

## Apollo 17 regolith, 71501,262: A record of impact events and mare volcanism in lunar glasses

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**Abstract**—Thirteen glasses from Apollo 17 regolith 71501,262 have been chemically analyzed by electron microprobe and isotopically dated with the <sup>40</sup>Ar/<sup>39</sup>Ar dating method. We report here the first isotopic age obtained for the Apollo 17 very low titanium (VLT) volcanic glasses, 3630 ± 40 Ma. Twelve impact glasses that span a wide compositional range have been found to record ages ranging from 102 ± 20 Ma to 3740 ± 50 Ma. The compositions of these impact glasses show that some have been produced by impact events within the Apollo 17 region, whereas others appear to be exotic to the landing site. As the data sets that include compositions and ages of lunar impact glasses increase, the impact history in the Earth-Moon system will become better constrained.

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### INTRODUCTION

Impact processes have played an important role in the history of the Earth-Moon system. Studies of lunar impact glasses and impact melt rocks that have combined geochemical compositions and isotopic ages have demonstrated the value of this approach for better constraining the bombardment history of the Moon (e.g., Eberhardt et al. 1973; Borchardt et al. 1986; Dalrymple and Ryder 1993, 1996; Ryder et al. 1996; Cohen et al. 2000; Duncan et al. 2004; Delano et al. 2007). In some instances, it has been possible to relate the isotopic ages and chemical compositions of specific lunar samples with the ages of specific impact craters and the chemical compositions of the regions surrounding those craters (e.g., Zellner et al. 2002; Duncan et al. 2004).

The Apollo 17 landing site is located in the Taurus-Littrow valley along the eastern margin of the Serenitatis impact basin (Fig. 1). The valley is underlain by high-Ti mare basalts that were erupted at ~3700 Ma (e.g., Heiken et al. 1974). The mountainous highlands regions contain Serenitatis ejecta and impact melt sheets that were emplaced at ~3900 Ma (e.g., Dalrymple and Ryder 1996; Ryder 1997; Stöffler and Ryder 2001). To the west within ~100 km of the Apollo 17

landing site are areas (central regions of Mare Serenitatis) where low-Ti mare basalts have been inferred from ground-based reflectance spectroscopy (e.g., Pieters and McCord 1976; Pieters 1978) and instruments onboard lunar orbiting spacecraft (e.g., Jolliff 1999). Basaltic rocks, volcanic glasses, and impact glasses presumed to have been ballistically transported to the Apollo 17 landing site from those areas to the west have been identified by previous investigators (e.g., Taylor et al. 1977; Vaniman and Papike 1977a, 1977b; Warner et al. 1979a; Wentworth et al. 1979). Station 1 soils, from which regolith sample 71501,262 was collected, have been found to contain nearly 18 wt% FeO, ~10 wt% TiO<sub>2</sub>, ~11 wt% Al<sub>2</sub>O<sub>3</sub> (Jolliff 1999 and references therein). Our lunar glasses have compositions that, in some cases, differ from this average composition, and thus show they are not typical of the local regolith.

The presence of secondary craters at the Apollo 17 landing site (i.e., Central Cluster), which are generally regarded as having been formed by the impact of ejecta from the Tycho event (e.g., Arvidson et al. 1976; Lucchitta 1977, 1979; Wolf et al. 1975, 1981), has led to searches for Apollo 17 samples that may have come from the Tycho region (e.g., Fruland et al. 1977; Vaniman et al. 1979). Cosmic-ray exposure ages of Apollo 17 samples associated with the

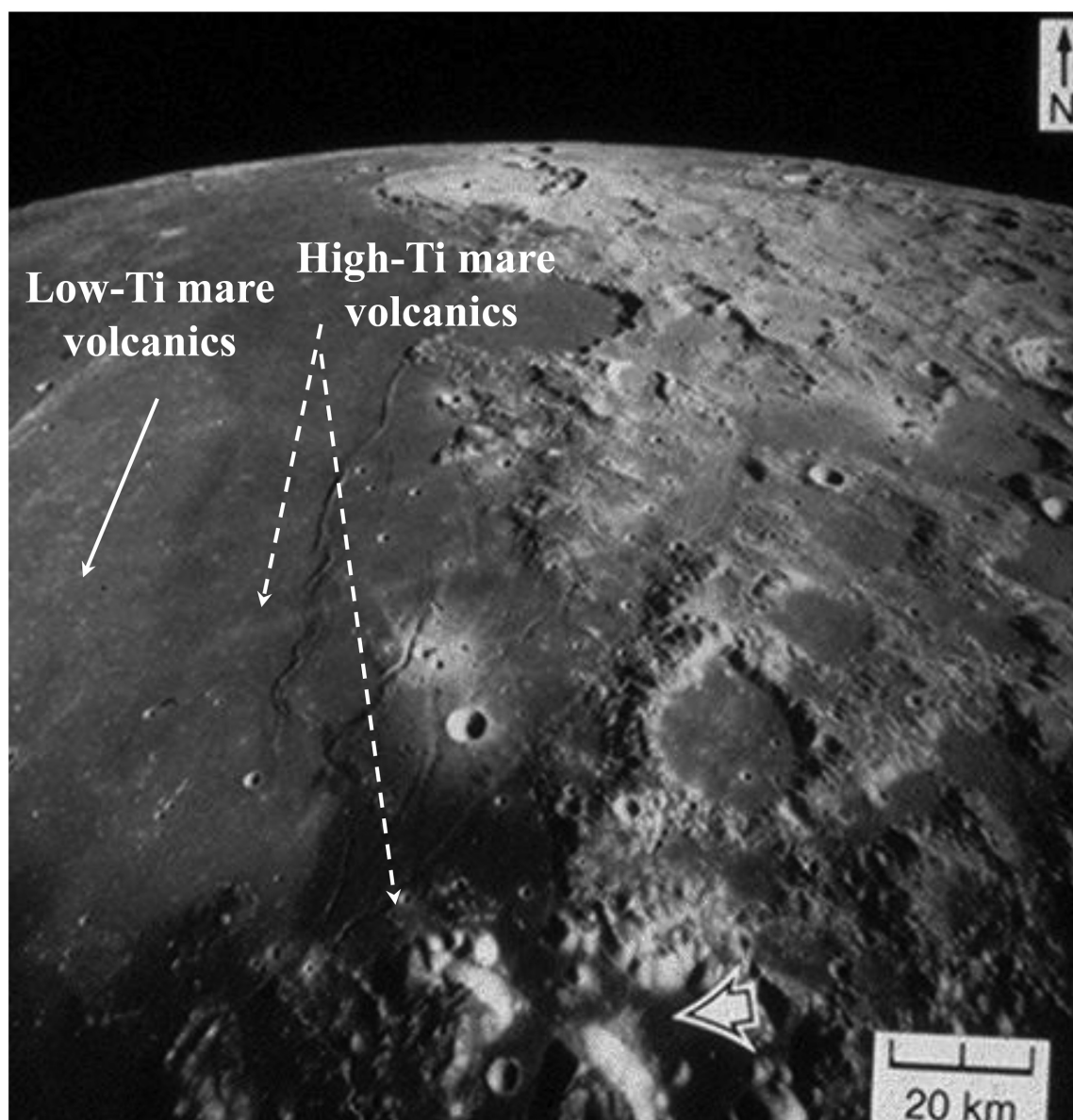


Fig. 1. Image of the region containing the Apollo 17 landing site (arrow at lower right corner) in the Taurus-Littrow valley (NASA photograph AS17-0939[M]). The eastern half of Mare Serenitatis is on the left half of the image with low-albedo, high-Ti mare volcanics along the basin's margin (typical regions noted by two dashed arrows) and higher-albedo, low-Ti mare volcanics within the basin's interior (typical region noted by solid arrow).

