**ARGON DIFFUSION IN LUNAR IMPACT GLASS** D. J. Gombosi[1], S. L. Baldwin[1], E. B. Watson[2], T. D. Swindle[3], J. W. Delano[4], W.G. Roberge[5] [1]Department of Earth Sciences, Syracuse University, Syracuse, NY (djgombos@syr.edu), [2]Department of Earth and Environmental Sciences, Rensselaer Polytechnic Institute, Troy, New York 12180, [3]Lunar and Planetary Laboratory, The University of Arizona, Tucson, AZ 85721, [4]Department of Earth and Atmospheric Sciences, University at Albany (SUNY), Albany, NY 12222. [5]Department of Physics, Applied Physics & Astronomy, Rensselaer Polytechnic Institute, Troy, New York 12180

**Introduction:** The lunar impact history has been assessed by dating impact glasses in lunar meteorites [1] and lunar impact glass spherules [2-4] using the $^{40}Ar/^{39}Ar$ technique. A larger number of $^{40}Ar/^{39}Ar$ ages over a given time period are interpreted to result from a higher rate of impact flux to the lunar surface. Previous studies have reported significant $^{40}Ar/^{39}Ar$ age differences for lunar impact glasses and assumed that glasses remained a closed system with no radiogenic argon ($^{40}Ar^*$) lost subsequent to glass formation.

We propose an alternate hypothesis to account for $^{40}Ar/^{39}Ar$ age differences reported in previous studies of lunar impact glass. If impact glasses do not act as closed systems subsequent to glass formation, they will not record their age of formation, but will yield younger $^{40}Ar/^{39}Ar$ ages from an either partially or totally reset system. We present results of argon diffusion experiments on lunar impact glasses that provide kinetic parameters required to assess whether $^{40}Ar^*$ can be lost at lunar surface conditions via volume diffusion.

**Prior Diffusion Studies:** Two prior studies determined diffusion kinetics of Ar in terrestrial basalt glasses. Hazelton et al., 2003 [5] observed non-linear Arrhenius behavior in basalt glasses at moderate temperatures (600-1,000°C), while a minimal quantity of $^{39}Ar$ was released <600°C preventing robust low temperature kinetic values from being calculated. Grove et al., 2010 [6] determined an $E_a$ of 17.57 ± .014 kcal/mol and frequency factor ($D_0$) of 1.8 ± 0.2 x10$^{-13}$ m s$^{-1}$ at <300°C for Ar diffusion in terrestrial basalt glass assuming a spherical geometry and an effective diffusion domain size of 1 cm. Both studies indicate a possible argon release mechanism transition at ~300°C corresponding to a change from linear behavior (i.e., loss of Ar via volume diffusion) to non-linear Arrhenius behavior.

**Methods:** Eight Apollo 16 lunar spherules (1-2 mm) were characterized with an electron microprobe. Samples were subsequently wrapped in Al-foil and irradiated for 35 hours at the Oregon State University CLICIT facility with a fast neutron flux.

After irradiation six glasses were heated for variable lengths of time in a double vacuum resistance furnace. Diffusivities were calculated based on the fraction of $^{39}Ar_{total}$ released for each temperature step following the approximations of [7] assuming diffusive loss from a sphere.

**Results (Geochemistry):** The geochemistry of glasses analyzed is approximately that of the "local" composition of Apollo 16 [8] defined by the comparison of refractory elements. The bulk composition is broadly similar a low-K terrestrial basalt. At the spatial scale analyzed all elements appear homogeneous.

**Results and Interpretation (Diffusion):** When calculating diffusivities only data with above blank $^{39}Ar$ values were used. Only sample 61503,13_7 is examined here since the range of temperatures is more comprehensive than other samples and all samples generally follow a similar trend.

