

The geochemistry and provenance of Apollo 16 mafic glasses

Ryan A. Zeigler *, Randy L. Korotev, Bradley L. Jolliff,
Larry A. Haskin, Christine Floss

Washington University, Campus Box 1169, St. Louis, MO 63130, USA

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Abstract

The regolith of the Apollo 16 lunar landing site is composed mainly of feldspathic lithologies but mafic lithologies are also present. A large proportion of the mafic material occurs as glass. We determined the major element composition of 280 mafic glasses (>10 wt% FeO) from six different Apollo 16 soil samples. A small proportion (~5%) of the glasses are of volcanic origin with picritic compositions. Most, however, are of impact origin. Approximately half of the mafic impact glasses are of basaltic composition and half are of noritic composition with high concentrations of incompatible elements. A small fraction have compositions consistent with impact mixtures of mare material and material of the feldspathic highlands. On the basis of major-element chemistry, we identified six mafic glass groups: VLT picritic glass, low-Ti basaltic glass, high-Ti basaltic glass, high-Al basaltic glass, KREEPy glass, and basaltic-andesite glass. These glass groups encompass ~60% of the total mafic glasses studied. Trace-element analyses by secondary ion mass spectroscopy for representative examples of each glass group (31 total analyses) support the major-element classifications and groupings. The lack of basaltic glass in Apollo 16 ancient regolith breccias, which provide snapshots of the Apollo 16 soil just after the infall of Imbrium ejecta, leads us to infer that most (if not all) of the basaltic glass was emplaced as ejecta from small- or moderate-sized impacts into the maria surrounding the Apollo 16 site after the Imbrium impact. The high-Ti basaltic glasses likely represent a new type of basalt from Mare Tranquillitatis, whereas the low-Ti and high-Al basaltic glasses possibly represent the composition of the basalts in Mare Nectaris. Both the low-Ti and high-Al basaltic glasses are enriched in light-REEs, which hints at the presence of a KREEP-bearing source region beneath Mare Nectaris. The basaltic andesite glasses have compositions that are siliceous, ferroan, alkali-rich, and moderately titaniferous; they are unlike any previously recognized lunar lithology or glass group. Their likely provenance is within the Procellarum KREEP Terrane, but they are not found within the Apollo 16 ancient regolith breccias and therefore were likely deposited at the Apollo 16 site post-Imbrium. The basaltic-andesite glasses are the most ferroan variety of KREEP yet discovered.

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1. Introduction

The Apollo 16 mission landed in the Feldspathic Highlands Terrane (Jolliff et al., 2000) of the Moon and most of the crystalline rocks collected there are rich in feldspar and poor in the mafic minerals, pyroxene and olivine. The feldspathic lithologies are those characteristic of the highlands, mainly, anorthosites and a variety of feldspathic breccias (James, 1980; Ryder, 1981; Lindstrom and Salpas,

1981, 1983; Stöffler et al., 1985). Because the ratio of feldspar to pyroxene plus olivine is large in such rocks, the rocks have high concentrations of Al and Ca, and low concentrations of elements associated with ferromagnesian minerals (e.g., Mg, Fe, Sc, Cr). They also have low concentrations of ITEs (incompatible trace elements) such as Th, characteristic of the Feldspathic Highlands Terrane (Lawrence et al., 1998; Jolliff et al., 2000).

The Apollo 16 regolith also contains mafic lithologies that do not originate in the feldspathic highlands. The most common mafic lithology at the Apollo 16 site is impact-melt breccia with high concentrations of ITEs and concentrations of Mg and Fe significantly greater than those of

* Corresponding author. Fax: +1 314 935 7361.

E-mail address: Zeigler@levee.wustl.edu (R.A. Zeigler).

the feldspathic lithologies (Stöffler et al., 1985; Korotev, 1997). The ITE-rich impact-melt breccias are common at the Apollo 16 site (and among nonmare materials of all other Apollo sites) because the site lies near the Th-rich, Procellarum KREEP Terrane (~350 km to the west) and because the last major basin-forming impact, Imbrium, struck that geochemically anomalous region, depositing ITE-rich material at the Apollo 16 site (Stöffler et al., 1981; Haskin, 1998; Haskin et al., 1998). In contrast, mafic, Th-rich impact-melt breccias are rare to absent as clasts in the feldspathic lunar meteorites, most of which are breccias composed of regolith from unknown locations in the Feldspathic Highlands Terrane, but locations that must be distant from the Procellarum KREEP Terrane (Korotev et al., 2003).

Other mafic lithologies that occur in the Apollo 16 regolith are nonmare plutonic rocks such as the gabbronorites of James and Flohr (1983) and the monomict mafic fragments of Zeigler et al. (2000a,b, 2002). Such material is rare and occurs mainly as small fragments (for a list of Apollo 16 plutonic samples see Warren, 1993). A third type of mafic material consists of the products of mare volcanism. Despite the Apollo 16 site being 220 km from the nearest mare, fragments of mare basalt and pyroclastic glass occur in the Apollo 16 regolith (Dowty et al., 1974a,b; Delano, 1975; Murali et al., 1976; Vaniman et al., 1978; Simon and Papike, 1987; Takeda et al., 1987; Zeigler et al., 2005a). Again, all known samples are small.

This work developed from mass-balance modeling of Korotev (1997), who attempted to quantitatively account for the composition of the Apollo 16 regolith in terms of a mixture of lithologies known to occur in the regolith. A first-order conclusion was that typical Apollo 16 soil (<1-mm regolith fines) consisted mainly of a 2-to-1 mixture of feldspathic, ITE-poor materials (mean: 32% Al₂O₃, 2% FeO, 0.3 ppm Th) and mafic, ITE-rich, impact-melt breccias (mean: 21% Al₂O₃, 8% FeO, 7 ppm Th; Tables 6 and 7 of Korotev, 1997). However, the soil is richer in Sc and Cr than any such mixture that accounts well for the other elements. The excess Sc and Cr can be explained if the regolith also contains 6% mare volcanic material and 2–3% gabbronorite. These model-derived values depend on assumptions made about the identity and composition of the rare mafic components of the regolith. To test this result, we initiated the projects described here and in Zeigler et al. (2000a,b, 2002) to better understand the nature and provenance of the mafic components of the Apollo 16 regolith.

The >1-mm grain-size fraction of the Apollo 16 regolith contains much less mare volcanic material (1% or less; Delano et al., 1973; Zeigler et al., 2005a) than the 6% predicted by the mass balance model for the <1-mm fraction. This discrepancy led us to suspect that most of the mare component of the Apollo 16 regolith occurs as pyroclastic “ash,” which typically occurs as glassy spherules of 40–50 μm diameter (Korotev, 1997). Lunar pyroclastic glass has a picritic composition (high Mg, 11–19 wt% MgO), one that is more

primitive than most crystalline lunar basalts (Delano, 1986; Shearer and Papike, 1993). Petrographic studies of the <1-mm grain-size fraction have found few lithic fragments of basalt, but have identified several percent yellow, orange, and volcanic green glass (Heiken et al., 1973; Houck, 1982a,b; Basu and McKay, 1984). Geochemical studies of glasses in the <1-mm fines identified the yellow and orange glass shards as a collection of basaltic and ITE-rich impact-melt glasses (Ridley et al., 1973; Meyer and McCallister, 1974; Delano, 1975; Meyer and Tsai, 1975; Naney et al., 1976; Vaniman et al., 1978; Kempa and Papike, 1980; Zellner et al., 2003) and a small subset of the green glasses as very low-Ti (VLT) picritic glass (Delano, 1986; Shearer and Papike, 1993).

Most glass in the Apollo 16 regolith is not of pyroclastic origin, however; it is the product of meteoroid impacts. All impacts, from massive basin-forming impacts such as Imbrium to tiny micrometeorite impacts, produce glass from fusion of target materials. Impact craters have saturated the lunar highlands around the Apollo 16 site, and impact-generated glass and agglutinates (glassy breccias formed in micrometeorite impacts) account for about half of the <150-μm particles in the Apollo 16 regolith (Heiken et al., 1973; Houck, 1982a,b; Taylor et al., 2003). Most of that glass is poor in Fe because it is formed from feldspathic rocks (Taylor et al., 2003; Zellner et al., 2003); however, there is disagreement about whether most of the feldspathic glass is formed locally by micrometeorite impacts (Taylor et al., 2003) or by larger regional impacts that ballistically distribute impact-generated glass over kilometers of distance (Zellner et al., 2003).

Some glasses that occur in the Apollo 16 regolith are too mafic, that is, too rich in Fe, to have plausibly formed at the Apollo 16 site (Table 1). In this study, we specifically target mafic glasses from several Apollo 16 soil samples, selecting against the more feldspathic glasses. In this way, we were able to identify 280 mafic glasses. Within this data set, we identified six main groups of glasses: (1) VLT picritic glass, (2) low-Ti basaltic glass, (3) high-Ti basaltic glass, (4) high-Al basaltic glass, (5) KREEPy glass, and (6) basaltic-andesite glass, as well as a large number of ungrouped mafic glasses. We present here the major- and trace-element composition of these mafic glasses, concentrating on the main groupings. For each group we discuss: the method of formation (impact vs. pyroclastic), likely parent materials, the relative age and transport mechanism, and the provenance.