Central Cluster and with the bright mantle (landslide from South Massif) are  $\sim 90$ – $115$  Ma ( $96 \pm 5$  Ma: Arvidson et al. 1976; and  $109 \pm 4$  Ma: Drozd et al. 1977), which is inferred to be the age of the Tycho impact event.

Impact glasses from regolith 71501,262 with interesting compositions and high K abundances were selected for isotopic dating by the laser, step-heating  $^{40}\text{Ar}/^{39}\text{Ar}$  method in order to determine the age of the impact event that produced each piece of impact glass. In this study, we report on impact glasses with compositions both typical and atypical of the local Apollo 17 regolith and put their impact ages in the context of lunar bombardment history.

## ANALYTICAL PROCEDURES

One 5-gram sample from Apollo 17 regolith 71501,252 was dry-sieved, then ultrasonically cleaned in acetone. Within the  $>125$ -micron fraction, 119 homogeneous and inclusion-free spherules and fragments of glass were handpicked with the aid of a binocular microscope. Glasses were individually mounted in a 6 mm diameter aluminum tubing with Crystalbond<sup>TM</sup> 509–3 adhesive (Aremco Products, Inc.) and carefully ground and polished to produce a smooth, planar surface (with minimal mass-loss of the sample) that could be chemically analyzed by electron microprobe (EM). Each

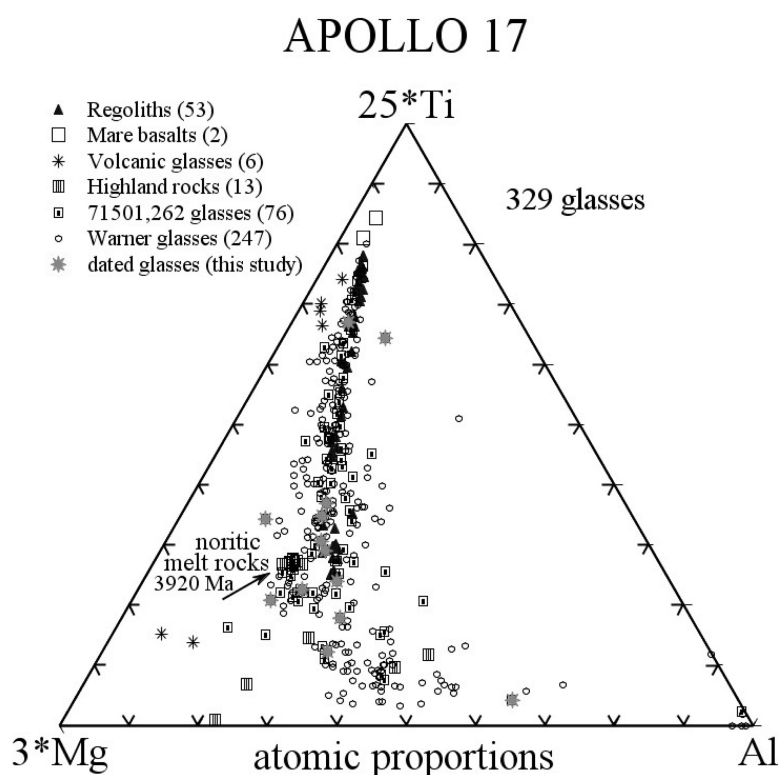


Fig. 2. Ternary diagram (atomic proportions of non-volatile elements) showing the compositions of Apollo 17 glasses analyzed by electron microprobe from 71501,262 (this study) and from Warner et al. (1979b). The 13 glasses that were also isotopically dated in this study are plotted to show their chemical context with Apollo 17 rocks and regoliths. Compositions of highlands rocks, mare basalts, and regoliths from the Taurus-Littrow landing site are from Duncan et al. (1974), Rhodes et al. (1974), Rose et al. (1974), and Korotev and Kremser (1992). The most compositionally primitive types (6) of Apollo 17 volcanic glasses from Delano (1986) are also plotted. The noritic impact melt rocks (e.g., boulders at Station 6) have an  $^{40}\text{Ar}/^{39}\text{Ar}$  ages of  $\sim 3920$  Ma (e.g., Cadogan and Turner 1976; Dalrymple and Ryder 1996).

glass was chemically analyzed at Rensselaer Polytechnic Institute in Troy, NY by a JEOL 733 Superprobe for Si, Ti, Al, Cr, Fe, Mn, Mg, Ca, Na, and K. Five X-ray spectrometers were tuned and calibrated for each element analyzed in the glass sample. A 15 keV electron beam with a specimen current of 50 nAmps was used. Lunar working standards were used to assess analytical precision throughout the study. Count times of 200 seconds were used for Na and K, while count times of 40 seconds were used for the other elements. Backgrounds were collected for every element on every analysis. Uncertainties in the measurements were usually  $<3\%$  of the amount present. In the absence of ferromagnetic resonance intensity (Stone et al. 1982), high Mg/Al ratios and high  $\text{Cr}_2\text{O}_3$  values were used to distinguish volcanic glasses from impact glasses (as described in Delano 1986). Lunar glass working standards were analyzed multiple times to assess the analytical precision of the electron microprobe (as described in Zellner et al. 2002).

Following chemical analysis, glasses (Figs. 2–4) with interesting chemical compositions, including high K abundances, were selected for isotopic dating, re-polished to remove the carbon coating needed for the EM analysis, removed from the Crystalbond adhesive, and cleaned in acetone to remove organics from the surfaces of the glasses.

They were then placed in aluminum sample holders, transferred to the geochronology facility at the University of Arizona, and irradiated for  $\sim 300$  hours in the Phoenix Ford Reactor at the University of Michigan along with MMhb-1 hornblende (but see Jourdan and Renne [2007]) for concerns about using this as a monitor] and  $\text{CaF}_2$  salt. The hornblende is used to determine the neutron fluence in the reactor, while the  $\text{CaF}_2$  is used to correct for reactor-produced interferences. K interferences were based on typical values measured for  $\text{K}_2\text{SO}_4$  included in irradiations at this reactor. The J factor for the irradiation of these glasses was  $0.05776 \pm 0.00030$ . Samples were analyzed in the noble gas mass spectrometry laboratory of the University of Arizona, and each sample was degassed in a series of temperature extractions using a continuous Ar-ion laser heating system. In the first heating step, a 5A beam was passed over the sample. The amperage was increased incrementally until  $^{40}\text{Ar}$  counts from the sample peaked, and then decreased to background levels. The isotopic composition of the released Ar was measured with a VG5400 mass spectrometer.

