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LA-UR 89-1791
CONF-8903111--2

LA-UR--89-1791
DE89 013456

Received by OSTI
JUN 07 1989

TITLE VOLATIZATION AND MIXING IN GLASSES OF SOME APOLLO 14 REGOLITH BRECCIAS

AUTHOR(S) D. T. Vaniman and G. H. Heiken

SUBMITTED TO Proceedings of the 20th Lunar and Planetary Science Conference

VOLATILIZATION AND MIXING IN GLASSES OF SOME APOLLO 14 REGOLITH BRECCIAS

D. T. Vaniman and G. H. Heiken
Earth and Space Sciences Division, MS D462
Los Alamos National Laboratory
Los Alamos, NM 87545

Three unique samples can distinguished by analysis of all glass types, including devitrified glasses, in a suite of 26 Apollo 14 regolith breccias. These unique samples include the well-studied sample 14315, which has an abundance of anorthositic gabbro glasses and devitrified glasses; 14004,77, which has no glasses other than those that match the local soil; and 14076,5, which contains no glasses similar to the local soil or to LKFM. Sample 14076,5 is clearly exotic, for it contains devitrified glasses of anorthositic composition and of a silica-volatilized (HASP) trend that stems from anorthosite; these silica-volatilized glasses contain the new mineral yoshiokite. HASP glasses in this exotic sample and HASP glass spheres that stem from the Apollo 14 soil composition differ greatly from the HASP glasses at Apollo 16. The various HASP glasses can be just as useful as non-volatilized glasses in searching for major crustal or regolith lithologies.

INTRODUCTION

Regolith breccias provide individual coherent soil samples that may or may not have formed from the surrounding regolith. A large part of the interest in regolith breccias is due to studies which indicate that some of them represent regoliths that are much older than the unconsolidated surrounding soil (McKay et al., 1986) or regoliths that are exotic to their collection locality (Jerde et al., in press). If old or exotic, the fragments within regolith breccias can provide c[illegible] to the lithology of regoliths that are not represented in known lunar samples or of fossil regoliths that no longer exist on the Moon.

Glasses in regoliths and regolith breccias are small fragments that can provide large amounts of information about the impact melt and volcanic lithologies that contributed to these samples. Delano (1988) has studied glasses from five large (140 to 1360 g) regolith breccias from the Apollo 14 site. His study showed that at least six pristine mare glasses occur in these samples, and that relative ages for the regolith breccias may be inferred from the number of pristine glasses in each sample (younger regolith breccias have more types of pristine glasses, since they sample a longer history of mare volcanism). The present study summarizes data for a larger number of smaller (mostly <40 g) regolith breccia samples from Apollo 14. Because of the small sizes of the subsamples analyzed (most are <0.5 cm in diameter), it was generally rare to find more than 10 to 20 glasses in a single thin section.

The goal of this effort was to provide a comparison between the glass populations in 27 thin sections with bulk sample chemistry and I_s/FeO data obtained by collaborators at UCLA (P. Warren and E. Jerde) and at NASA/JSC (R. Morris). The chemical study was designed mainly as a search for exotic regolith breccias that may provide new information not previously extracted from the Fra Mauro regolith. It was hoped that the glass fragments in thin section, as representatives of larger rock and soil types, might show a correspondingly exotic nature in those regolith breccias that had unique chemical compositions. Indeed, one very unique sample representing half of the 2 g sample 14076 stands out not only for its very anorthositic composition (Jerde et al., in press) but also for the presence of a very unique set of devitrified glass fragments that represent impact in an almost "pure" anorthosite terrain with extreme SiO_2 volatilization. These devitrified glasses have yielded yoshiokite, the first new mineral unique to the lunar highlands (Vaniman and Bish, in prep.).

Because this study of glass fragments was intended to be a comparison with bulk chemistry, it was decided to analyse not only the small glass spheres but also to analyze glasses that had undergone obvious devitrification, glasses with vesicles and small inclusions, agglutinates, matrix glasses, and ropy glasses. Although these analyses might be argued to include features that are too varied for uniform interpretation in one study, it would be unacceptable to ignore large but "messy" glass types in a search for explanations of chemical variation in the bulk samples. Thus a wide variety of glass types is represented here, and the results include a consideration of the relations between glass type and size as well as chemistry.

