**MAGNESIUM AND SILICON ISOTOPES IN HASP GLASSES FROM APOLLO 16 LUNAR SOIL 61241.** G.F. Herzog[1], J. S. Delaney[1], F. Lindsay[1], C. M. O'D. Alexander[2], R. Chakrabarti[3], S. B. Jacobsen[3], S. Whattam[4], R. Korotev[5] and R. A. Zeigler [6]. [1]Rutgers Univ., Piscataway, NJ 08854, US. [2]Dept. Terrestrial Magnetism, Washington, DC 20015, US. [3]Harvard University, Cambridge, MA 02138, US. [4]Korea University, Seoul 136-713 Rep. Korea [5]Washington Univ., St. Louis, MO 63130,US. [6] NASA Johnson Space Center, KT, Houston TX 77058.

Introduction: The high-Al (>28 wt %), silica-poor (<45 wt %) (HASP) feldspathic glasses of Apollo 16 are widely regarded as the evaporative residues of impacts in the lunar regolith [1-3]. By virtue of their small size, apparent homogeneity, and high inferred formation temperatures, the HASP glasses appear to be good samples in which to study fractionation processes that may accompany open system evaporation. Calculations suggest that HASP glasses with present-day Al_2O_3 concentrations of up to 40 wt% may have lost 19 wt% of their original masses, calculated as the oxides of iron and silicon, via evaporation [4].

We report Mg and Si isotope abundances in 10 HASP glasses and 2 impact-glass spherules from a 64-105 μm grain-size fraction taken from Apollo 16 soil sample 61241.

Experimental methods: Through examination of back-scattered electron mosaics and elemental x-ray maps of a portion of the 61241,4 grain mount containing >8000 particles, Korotev et al. [3] identified 18 HASP glasses and determined major element com-positions using the JEOL 8200 at Washington University. Ten HASP glasses and 2 impact-glass spherules were selected for Mg and Si isotopic analyses, which were carried out using the Cameca 6f ion probe at the Carnegie Institution using an O⁻ primary beam, a spot size of **XX-yy** μm, a 10-kV secondary accelerating voltage, 50 eV energy window, a mass resolution of ~3500, field aperture **.....** To compensate for possible matrix effects in the ion microprobe measurements, we prepared and analyzed a set of synthetic glass standards with elemental compositions comparable to those of the HASP glasses. The elemental compositions of these glass standards were measured using the JEOL 8200 electron microprobe at Rutgers University (Figure 1). To tie the isotope
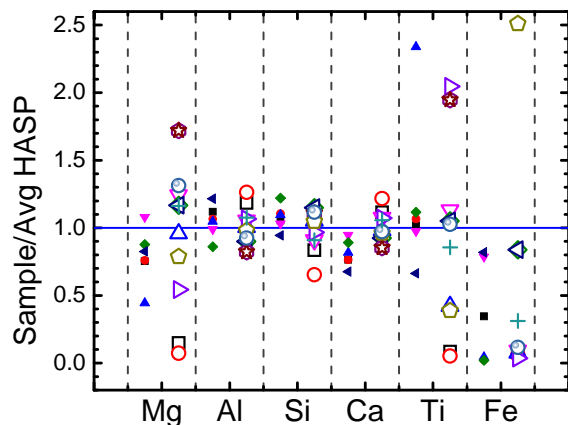
data from the ion-probe analyses to the widely used inter-laboratory standards for Mg (DSM3) and Si (NBS28), we dissolved aliquots of the synthetic glasses in mineral acids, separated Mg and Si by ion chromotography; and measured the Mg and Si isotope abundances by MC-ICP-MS at Harvard University [5].
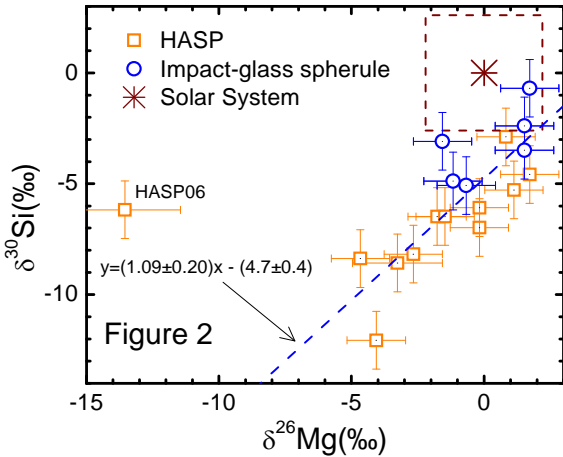
Results and discussion: Table 1 summarizes the isotopic data. To calculate these values, we used the relation $\delta = \delta(6f)_{sample} - \delta(6f)_{avg\ glass\ std} + [\delta(ICP)_{avg\ glass\ std} - \delta(ICP)_{DSM3\ or\ NBS28}]$, with small numerical corrections for non-linearity. Plots of $\delta^{26}Mg$ *vs.* $\delta^{25}Mg$ and of $\delta^{30}Si$ *vs.* $\delta^{29}Si$ for the lunar sample data of Table 1 (not shown) have slopes of 1.79±0.12 and 1.83±0.11, respectively, within <2-σ of the value of ~2.00 expected for mass-dependent fractionation. The values of $\delta^{26}Mg$ and $\delta^{30}Si$ for the glass standards show no systematic variation with composition except that the values of $\delta^{29,30}Si$ for Gstd4 are twice as large as those for the other synthetic glasses. Inclusion of Gstd4 has little effect on the values of $\delta^{29,30}(ICP)_{avg\ glass\ std}$.