Data corrections included system blanks, radioactive decay, and reactor-induced interferences. Although we have data that could be used to determine Ca/K ratios for each step, we are dealing with a glass, rather than a polymineralic

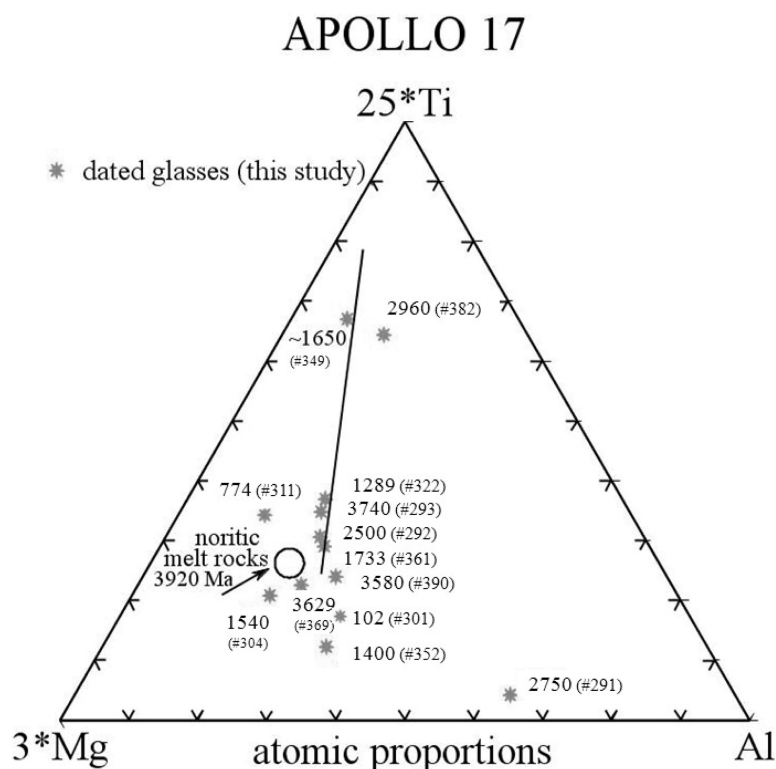


Fig. 3. Ternary diagram (atomic proportions of non-volatile elements) showing the ages (Ma) of the 13 glasses dated in this study along with the sample numbers. The chemical compositions of these glasses are listed in Table 1. The sample numbers of the individual glasses can be identified using their ages near the bottom of Table 1. The solid line shows the compositional range of regoliths sampled at the Apollo 17 landing site.

sample, so the Ca/K ratios tend to be uniform throughout a sample and are not considered further. We corrected for cosmic-ray spallation based on the  $^{38}\text{Ar}/^{36}\text{Ar}$  ratio of each sample, assuming  $^{38}\text{Ar}/^{36}\text{Ar}$  of air for the “trapped” component. Although difficult or impossible on irradiated meteorites, such a correction is possible on these lunar samples because there is no apparent contribution at  $^{38}\text{Ar}$  from Cl. Three-isotope plots were then used to determine the  $^{40}\text{Ar}/^{36}\text{Ar}$  ratio for the trapped solar wind within each sample, and that contribution was subtracted, as described in Delano et al. (2007). Typically a step or two with a high enough ratio of solar wind to radiogenic gas allowed us to determine a well-defined value. In all cases except for sample #382, the  $^{40}\text{Ar}/^{36}\text{Ar}$  ratio is low enough that we suspect it is solar wind  $^{36}\text{Ar}$  mixed with re-implanted  $^{40}\text{Ar}$ , the typical lunar “solar wind” Ar component, so we refer to this as “solar wind” Ar. Since the samples contained small amounts of K (from <1 ng to a few hundred ng), measuring Ar can be difficult. Temperature extraction steps were therefore large in order to maximize the amount of Ar released at each step. The ages discussed in this paper were derived from plateaus and the uncertainties in those ages were calculated as weighted averages based on the amount of  $^{39}\text{Ar}$  released at each step. The uncertainties in the ages reported here are  $2\sigma$ . Several spherules of Apollo 15 volcanic green glass from 15426 (e.g., Delano 1979; Steele et al. 1992), with a well-defined  $^{40}\text{Ar}/$

$^{39}\text{Ar}$  age of ~3340 Ma (Podosek and Huneke 1973; Huneke et al. 1974; K ~200 ppm) were used as isotopic working standards. Our analyses of single spherules were typically within 5% of the accepted age.

## RESULTS AND DISCUSSION

Lunar impact glasses are droplets of melt (produced by energetic impact events) that have been quenched during ballistic flight. They are presumed to preserve the ratios of non-volatile element ratios in the original target materials that had been fused at the site of impact (e.g., Delano 1991). Based on this geochemical perspective, a ternary diagram involving three non-volatile lithophile elements (Mg, Ti, Al) can be informative. Figure 2 shows this geochemistry for 329 Apollo 17 glasses, including the 13 reported here. This ternary diagram displays the ratios of these conserved elements, in which fractional losses of volatile elements do not move the location of compositions in the diagram relative to that of the original target materials, as described in Delano et al. (2007). Since the 13 dated glasses in this study show (with the exception of glass #311) that the glasses have reasonable abundances of the highly volatile element Na (Table 1), it appears that these glasses have not experienced significant open-system behavior of the major elements during their formation. As a result, it appears justifiable to plot their

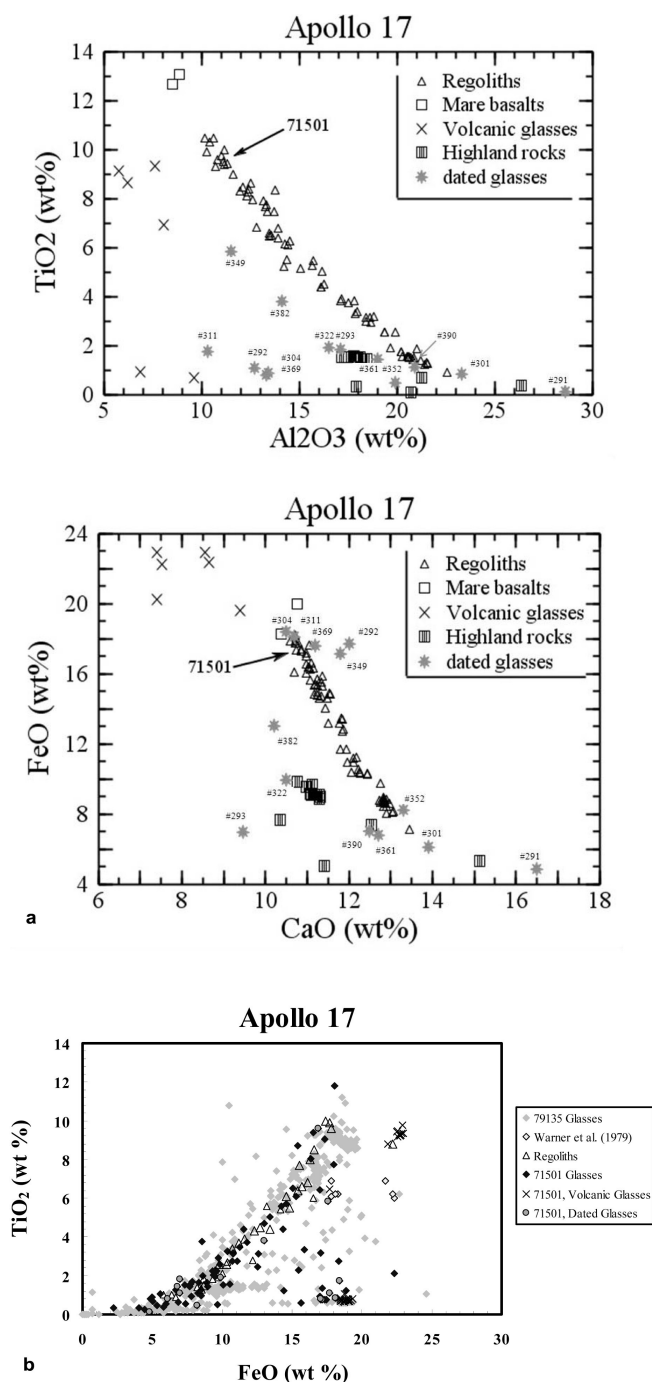


Fig. 4. a) Top and center panels show the compositional comparison of the isotopically dated Apollo 17 glasses with Apollo 17 highlands rocks, mare basalts (70215; 74275), regoliths, and picritic volcanic glasses. Sources of data are listed in the caption to Fig. 2. b) Bottom panel shows the compositional comparison of the isotopically dated Apollo 17 glasses with Apollo 17 regoliths from Miller et al. (1974), Wänke et al. (1974), Rose et al. (1974), Rhodes et al. (1974), Laul et al. (1974), Duncan et al. (1974), and Korotev and Kremser (1992), and glasses from Warner et al. (1979a) and J. Delano (unpublished data). Compare the range of these data to the range of Clementine data in Fig. 14 (Jolliff 1999).