2. Analytical methods

We analyzed mafic glasses in four thin sections from regolith drive tube section 68001 and 14 grain mounts that we prepared from surface regolith samples 60601, 62281, 65511, 65701, and 68501, all <1-mm fines. Samples 60601 and 62281 were taken 1.5 and 0.9 km west of the landing site. Samples 65511 and 65701 were collected at station 5, 3.1 km south, and 68001 and 68501 were

Lithology	Mare-highlands mixed glasses						HT picritic		Green glass beads						High Mg											
	(11)	sd	(5)	sd	(7)	sd	(4)	sd	(2)	sd (1)	sd (1)	sd (5)	sd	(3)	sd	(5)	sd	(17)	sd	(3)	sd	(5)	sd			
SiO ₂	44.29	0.920	42.89	1.170	47.78	2.060	39.10	1.000	44.70	—	45.36	—	44.26	—	43.50	0.300	44.19	0.470	45.22	1.560	44.14	0.560	44.14	0.480	44.32	3.010
TiO ₂	4.04	0.700	4.99	1.000	1.55	1.010	8.90	0.500	0.47	—	0.54	—	0.39	—	0.36	0.050	0.62	0.480	0.84	0.450	0.45	0.090	0.37	0.060	0.80	0.550
Al ₂ O ₃	15.39	1.500	14.83	1.080	11.64	1.380	7.30	0.800	7.90	—	9.07	—	7.75	—	9.50	0.600	8.59	0.680	9.04	0.860	8.14	0.670	7.81	0.020	14.45	2.370
Cr ₂ O ₃	0.30	0.060	0.36	0.110	0.40	0.120	0.68	0.030	0.46	—	0.49	—	0.48	—	0.47	0.600	0.47	0.050	0.49	0.150	0.44	0.100	0.33	0.070	0.20	0.140
FeO	13.44	1.770	14.39	1.100	13.68	2.910	21.50	0.500	20.83	—	20.81	—	21.34	—	20.80	0.200	19.97	0.810	19.77	1.010	21.67	0.260	21.05	0.360	11.42	2.430
MnO	nr	—	0.20	0.060	0.20	0.070	0.32	0.030	0.34	—	0.22	—	0.25	—	0.26	0.050	0.23	0.020	0.28	0.080	nr	—	nr	—	0.19	0.120
MgO	10.46	0.400	10.03	2.220	13.87	2.400	12.80	0.800	16.74	—	14.10	—	17.19	—	15.70	0.600	15.83	1.200	13.74	2.130	16.06	1.660	16.72	0.240	19.79	1.810
CaO	10.92	0.450	11.51	0.430	9.88	2.200	8.60	0.300	8.27	—	8.93	—	8.64	—	9.00	0.200	8.58	0.320	9.64	1.290	8.61	0.600	8.41	0.230	8.35	0.550
Na ₂ O	0.48	0.150	0.50	0.290	0.28	0.290	0.34	0.060	0.32	—	0.11	—	0.13	—	0.16	—	0.04	0.030	0.27	0.110	0.22	0.120	0.13	0.070	0.22	0.160
K ₂ O	0.13	0.040	0.15	0.090	0.18	0.220	0.08	0.020	nd	—	nd	—	0.03	—	0.04	—	nd	—	0.05	0.030	0.08	0.010	0.03	0.030	0.11	0.100
Sums	99.45	—	99.85	—	99.46	—	99.60	—	100.0	—	99.63	—	100.5	—	99.80	—	98.52	—	99.34	—	99.81	—	98.99	—	99.85	—
Mg'	58.1	—	55.4	—	64.4	—	51.5	—	58.9	—	54.7	—	58.9	—	57.4	—	58.6	—	55.3	—	56.9	—	58.6	—	75.5	—
CaO/Al ₂ O ₃	0.71	—	0.78	—	0.85	—	1.18	—	1.05	—	0.98	—	1.11	—	0.95	—	1.00	—	1.07	—	1.06	—	1.08	—	0.58	—
MgO/Al ₂ O ₃	0.68	—	0.68	—	1.19	—	1.75	—	2.12	—	1.55	—	2.22	—	1.65	—	1.84	—	1.52	—	1.97	—	2.14	—	1.37	—
Reference	(1)		(4)		(4)		(5)		(4)		(4)		(4)		(5)		(4)		(4)		(1)		(2)		(4)	

Apollo 16 mafic glasses found in the literature. Names follow our scheme in this paper. Abbreviations are as follows: Green glass bead (GGB), high-Al basaltic glass (HABG), and basaltic andesite glass (BAG). Mg' = molar Mg/(Mg + Fe) * 100. N, number of glasses in group L, HT, high-Ti. References are: (1) Naney et al. (1976); (2) Ridley et al. (1973); (3) Meyer and Tsai (1975); (4) Kempa and Papike (1980); (5) Delano (1975); (6) Delano et al. (1981).

collected at station 8, 3.8 km south of the landing site. The specific thin sections from drive tube 68001 were numbers 6024 (33–33.5 cm depth interval), 6033 (41.5–44 cm), 6036 (44.5–47 cm), and 6045 (53.5–56 cm). The grain mounts consisted of material from the 1000–525 μm , 525–150 μm , 150–75 μm , and 75–35 μm size fractions. In almost all cases, highly feldspathic material had been removed for a previous study (Kitts et al., 2003) using a Franz isodynamic magnetic separator. All of the analyzed particles in the 1000–525 μm size range are glass fragments and spheres that we picked by hand. We prepared five grain mounts from sample 60601: 1000–150 μm ($N=1$), 525–150 μm (1), 150–75 μm (2), and 75–35 μm (1); four grain mounts from sample 62271: 1000–150 μm (1) and 150–75 μm (3); three grain mounts from sample 65701: 525–150 μm (1) and 150–75 μm (2); and a single grain mount from sample 65511: 1000–150 μm . Also included in this study was grain mount 68501,159 (prepared by NASA) that appears to have been prepared from unsorted sieved soil (\sim 525–150 μm size range).

We determined the major-element compositions of the glasses in this study by electron microprobe analysis using a JEOL 733 Superprobe equipped with Advanced Microbeam IncTM automation at Washington University in St. Louis. All analyses used wavelength dispersive spectrometers at 15 kV accelerating voltage, 20 nA beam current, and a spot size ranging from 10 to 50 μm (with 20 μm the most common size). Mineral, glass, and oxide standards were used for calibration. Only those “clean” glasses with >10 wt% FeO were considered in this study (this was our arbitrary cutoff for “mafic” materials at Apollo 16 site). We define “clean” as not containing more than a few small clasts, having no obvious brightness variation in BSE images, and not being extensively devitrified.

We determined the trace element compositions of 31 glasses from all six of the main glass groups by secondary ion mass spectrometry (SIMS) using the modified Cameca 3f ion microprobe at Washington University. The details of the experimental procedures can be found in Zinner and Crozaz (1986) and the data reduction procedures are given in Floss (2000). To fully characterize the trace element chemistry of the these glasses and to account for interferences we measured at masses corresponding to the following elements: Na (mass 23), Mg (masses 25, 26), Si (masses 29, 30), P (mass 31), K–Ca–Sc–Ti (masses 39, 41, 42, 43, 44, 45, 46, 47, 48, 49), V (mass 51), Cr (masses 52, 53), Mn (mass 55), Fe (mass 57), Co (mass 59), Ni (masses 60, 61, 62), Rb–Sr–Y–Zr (masses 84, 85, 86, 87, 88, 89, 90, 91), Nb (mass 93), Ba–REE (137, 138, 139, 140, 141, 143, 144, 146, 147, 148, 150, 151, 153, 154, 155, 156, 157, 158, 159, 160, 161, 163, 164, 165, 166, 167, 168, 169, 170, 171, 172, 174, 175), Th (mass 232). Corrections for interferences are made by deconvolving the mass spectrum in the mass regions for K–Ca–Sc–Ti, Rb–Sr–Y–Zr, and Ba–REEs (e.g., Alexander, 1994).

3. Results

When viewed in plane polarized light, most glasses range in color from pale yellow to a dark orange. In a few cases

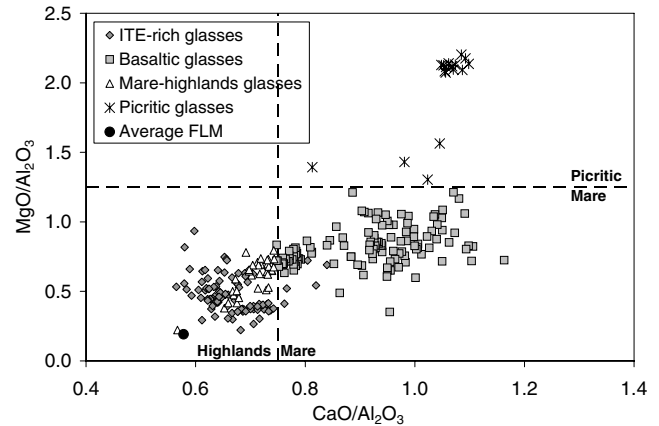


Fig. 1. The major element ratios $\text{CaO}/\text{Al}_2\text{O}_3$ and $\text{MgO}/\text{Al}_2\text{O}_3$ distinguish between highlands, mare, and picritic glasses. The vertical dashed line highlights the $\text{CaO}/\text{Al}_2\text{O}_3$ ratio used by Naney et al. (1976) and others as a dividing line between purely mare and mare-highlands mixed glasses (with “pure” highlands materials having a ratio \sim 0.58). Similarly, the horizontal dashed line highlights a $\text{MgO}/\text{Al}_2\text{O}_3$ ratio of 1.25, which Delano (1986) recognized as a good discriminator between picritic and mare glasses (except for the most olivine rich basalts). This plot can not differentiate between mare-highlands mixed glasses and ITE-rich glasses, which requires a plot that has K_2O (or some other ITE; see Fig. 2). The large black circle is the average composition of the feldspathic lunar meteorites (FLM; Korotev et al., 2003).

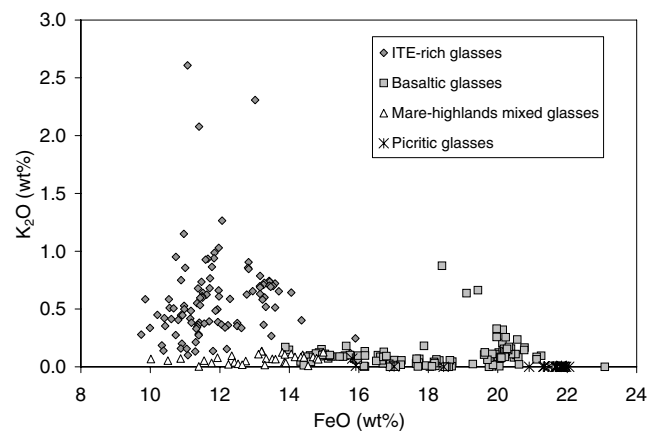


Fig. 2. K_2O concentrations differentiate between mare-highlands mixed glasses and the ITE-rich glasses. Several investigators (e.g., Housley, 1979; Delano et al., 1981) have noted that K can be lost due to volatilization during lunar impact melting events. The affects of vaporization of K and Na are observed in this study (see discussion section), and thus it is a possibility that a few ITE-rich glasses which have undergone extensive volatilization would be missed using this method. Glasses that have undergone such a complete K loss often show obvious Si (or even Fe) volatilization (Naney et al., 1976), however, neither Si or Fe volatilization was observed in the glasses of this study. Although it is not ideal, K_2O is the best ITE determined by EMPA that could be used in this manner (P might also be used, but it is also volatile and present in lower concentrations).