The decision which points to include in the kinetic calculations were made by noting the weighted fit for each data point following the methods of [9]. The best fit is defined as the line fit between the first release of $^{39}Ar$ and the point before which the weighted fit begins to decrease. This procedure results in a calculated $E_a$ of 17.89 ± 0.52 kcal/mol and log ($D_0/a^2$) of -6.85 ± 0.17 s$^{-1}$ (Fig. 1).



Arrhenius Plot of $^{39}Ar$ from Sample 61503,13_7

$E_a$=41.60 ± 7.27 kcal/mol
log($D_0/a^2$) = 2.98 ± 2.90 s$^{-1}$
$R^2$=0.9965
Reduced $\chi^2$=0.03
$T_c$= 277.5C ± 177.5 (100°C Myr$^{-1}$)

$E_a$=17.89 ± 0.52 kcal/mol
log($D_0/a^2$) = -6.85 ± .017 s$^{-1}$
$R^2$ = 0.9523
Reduced $\chi^2$ = 2.04
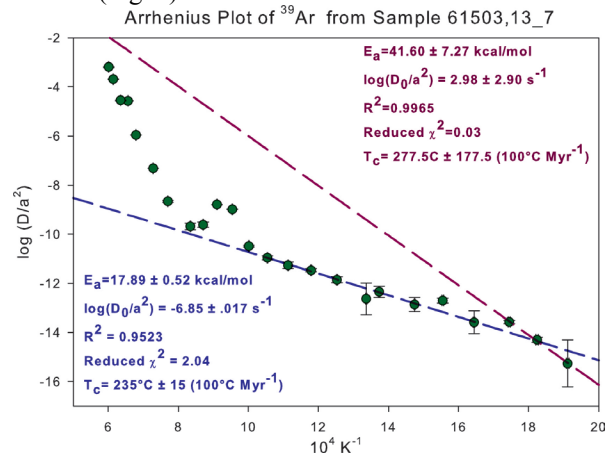$T_c$= 235°C ± 15 (100°C Myr$^{-1}$)

**Figure 1**. Arrhenius plot of argon loss from sample 61503,13_7. The blue line is the linear regression using data corresponding to temperatures $\leq$ 675°C. The red line is the linear regression based on data for temperature steps $\leq$ 300 °C.

If the radius of the diffusion dimension is assumed to be the radius of the spherule ($a$=.0825 cm) this becomes $D_0$=9.64x10$^{-10}$ ± 3.86x10$^{-10}$ cm² s$^{-1}$, a significantly higher value than silica glasses [10, 11], but

reproduces nearly identical activation energies and $D_0$ values from [6].

A subset of the first three data points (250-300°C) visually appear linear (Fig. 1), however both the paucity of data and relatively high uncertainty of the analysis contribute to high uncertainties in calculated kinetic parameters of $\log(D_0/a^2) = 2.98 \pm 2.90$ s$^{-1}$ and $E_a = 41.6 \pm 7.27$ kcal/mol. Both of these $E_a$ and $D_0$ values are distinguishable as higher values than values from the line based on best weighted fit, however due to the high uncertainty little else can be determined from the data.

**Ages:** Although the primary objective of the study was to calculate argon diffusion in lunar impact glasses, $^{40}Ar/^{39}Ar$ ages were determined for each spherule. In cases where glass ages are <100Ma, $^{40}Ar^*$ was at or just above blank levels. These young glasses are possibly sourced from the nearby young North and South Crater Rays (~50 Ma and ~2 Ma respectively), or have been completely reset due to diffusive argon loss. Other glasses yielded complex spectra with $^{40}Ar/^{39}Ar$ ages as old as 1.4 Ga (61503,13_1). Two samples (61503,13_6, 61503,13_7) show clear age gradients with blank levels of $^{40}Ar^*$ in the first ~20% of $^{39}Ar$ released to several hundred million years in latter steps (Fig. 2).
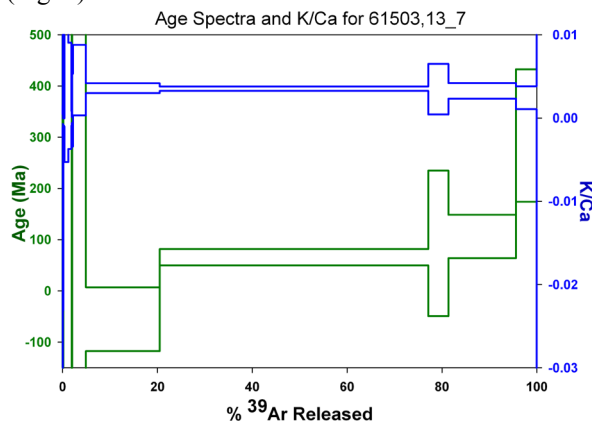