abundances of oxides on x-y diagrams for comparison with rocks and regoliths from the Apollo 17 landing site (Fig. 4a). Jolliff (1999) noted that a plot of FeO versus TiO<sub>2</sub> concentrations of soils, derived from Clementine images of the Taurus-Littrow Valley and the surrounding highland regions, suggests that there may be important unsampled rock types there. He showed that the range of Clementine compositional data is far greater than that shown by the average soil compositions at the Apollo 17 stations. Indeed, when glass and regolith data are plotted (including samples from 79135; J. Delano, unpublished data), as shown in Fig. 4b, the range of Clementine data (Fig. 14; Jolliff 1999) is seen in the additional samples. Among the 13 isotopically dated glasses, four have a low-Ti mare provenance (glasses #369, 304, 311, 292; Table 1) and eight have a highlands provenance (glasses #291, 293, 301, 322, 352, 361, 382, 390; Table 1). One has an intermediate-Ti mare provenance (glass #349).

Our preferred estimates of ages (Table 1) are based on summing multiple steps containing 87% or more of the sample's <sup>39</sup>Ar in every case but #349 and #301, which are discussed separately below. This is usually only two or three steps, because of the rather coarse steps we used to obtain a high enough signal-to-noise ratio. However, these steps typically agree reasonably well with each other. While we cannot be as confident in these ages as we would be in an age based on many steps, we have far more confidence than we would in a single-step extraction, and we have tried to assign realistic uncertainties. Uncertainties in the ages are reported at the 2σ level to account for heterogeneity in the hornblende monitor and to account for any errors resulting from the data analysis procedures. These conservative uncertainty values are large enough so that any ages included in the calculation are usually no more than twice that away from the weighted age.

As expected, the compositional range displayed by the 329 glasses (Warner et al. 1979b; this study) plotted in Fig. 2 shows a broad compositional similarity to the rocks and regoliths at the Apollo 17 landing site (at least for the ratio of Ti/Al/Mg). This agreement supports the idea that the ratios of non-volatile element ratios in impact glasses preserve the ratios in the original target-materials, thereby providing chemical information about their provenance. In combination with isotopic ages that constrain the time of the impact event that generated each glass, these glasses preserve useful information about the Moon's bombardment history and chemical evolution. We would expect impact glasses of local regolith composition to have a wide range of ages, not necessarily coincident with any large impact event, and that is indeed what we see. In addition, a few glasses have ages consistent with previously suggested events.

### Glasses with Mare Compositions

**Glass #369** was a green angular fragment with a very-low titanium (VLT) mare provenance (Table 1; Figs. 4, 5, and

Table 1. Chemical compositions (wt%) of 13 glasses from Apollo 17 regolith 71501,262 that have been isotopically dated in this study. The compositional groupings listed in row 2 of this table are generic only: VLT = very low-Ti; LKFM = low-K Fra Mauro; HB = highland basalt; HKFM = high-K Fra Mauro; ImHKFM = low-Mg high-K Fra Mauro of Delano et al. (2007) = “basaltic andesite” of Zeigler et al. (2006a). Ages are reported with  $\pm 2\sigma$  uncertainty. Individual results for each heating step can be seen in Table A1 (online appendix). In the text, the glasses are described in the same order as listed in this table.

	#369	#304	#311	#292	#349	#322	#352	#361	#390	#382	#293	#291	#301
(wt%)	VLT mare	low-Ti mare	low-Ti mare	low-Ti mare	mare	LKFM	LKFM	LKFM	LKFM	ImHKFM	HKFM?	HB	HB
SiO <sub>2</sub>	48.6	45.9	46.8	47.4	43.7	51.3	47.4	49.9	47.3	50.3	50.1	44.7	46.0
TiO <sub>2</sub>	0.79	0.86	1.74	1.08	5.84	1.89	0.47	1.44	1.11	3.80	1.81	0.12	0.82
Al <sub>2</sub> O <sub>3</sub>	13.3	13.4	10.3	12.7	11.5	16.5	19.9	19.0	20.9	14.1	17.1	28.6	23.3
Cr <sub>2</sub> O <sub>3</sub>	0.41	0.51	0.37	0.35	0.54	0.30	0.35	0.29	0.16	0.24	0.32	0.10	0.20
FeO	17.1	18.1	18.4	17.7	17.6	9.92	8.20	6.77	6.98	13.0	6.96	4.82	6.07
MnO	0.27	0.27	0.24	0.27	0.29	0.15	0.17	0.10	0.08	0.17	0.11	0.07	0.08
MgO	7.90	10.4	11.4	6.99	9.11	9.29	8.87	9.84	9.36	5.16	9.80	3.89	9.83
CaO	11.8	10.7	10.5	12.0	11.1	10.5	13.3	12.7	12.5	10.2	9.47	16.5	13.9
Na <sub>2</sub> O	0.21	0.24	0.04	0.26	0.32	0.24	0.76	0.22	0.71	1.16	1.83	1.11	0.75
K <sub>2</sub> O	0.03	0.03	0.01	0.04	0.05	0.17	0.29	0.04	0.35	0.73	2.11	0.05	0.10
Total	100.4	100.4	99.8	98.8	100.1	100.3	99.7	100.3	99.5	98.8	99.6	100.0	101.1
Color	green	yellow green	opaque	lt.green	red	lt.green	green	lt.green	green	opaque	yellow green	lt.green	green
Form	frag	frag	sphere	frag	frag	frag	sphere	sphere	frag	frag	frag	sphere	sphere
Size ( $\mu$ m)	—	~280	310	~340	~400	~400	190	370	~400	~150	~450	140	570
Age (Ma) $\pm$	3630 40	1540 140	774 114	2500 1500	1650 400	1289 415	1400 300	1733 40	3580 45	2960 1600	3740 50	2750 60	102 20
% <sup>39</sup> Ar in plateau	87.2	97.9	96.2	94	99.5	100	88.5	99.7	100	100	91.7	100	62.2
# of steps in plateau	3	3	3	4	4	3	3	3	4	3	3	2	2
Solar wind ( <sup>40</sup> Ar/ <sup>36</sup> Ar) $\pm$	0.343 0.073	0.399 0.011	0.275 0.005	0.123 0.011	0.526 0.003	0.413 0.004	0.282 0.004	0.824 0.003	0.255 0.002	460.6 180.6	0.71 0.1	0.255 0.008	0.102 0.001