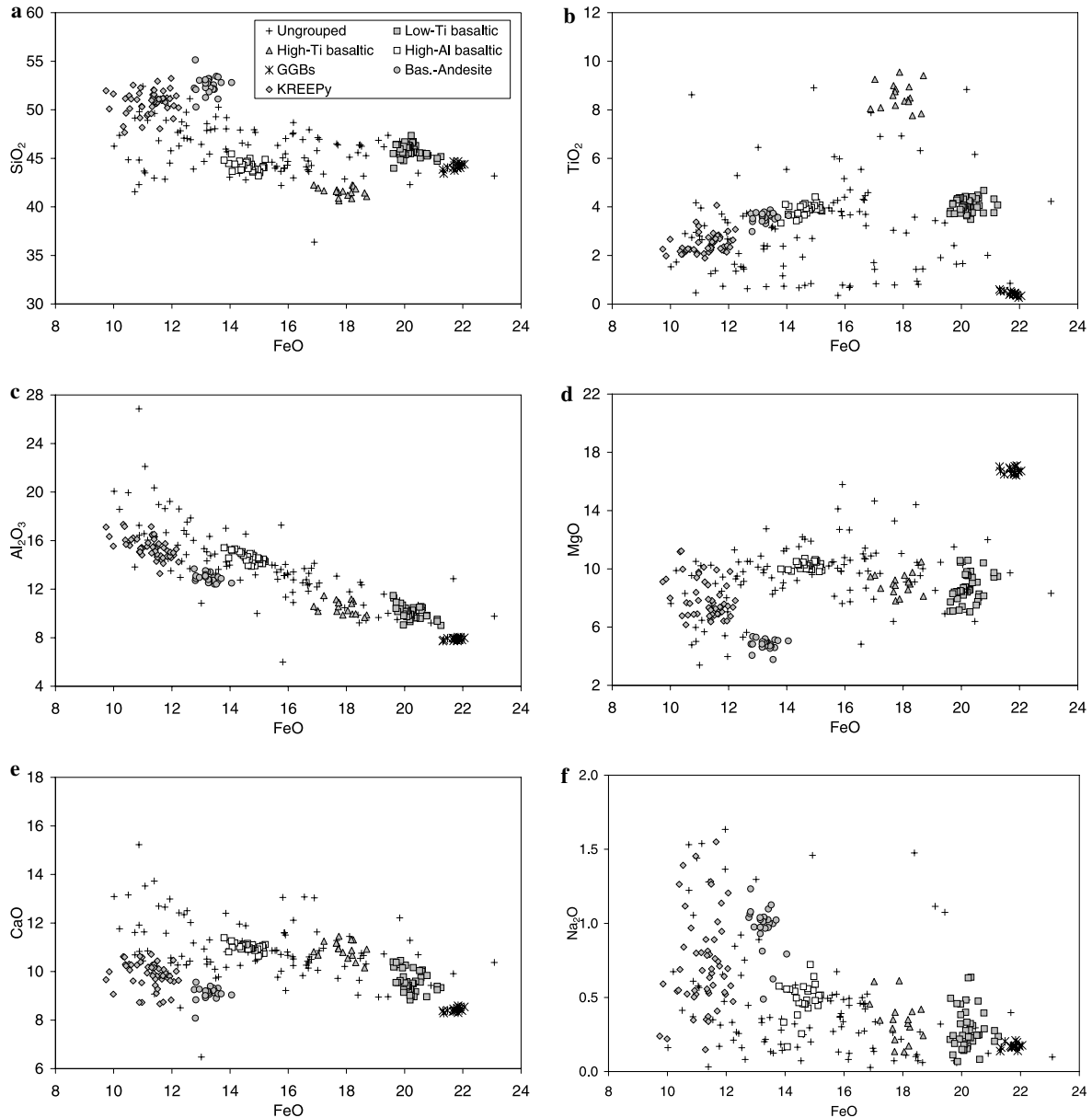


Fig. 3. Two element discrimination diagrams such as these differentiate between the six main groups of glasses discussed in this paper. The glasses form tight compositional clusters for most elements. The most variation is seen in MgO concentrations (for reasons as yet unresolved) and Na₂O concentrations (likely due to volatilization; see Fig. 11). The legend in part (a) is consistent for all of the figures. (a) FeO vs. SiO₂. (b) FeO vs. TiO₂. (c) FeO vs. Al₂O₃. (d) FeO vs. MgO. (e) FeO vs. CaO. (f) FeO vs. Na₂O. GGBs, green glass beads.

the glasses have a black or green color. The color in the yellow-orange glasses appears to be controlled primarily by the TiO₂ concentration, with the lowest TiO₂ glasses being yellow, and the highest Ti glasses being orange and black. Most green glass observed in thin section has a composition close to that of the Apollo 16 soil (e.g., 5.5 wt% FeO, 6.0 wt% MgO), however a small subset of the green glasses have picritic, very low-Ti basalt compositions. The picritic glasses are the only spherical glasses found in this study. All other glasses analyzed are fragments that have jagged edges. None of the other glasses even had a partial spheroidal edge. Some glasses from each group

(except the green glass beads) contain small blebs of Fe,Ni metal, likely of meteoritic origin.

3.1. Geochemistry

The mafic glasses have a wide range of chemical compositions that can be classified into four compositional classes: (1) basaltic (45%), (2) ITE-rich (36%), (3) mare-highlands mixed (13%), and (4) picritic (6%). We make this classification based on MgO/Al₂O₃ and CaO/Al₂O₃ ratios, as well as K₂O concentrations (Figs. 1–3). Basaltic (mare-derived) and picritic glasses both have CaO/Al₂O₃ ratios

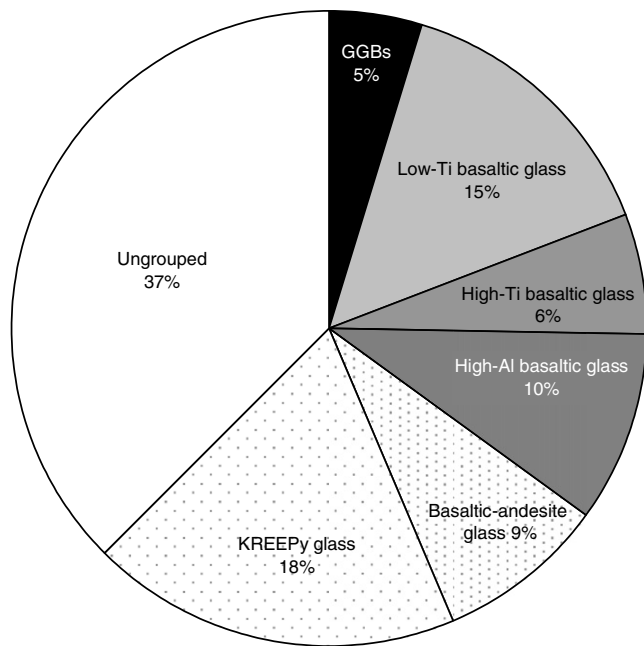


Fig. 4. Relative percentages of the six mafic glass groups and the ungrouped glasses in the Apollo 16 regolith. The total number of glasses in the study is 280. GGBs, green glass beads.

>0.75, but picritic glasses have $\text{MgO}/\text{Al}_2\text{O}_3$ ratios >1.25, whereas mare basalts, and everything else at the Apollo 16 site, have $\text{MgO}/\text{Al}_2\text{O}_3$ ratios <1.25 (Fig. 1; Delano, 1986). Feldspathic highlands samples typically have $\text{CaO}/\text{Al}_2\text{O}_3$ ratios ~ 0.6 (Korotev et al., 2003) and in previous studies Apollo 16 glasses that have $\text{CaO}/\text{Al}_2\text{O}_3$ ratios between 0.6 and 0.75 and low K_2O concentrations have been classified as mixtures of mare and highlands materials (e.g., Naney et al., 1976). The concentration of K_2O is important because many ITE-rich materials have $\text{CaO}/\text{Al}_2\text{O}_3$ ratios between 0.60 and 0.75, but have no genetic association with mare material. Potassium is the best discriminator in this case because almost all samples of the feldspathic highlands and mare have very low K_2O concentrations. Thus we classify any glass with >0.15 wt% K_2O (Fig. 2) as an ITE-rich glass. Although this classification scheme is broad, these four compositional classes (basaltic, ITE-rich, mare-highlands mixed, and picritic) are useful as a starting point to determine source materials for these groups and the processes that formed them.

Within the basaltic, picritic, and ITE-rich glass classes are six compositional groups that encompass 60% of the glasses (Fig. 4). The six groups are: (1) very low-Ti picritic green glass beads (GGBs), (2) low-Ti basaltic glass, (3)