It is well documented that impact glasses (1) are products of impact melting events that sample regolith rather than rocks and (2) often have compositions that are skewed to lower K, Na, and Si content because of impact volatilization. Naney et al. (1976) documented the effects of Si volatilization, and Delano et al. (1981) have used refractory-element ratios to "see through" this effect and recover part of the original soil chemistry. In this report as much emphasis will be given to the effects of fractional vaporization as to the decipherment of original constituents.

METHODS

Electron microprobe analyses were obtained on a Cameca Camebax instrument with Tracor Northern electronics. Microprobe automation is described in Chambers (1985); data reduction using modified Bence-Albee empirical correction factors is described in Chambers (in press). A beam current of 15 nA was used. Analyses were obtained either in rastered areas that covered large portions of homogeneous glasses and devitrified glasses, or with focused beams to avoid vesicles, inclusions, and local devitrification. Glasses forms were classified and measured by petrographic microscopy.

RESULTS: CLASSIFICATION

Glasses were classified by color, form, special features, and size prior to analysis. Colorless, yellow, green, orange, black, and brown color classifications were used. Glass forms were classified as spheres (or sphere fragments), angular, splash coats, agglutinates, ropy glasses, and matrix glasses (those that saturate a porous matrix). Special features were defined for those fragments that were not clear glass; these features were devitrification avoided in microprobe analysis, pervasive devitrification that was analyzed by broad-beam methods, edge or rim crystallization avoided in microprobe analysis, inclusions or quench crystals avoided in analysis, and vesicles.

For systematic chemical classification, compositions were categorized according to a modified scheme based on Naney et al. (1976, 1977). These references provide a classification scheme for highland glass types based on major-element composition. The Naney scheme was used as-is to classify plagioclase glass (~34% Al_2O_3), gabbroic anorthosite (~31% Al_2O_3), anorthositic gabbro (~26% Al_2O_3), LKFM (low-K Fra Mauro, ~22% Al_2O_3) and Apollo 14 soil (equivalent to typical Apollo 14 regolith composition, ~16% Al_2O_3). In addition, mixed mare glasses were defined as those that have CaO/Al_2O_3 weight ratios above 0.75 but do not fit the "pristine" Apollo 14 glass classifications of Delano (1988); pristine mare are those that do fit his criteria. Rhyolitic glasses were defined as those with SiO_2 weight contents greater than 60%. Feldspathic highland glasses with >16% Al_2O_3 and <40% SiO_2 are classified as "HASP", in a modification of the use of this acronym by Naney et al. (1976). Although Naney et al. (1976) used this term for glasses derived by SiO_2 volatilization from anorthositic gabbro (~26% Al_2O_3), the genetic implications of the term (high-Al residue due to Si volatilization) make it applicable to a broad range of impact-volatilized glasses. The HASP compositions in Apollo 14 regolith breccias are especially complex, since volatilization from both Fra Mauro and anorthositic sources is observed. This complexity, however, allows a general comparison of the volatilization process.

The results of this classification scheme applied to all of the glass and devitrified glass constituents is listed in Table 1. Table 1 also shows the application of this classification scheme to the 357 glass analyses from soil sample 14259 obtained by Brown et al. (1971). The analyses of form, size, and chemical composition on which the regolith breccia glass and devitrified glass classifications are based can be obtained by writing to the authors.

DISCUSSION

Systematic Chemical Variation

Refractory-element Ratios. All of the glasses and devitrified glasses analyzed can be considered as a group, and as separate glass types. As a group, the effects of impact volatilization can be suppressed by examining the variation among refractory elements. In this manner, Delano et al. (1981) examined glasses from all of the Apollo sites except Apollos 14 and 17. They did not rely on the volatile constituents (K_2O, Na_2O, SiO_2, Fe) but instead developed hyperbolic mixing curves based on refractory-element ratios (Ti/Al vs. Ca/Ti, and Mg/Al vs. Ca/Ti). These curves could be shown to match the larger-scale variation in soils due to mixing at each site, even though many of the glasses analyzed had suffered volatile-element losses. Similar curves are shown in Fig. 1 for all of the glasses analyzed in this study.