6). Unlike VLT glass #304 (below), which is inferred to have had an impact origin, glass #369 appears to be an extreme magmatic differentiate of the Apollo 17 VLT volcanic glasses (Fig. 5). Specifically, glass #369 lies near the crystal/liquid fractionation trend noted by Warner et al. (1979a) for the VLT volcanic glasses (Fig. 5). If this interpretation is correct, the <sup>40</sup>Ar/<sup>39</sup>Ar age of  $3630 \pm 40$  Ma (Table 1; Fig. 7a) is the time of magmatic fire-fountaining that produced the Apollo 17 VLT volcanic glasses. While Apollo 17 VLT mare basalts have been chemically and petrologically described (Wentworth et al. 1979; Vaniman and Papike 1977a,b), this is the first isotopic age obtained for the Apollo 17 VLT volcanic glasses. The age is based on three consecutive steps, with 87% of the <sup>39</sup>Ar. The next step, containing most of the remainder of the gas, is 200 Ma older ( $3846 \pm 58$  Ma). That step could suggest that the true crystallization age is somewhat older, or it could be an outlier, perhaps caused by a tiny relict inclusion. We will assume it is an outlier, although a 200 Ma older age cannot be ruled out and would not change any conclusions.

This age of Apollo 17 VLT mare volcanism ( $3630 \pm 40$  Ma) overlaps with the known age of Apollo 17 high-Ti mare volcanism (3600–3700 Ma; Taylor 1982) and the orange picritic glass, 74220 ( $3600 \pm 40$  Ma; Huneke 1978). In contrast, this age is distinctly different from the well-documented age of VLT volcanism (~3300 Ma) that occurred at the Luna 24 landing site (e.g., Schaeffer et al. 1978; The Lunatic Asylum 1978; Hennessy and Turner 1980; Burgess

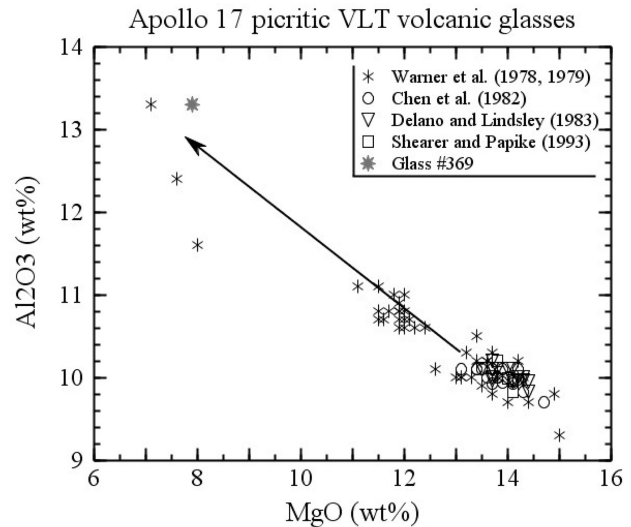


Fig. 5. Compositional range of VLT volcanic glasses at the Apollo 17 site as determined by the following investigators: 20 VLT glasses from Chen et al. (1982); 20 VLT glasses from Delano and Lindsley (1983); 41 VLT glasses from Warner et al. (1979a, 1979b); 3 VLT glasses from Shearer and Papike (1993). Since the trend shown by the arrow is likely due to magmatic fractionation prior to volcanic fire-fountaining at ~3630 Ma, glass #369 appears to be an extreme differentiate of the picritic VLT magma.

and Turner 1998; Cohen et al. 2001; Fernandes and Burgess, 2005). While it would be difficult to definitively determine the origin of this volcanic glass, sources could include flows

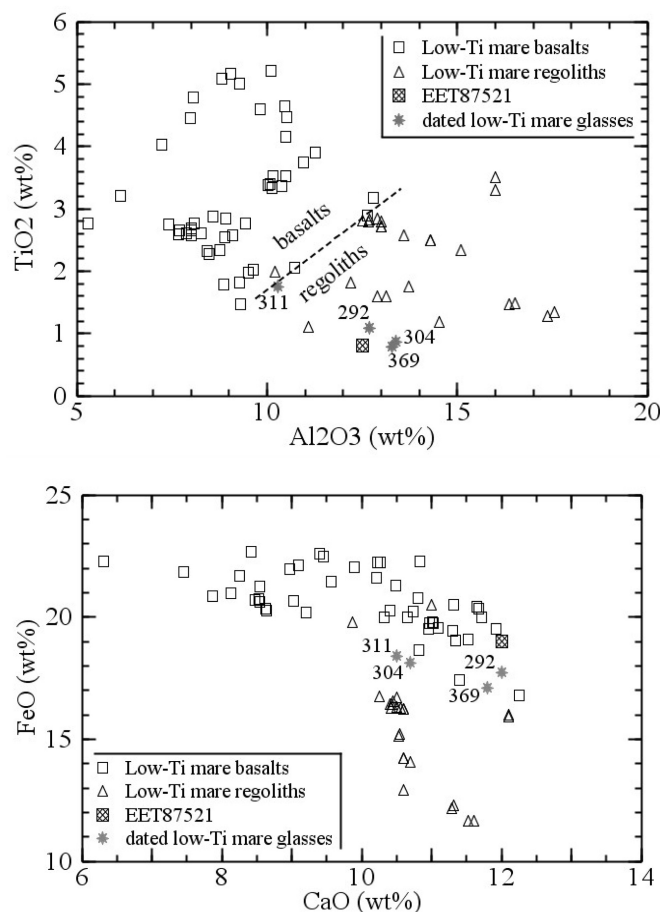


Fig. 6. Compositional comparison of the four isotopically dated, low-Ti mare glasses with low-Ti mare basalts and associated regoliths from Apollo 12, Apollo 15, Luna 16, Luna 24, and lunar meteorite EET 87521 (Arai and Warren 1999; Blanchard et al. 1978; Cuttitta et al. 1971; Engel et al. 1971; LSPET, 1972; Rhodes and Hubbard 1973; Rhodes et al. 1977; Willis et al. 1971). The dashed line is the approximate compositional boundary between crystalline mare basalts and mare regoliths overlying those mare basalts.

within Mare Crisium, flows within Mare Serenitatis, or VLT basalts that are not present at the surface.

Finally, several episodes of VLT volcanism have been reported at the Apollo 14 (e.g., Delano 1986, 1988) and Apollo 16 landing sites (e.g., Zeigler et al. 2006b), as well as in lunar meteorites (e.g., EET 87521; Asuka-881757; Y-793274; Y-793169; Asuka-31; QUE 94281; and NWA 773) with one reported U-Pb age of  $\sim 3840$  Ma (Misawa et al. 1993) and another reported U-Pb age of  $\sim 4350$  Ma (Terada et al. 2007). These occurrences suggest that VLT mare volcanics are not only widely distributed on the Moon but also have a large range of isotopic ages ( $\sim 2700$  Ma to  $\sim 4350$  Ma). Additionally, the large range in Ti contents of mare basalts (as summarized for example in Giguere et al. 2000), in combination with the range of ages, suggests complex mantle dynamics over a long range of time.

