of clast cogeneticity in lunar breccias must be more robustly demonstrated rather than presumed based solely on textural affinities. Our results necessitate critical re-evaluation of the contextual framework for samples destined for interpretation of planetary-scale process through local geochemical proxies.