The plot of Ti/Al versus Ca/Ti in Fig. 1a indicates a general hyperbolic mixing curve for all of the glasses and devitrified glasses analyzed. The alignment of compositions along this curve shows a mixing relationship (or several families of mixing relationships) that extends from high-Ti basalts (Ti/Al > 1.8) to the plagioclase-like glasses (Ca/Ti > 1000). This alignment passes through the typical Apollo 14 (Fra Mauro) soil composition. Those glass compositions that deviate greatly can not be major contributors to the Fra Mauro soils and regolith breccias. Figure 1a indicates two exotic glass types: a high-K (> 7% K_2O) rhyolite that falls below the curve, and the low-Ti (<2% TiO_2) pristine mare glasses that fall above the curve. The rhyolite compositions, and end-members for the apparent low-Ti pristine mare trend, are listed in Table 2. High-K rhyolite occurs both as a single clear glass sphere and as a ropy glass; ropy glasses in general have higher Si content than the typical Fra Mauro soil glasses.

Refractory-element mixing variations form a more diffuse hyperbola where an element is not held in common between the ratios plotted. Nevertheless the plot of Mg/Al versus Ca/Ti in Fig. 1b shows the same distinctive separation of high-K rhyolites below the main trend, and low-Ti pristine mare glasses above the trend. The other glass/devitrified glass types scatter along the trend, but indicate complex groupings and multiple mixing relationships.

In both Figs. 1a and 1b, the best-fit hyperbolic curves through the major glass clusters are those that tie high-Ti mare compositions to a variety of feldspathic highland compositions. The importance of high-Ti basalts in mixing may well be due to their greater age: Delano (1988) proposed that the high-Ti pristine glasses in Apollo 14 regolith breccias are older than the other pristine mare glasses. This inference was based on the occurrence of high-Ti compositions as the sole mare glass in some regolith breccias, whereas the the low-Ti compositions are often mixed with the high-Ti types (thus suggesting that there was an early episode of regolith breccia formation when only the high-Ti types were present). A greater age for the high-Ti mare composition would allow an earlier (perhaps more intense) and longer period of impact mixing to incorporate this component into glasses, regolith, and regolith breccias among the Apollo 14 samples.

In Fig. 1b, the scatter of glass compositions other than high-K rhyolite or low-Ti pristine mare allows a wide range of hyperbolic mixing curves. Two such curves are shown, one through the high Mg/Al part of the Fra Mauro cluster and into the anorthositic gabbro cluster, the other at lower Mg/Al and passing close to the x-axis toward HASP-like and plagioclase glasses. Clearly, the more anorthositic compositions (Ca/Ti > 500) do not fall along a single simple mixing trend that includes most anorthositic gabbros. Delano et al. (1981) proposed that the refractory-element ratio curves may be used to constrain the original lithologic components in a regolith sample; for the glasses in Fig. 1, separate mixing trends for mafic anorthositic gabbro (high Mg/Al) and for anorthosite (low Mg/Al) can be perceived, although the high Ca/Ti members themselves are impact mixtures rather than pristine igneous rocks.

Volatile-element Variation. Volatilization of constituents such as K_2O, Na_2O, SiO_2, and Fe modifies the chemical trends due to impact mixing (Delano et al., 1981). However, the volatilization process itself is a measure of how severe the impact history has been for specific glass groups. Naney et al. (1976) related HASP glasses in Apollo 16 regolith to an anorthositic gabbro (~26% Al_2O_3) parent composition. Figure 2 plots a major refractory oxide (Al_2O_3) against relatively volatile SiO_2. Compositions above 40% SiO_2 may include some samples with SiO_2 loss by volatilization, but generally contain samples with little or no SiO_2 volatile loss. Feldspathic highland glasses with SiO_2 <40% are are mostly if not all attributable to some amount of SiO_2 volatilization (note that mafic highland glasses from dunitic sources and Ti-rich mare glasses can have such low SiO_2 contents without SiO_2 volatilization).

In Fig. 2 there are two HASP trends. One is common to a broad range of regolith breccias (columns 5 and 6 in Table 2) and can be tied to a Fra Mauro-type (~16% Al_2O_3) source composition; we refer to this as the "Apollo 14 HASP trend". The other occurs only in regolith breccia 14076,5 and can be tied to an anorthositic (~34% Al_2O_3) source. Both are far different from the Apollo 16 HASP described by Naney et al. (1976), and both provide further constraints on the SiO_2-volatilization process.