**Glass #304** was a clast-free, angular impact fragment measuring  $\sim 340 \mu\text{m} \times 430 \mu\text{m}$  with a yellowish green color

and is compositionally similar to a group of VLT glasses identified by Warner et al. (1979a), which were designated as “Mare 6” (Table 2). These mare glasses are not likely to be of volcanic origin (Delano 1986). Since low-Ti mare basalts have been spectrally identified within  $\sim 100$  km west of the Apollo 17 landing site (e.g., Pieters 1978; Fig. 1), this VLT impact glass (Figs. 2, 4, 5, and 6) may have been derived from somewhere within the low-albedo regions of Mare Serenitatis (Fig. 1). The  $^{40}\text{Ar}/^{39}\text{Ar}$  age of  $1540 \pm 140$  Ma (Table 1) for glass #304 (Fig. 7b) is based on the fact that all three steps give the same apparent age (though with different uncertainties), and is interpreted as being the age of an impact event into a VLT mare regolith.

**Glass #311** was an opaque impact sphere having a diameter of  $310 \mu\text{m}$ . In fact, this VLT glass has the highest FeO and lowest  $\text{Al}_2\text{O}_3$  abundances of the four low-Ti mare glasses analyzed in the study (Table 1; Figs. 4, 5, and 6). We therefore interpret this to mean that the glass was formed during a large distant impact and transported ballistically to the Apollo 17 landing site, since its composition is atypical of the local regolith composition. Its age of  $774 \pm 50$  Ma, based on three steps containing 97% of the  $^{39}\text{Ar}$  (Fig. 7c), is important because it is similar to ages found by other authors (e.g., Barra et al. 2006) at other lunar sites. This may imply a global lunar impact event (or group of events), perhaps coincident in time with the formation of Copernicus  $\sim 800$  Ma ago (Bogard et al. 1994; Zellner et al. 2009).

**Glass #292** was a clast-free, angular fragment measuring  $\sim 280 \mu\text{m} \times 430 \mu\text{m}$  with a light green color and a VLT mare composition (Table 1; Figs. 4, 5, and 6). This glass is interpreted as an impact glass (Delano 1986) and was probably generated by melting of a regolith developed on VLT lavas (Figs. 4 and 5). Since the temperature steps are discordant, we believe the  $^{40}\text{Ar}/^{39}\text{Ar}$  age is essentially unconstrained—we use the range of apparent ages,  $2500 \pm 1500$  Ma (Table 1; Fig. 7d).

**Glass #349** was a large, red, angular glass fragment measuring  $370 \mu\text{m} \times 425 \mu\text{m}$  and is similar in overall composition to the intermediate-Ti mare glasses studied by Warner et al. (1979a). They suggest that glasses like this one are the result of mixing of mare basalts with aluminous nonmare rocks and may be representative of unsampled mare basalt flows (Warner et al. 1979a). The four steps that released  $>99\%$  of the  $^{39}\text{Ar}$  do not agree well with each other, but all yield ages between 1250 Ma and 2080 Ma, so we estimate the age as  $1650 \pm 400$  Ma (Table 1; Fig. 7e).

### Glasses with Highlands Compositions

**Glass #322** was a clast-free, angular impact glass fragment measuring  $310 \mu\text{m} \times 450 \mu\text{m}$  with a light green color. Although this sample plots near the field defined by the noritic impact melt breccias sampled at Stations 6 and 7 at the Apollo 17 site (Fig. 4), it is enriched in  $\text{SiO}_2$  and depleted in alkalis compared to those rocks (Tables 1 and 2). Three steps

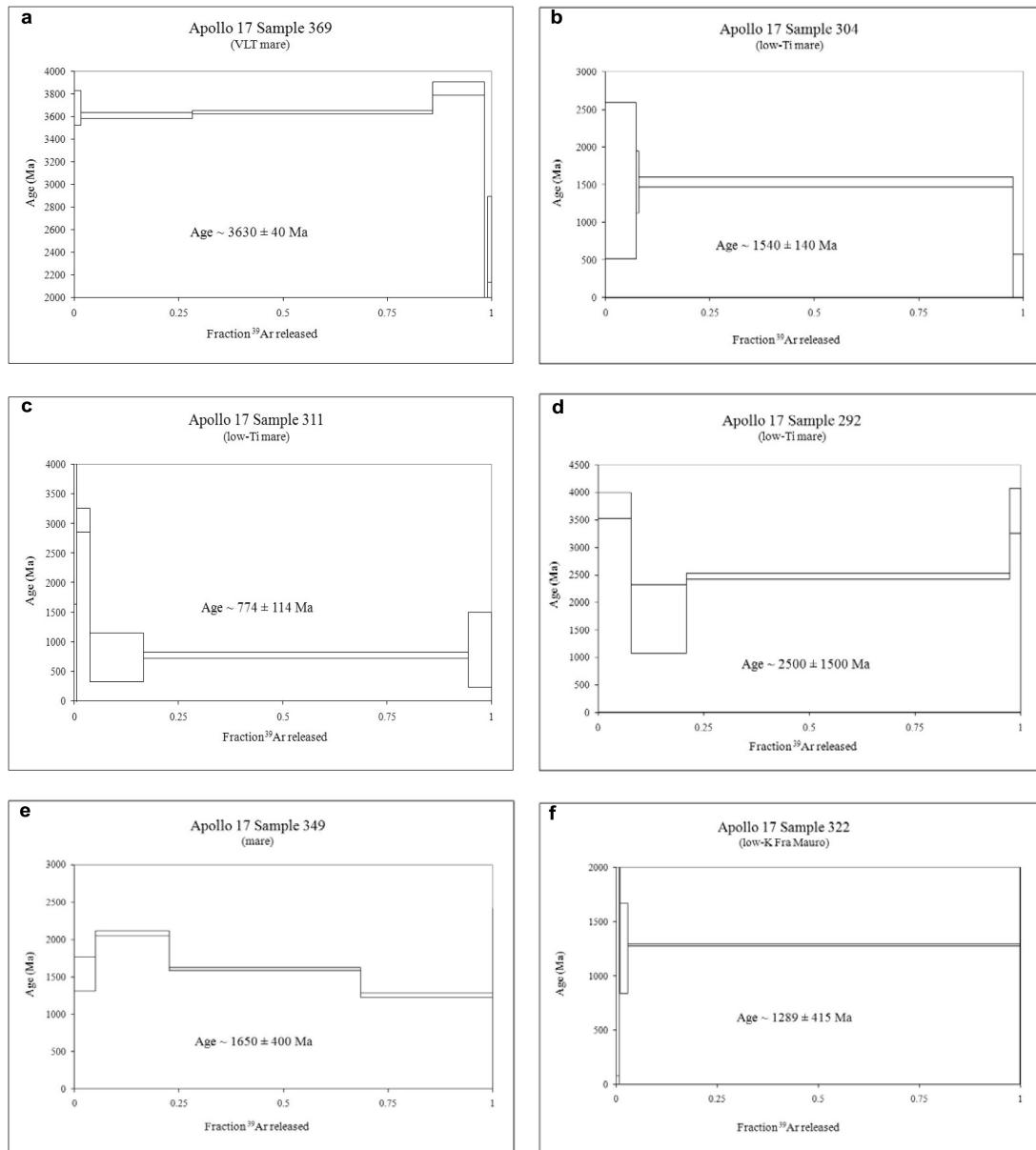


Fig. 7a–f. Plateau plots of apparent ages versus fraction of  $^{39}\text{Ar}$  released for all glasses discussed. In all cases, preferred estimates of ages are based on the sums of steps containing  $>87\%$  of the  $^{39}\text{Ar}$  (see Table 1).

give consistent  $^{40}\text{Ar}/^{39}\text{Ar}$  ages, though with uncertainties spanning two orders of magnitude. Our quoted age of  $1289 \pm 415$  Ma (Table 1; Fig. 7f) uses the precisely determined value of the largest step, but includes the uncertainty of the step intermediate in size.

