DETERMINATION OF TRACE AND VOLATILE ELEMENT ABUNDANCE SYSTEMATICS OF LUNAR PYROCLASTIC GLASSES 74220 AND 15426 USING LA-ICP-MS.

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Introduction: Since their recognition as pyroclastic glasses generated by volcanic fire fountaining on the Moon, 74220 and 15426 have garnered significant scientific interest. Early studies recognized that the glasses were particularly enriched in volatile elements on their surfaces [1,2]. More recently, detailed analyses of the interiors of the glasses, as well as of melt inclusions within olivine grains associated with the 74220 glass beads, have determined high H_2O, F, Cl and S contents [3]. Such elevated volatile contents seem at odds with evidence from moderately volatile elements (MVE), such as Zn [4] and K [5], for a volatile-depleted Moon. In this study, we present initial results from an analytical campaign to study trace element abundances within the pyroclastic glass beads. We report trace element data determined by laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) for 15426 and 74220.

Samples: We were provided with polished thick sections of 74220 (,701) and 15426 (,180) by CAPTEM and the NASA JSC Curation staff. We determined the average bead size of 74220, 701 as 48 ±29 µm for 74220, 701 (*Figure 1*). The beads in 15246 are significantly larger, consistent with prior work [6].

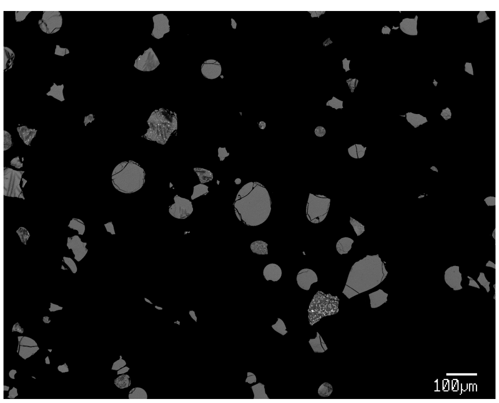

Figure 1: *Back-scatter electron image of a portion of 74220, 701 illustrating the shape and size of the glass beads.*

Methods: Thick polished sections of 74220 and 15426 were analysed for 44 trace elements using a *New Wave* UP-213nm laser ablation system coupled to a *ThermoScientific* iCAPq inductively coupled plasma mass spectrometer (ICP-MS) at the *Scripps Isotope Geochemistry Laboratory* (SIGL). NIST 610, BHVO-2g and BCR2-g glasses were used for standardization. To accurately determine elemental abundances by LA-ICP-MS, we focused on larger grains in 74220, 701. Samples were analyzed for major element compositions using a *JEOL JXA 8200* electron microprobe at the *University of New Mexico.*

Results: New major element chemistry for the glass beads are consistent with prior work [7]. For trace elements determined by LA-ICP-MS, we only report concentration data for spots in the centers of large beads in 74220 (n = 33) and for spots and rasters within larger beads in 15426 (n = 20). As also determined previously [8], 74220 and 15426 exhibit distinct differences in absolute and relative abundances of the rare earth elements (REE) (*Figure 2*). Sample 74220, 701 has a convex-up REE pattern at ~55 × CI chondrite, with a slight negative Eu-anomaly, whereas 15426 has a flatted CI chondrite pattern (~5.7 × CI chondrite) and a slight negative Eu anomaly.

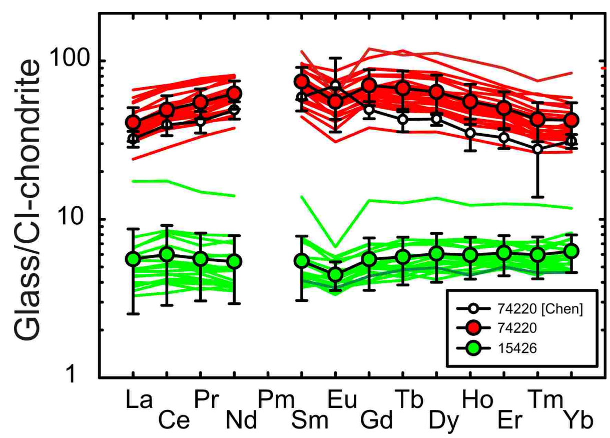

Figure 2*. CI chondrite normalized REE abundances for lunar pyroclastic glasses 74220 and 15426 determined by LA-ICP-MS. Data for individual beads shown as solid lines; averages and 1 S.D. uncertainties shown as black lines and symbols. Previously published data by Chen et al. [9] are also shown.*

For refractory trace elements with broadly similar geochemical behaviour, we find that the lunar pyroclastic glasses span similar variations in Zr/Hf and Nb/Ta to those published previously (*Figure 3*). Munker et al. [10] explained Nb/Ta ratios below the chondritic value as reflecting removal of Nb into planetary cores. We find that data for 74220 are sub-chondritic for both Nb/Ta and Zr/Hf, but that data for 15426 disperse around the chondritic ratio. In general, our data are consistent with limited fractionation of trace elements occurring within the beads.