When the term HASP was first employed (Naney et al., 1976), it was used to describe a range of Si-volatilized glasses at Apollo 16 related to an anorthositic gabbro parent composition. The local soils at Apollo 16 have compositions intermediate between anorthositic gabbro and gabbroic anorthosite (about 25% to 30% Al_2O_3); thus the soils themselves are not especially appropriate parent material for the Apollo 16 HASP. Clusters of appropriate composition (~26% Al_2O_3), however, are represented by the Apollo 16 dimict breccias and perhaps one group of impact-melt splashes (See et al., 1986). The Apollo 16 HASP may have related origins, perhaps as silica-volatilized impact droplets formed from melts equivalent to the veined breccias formed beneath large impact craters.

Figure 2 shows that none of the HASP-like glasses or devitrified glasses in Apollo 14 regolith breccias follow the Apollo 16 HASP trend. The Apollo 14 HASP trend is common to a number of Apollo 14 regolith breccias. There is no significant difference between the composition of Apollo 14 regolith and the projected parent composition for the Apollo 14 HASP trend. If the Apollo 14 HASP formed in a manner similar to the Apollo 16 HASP, it is possible that at Apollo 14 the impact regime equivalent to that of Apollo 16 dimict breccia formation occurred entirely within a thick regolith sequence of uniform Fra Mauro regolith composition.

The high-Al HASP trend is unique. It occurs only in the sample 14076,5. The projected parent composition for this HASP trend is anorthositic, with ~34% Al_2O_3. The implications of this trend are far-reaching, because the regoliths collected from Apollo and Luna sampling sites do not include such pure anorthositic material. However, maps generated from Apollo orbital geochemical data reveal extensive terrains of anorthositic regolith on the lunar limbs and farside (Davis and Spudis, 1987). Although the closest of these terrains to Apollo 14 is near the crater Grimaldi, similar ancient anorthositic terrains may be buried at closer proximity. The thin section 14076,5 - and the related bulk sample 14076,1 (Jerde et al., in press) - may be a product of impact into such terrains.

In addition to its unique composition, the high-Al HASP trend in 14076,5 is unique because (1) it occurs in devitrified rather than glassy fragments, (2) the fragments are angular rather than spheres, and (3) the devitrification product is the new mineral yoshiokite (Vaniman and Bish, in prep.). This new mineral is discussed below, in the more detailed description of 14076,5. All other HASP compositions are glassy spheres; this is so for the Apollo 16 HASP (Naney et al., 1976) and for the Apollo 14 HASP (note the circles around all Apollo 14 HASP analyses in Fig. 2, indicating that the samples are either spheres or sphere fragments). The angular shapes and devitrification of the yoshiokite-bearing high-Al HASP samples may reflect their very Ca,Al-rich composition (Table 2) or a different method of formation. Many of the answers to questions about these puzzling high-Al HASP fragments probably will not be answered until samples are obtained from the anorthositic lunar highland terrains.

Effects of size. The largest glass constituents in the regolith breccias resemble the local Apollo 14 Fra Mauro regolith or the LKFM composition. Four glasses were found with areas greater than 0.9 mm^2; the largest of these was a 8 mm^2 splash coat draping sample 14160,147 (this is the only glass analyzed in this sample, and is thus the only data point shown for 14076,147 in Table 1). The other three are splash coats (14160,149 and 14232,5) and an agglutinate (14160,145).

In the size range of 0.2 to 0.4 mm^2, a greater variety of compositions and glass types is observed. Splash coats, ropy glass, matrix-soaking glasses, and angular fragments of composition similar to Apollo 14 soil or LKFM are common. In addition, angular devitrified fragments of anorthositic gabbro glass in this size range occur in 14250,8, 14251,5, and 14315,26. The exotic regolith breccia 14076,5, which includes the high-Al HASP fragments, also has a large (0.32 mm^2) fragment of devitrified plagioclase-like (anorthositic) glass.

The largest glassy sphere found (in 14004,78) is 0.2 mm^2, consisting of brown glass of Apollo 14 soil composition and containing vesicles and inclusions. The largest inclusion-free and non-vesicular glass sphere found was also of Apollo 14 soil composition (0.06 mm^2 yellow glass in 14004,77). Over 90% of the glass spheres found and analyzed were in the size range 0.001-0.01 mm^2.