**Glass #352** was a clast-free sphere measuring  $190\text{ }\mu\text{m}$  in diameter with a green color. This impact glass has a KREEP composition (Fig. 4; Table 1). A weighted average of the  $^{39}\text{Ar}$  gives a  $^{40}\text{Ar}/^{39}\text{Ar}$  age of  $1400 \pm 300$  Ma (Table 1; Fig. 7g) and roughly spans the range of the three largest steps.

**Glass #361** was a clast-free, broken sphere with an initial diameter of  $370\text{ }\mu\text{m}$  that had been reduced to  $260\text{ }\mu\text{m}$  on one side. Like glass #322, this sample plots near the field defined

by the noritic impact melt breccias sampled at Stations 6 and 7 at the Apollo 17 site (Fig. 4). While it has a composition typical of the local Apollo 17 regoliths, it is enriched in  $\text{SiO}_2$  and depleted in alkalis compared to those rocks (Tables 1, 2). The  $^{40}\text{Ar}/^{39}\text{Ar}$  age is  $1733 \pm 40$  Ma (Table 1; Fig. 7h), a value consistent with each of the three steps that combine to release  $>99\%$  of the  $^{39}\text{Ar}$ .

**Glass #390** was a clast-free, angular fragment measuring  $230\text{ }\mu\text{m} \times 630\text{ }\mu\text{m}$  with a green color. This glass has a KREEP composition (Fig. 4; Table 1). A weighted average of the  $^{39}\text{Ar}$  gives a  $^{40}\text{Ar}/^{39}\text{Ar}$  age of  $3580 \pm 45$  Ma (Table 1; Fig. 7i), based on four steps that contain virtually all of the Ar and are all concordant with one another. An alternative interpretation



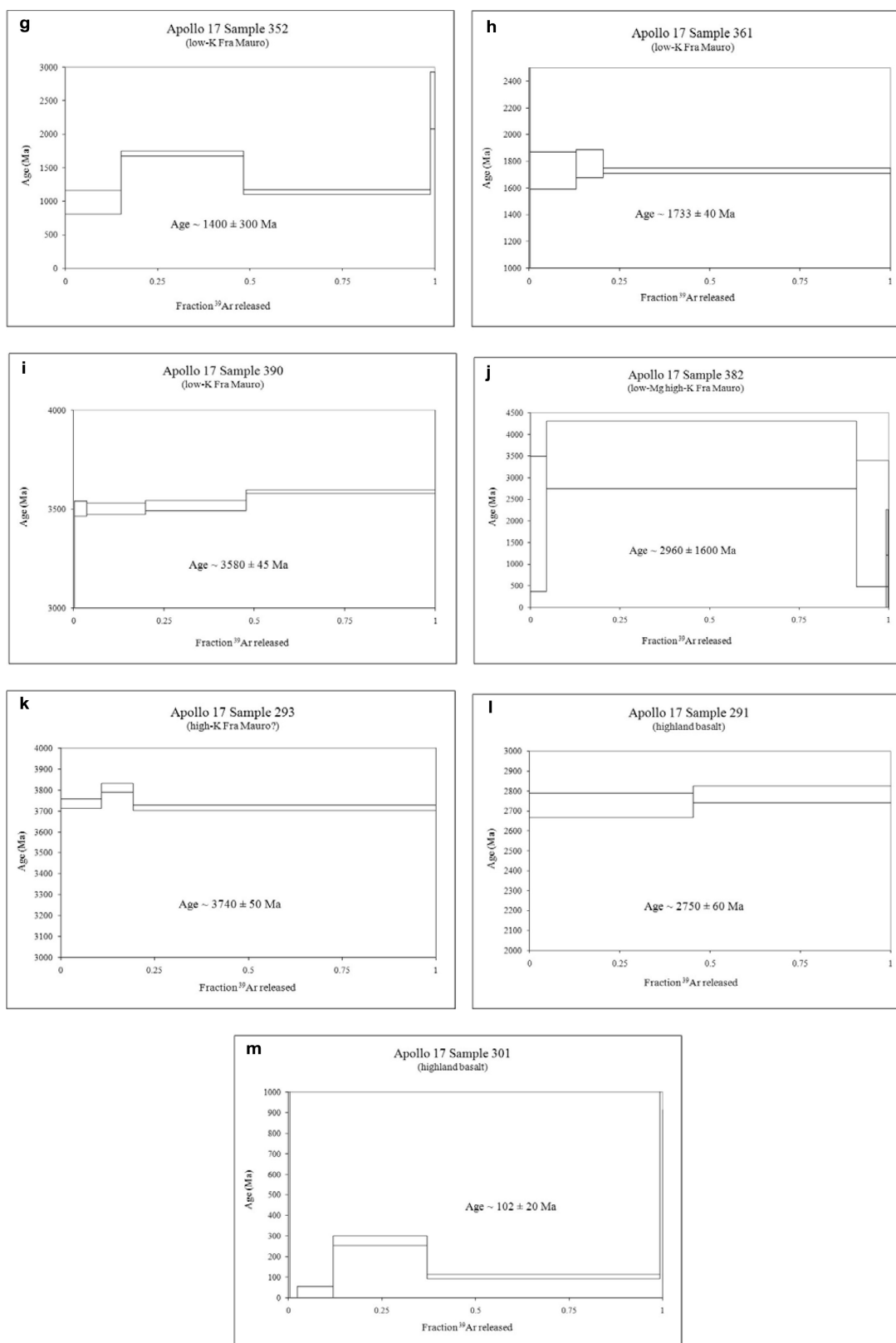


Fig. 7g–m. Plateau plots of apparent ages versus fraction of  $^{39}\text{Ar}$  released for all glasses discussed. In all cases except #301 (see discussion in text), preferred estimates of ages are based on the sums of steps containing  $>87\%$  of the  $^{39}\text{Ar}$  (see Table 1).

Table 2. Major-element compositions (wt%) of lunar samples that have many chemical similarities to the glasses isotopically dated in this study.

(wt%)	73131 regolith <sup>1</sup>	"Mare 6" <sup>2</sup>	Ropy glass <sup>3</sup>	Noritic breccias <sup>4</sup>	Highland surface <sup>5</sup>	EET 87521 mare <sup>6</sup>
SiO <sub>2</sub>	45.0	46.6	45.4	46.6	44.7	48.3
TiO <sub>2</sub>	0.92	0.85	0.48	1.48	0.22	0.80
Al <sub>2</sub> O <sub>3</sub>	21.3	12.5	23.1	18.0	28.2	12.5
Cr <sub>2</sub> O <sub>3</sub>	0.18	0.51	0.17	n.a.	0.096	0.23
FeO	7.13	18.0	6.11	9.10	4.4	19.0
MnO	n.a.	0.27	n.a.	0.12	0.063	n.a.
MgO	9.36	10.5	9.24	12.4	5.4	7.0
CaO	13.5	10.5	13.6	11.1	16.3	12.0
Na <sub>2</sub> O	0.43	0.14	0.29	0.75	0.35	0.38
K <sub>2</sub> O	n.a.	0.04	0.10	0.29	0.027	0.06
Total	97.8	99.9	98.5	99.8	99.8	100.3

<sup>1</sup>Friable, immature regolith breccia from Korotev and Kremser (1992).

<sup>2</sup>VLT mare glasses belonging to group 'Mare 6' of Warner et al. (1979a).