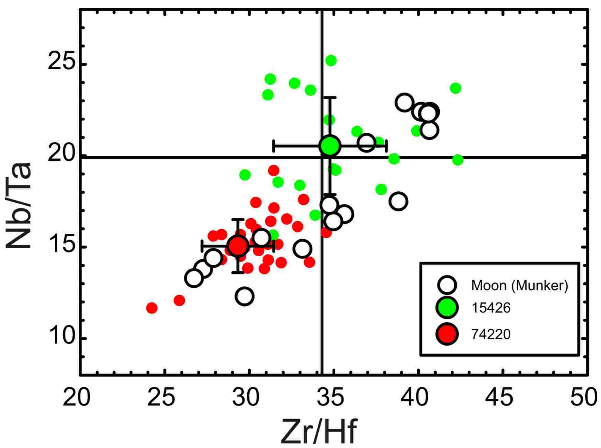

Figure 3. Plot of Nb/Ta versus Zr/Hf from lunar pyroclastic glasses 74220 and 15426 versus previously published data from lunar samples [10], and the chondritic average (Zr/Hf = 34.3±0.3; Nb/Ta = 19.9 ±0.6).

Of particular interest to us was the observed variations in MVE. We performed rasters across glass beads and within glass beads. Qualitatively, we observed 'kicks' and elevated count rates for some of the MVE close to the rims of some glass beads. These observations are consistent with prior work showing significant enrichment of these elements on the bead rims and surfaces (e.g., [1]). Average abundances of elements, double-normalized to CI chondrite composition and to Fe content are shown in *Figure 4*. We find that both pyroclastic glasses are more depleted in the MVE than the BSE estimate, and similar to estimates for the bulk silicate Moon. We determined Zn/Fe ratios for 74220 and 15426 of 0.00022 ±19 and 0.00008 ±14, respectively, which are moderately higher than data reported for the glasses by Albarède et al. [11], but that are still 5 to15 times lower than in BSE.

Discussion: It has been suggested that the lunar glasses represent primitive liquid compositions [12]. We find some trace element variability within 74220 and 15426, illustrated in *Figure 1*, reflecting minor fractional crystallization. There are also slight Eu anomalies in both 15426 and 74220, indicating plagioclase removal from their sources. The connection between mare basalts and the picritic glasses is enigmatic, with subtle differences between source compositions of mare basalt magmas [13] and the picritic glasses [12]. Nonetheless, our data support formation of the beads from interior reservoirs with components similar to high- and low-Ti mare basalt sources.

The Moon has been considered to be depleted in volatile elements [17], however higher volatile concentrations than those in mare basalts have been found in pyroclastic glasses [3]. Our results support MVE enrichment in the glass beads compared with mare basalts (e.g., [11]).

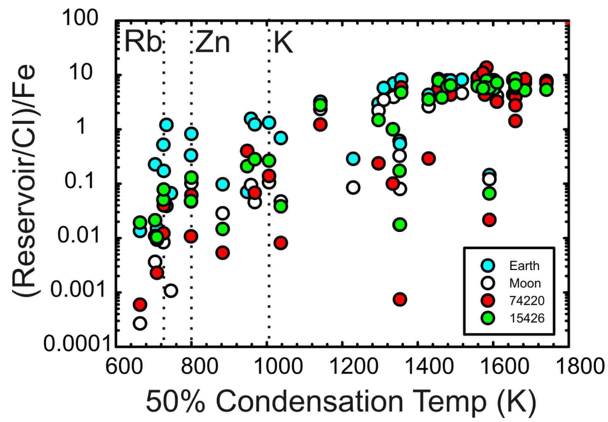

***Figure 4.** Double normalized patterns (to CI-chondrite and Fe) versus 50% condensation temperatures. Bulk silicate Earth (BSE) is represented in blue, the bulk silicate Moon (BSM) as unfilled symbols. Dotted lines represent the condensation temperatures of Rb, Zn, and K. Data for 74220 are divided by a factor of 10 for comparison with 15426 data. Data for condensation temperatures from [14], and BSE and BSM from [15] and [16], respectively.*

Volatiles on the glass beads have been shown to be surface correlated due to vapor deposition [18,19], or that these glasses were formed from local interaction with a volatile rich crustal source [11]. Elevated count rates for MVE at the rims of the beads support the concept that the volatiles are partly the result of vapor deposition, with possible decoupling between magmatically degassed volatiles (e.g., H2O, F, Cl, S) and the MVE (e.g., Zn, K).

References: [1] Tatsumoto, M. et al. (1973) *EOS Trans AGU, 54*, 614; [2] Ganapathy, R. et al. (1973) *LPS IV,* 1239; [3] Hauri, E.H. et al. (2011) *Science, 33,* 213. [4] Kato, C. et al. (2015) *Nat. Comm*., *6,* 7617. [5] Delano, J.W. & Lindsley, D.H. (1983) *JGR*, 88, B1. [6] Carusi et al. (1972) *Geol. Romana*, 11, 137; [7] Delano, J.W. (1986) *JGR*. [8] Philpotts, J.A. et al. (1974) *PLSC 5th,* 1255; [9] Chen, Y. et al. (2015) *EPSL*. 427, 37. [10] Münker, C. et al. (2003) *Science*. 301, 84. [11] Albarède, F. et al. (2015) *M&PS*, 50, 568. [12] Shearer, C.K. & Papike, J.J. (1993) *GCA,* 57, 4785. [13] Neal, C.R. & Taylor, L.A. (1992) *GCA*, 56, 2177. [14] Lodders, K. (2003) *Ap. J.*, 59, 1220. [15] McDonough, W.F. & Sun, S. (1995) *Chem. Geol.* 120, 223. [16] O'Neill, HStC (1991) GCA, 55, 1135. [17] Ganapathy, R. et al (1970) *PLSC Apollo 11*, 1117. [18] Sato, M. (1979). *PLPSC,* 10, 311. [19] Fogel, R.A. & Rutherford, M.J. (1995). *GCA*, 59, 201-215.