Ropy glasses. Ropy glasses in the regolith breccia samples have a wide range of compositions, from an anorthositic (33% Al_2O_3) ropy glass in

14076,11 to the high-K rhyolitic ropy glass in 14281,20 (second column of Table 2). Regolith breccias 14160,150 and 14282,5 also contain ropy glasses with anorthositic gabbro composition (~26% Al_2O_3). However, most of the ropy glasses analyzed have compositions similar to the Apollo 14 soil.

The Apollo 14 soil composition is also represented by fragments of angular glass, glass beads, agglutinates, splash coats, and matrix glasses. Ropy glasses of the Apollo 14 soil type differ slightly from these other soil-like glasses by having a higher average SiO_2 content (51 ± 3% SiO_2 versus 48 ± 2% SiO_2). Although the 1σ ranges in these silica contents overlap, the largest Fra Mauro ropy glass (0.35 mm^2; 14281,20) has the high-silica average composition (50.8% SiO_2), and the ropy glass compositional range is stretched toward compositions of higher silica and lower alumina (13% versus 16% Al_2O_3). A higher proportion of rhyolitic components appears to be present in the ropy glasses.

Glasses in Distinctive Regolith Breccias

The glass constituents in soil 14259 (Table 1) reflect the predominant input of anorthositic gabbro, LKFM, and recycled soil compositions in Apollo 14 soils. The average composition of Apollo 14 soil is well represented, but the glass type next in abundance is not LKFM but anorthositic gabbro. Approximately similar distributions of glass types are seen in the regolith breccias, but there are notably more HASP, plagioclase-like (anorthositic), and gabbroic anorthosite glasses in the regolith breccias than in soil 14259 - even when the data from the anomalous regolith breccia 14076,5 are disregarded. This greater abundance of aluminous glasses in the regolith breccias than in the soil suggests sampling of more aluminous terrain at the time of regolith breccia formation. It is also significant that the sole HASP fragment found by Brown et al. (1971) in the soil is similar to Apollo 16 HASP; they found no Apollo 14 HASP, which represents all but one of the HASP spheres (exclusive of the HASP in 14076,5) listed in Table 1. It is apparent that the impacts which formed HASP glasses from the Apollo 14 soil were active before or during the episode of regolith breccia formation, and were not an important part of bulk regolith maturation.

Several regolith breccias stand out because of particular glass types (e.g., the devitrified high-Al HASP in 14076,5). Exotic components often reflect constituents that account for chemically deviate regolith breccias, and may help to clarify the origins of regolith breccias that have unique compositions.

14004,77: This breccia, rather than being exotic, has a notable lack of glasses that do not mimic the local soil. Although its glass abundance is small, the absence of glasses other than those formed in the immediate vicinity may indicate derivation from a regolith of almost pure Fra Mauro composition with very little exotic material worked in.

14076,5: This is by far the most unique of the Apollo 14 regolith breccias studied. The regolith breccia from which this sample comes is not homogeneous; Jerde et al. (in press) describe the portion from which thin section 14076,5 comes as anomalously aluminous (30% Al_2O_3) and clearly exotic to the Apollo 14 sampling area. The other part (represented by thin section 14076,11) has the typical Fra Mauro regolith breccia composition.

The exotic portion (14076,5) contains a minor high-Ca rhyolite constituent as devitrified glass spheres, and a significant amount of the devitrified high-Al HASP glass described above. This type of HASP is unique to this sample. This HASP composition occurs not only as devitrified glasses, but has also been found in single crystals up to 250 μm long in 14076,5. X-ray diffraction analysis of mineral separates from the equivalent sample powder (14076,1) has confirmed that these devitrified glasses and the single crystals are a new mineral; this mineral has been named yoshiokite (Vaniman and Bish, in prep.), after the researcher who synthesized and studied similar materials. Yoshiokite is a hexagonal nepheline-like mineral, ($Ca_{8-(x/2)}[]_{(x/2)}Al_{16-x}Si_xO_{32}$), that forms metastably in glasses equivalent to Si-depleted anorthite that have devitrified at about 950-1200°C. Vaniman and Bish (in prep.) suggest that yoshiokite forms in impact glasses from relatively "pure" anorthositic terrains. The occurrence of yoshiokite in this sample is in accord with the chemical data of Jerde et al. (in press); both the aluminous composition and the unique occurrence of this new mineral indicate that anorthositic terrains are more important in the lunar highlands than the Apollo and Luna regoliths suggest.