Table 2
Average major-element composition and normative mineralogy of the groups

Group	GGB		LTBG		HTBG		BAG		HABG		KREEPy	
N	13	sd	41	sd	17	sd	24	sd	27	sd	53	sd
<i>EMPA derived major-element composition</i>												
SiO ₂	44.14	0.359	45.77	0.666	41.53	0.488	52.53	0.938	44.20	0.525	50.79	1.191
TiO ₂	0.43	0.094	4.06	0.280	8.58	0.534	3.58	0.191	3.89	0.242	2.47	0.399
Al ₂ O ₃	7.88	0.114	10.06	0.537	10.49	0.551	12.90	0.351	14.60	0.435	15.47	0.841
Cr ₂ O ₃	0.47	0.037	0.30	0.089	0.44	0.068	0.13	0.035	0.35	0.031	0.18	0.053
FeO	21.73	0.232	20.23	0.392	17.88	0.510	13.28	0.309	14.64	0.393	11.24	0.596
MnO	0.26	0.033	0.26	0.055	0.25	0.042	0.18	0.037	0.19	0.032	0.15	0.031
MgO	16.74	0.230	8.69	0.981	8.98	0.693	4.82	0.357	10.22	0.263	7.87	1.268
CaO	8.43	0.093	9.57	0.434	10.90	0.354	9.10	0.273	11.00	0.162	9.89	0.528
Na ₂ O	0.17	0.022	0.28	0.136	0.34	0.140	0.97	0.157	0.49	0.113	0.73	0.323
K ₂ O	0.00	0.003	0.13	0.070	0.05	0.039	0.68	0.117	0.09	0.027	0.52	0.247
P ₂ O ₅	0.04	0.011	0.07	0.050	0.09	0.037	0.51	0.248	0.11	0.041	0.18	0.221
Sums	100.3		99.4		99.5		98.7		99.8		99.5	
<i>Ratios</i>												
Mg'	57.9		43.2		47.2		39.2		51.3		55.2	
CaO/Al ₂ O ₃	1.07		0.95		1.04		0.71		0.75		0.64	
MgO/Al ₂ O ₃	2.12		0.87		0.86		0.37		0.65		0.51	
<i>Modified CIPW normative composition (no Fe³⁺ allowed)</i>												
Quartz	0.0		1.0		0.1		13.5		0.0		6.8	
K-feldspar	0.0		0.8		0.3		4.1		0.5		3.1	
Albite	1.5		2.4		2.9		8.3		4.2		6.2	
Anorthite	20.7		26.0		27.1		29.2		37.5		37.6	
Clinopyroxene	17.2		17.9		21.9		11.0		13.5		8.7	
Orthopyroxene	22.6		43.7		30.5		25.5		27.2		32.2	
Olivine	36.5		0.0		0.0		0.0		9.0		0.0	
Ilmenite	0.8		7.8		16.4		6.9		7.4		4.7	
Chromite	0.7		0.4		0.6		0.2		0.5		0.3	
Apatite	0.1		0.2		0.2		1.2		0.3		0.4	

Green glass bead (GGB), low-Ti basaltic glass (LTBG), high-Ti basaltic glass (HTBG), basaltic andesite glass (BAG), and high-Al basaltic glass (HABG). Mg' = molar Mg/(Mg + Fe) * 100. N, number of glasses in group.

Table 3
Trace-element concentrations of the main glass groups

N	BAG		KREEPy		HKFM		HTBG		LTBG	GGB
	(7)	sd	(5)	sd	(12)	sd	(4)	sd	(1)	(1)
Na	7755	1440	3311	1073	4273	2084	2802	1040	2011	1495
P	3723	1016	949	164	1487	979	1438	524	1719	977
K	4969	837	753	215	3425	2088	568	231	1212	143
Sc	32.2	3.12	38.8	2.12	28.9	2.36	74.7	4.58	48.1	38.3
V	40.8	10.9	85.9	11.1	48.9	7.4	175.1	38.6	130.2	95.2
Cr	791	43	2172	131	1014	188	2739	400	1847	2695
Mn	1425	39	1740	59	1151	102	2490	79	2350	2617
Co	40.6	5.2	64.4	10.3	35.8	6.6	62.5	14.6	108	207
Rb	12.8	3.2	2.1	0.5	7.9	6.2	1.7	0.8	4.7	1.7
Sr	229	9	151	5	168	12	136	13	157	39.5
Y	563	18	64.8	1.4	330	32	111	37	166	9.7
Zr	3220	101	285	10	1739	280	356	102	785	27.0
Nb	180	5.1	18.7	1.2	119	14	24.2	5.8	66.8	2.0
Ba	1108	35	98.7	3.8	797	151	91.1	39.7	391	11.9
La	144	3.6	11.0	0.6	81.5	9.0	12.5	6.4	39.6	1.2
Ce	401	12.0	32.9	0.85	222	23.4	40.2	19.39	106.3	3.3
Pr	55.1	1.6	4.6	0.10	29.4	3.2	6.0	2.74	14.6	0.5
Nd	224	5.9	21.2	0.98	119	14.1	30.0	12.59	57.6	2.1
Sm	58.6	3.0	6.5	0.28	32.1	3.7	9.7	3.78	16.9	0.7
Eu	3.0	0.6	1.1	0.12	1.9	0.4	1.2	0.12	1.6	0.2
Gd	68.8	3.8	7.7	0.95	37.8	5.5	12.6	4.51	18.8	0.9
Tb	12.4	0.9	1.6	0.14	7.0	0.8	2.5	0.89	3.7	0.2
Dy	78.0	5.5	9.5	0.50	46.6	6.5	15.5	5.24	23.9	1.3
Ho	15.7	0.8	2.0	0.08	9.5	1.7	3.4	1.20	5.0	0.3
Er	47.6	2.6	5.8	0.44	29.4	4.4	9.8	3.40	15.3	0.9
Tm	6.2	0.3	0.8	0.05	4.0	0.7	1.3	0.51	2.3	0.1
Yb	37.8	2.6	4.9	0.28	25.7	3.7	8.6	2.72	14.0	0.8
Lu	5.7	0.7	0.7	0.06	4.0	0.8	1.4	0.43	2.2	0.2
Th	17.4	1.2	1.3	0.11	13.9	2.0	0.9	0.55	5.1	0.1

All concentrations in ppm. Sample abbreviations the same as Table 2 Mg' = molar Mg/(Mg + Fe) * 100. N, number of glasses in group.

high-Ti basaltic glass, (4) high-Al basaltic glass, (5) basaltic-andesite glass, and (6) KREEPy glass. The basaltic glass class contains three of the groups (low-Ti, high-Ti, and high-Al basaltic glasses), the ITE-rich glass class contains two of the groups (basaltic-andesite and KREEPy glass), and the picritic glass class contains one of the groups (the very low-Ti picritic GGBs). There is no compositional group observed within the mare-highlands mixed glass class.

We initially identified the six groups visually based on similarities in the major-element composition of the individual glasses (Table 2); subsequent trace-element data on representative glasses from each group (Table 3) indicate that the groupings are robust for trace- as well as major-element compositions. In some cases, we suspect that all glasses within a given group are geologically related (green glass bead group, low-Ti basaltic glass group, basaltic-andesite glass group); for others the evidence is less compelling (high-Ti and high-Al basaltic glass groups), or there is little to no evidence for a common origin (KREEPy glasses). Below, we describe each group and compare each to glasses previously described at the Apollo 16 site.

3.1.1. Green glass beads

The 13 glasses in the green-glass group have an average major- (e.g., 0.43 wt% TiO₂, MgO/Al₂O₃ = 2.1) and trace-

element composition (38 ppm Sc, 3.3 ppm Ce) indistinguishable from the pyroclastic green glass previously described at the Apollo 16 site (Delano and Rudowski, 1980; Delano, 1986; Shearer and Papike, 1993).

3.1.2. Low-Ti basaltic glasses

The 41 glasses in the low-Ti basaltic group have an average major element composition and oxide ratios consistent with low-Ti mare basalts (20 wt% FeO, 4 wt% TiO₂; MgO/Al₂O₃ = 0.84). This group has a major-element composition and normative mineralogy similar to Apollo 12 pigeonite basalts (Neal et al., 1994), albeit with slightly higher TiO₂ concentrations. Although the ferromagnesian trace elements (e.g., Sc, V, Cr), phosphorus, and the alkali elements (e.g., K, Na, Rb, Sr) are typical of lunar low-Ti basalts, the absolute ITE concentrations are elevated, particularly in the light REEs (rare earth elements) relative to other low TiO₂ basalts (Fig. 5). Furthermore, the low-Ti basaltic glass group has the highest Th/REE ratio of any lunar basalt reported thus far (0.304 vs. 0.285 in NWA 032; Zeigler et al., 2005b). The group-1, high-Al basalts of Apollo 14 (Dickinson et al., 1985) have similar concentration of REEs, although they are marginally depleted in heavy REEs. Also, the basaltic lunar meteorites LAP 02205 and NWA 032 have a similarly shaped REE pattern, but at about half the absolute concentrations. Delano et al. (1981)

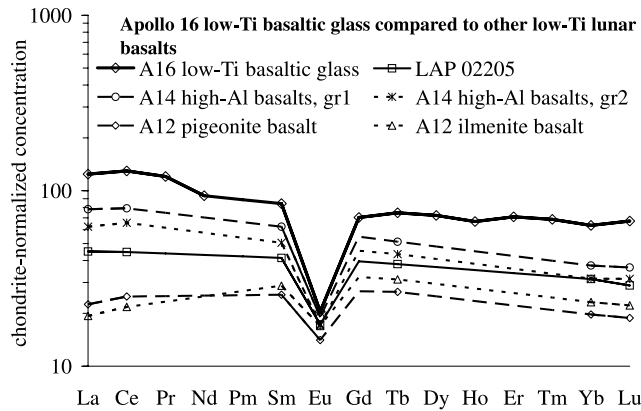


Fig. 5. The chondrite-normalized REE concentrations and pattern observed in the low-Ti basaltic glass fragment is dissimilar from the previously observed lunar low-Ti mare basalts due to its high absolute concentrations and light REE enriched pattern. The only low-Ti basalts in the lunar collection that show a similar LREE-enriched pattern are the Apollo 14 high-Al basalts and the lunar meteorites LAP 02205 and NWA 032 (not shown). Apollo 12 pigeonite and ilmenite basalt data are from: Goles et al. (1971), Wänke et al. (1971), Neal et al. (1994). Apollo 14 group 3 data are from Dickinson et al. (1985). LAP data are from Zeigler et al. (2005b). Chondrite normalization factors are from Anders and Grevesse (1989).

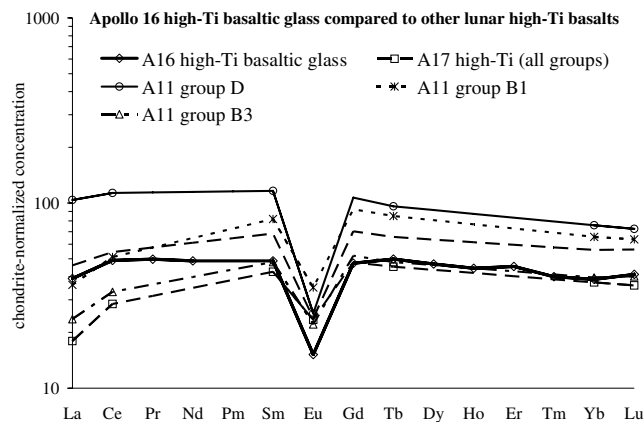


Fig. 6. The chondrite-normalized REE concentrations and pattern observed in the high-Ti basaltic glasses are similar to the Apollo 11 group D basalts in shape, albeit at about half the absolute concentrations. The average composition is plotted here, although there is a considerable spread in the REE-concentrations (see Table 3) in this group. The shape of the REE pattern is nearly identical in each bead, however. It is notable that the Apollo 11 group D basalts are the lowest-Ti group of lunar high-Ti basalts, and that those lunar high-Ti basalts with higher Ti concentrations (particularly the Apollo 17 basalts) show a much more LREE-depleted pattern. Apollo 17 data from: Neal et al. (1990), Rhodes et al. (1976), Warner et al. (1979). Apollo 11 data from: Beatty et al. (1979), Gast et al. (1970), Goles et al. (1970), Haskin et al. (1970), and Jerde et al. (1994).

reported compositions of individual glasses from the Apollo 16 regolith that are nearly identical to this group. Other investigators (Ridley et al., 1973; Meyer and Tsai, 1975; Naney et al., 1976; Kempa and Papike, 1980) reported low-Ti basaltic glass group compositions, none of which are similar to the low-Ti basaltic glasses in this study.