Figure 2 shows the isotopic data of Table 1 re-

Table 1. Isotopic composition (‰) of lunar samples

Sample	$\delta^{25}Mg$	$\delta^{26}Mg$	$\delta^{29}Si$	$\delta^{30}Si$
HASP06	-6.8±2.0	-14.1±2.1	-3.3±1.1	-6.6±1.3
HASP08	-5.4±2.3	-3.8±1.7	-4.1±1.0	-9.0±1.3
HASP09	-2.1±1.2	-2.3±1.1	-3.5±0.9	-6.9±1.3
HASP18	-0.4±1.2	-2.0±1.1	-4.0±1.1	-6.9±1.3
HASP19	0.5±1.2	1.2±1.1	-3.8±0.9	-5.0±1.3
HASP19b	0.5±1.2	0.6±1.1	-4.5±0.9	-5.7±1.3
HASP20	-0.5±1.2	-0.7±1.1	-4.2±1.0	-7.4±1.3
HASP30	0.0±1.2	0.3±1.1	-1.8±0.9	-3.3±1.3
HASP30b	-0.1±1.2	-0.7±1.1	-2.7±0.9	-6.5±1.3
HASP36	-1.2±1.2	-3.2±1.1	-5.1±0.9	-8.6±1.3
HASP38	-2.9±1.2	-5.2±1.1	-3.2±0.9	-8.8±1.3
HASP40	-3.2±1.2	-4.6±1.1	-6.5±0.9	-12.4±1.3
Avg	-1.8±1.4	-2.9±2.4	-3.9±1.2	-7.3±2.3
Impact glass 3	-2.0±1.2	-2.1±1.1	-1.8±0.9	-3.5±1.3
Impact glass 3c	1.5±1.2	1.0±1.1	-2.0±0.9	-3.9±1.3
Impact glass 3d	1.2±1.2	1.0±1.1	-1.3±0.9	-2.8±1.3
Impact glass 4	0.6±1.2	1.2±1.1	-1.7±0.9	-1.1±1.3
Impact glass 4b	-1.2±1.2	-1.7±1.1	-3.5±1.0	-5.3±1.3
Impact glass 4c	-0.3±1.2	-1.2±1.1	-1.1±0.9	-5.5±1.3
Avg	0.0±0.8	-0.3±0.9	-1.9±0.9	-3.7±1.7
Gstd1a	-0.8±0.1	-1.6±0.2	-1.3±0.1	-2.6±0.2
Gstd1b	-0.8±0.1	-1.5±0.1	-1.1±0.1	-2.2±0.3
Gstd2	-0.9±0.1	-1.7±0.2	-1.5±0.1	-2.8±0.2
Gstd3	-0.7±0.1	-1.4±0.1	-1.4±0.1	-2.4±0.2
Gstd4	-0.7±0.1	-1.4±0.2	-3.2±0.1	-6.4±0.3
Gstd5	-0.8±0.1	-1.5±0.2	-1.6±0.1	-3.2±0.2
Avg	-0.8±0.1	-1.5±0.1	-1.7±0.6	-3.3±1.3