**Figure 2**. Age spectrum for sample 61503,13_7 showing an apparent $^{40}Ar/^{39}Ar$ age gradient corresponding to ages within error of zero over the initial 20% of gas released to 300Ma in last steps.

These age gradients may be evidence for argon diffusive loss in the lunar impact glasses. One sample (61503,13_4) yielded a reverse age gradient from 5.3 Ga to near 0 Ma, attributed to inheritance of $^{40}Ar$ from implantation as described in [12].

**Discussion:** Linear Arrhenius trends based on data corresponding to temperatures steps between 250°C and 675°C are interpreted to result from volume diffusion over this temperature range. This is in contrast to Ar diffusion studies on terrestrial basalts [5, 6]. Above

675°C a second highly retentive linear region occurs. This abrupt transition from relatively low $E_a$ and $D_0$ values to much higher values is interpreted to coincide with a transition to a highly viscous melt. This hypothesis is substantiated by taking a mean composition of the 61503,13 glasses and calculating what the glass transition temperature ($T_g$) is using methods outlined in [13]. The result is a predicted $T_g$ temperature of 661.3°C, a near perfect match to the experimental data.

Assessment of the kinetics corresponding to temperatures <300°C remains an area of ongoing research as does constructing a model to quantify the amount argon production and loss in lunar glasses over Myr timescales. Results presented here indicate that all $^{39}Ar$ lost can be ascribed to transport via volume diffusion.

The implications for retentive kenetics, as the 250-675°C data describe, are lunar glasses with similar compositions should retain ages which pre-date a late heavy bombardment. No ages have been observed which are >3.9 Ga, implying glasses before this time were either destroyed or had their $^{40}Ar^*$ isotopic system reset due to temperatures which exceed the ambient temperature of the lunar surface over the synodic month.

**References:** [1] Cohen B. A., et al. (2000) *Science* 290, 1754. [2] T. S. Culler T. A. et al. (2000) *Science* 287, 1785. [3] Muller R. A. et al. (2001), in *Accretion of Extraterrestrial Matter Throughout Earth's History,* B. P.-E. a. B. Schmitz, Ed. 447-452. [4] Levine J., et al. (2005) *Geophys. Res. Lett.* 32, L15201. [5] Hazelton G. B. et al.(2003) *Contrib. to Min. & Pet.* 145, 1. [6] Grove M. and Manganelli S., (2010) *AGU Fall Confrence*, 1, 2170. [7] Reichenberg D. (1953) *J. of the Am. Chem. Soc.* 75, 589. [8] Delano J. W. et al. (2007) *Meteoritics & Planet. Sci.* 42, 993. [9]. Weirich J. R. et al. (2012), *Geochim. et Cosmochim. Acta* 77, 546. [10] Roselieb K.et al. (1995) *Chem. Geol.* 120, 1. [11] Carroll M. R. et al. (1991) *Earth & Planet. Sci. Lett.* 103, 156. [12] Eugster O. et al. (2001) *Meteoritics &Planet. Sci.* 36, 1097. [13] Giordano D. et al. (2008) *Earth & Planet. Sci. Lett.* 271, 123.