3.1.3. High-Ti basaltic glasses

Seventeen of the glasses have major-element compositions similar to high-Ti mare basalts. In detail, the glasses have somewhat lower TiO_2 (8.6 wt%) concentrations than most of the Apollo 11 and all of the Apollo 17 high-Ti basalts and slightly higher MgO concentrations (9 wt%) than either Apollo 11 or 17 high-Ti basalts. The trace-element composition is also consistent with high-Ti mare basalt compositions (e.g., 77 ppm Sc and low light REE/heavy REE ratio; Fig. 6), but it does not match any of the Apollo 11 or 17 high-Ti basalt suites. Glasses of this composition have been described in almost all of the previous surveys of Apollo 16 glass and several lithic basalts with a similar major element composition have been identified in the Apollo 16 regolith (Delano, 1975; Vaniman et al., 1978; Zeigler et al., 2005a).

3.1.4. High-Al basaltic glasses

The average composition of the 27 glasses in the high-Al basaltic glass group is broadly similar to previously studied lunar high-Al basalts. In detail, however, their average composition differs from that of any known type of crystalline high-Al basalt. The Apollo 16 glasses are more magnesian ($\text{Mg}' = 56$) and have a lower $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio (3.0) than either Apollo 14 (50–42, ~ 3.8) or Luna 16 (42, ~ 3.3 ; Fig. 7). They are also considerably richer in TiO_2 on average than the Apollo 14 high-Al basalts (3.9 vs. 2.5 wt%, respectively). Thus far, we have been comparing the composition of this group to known lunar lithologies, but the composition could correspond to a mixture of two or more lunar lithologies, such as a moderately Ti-rich basalt (5–6 wt% TiO_2) and some unspecified feldspathic lithology or lithologies. These competing hypotheses will be explored further in the discussion section. Glass groups with a similar compo-

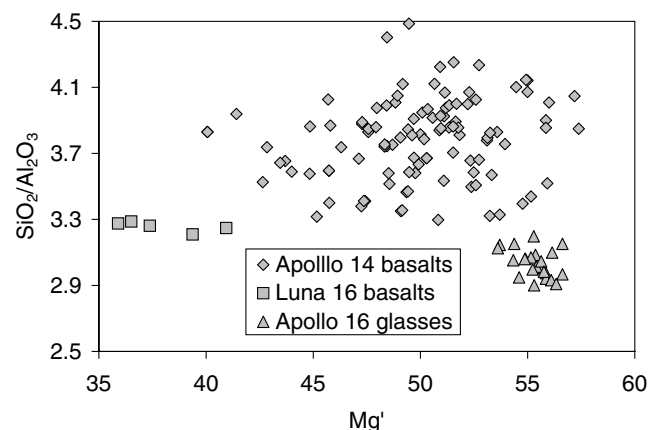


Fig. 7. The Apollo 16 high-Al basaltic glass group is more magnesian [$\text{Mg}' = \text{molar Mg}/(\text{Mg} + \text{Fe}) \cdot 100$] than the Luna 16 high-Al basalts and all but the most magnesian of the Apollo 14 high-Al basalts. The $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio in the Apollo 16 high-Al basaltic glass is also clearly different from either of the previously observed lunar high-Al basalts, although it is worth noting that SiO_2 is determined by difference for all of the literature basalts. Apollo 14 data is from Dickinson et al. (1985), Shervais et al. (1985), and Neal et al. (1989a,b). Luna 16 data are from: Ma et al. (1979), Philpotts et al. (1971), and Korotev et al. (1988).

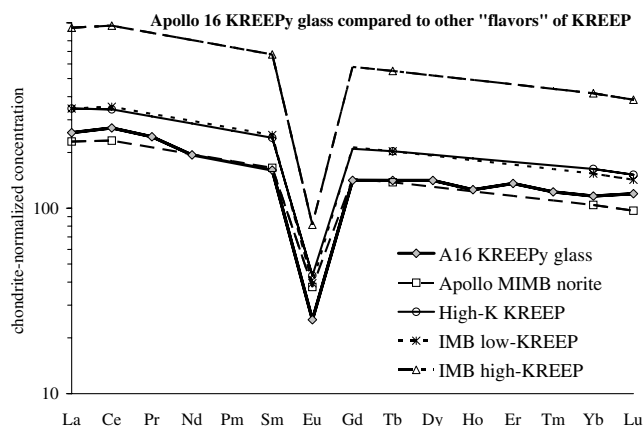


Fig. 8. Chondrite-normalized REE concentrations and patterns in the KREEPy glasses compared to various types of KREEP. Only the average composition of the KREEPy glass group is shown. There is some variability in the absolute concentrations of the REEs in different beads, however, the shape of the REE patterns in different beads is invariant. The closest match is the noritic component of the Apollo mafic impact melt breccias (MIMB) of Korotev (2000). The high-K KREEP data are from Warren (1989) and the IMB low- and high-KREEP data are from Jolliff (1998).

sition have been previously reported (Meyer and Tsai, 1975; Naney et al., 1976; Kempa and Papike, 1980).

3.1.5. KREEPy glasses

A large number of the glasses, 53, are those whose compositions correspond to glasses previously categorized as high-K Fra Mauro (HKFM) “basaltic” glasses (Ridley et al., 1973; Meyer and Tsai, 1975; Naney et al., 1976; Vaniman et al., 1978; Kempa and Papike, 1980; Zellner et al., 2005). We designate this group KREEPy glasses because they have high concentrations of K, REE, P, and other incompatible elements and major-element compositions similar to rocks of KREEP composition. The KREEPy glass group has a wider compositional range than any of the other groups in this study. On average, however, absolute concentrations of incompatible elements are similar to those of Apollo 15 KREEP basalt and the average KREEP component of the mafic impact-melt breccias of the Apollo sites (Fig. 8) but less than (~70%) those of high-K KREEP (Warren, 1989). In detail, the average major- and ferromagnesian trace-element composition of the KREEPy glasses does not match that of rocks identified as KREEP. The concentrations of Ti, Fe, and Sc are somewhat greater and those of Mg and Cr are lower. The closest match would be to the noritic melt component in Apollo mafic impact melt breccias (Korotev, 2000).

3.1.6. Basaltic-andesite glasses

The 24 glasses in the basaltic-andesite glass group have a composition that is similar to samples identified as KREEP in a broad, generic sense, but there are important differences. Compared to “high-K KREEP,” that is, the impact-melt breccias of Apollo 14 (Warren, 1989), this group is enriched in FeO (1.3 \times) and TiO₂ (1.8 \times) and depleted in

MgO (0.6 \times) and Cr (0.7 \times). These concentrations lead to a very low value of Mg' (39) compared to KREEP basalt or Apollo 14 impact-melt breccias (~60). At 52.5%, the silica concentration is at the high end of the range of lithologies of KREEP composition and is more similar in this regard to Apollo 15 KREEP basalt than to KREEP impact-melt breccias (see compilation of Korotev, 2000). Concentrations of REE are 10–40% greater than in high-K KREEP, a factor of two greater than in Apollo 15 KREEP basalt, and the light REEs are relatively more enriched than any of the various manifestations of KREEP (Fig. 9). In detail, this group has a composition that does not match that of any lithology or mixture of lithologies previously described in the lunar sample collection. Glasses of this composition were reported previously by Meyer and Tsai (1975) and Zellner et al. (2005) as HKFM glasses, whereas others (e.g., Naney et al., 1976) have used the term HKFM for more Mg-rich and Si-poor glasses.

3.1.7. Ungrouped glasses

The rest of the glasses in this study are not part of a tight compositional group. Most of them do fit into the following broad compositional categories, however (see Fig. 10). Eighteen glasses have a major-element composition similar to low-Ti or VLT basalt (0.5–2.5 wt% TiO₂ and >16 wt% FeO). Six glasses have a composition similar to high-Ti basalt (>5 wt% TiO₂ and >15 wt% FeO). None of these ungrouped basaltic glasses fall near the tight compositional cluster of the high-Ti basaltic glass group discussed above. Twenty-one glasses have many of the same characteristics as the high-Al basaltic glass group, although they are slightly more mafic (~4 wt% TiO₂, 16 wt% FeO). We excluded them from the high-Al basaltic glass group because of a compositional gap. The compositions of the remaining glasses do not match any known lunar lithology,

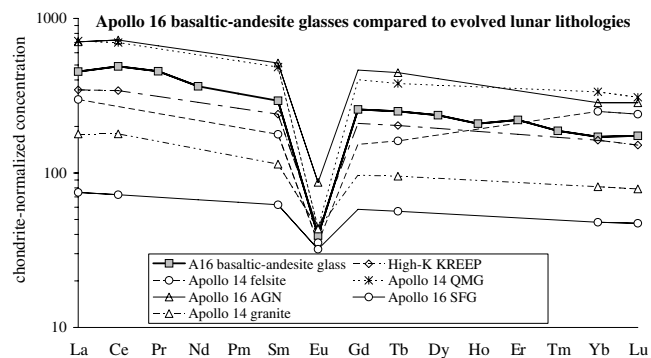


Fig. 9. The chondrite-normalized REE concentrations and pattern observed in the basaltic-andesite glass group compared to various evolved lunar lithologies. Only the average composition of the basaltic andesite glass group is shown. Little variability is seen in absolute REE concentrations or the shape of the REE pattern in different beads. No material is an exact match, although Warren's (1989) high-K KREEP and the Apollo 16 alkali gabbro (AGN; Jolliff, 1998) have similar shapes. Apollo 16 sodic ferrogabbro (SFG) data are from Marti et al. (1983) and Lindstrom and Salpas (1983). All other data are from Jolliff (1998) and the references therein. QMG, quartz monzogabbro.