Mg relative to DSM3 and Si to NBS28.

Figure 1. Elemental compositions (wt%) of synthetic glass standards (left columns; small symbols) and HASP glasses (right columns, large symbols) normalized to the average elemental composition of 10 Apollo 16 HASP glasses (wt%): Mg 3.61; Al 19.4; Si 16.3; Ca 14.8; Ti 0.16; Fe 1.35.

Figure 2

normalized to the average solar system (SS) values: $\delta^{26}Mg \equiv 0$ (SS) = -0.535 (DSM3) [5]; $\delta^{30}Si \equiv 0$ (SS) = -0.39 (NBS28) [6]. The box surrounding the SS point represents the average 2-σ uncertainty of the ion microprobe measurements. Values of $\delta^{26}Mg$ for 5 of the 10 HASPs and both the lunar glasses analyzed plot within 2σ of the SS value. For $\delta^{30}Si$, all the samples are on average more than 1σ below 0. Averages and one standard deviation of the means for the HASP glasses and the impact-glass spherules are, respectively: $\delta^{26}Mg$ = -2.3±1.2 and 0.23±0.62; $\delta^{30}Si$ = -6.9±0.7‰ and -3.3±0.7. $\delta^{30}Si$ and $\delta^{26}Mg$ correlate modestly with eachother (R^2=0.64). HASP glasses 6, 8, 36, 38, and 40 have $\delta^{26}Mg$ values more negative than -2.0‰.

In assessing these observations, we considered several possible instrumental artifacts. 1) Unidentified interferences at masses 24 and 28 could explain the low values of $\delta^{26}Mg$ and $\delta^{30}Si$. With a mass resolution of ~3500 we were able to separate $^{12}C_2^{2+}$ from ^{24}Mg and $^{27}Al^1H^+$, $^{14}N_2^+$, and $^{12}C^{16}O^+$ from $^{28}Si^+$. 2) High-energy tailing of ^{27}Al at mass 28 ought to have led to a strong, but unobserved correlation between Al/Si and $\delta^{30}Si$ and would have produced similar (and hence compensating) results in the standard glasses. 3) N_2^+ is very inefficiently produced with an O$^-$ beam.

We also considered the possibility that the results might be accurate. We are not the first to observe isotopically light Mg in lunar samples. Esat et al. [7] reported values of -1.2,±0.5 -1.7±0.2, and -2.0±0.2‰ (relative to a 'normal' $^{26}Mg/^{24}Mg$ ratio of 0.13569) for three directly-loaded samples of Apollo 15 green glass. Those authors regarded the results reservedly, in part because analyses of the same samples after chemical separation of Mg gave 'normal' values. In another study [2], Warren et al. used laser ablation ICP-MS to measure $\delta^{26}Mg$ of -1.5‰ for one Apollo 15 highland breccia relative to San Carlos Olivine (USNM 136718). Those authors also found values of $\delta^{26}Mg$ between 0 and +0.5‰ in Apollo 15 green glasses. Chakrabarti and Jacobsen [9] reported one Apollo 16 soil with $\delta^{26}Mg$ = -1.2.