The extremely low I_s/FeO of 14076,5 (0.03; Jerde et al., in press) and the absence of agglutinates in this sample might be construed to cast some doubt on whether it is indeed a regolith breccia. However, 5 of the 20 devitrified glass fragments larger than 0.001 mm^2 in this sample are spheres or sphere fragments (Vaniman et al., 1988). Smaller spheres can be found throughout the matrix. This sample's non-friable nature and relatively low porosity (~15%) suggest that it is an exceptionally well-sintered regolith breccia; the lack of agglutinates also suggests that the parent regolith was immature. The very low I_s/FeO may be due to both extreme sintering and immaturity.

14315,26: This sample is the "chondrule"-bearing regolith breccia studied recently by Jerde et al. (1987) and earlier by other researchers (e.g., Simonds et al., 1977). The "chondrules" in 14315,26 have an anorthositic gabbro composition that accounts for its anomalously Al-rich composition contrasted with other Apollo 14 regolith breccias. Although less abundant than the "chondrules", the glasses in this sample also have a predominantly anorthositic gabbro composition. It is noteworthy that next to the Fra Mauro glasses, the most abundant glass constituent in Apollo 14 regolith is anorthositic gabbro (soil 14259, Table 1). The regolith breccias 14004,77 and 14315,26 may provide examples of relatively "unmixed" Fra Mauro and anorthositic gabbro soil types, respectively, preserved as regolith breccias at the Apollo 14 site.

CONCLUSIONS

Among Apollo 14 regolith breccias, compositions that deviate from that of the Apollo 14 soil are rare (Fruland, 1983). Simonds et al. (1977) analyzed 14 regolith breccias and, with the exception of 14315, found that all clustered around the composition of Apollo 14 soil. Jerde et al. (1987) re-analyzed 14315 and studied 18 additional small (4-10 mm) regolith breccias; they found only one other anomalous sample, 14004,55 (our thin section 14004,77), which stands apart from the Apollo 14 regolith only in terms of its higher (~1.4X) incompatible element contents. In the completion of this study, Jerde et al. (in press) analyzed another 9 of these small regolith breccias and added one portion of 14076 (14076,1; our thin section 14076,5) to the final list of three deviate regolith breccias out of 41.

Our study of glass compositions, including devitrified glasses, reveals compositions that match the bulk chemical anomalies in these three odd regolith breccias. Sample 14315 stands apart because the glasses and devitrified glasses it contains are largely of anorthositic gabbro composition; it has a notable paucity of glasses that match the local soil (Table 1). Sample 14004,77 on the other hand is unique in that it contains only glasses (ropy glasses, spheres, angular glass fragments, and matrix glasses) that match the local soil; its lack of other more aluminous glasses is reflected in the higher incompatible element composition found by Jerde et al. (1987). Sample 14076,5 is by far the most unique. This sample is not only aluminous in bulk composition (Jerde et al., in press), it is the only sample with no glasses that match either the local soil or LKFM compositions (Table 2). Moreover, all of the glasses in this subsample of 14076 are devitrified and are dominated by anorthositic gabbro, anorthosite, and high-Al HASP compositions - including the new aluminous mineral yoshiokite. This part of 14076 is clearly exotic. If it formed from impacts near the Apollo 14 site, then the target area is presently hidden. Our only sighting of appropriate highland terrains for this sample is in the far distant anorthositic surfaces mapped by Davis and Spudis (1987).

The high-Al HASP in 14076,5 and the Fra Mauro HASP found in many of the other regolith breccias broaden our understanding of silica volatilization processes. At both Apollo 14 and Apollo 16, the silica volatilisation trends stem from compositions that match either the local soil or the dimict breccias that may arise from impacts through the local regolith. In the exotic regolith breccia 14076,5, the HASP trend indicates a comparable origin but in a regolith of essentially pure anorthosite. Regolith of this type was not sampled by the Apollo or Luna explorations; the devitrified glasses in regolith breccia 14076,5 are our only samples. The suggestion of Delano et al. (1981) - that surveys of glass compositions in grab-samples are a powerful tool to explore the chemistry of crustal lithologies - is amply borne out in 14076,5.