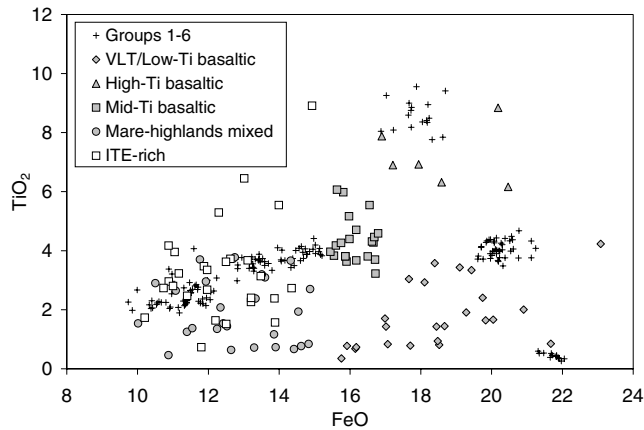


Fig. 10. Similar to Fig. 3b, but the grouped glasses have been deemphasized (small black crosses), and the previously ungrouped glasses are lumped into general categories based on their major element composition.

and in many cases the compositions of individual ungrouped glasses are hard to account for as a mixture of known lunar lithologies. They all have intermediate FeO (10–15 wt%) and most have low TiO_2 (0.5–4 wt%) concentrations. About half of the glasses in this final “group” have <0.15 wt% K_2O and are likely mare-highlands mixed glasses, whereas the other half have >0.15 wt% K_2O and likely have an origin similar to the KREEPy glass group (see discussion section).

4. Discussion

There are two processes that produce glass on the Moon: impact melting and pyroclastic eruption. Given the ubiquity of impact craters on the Moon and the paucity of obvious explosive volcanic features, it is no surprise that five of the six glass groups in this study, and $>95\%$ of the glasses studied here, almost certainly formed through impact processes. Only the green-glass group has an obvious eruptive origin (Delano, 1986; Shearer and Papike, 1993). The impact origin of the rest of the glasses is indicated by the presence of metal with meteoritic Fe:Ni ratios ($\sim 94:6$) in many glass fragments, by the apparent volatilization of alkali elements in most glass groups (Fig. 11), and by the fact that none of the groups has a composition similar to previously recognized eruptive lunar samples. Even the low-Ti and high-Ti basaltic glass groups, which appear to have almost purely basaltic precursor lithologies (not mixtures), have $\text{MgO}/\text{Al}_2\text{O}_3$ ratios (~ 0.86) that are distinct from the range of known pyroclastic glasses.

Because an impact origin is probable for such a high proportion of the glasses in this study, and by proxy, the Moon as a whole, the question becomes: what materials were melted to form the glasses observed in the Apollo 16 regolith? Do the glasses have a single lithologic precursor, or are they typically multi-lithologic (e.g., regolith compositions)? Previous investigators (Naney et al., 1976; Kempa and Papike, 1980; Zellner et al., 2003) have noted

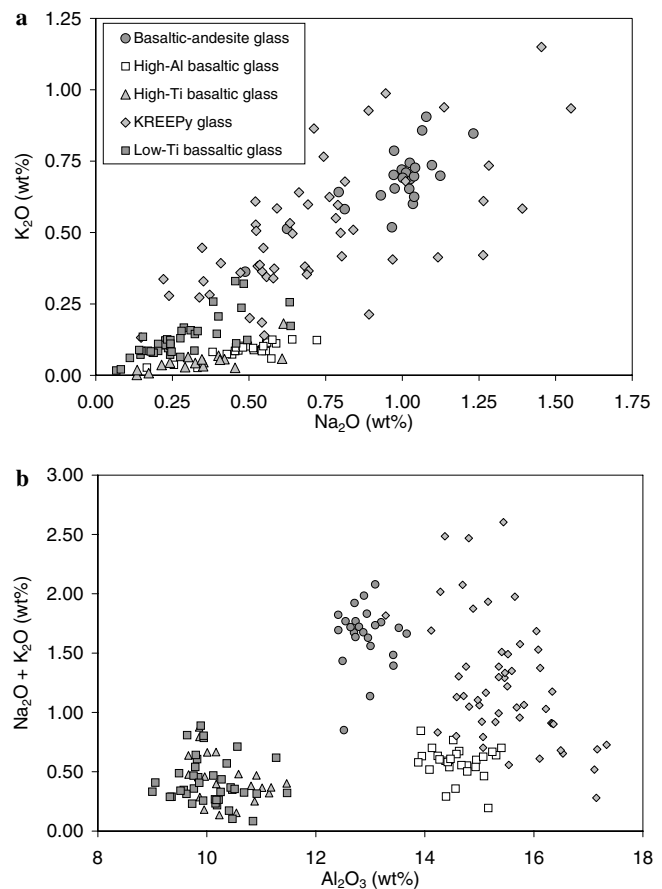


Fig. 11. The concentrations of Na_2O and K_2O in a given group of glasses are positively correlated with each other (a), but the concentration of Na_2O and K_2O is not correlated with Al_2O_3 (b). This indicates that it is most likely volatilization due to impact processes that is causing the large spread in alkali concentrations within the glass groups (Na_2O and K_2O are by far the most volatile of the major elements), not variable amounts of feldspar in the precursor materials for the glasses.

that most of the feldspathic glasses at the Apollo 16 site (by far the most abundant glass type at the Apollo 16 site) have compositions similar to average Apollo 16 soil. This clearly indicates that multi-lithologic precursor material is most common in Apollo 16 glasses. Furthermore, Delano (1975) and Delano et al. (1981) has advocated linear and hyperbolic mixing trends between mare and highlands end-members as the precursor material for glasses with a mare affinity in Apollo 16 glasses.

Although we find little evidence for linear mixing trends in the mafic glasses of this study, many of these mafic glasses, particularly the ungrouped glasses, likely have multi-lithologic precursors (i.e., regolith). Their bulk compositions are not consistent with any known lunar lithology. At the same time, the data are consistent with a significant number of mafic glasses in the Apollo 16 soils having a single lithologic precursor, such as the high-Ti, low-Ti, and high-Al basaltic-glass groups and the basaltic-andesite glass group (see below). These glass groups represent 40% of the mafic glasses found in this study. That the mafic glass beads in this study seem to have both multiple and

single lithologic precursors is of note, as previous work by Hörz and Cintala (1997) concluded that the only way to make a homogenous impact glass bead is from a single lithologic precursor, i.e., a crystalline rock surface.

What follows is a discussion of the transport mechanism and time of emplacement for the mafic glasses in this study, with an emphasis on the likely precursor materials and specific provenance of the six glass groups previously discussed in detail.

4.1. Post-basin origin of basaltic glasses at Apollo 16

The concept that basaltic material at the Apollo 16 site was deposited by post-basin impacts was first presented in Zeigler et al. (2005a), so only a brief summary is provided here for convenience. The Apollo 16 ancient regolith breccias (McKay et al., 1986) and the soils collected near North Ray Crater contain material from Imbrium, the last basin ejecta deposit at the Apollo 16 site, but practically no material deposited by post-Imbrium impacts. Since neither of these sample suites contains appreciable amounts of basaltic material, it follows that all, or very nearly all, of the basaltic material at the Apollo 16 site was not deposited as part of basin ejecta deposits. Instead, basaltic material in the Apollo 16 regolith occurs mainly as ejecta from small to medium (<150 km) sized post-Imbrium cratering events into the maria near the Apollo 16 site.

Previous investigators (Milton and Hodges, 1972; Delano, 1975) have made a strong case for Theophilus ejecta from Mare Nectaris as the source of both high- and low-Ti basaltic material at the Apollo 16 site. These studies did not have the benefit of global remotely sensed TiO₂ data, however, which shows that Mare Nectaris (220 km east) is the most likely source region only for low-Ti and VLT basaltic material at the Apollo 16 site. This includes the low-Ti and high-Al basaltic glass groups, as well as the ungrouped low-Ti and VLT basaltic glasses. In addition to Theophilus, the craters Madler and Torricelli, are possible source craters within Mare Nectaris.

Remotely sensed TiO₂ concentrations show that Mare Tranquillitatis is the closest (~300 km north) and most expansive high-Ti mare near the Apollo 16 site, making it the most likely source region for high-Ti basaltic glasses at the Apollo 16 site. There are several small craters along the southwestern edge as likely source craters: Ross, Arago, Dionysius, Maskelyne, Moltke, Sosigenes, and Schmidt.

4.1.1. Low-Ti and high-Ti basaltic glass groups

Earlier we referred to the low-Ti and high-Ti basaltic glass groups as having single lithologic precursors (i.e., a single rock type was melted to produce these impact glasses); these would be low-Ti and high-Ti mare basalts, respectively. We make this assertion because the major-element compositions of the basaltic glass groups are more similar to lithic mare basalts in the lunar sample collection, that is, the glasses do not have compositions consistent with a regolith composed mainly of mare basalt but with

some feldspathic material from the highlands. Specifically, the low-Ti basaltic glasses are very similar to the Apollo 12 pigeonite basalts and the high-Ti basaltic glasses are broadly similar to both the Apollo 11 and 17 high-Ti basalts. The standard deviation of the ITE concentrations is nearly 50% in the high-Ti basaltic glass group, although the shape of the REE patterns are similar in each case. This suggests that individual glass beads within the high-Ti basaltic glass group came from more than one basalt flow, likely transported to the Apollo 16 site by more than one source crater.