In the conventional view of HASP glasses as evaporation residues, $\delta^{26}Mg$ and $\delta^{30}Si$ should be the same as or heavier than those of the possible source materials. Lunar

basalts, one possible source, show a limited range of mass-dependent variation in Mg isotope abundances (‰): $-0.8 \le \delta^{26}Mg \le +0$ [2]; $-0.56 \le \delta^{26}Mg \le -0.49$ [5]; $-0.53 \le \delta^{26} \le +0.05$ [8], where $\delta^{26}Mg$ is taken relative to standard DSM3. More to the point, with the exception mentioned above, the Mg isotope abundances in Apollo 16 lunar soils lie in the range from $-0.56 \le \delta^{26}Mg \le 0.1$ [9]. Isotopic results for silicon in lunar basalts and a breccia all fall in a restricted range: $-0.35 \le \delta^{30}Si \le 0.27$ [10]; $0.33 \le \delta^{30}Si \le 0.27$ [11], where $\delta^{30}Si$ is taken relative to standard NBS 28. In lunar soils, heavier silicon isotopes are enriched in grain surfaces (see [12]) although [13] suggested that the fractionation was an artifact. Few data are available, however, for the source rocks of the Apollo 16 regolith: anorthosites, feldspathic breccias from which most of the Si derives.

In summary, in the likeliest lunar source materials for the HASP glasses, $\delta^{26}Mg$ and $\delta^{30}Si$ are mostly close to or greater than 0 relative to SS. Thus on average we would expect $\delta^{26}Mg$ and $\delta^{30}Si$ >0 in HASP glasses, contrary to observations. The HASPs could, perhaps, include re-condensed vapor. If the vapor were isotopically unfractionated, then with partial condensation a proto-HASP might have acquired a large fraction of the more refractory Mg, which, accordingly, would be close in isotopic composition to that of the vapor; the proto-HASP might also acquire a smaller fraction of the condensing, more volatile Si, which therefore would be more fractionated in favor of the lighter isotopes than the vapor. Another possible explanation is that the Moon harbors, somewhere, heretofore unidentified reservoirs of isotopically light Mg and Si.

Conclusions: The Mg isotopic compositions of 2 impact glass spherules and 5 HASP glasses are consistent with average Solar System values. Values of $\delta^{26}Mg$ in 5 other HASP samples are more negative than SS values. The Si isotopic compositions of 2 impact-glass spherules and 10 HASP glasses are all isotopically lighter by more than 2-σ than SS values. Perhaps we have tapped lunar reservoirs of isotopically light Mg and Si at the Apollo 16 site. Alternatively, partial condensation of Si, and for a few samples Mg, could explain the low values of $\delta^{26}Mg$ and $\delta^{30}Si$. We do not rule out an unidentified artifact.

References: **[1]** Naney M.T. et al. (1976) *Proc. LSC*, *7*, 155-184. **[2]** Warren P.H. (2008) *GCA*, *72*, 3562-3585. **[3]** Korotev R.L. et al. (2010) *GCA*, *74*, 7362-7388. **[4]** Yakovlev O.I. et al. (2009) *LPS*, *40*, 1261.pdf. **[5]** Chakrabarti R. and Jacobsen S. (2010) *EPSL*, *293*, 349-359. **[6]** Chakrabarti R. and Jacobsen S. (2011) *GCA*, *74*, 6921-6933. **[7]** Esat T.M. et al. (1979) *Science*, *206*, 190-197. **[8]** Wiechert and Halliday (2007) *EPSL*, *256*, 360–371. **[9]** Charkabarti R. and Jacobsen S.B. (2011) *LPS*, *42*, 2006.pdf. **[10]** Georg R.B. et al. (2007) *Nature*, *447*, 1102-1106; Armytage R.M.G. et al. (2010) *MPS*, *73*, 5272.pdf. **[11]** Fitoussi C. et al. (2010) *LPS*, *41*, 2653.pdf. **[12]** Beckinsale R.D. (1977) Phil. Trans. Royal Soc. London A: *285*, 417-26. **[13]** Esat T.M. and Taylor S.R. (1992) *GCA*, *56*, 1025-1031.