<sup>3</sup>Ropy glass of Fruland et al. (1977) from gray soils at Station 4 (74240 and 74260).

<sup>4</sup>Noritic impact melt breccia, 76015, from Rhodes et al. (1974).

<sup>5</sup>Estimate for average highlands surface composition from Korotev et al. (2003).

<sup>6</sup>VLT mare lithology in lunar meteorite EET 87521 from Arai and Warren (1999).

n.a. = not analyzed.

would be that it is demonstrating partial diffusive loss, since the last three of those four are monotonically increasing. However, all four steps are between 3500 Ma and 3600 Ma, and most agree at the 1 $\sigma$  level. As with #293 (below), its age falls at the end of the Late Heavy Bombardment or just after the primary Lunar Cataclysm, if it occurred.

**Glass #382** was an opaque glass measuring 115  $\mu\text{m} \times 190 \mu\text{m}$  and has a composition that broadly resembles the "basaltic andesite glasses" (Zeigler et al. 2006a) and "low-Mg high-K Fra Mauro" (ImHKFM; Delano et al. 2007) at the Apollo 16 site that have an isotopic age of  $3730 \pm 40$  Ma (Delano et al. 2007). However, none of our steps had  $1\sigma < 750$  Ma, so we do not believe we have determined the  $^{40}\text{Ar}/^{39}\text{Ar}$  age of this Apollo 17 impact glass to any better than  $\sim 3000 \pm 1600$  Ma (Table 1; Fig. 7j), which does not allow for a correlation of this compositional suite between these two widely separated landing sites. Although this compositionally distinctive group of mafic KREEP glasses has been proposed to have been ballistically transported from the KREEP-rich Procellarum region (Zeigler et al. 2006a), their presence has not yet been detected at the Apollo 14 site (Brown et al. 1971; Simon et al. 1989; Vaniman, 1990; Zellner et al. 2002) where the compositions of  $\sim 1200$  glasses have been reported (i.e., this composition likely makes up  $<0.1\%$  of all Apollo 14 glasses).

**Glass #293** was a clast-free, angular fragment measuring  $340 \mu\text{m} \times 510 \mu\text{m}$  with a yellowish green color. Its KREEP composition falls along the line showing the compositional range of Apollo 17 regoliths (Table 1) distinct from the dominant rocks at the Apollo 17 landing site (Fig. 4). Its age of  $3740 \pm 50$  Ma (based on three nearly concordant steps; Fig. 7k) suggests it, like #390 (above), may be part of the tail end of the Late Heavy Bombardment (e.g. Hartmann et al. 2000) or putative Lunar Cataclysm. Although ages

of macroscopic lunar impact melts are typically 3800–4000 Ma, which led to the suggestion of a "cataclysm" (e.g., Turner et al. 1973; Ryder 1990), impact glasses (e.g., Delano et al. 2007) and impact melts (Cohen et al. 2000, 2005) frequently fall in the range 3500–4000 Ma, as is the case for this sample and sample 390.

**Glass #291** was a clast-free impact sphere measuring 140  $\mu\text{m}$  in diameter with a light green color. Its chemical composition (Table 1; Fig. 4) is broadly similar to the average highlands composition and may imply that the Apollo 17 site is influenced by components from the lunar farside or by anorthositic components near the crater or not present at the site's surface (as described for some Apollo 14 impact glasses in Zellner et al. 2002). Although only two steps contain significant amounts of Ar, they each contain roughly half the total and are both consistent with a  $^{40}\text{Ar}/^{39}\text{Ar}$  age of  $2750 \pm 60$  Ma (Table 1; Fig. 7l). Since the processes that can typically lead to an incorrect age when apparent  $^{40}\text{Ar}/^{39}\text{Ar}$  ages within a sample are averaged (partial degassing, recoil, atmospheric contamination) would not be expected to operate to the same degree for high- and low-temperature steps, we tentatively assume this is the true age of the glass.

**Glass #301** was a clast-free impact spherule measuring 570  $\mu\text{m}$  in diameter with a green color and a thin, discontinuous coating of fine debris on its surface. Its chemical composition (Table 1; Fig. 4) is similar to, but distinct from, the group of ropy impact glasses (Table 2) described by Fruland et al. (1977) in the gray soils at Station 4. It shows an apparent age of  $102 \pm 20$  Ma in a single step with 62% of the  $^{39}\text{Ar}$  (Table 1, Fig. 7m), which may be coincident with the Tycho event at  $\sim 90$ –115 Ma (Arvidson et al. 1976; Drozd et al. 1977). Since glass #301 has a young age, significant contributions from solar wind to the  $^{40}\text{Ar}/^{36}\text{Ar}$  value are not anticipated. Indeed, the observed value of

reimplanted  $^{40}\text{Ar}$  to solar wind  $^{36}\text{Ar}$  is  $0.1017 \pm 0.0015$  (i.e.,  $<1$ ), consistent with a young age for this impact glass. Ignoring the solar wind component, the average age of the three largest steps is  $154 \pm 11$  Ma, which we consider an upper limit to the age of this glass. A weighted average of these three steps, including all corrections, gives an age of  $130 \pm 25$  Ma. However, since the last ~62% of the  $^{39}\text{Ar}$  released from this glass was presumably released from interior of the glass spherule, the most likely age is  $102 \pm 20$  Ma (Fig. 7m), although we believe this is less certain than most of the ages we quote.

Glass #301 is also compositionally similar to friable, compositionally unique (Korotev 1988), immature (Morris 1978) regolith breccia 73131 (Table 2; Fig. 4). This breccia contains little to no mare component (Korotev and Kremser 1992) and may have been locally derived from the lower stratigraphic levels of the Apollo 17 massifs, as suggested by Korotev and Kremser (1992). Glass #301 may be an impact melt of local materials having a 73131 composition produced during the impact of Tycho secondary debris, especially on the summit of the South Massif, at ~100 Ma. If correct, glass #301 and regolith 73131 are samples from the top of the South Massif, which was not directly sampled by the Apollo 17 astronauts. It is uncertain whether or not this sample is from the Tycho impact crater.

## CONCLUSIONS

We have geochemically and isotopically analyzed Apollo 17 glasses from regolith 71501,262. Of the 13 glasses with defined ages, one is of volcanic origin, and 12 are of impact origin.

- Sample #369 is a VLT volcanic glass with an age of  $3630 \pm 40$  Ma. This is the first isotopic age obtained for the Apollo 17 VLT volcanic glasses, and corresponds to the time of magmatic fire-fountaining. This age overlaps with the ages of *high-Ti* mare volcanism (i.e., mare basalts and 74220 picritic glass) at the Apollo 17 site.
- Twelve impact glasses show a wide range of ages (~102 Ma to ~3740 Ma) and compositions that are a record of impact events at local and remote locations. Although our sample set is small, we see no evidence for a recent increase in the bombardment flux for samples extracted from the Apollo 17 soils.
- The pair of older impact ages (3500–3800 Ma, #293 and #390) may reflect the tail end of the Late Heavy Bombardment or putative Lunar Cataclysm.
- Impact glass #301 may have been associated with the Tycho impact event at ~100 Ma.
- Impact glass #311 was formed in an event at ~800 Ma within a region of low-Ti mare. There are suggestions that this time interval may have been characterized by an increased meteorite flux. Alternatively, this glass may be related to the Copernicus impact event in the Procellarum region of the Moon.

Through composition and chronology, these samples do give us insight into the impact flux in the Earth-Moon system and illustrate the potential of the dating of well-characterized impact glasses.

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