4.1.2. High-Al basaltic glass group

The likely provenance of the high-Al basaltic glass group is less well constrained than the other basaltic glass groups. The composition of the high-Al basaltic glass group is consistent with the precursor material being either (1) a crystalline high-Al basalt or (2) a mixture of basalt and Feldspathic Highlands Terrane material. Although the major-element composition of the high-Al basaltic glass group can be explained as a mixture of two parts intermediate-Ti basalt (~6 wt% TiO₂) and one part feldspathic material (the average composition of Apollo 16 soils or feldspathic lunar meteorites works; Fig. 12), their trace-element composition appears to preclude them being a mixture of any known mare and highlands materials (Fig. 13a). It is not possible to mix known mare basalt compositions with known feldspathic highlands compositions to achieve the level of light REE enrichment seen in the high-Al basaltic glass group. Despite having REE concentrations and REE patterns (Fig. 13b) similar to the Apollo 14 high-Al basalts (group 3), differences in major-element composition (e.g., Fig. 7) show that these glasses represent a new lunar high-Al basaltic composition. The lack of high-Al basaltic glasses in the Apollo 16 ancient regolith breccias likely requires them to be a post-Imbrium product. In light of these observations, the most straightforward provenance for this group is Mare Nectaris (based on Ti concentrations). Lending further support to this provenance is the recent classification of large areas of Mare Nectaris as possible high-Al basalt flows by Kramer et al. (2004).

A problem with a Nectaris origin for the high-Al basalt glass group (and the low-Ti basaltic glass group discussed earlier) is the light REE enrichment. Typically, a light REE enrichment of this type in lunar materials (e.g., mafic impact melt breccias, Apollo 14 high-Al basalts) has been explained by the assimilation or incorporation of KREEP at some point in the sample's history (Dickinson et al., 1985; Warren, 1988, 1989; Haskin et al., 1998; Korotev, 2000). If the light REE enrichment is due to KREEP, it would either require there to be a KREEP layer beneath the Nectaris basin (something not supported by the remotely sensed data), which the erupting basalts assimilated during ascent through the crust, or that there was a KREEPY component in the source region for the basaltic precursors of these glasses. In the later case, this would be the first evidence for such an occurrence outside of Procellarum KREEP Terrane.

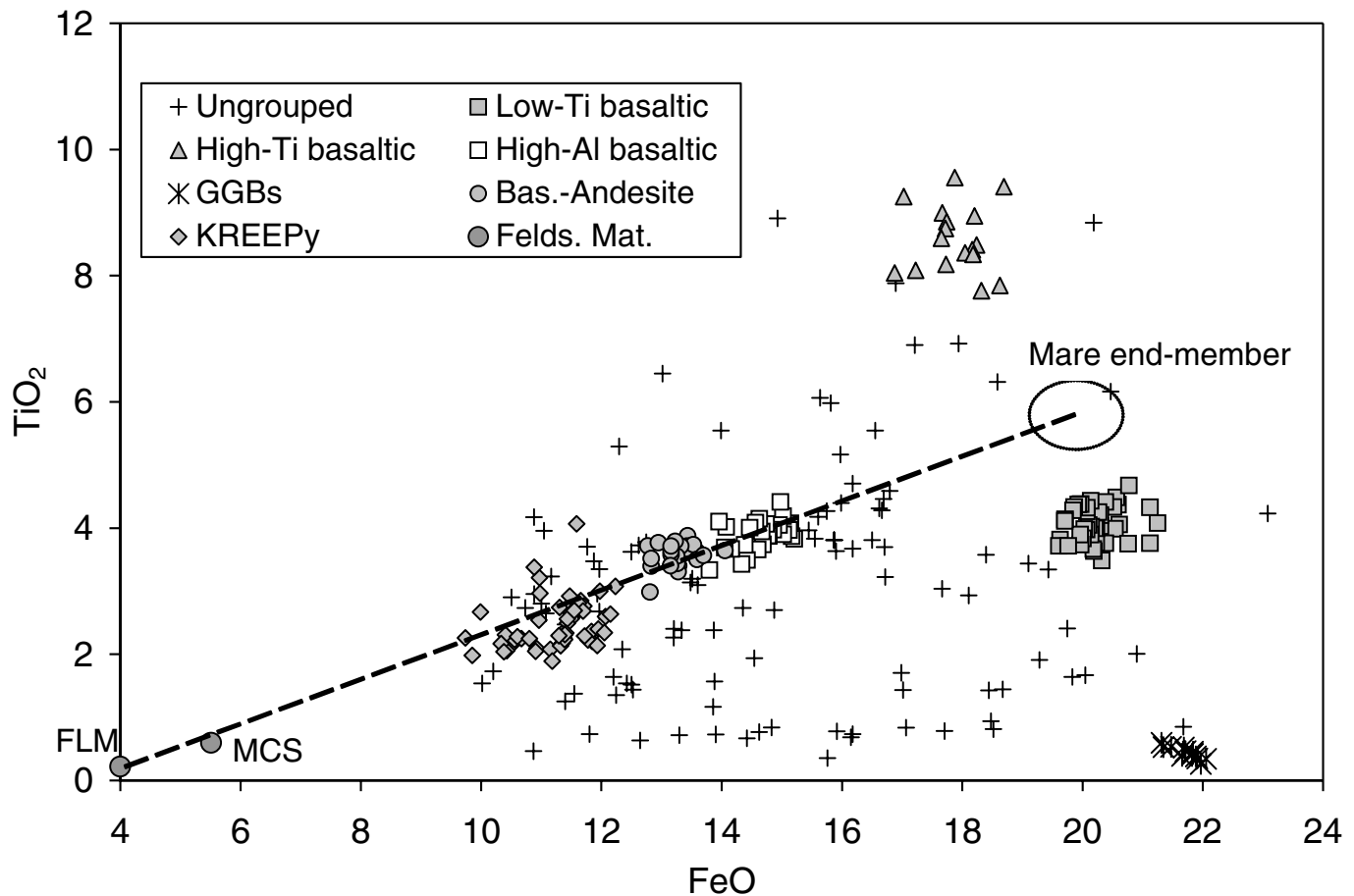


Fig. 12. The feasibility of the high-Al basaltic glass group being a mare-highlands glass mixture is shown here. Similar to Fig. 3b, but the FeO axis has been extended to lower concentrations and two typical feldspathic lunar materials (Felds. Mat.) have been added, mean Cayley soil composition (MCS; Korotev, 1997) and the average composition of the feldspathic lunar meteorites (FLM; Korotev et al., 2003). A mixing line (dashed) extends from these feldspathic materials, through the high-Al basaltic glass group, to extrapolate to a theoretical mare-endmember mixing component. This mare endmember would have about 6 wt% TiO_2 and 20 wt% FeO. GGBs, green glass beads.

4.2. Origin of mare-highlands mixed glasses

Clearly mare-highlands mixed glasses have multiple lithologic precursors that were melted and mixed; however, it is not known where and how this occurred. One possibility is that impacts that were large enough to completely punch through a mare veneer into the underlying highlands crust (e.g., Theophilus) might have melted both mare and non-mare material. It is also possible, if unlikely, that mare-highlands mixed glasses form when mare and highlands materials in the local soils are remelted and combined during the “gardening” of the Apollo 16 site by micrometeorite impacts. The lack of trace element data on these glasses makes reaching a definitive answer difficult. Clearly, this is an area that warrants further study.

4.3. Picritic glasses of unknown origin

The only picritic glasses found in this study are those of the green glass bead group and the discussion that follows is tailored toward them, although the discussion would be

applicable to any picritic glass found at the Apollo 16 site. The green glass beads found in this study are virtually identical in composition to previous Apollo 16 green glass beads (e.g., Delano, 1975, 1986). Green glass beads were not observed in the ancient regolith breccias (Simon et al., 1988; Wentworth and McKay, 1988), which means they are likely a post-basin addition to the Apollo 16 site. Other post-basin basaltic materials at the site have been postulated to be ejecta from craters in the surrounding maria (Zeigler et al., 2005a). The green glass beads appear to be unaffected by impact processes, with spherical shapes intact and no evidence for remelting, mixing, fracturing, or meteoritic contamination.

If the green glass beads were not deposited by impact processes, then they must have been delivered to the Apollo 16 site by direct pyroclastic deposition. Very-low Ti pyroclastic deposits are difficult to discern from orbit and thus potential sources are not readily apparent. The few sites proposed for VLT pyroclastic deposits are very far from the Apollo 16 site (>1000 km; Gaddis et al., 1985). Assuming VLT pyroclastic deposits occur spatially associated

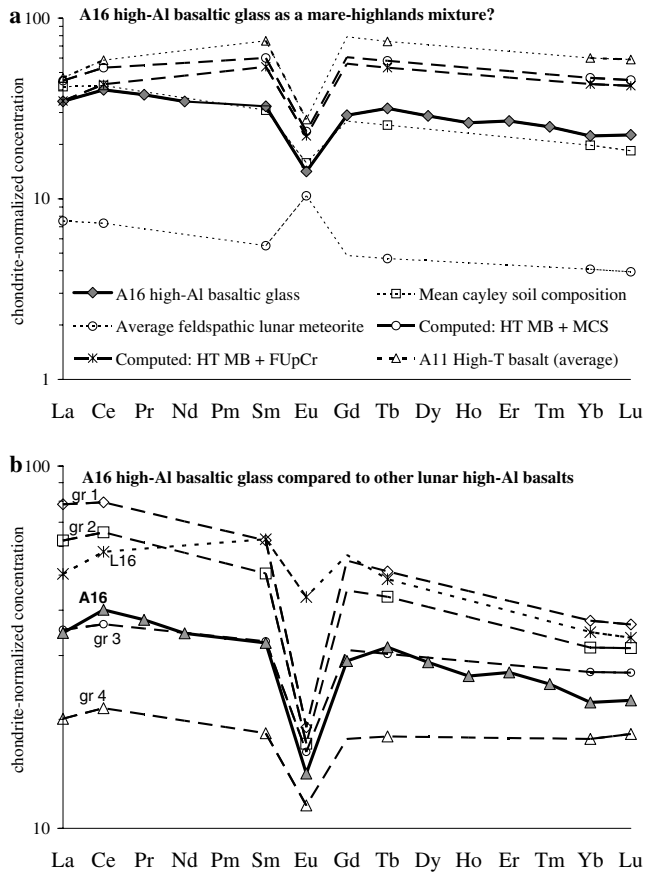


Fig. 13. (a) Comparison of REE concentrations in the high-Al basaltic glasses to the REE patterns in hypothetical mare-highlands glass mixtures (dark dashed lines). Average Apollo 11 high-Ti basalt (see references in Fig. 8) was used as the hypothetical mare endmember and mean Cayley soil (MCS) and feldspathic lunar meteorites (FLM) were used as feldspathic materials (Korotev, 1997, 2003). The basalt was combined in a ~2:1 ratio with mean Cayley soil and feldspathic lunar meteorites (in order to match the major element composition in the Apollo 16 glass). Neither of the resultant REE patterns is able to match the LREE-enrichment of the high-Al basaltic glass. (b) The Apollo 16 high-Al basaltic glass REE pattern compared to the Apollo 14 high-Al basalts groups 1–4 (dark dashed lines) and the Luna 16 high-Al basalts (dotted line). The concentrations and overall shapes of the Apollo 16 high-Al basaltic glass patterns are similar to the Apollo 14 high-Al group 3 basalts, with a possible diversion in the HREEs. Only the average composition of the high-Al basaltic glass group is shown. Little variability is seen in absolute REE concentrations or the shape of the REE pattern in different beads. References for the high-Al mare basalts are the same as Fig. 9.

with some mare basalts (as high-Ti pyroclastic deposits do) and that we are simply unable to discern them, the closest areas of volcanic activity to the Apollo 16 site are at least four times farther away than the proposed eruptive distances for “local” (<50 km²; Head and Wilson, 1979; Wilson and Head, 1981) lunar pyroclastic deposits (presumably if there were large regional VLT pyroclastic deposits covering thousands of square miles, they would have been identified). It seems unlikely that eruptive distances for lunar pyroclastic deposits can reach that far. Neither of the two options for emplacement of VLT green glass beads at the site is particularly appealing.

4.4. Procellarum KREEP Terrane origin of KREEPy materials at Apollo 16

The view of the Moon as a globally uniform “layer cake” of anorthosite overlying a mafic mantle with a globally distributed KREEP sandwich horizon (see Vaniman et al., 1991; for a summary) has given way to a more complicated model in which the Moon is divided into geologic/geochemical terranes that have significant chemical differences extending to considerable depths (Jolliff et al., 2000; Wieczorek and Phillips, 2000). The Procellarum KREEP Terrane, which encompasses most of the Oceanus Procellarum-Mare Imbrium region, contains an exceptional proportion of the Moon’s ITE content (Jolliff et al., 2000; Taylor et al., 2002). The Imbrium basin is the largest and most recent impact event into this region and it redistributed significant amounts of material from this terrane over much of the Moon’s surface (Haskin, 1998). Imbrium is the only impact into the Procellarum KREEP Terrane to contribute a significant amount of material to the regolith at the surface of the Apollo 16 site (Haskin et al., 2003). As no other region of the Moon has elevated ITE-concentrations comparable with those seen in the Procellarum KREEP Terrane, this leads us to speculate that the KREEPy materials at the Apollo 16 site most likely came from the Procellarum KREEP Terrane, including the ungrouped ITE-rich glasses and the KREEPy and basaltic-andesite glass groups in this study (for a more extensive treatment of this subject see Haskin et al., 1998 and Korotev, 2000).

4.4.1. KREEPy glass group

Given the similarities of the KREEPy glass group to the noritic melt component in Apollo mafic impact-melt breccias (Korotev, 2000), it seems likely that these KREEPy glasses are either noritic melt similar to that in the mafic impact-melt breccias that quenched before it picked up an appreciable clast load, or they actually represent pieces of broken up mafic impact-melt breccias that simply contain little or no clastic material. The KREEPy glass group was likely delivered to the site as Imbrium ejecta.

4.4.2. Basaltic-andesite glasses

The basaltic andesite glass group stands apart compositionally from other petrologically “evolved” ITE-rich lunar lithologies (Snyder et al., 1995; Jolliff, 1998; Papike et al., 1998). The KREEPy impact samples (e.g., mafic impact-melt breccias) have higher Mg’ numbers and lower concentrations of FeO and TiO₂ than the basaltic-andesite glass group (Korotev, 1994). KREEP basalts also have a higher Mg’ (50–60) and lower TiO₂ than this glass group. Lunar granites/felsites and alkali anorthosites are much less mafic than the basaltic andesite glasses, and have different inter-element ratios among the ITEs. Alkali gabbro-norites have comparable TiO₂ and FeO concentrations (3.5 and 14.5 wt%, respectively), but higher Mg’ (55) and lower Na₂O concentrations (0.4 wt%). Sodic ferrogabbros have higher SiO₂ and TiO₂ (56.5 and 5.6 wt%, respectively), low-

er Mg' (~ 30), and lower Al_2O_3 (10.2 wt% vs. 12.9 wt%) than this glass group (Lindstrom and Salpas, 1983; Marti et al., 1983). Quartz monzogabbros typically have lower TiO_2 (< 2 wt%), higher FeO (usually > 14 wt%), and usually much higher P_2O_5 (commonly upwards of several wt%).

The presence of meteoritic metal and mineral clasts indicates that the basaltic andesite glasses are products of impact melting. However, because of their extreme composition (Fig. 14), these glasses cannot be explained as a mixture of the known lithologies. This indicates that the basaltic-andesite glasses represent a previously unknown evolved lunar lithology that crops out on a large enough scale to produce an impact melt of this composition. The precursor material remains enigmatic. Most KREEPy materials are both ITE-rich and magnesian, an apparent geochemical contradiction (Warren, 1988). The basaltic andesite glasses have similar ITE-interelement ratios as other KREEPy materials, but have higher concentrations of ITEs (including TiO_2) and are more ferroan than other varieties of KREEP-rich materials. This composition is what would be expected of a magma ocean residuum that did not mix with magnesian components (Warren, 1988).

As stated earlier, based on their compositions, the basaltic andesite glasses are most likely products of the Procellarum KREEP Terrane. The available evidence suggests that unlike the other ITE-rich glasses at the Apollo 16 site, the basaltic andesite glasses are not pieces of Imbrium ejecta. Zellner et al. (2005) dated three basaltic-andesite glass fragments by the Ar–Ar technique, acquiring ages of 3.78, 3.78, and 3.74 Ga (all with errors of ~ 0.05 Ga). These ages are younger than the accepted age of Imbrium impact (3.85 Ga) and the absence of basaltic-andesite glass from the Apollo 16 ancient regolith breccias (Simon et al., 1988; Wentworth and McKay, 1988) means it is unlikely that they were deposited at the Apollo 16 site by the Imbrium impact. Perhaps one of the later impacts into the Procellarum KREEP Terrane such as Copernicus, Eratosthenes, Archimedes, or Aristillus deposited them at the site. However, these craters are all relatively small (< 100 km) and very distant (> 1000 km), which makes it unlikely that they

deposited a significant amount of material at the Apollo 16 site. Furthermore, the Ar–Ar systematics of suspected Copernicus ejecta (both glass and lithic fragments) at the Apollo 12 site have been reset (or at least disturbed; Eberhardt et al., 1973; Alexander et al., 1976; Barra et al., 2006), which is not the case for the basaltic andesite glasses of Zellner et al. (2005). Another possible source crater is the lower Imbrium crater Arzachel ($18^\circ S, 2^\circ E$; Wilhelms, 1987). This crater is comparable in size (100 km) and much closer to the Apollo 16 site (~ 500 km) than the later impacts into the Procellarum KREEP Terrane. Being much older (pre-Orientalis) it could satisfy the Ar–Ar age observed in the basaltic-andesite glasses, however there is no evidence that this crater exhumed high-Th materials such as the basaltic-andesite glasses. Whatever the source crater, the Procellarum KREEP Terrane seems to be the only likely source region for these glasses; what is puzzling is that they have not been found among the soils from other landing sites.

5. Conclusions

To a first order, this study shows that the mafic glass population of the Apollo 16 regolith consists of approximately equal amounts of basaltic glasses from the surrounding maria and KREEPy glasses derived from the Procellarum KREEP Terrane, with small amounts of mare-highlands mixed glass and picritic glass also present. Almost all of these glass ($> 95\%$) have an impact origin; only the group of green glass beads is pyroclastic in origin. Unlike the feldspathic glasses at the Apollo 16 site, almost all of which have multi-lithologic precursor materials, a significant proportion ($\sim 40\%$) of the Apollo 16 mafic glasses have a single lithology as a precursor material. A large sample set and SIMS-derived trace-element chemistry permits recognition and characterization of six groups of glasses: picritic VLT green glass beads, low-Ti basaltic glass, high-Ti basaltic glass, high-Al basaltic glass, “HKFM” KREEPy glass, and basaltic-andesite glass. The glasses in the high-Ti group likely represent a new high-Ti mare basalt composition from Mare Tranquillitatis, one not sampled at the Apollo 11 site. The group of low-Ti basaltic glasses and high-Al basaltic glasses likely represent the best estimates of the composition of Mare Nectaris basalts in the lunar sample collection. Furthermore, if the light-REE-enriched patterns observed in these basaltic groups are indigenous to the parent melts (and not the result of impact mixing or assimilation during eruption), that would indicate the presence of either a KREEPy region beneath the Nectaris Basin or the presence of KREEPy or KREEP-like materials in the source regions for these basalts. The high-Al basaltic glasses in this study represent a new type of lunar high-Al basalt, probably from Mare Nectaris. Finally, the basaltic andesite glasses represent a new evolved lunar composition, with a likely origin in the Procellarum KREEP Terrane. This study shows that a significant proportion of material was added to the Apollo 16 site by post-basin lateral mixing. Such lateral mixing with in many cases identifiable

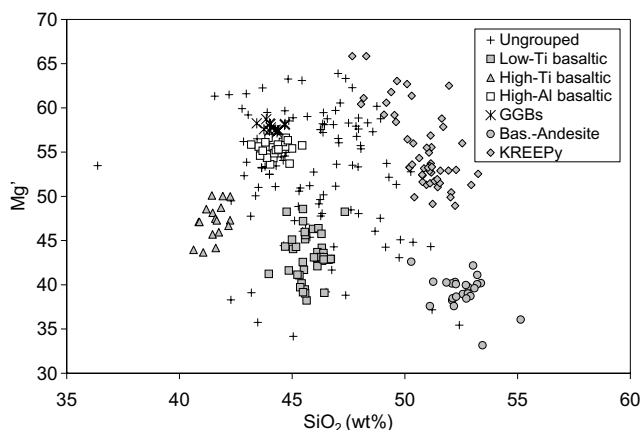


Fig. 14. The basaltic andesite glass is rich in silica and ferroan (low Mg').

source regions has implications for future sample return missions where the sample might consist only of regolith materials.

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