ACKNOWLEDGEMENTS

This study was supported in part by the Institute of Geophysics and Planetary Physics of the University of California, grant #86-129. The work was done under the auspices of the U. S. Department of Energy. We owe much to other members of our informal consortium (P. Warren, E. Jerde, and R. Morris). Review comments by A. W. Laughlin are greatly appreciated.

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TABLE 1
Glass Compositions in Apollo 14 Regolith Breccias

thin section	NAA/EP split	"HASP" -like	Plag. Glass	Gabb. Anorth.	Anorth. Gabb.	LKFM	A-14 soil	Rhyol.	mixed mare	pristine mare
14004,77	(,55)*						8			
14004,78	(,56)*				1	1	3			2[a]
14004,79	(,57)*						4		1	
14004,80	(,58)*				1		5			
14004,81	(,59)*			2	1	3	8			1
14004,82	(,60)*			1	1	3	10			1[a]
14076,5[b]	(,1)**	5[c]	6	5	1			3		
14076,11	(,6)**		1	2	1	2	4			
14160,144	(,113)*	1	2	2	1	3	4	1	2	3
14160,145	(,114)*		1		3	8			1	
14160,147	(,116)*					1				
14160,148	(,117)*	2			1	1			2	
14160,149	(,118)*	1	1		4	1	4			
14160,150	(,119)*			4	1	7			1	
14194,5	(,1)**		1	2	2	2	10			
14250,8	(,5)**	1			1	1	12		5	2
14251,5	(,2)**			3	9	3	3		3	1
14252,5	(,2)**	1			7	3	18		1	1
14263,23	(,8)*	1		1	1		4			1
14263,24	(,9)*			1	1		2			1
14263,25	(,10)*	1			5		4			1
14263,26	(,11)*		1			1	2	1		
14281,20	(,17)**				1	5	1	1		
14282,5	(,2)**				5	1	11		2	2
14309,10	(,8)**		1	1			18			2
14315,26	(,24)*			3	7		1			
14316,16	(,13)**	1		2	4	5		4		
Σ		14	14	29	59	51	136	10	18	18
soil 14259[d]		1	1	8	100	48	155	6	23	15

*NAA/EP (neutron activation/electron microprobe) analysis reported in Jerde et al. (1987); **NAA/EP analysis reported in Jerde et al. (in press)
[a]the pristine mare glasses in 14004,78 and ,82 have exceptionally high TiO_2 contents (16-17% TiO_2); they are similar to the Ti-rich mare glasses from Apollo 14 described by Delano (1988); [b]all of the glasses in 14076,5 are devitrified; [c]HASP glasses in 14076,5 are Al-rich and have devitrified to form the new mineral yoshiokite; [d]classification of glass analyses listed in Brown et al., 1971

TABLE 2

Distinctive Glass Sphere, Ropy Glass, and Devitrified Glass Compositions in Apollo 14 Regolith Breccias

	High-K Rhyolites		Pristine Low-Ti Mare		Fra Mauro HASP		HASP* in	
	14160,144	14281,20	14160,144	14160,145	14263,23	14160,148	14076,5	
	sphere	ropy glass	sphere	sphere	sphere	sphere	devitrified	
SiO_2	75.7	72.6	46.8	46.3	38.9	35.6	27.3	19.3
TiO_2	0.86	0.27	1.92	0.52	2.51	2.61	0.04	0.11
Al_2O_3	12.6	14.5	8.01	9.75	21.5	23.7	45.8	52.4
FeO	0.41	0.30	20.3	17.9	11.0	10.4	0.02	0.02
MgO	0.07	0.00	13.8	15.6	12.5	12.3	0.20	0.21
CaO	0.61	0.79	8.50	8.99	13.5	14.5	27.2	27.6
Na_2O	1.00	1.62	0.10	0.24	0.00	0.00	0.18	0.00
K_2O	7.77	7.20	0.04	0.07	0.01	0.00	0.00	0.00
BaO	0.00	2.86	n.a.**	n.a.	n.a.	n.a.	n.a.	n.a.
Σ	99.1	100.1	99.5	99.4	99.9	99.1	100.7	99.6
Ca/Ti	5.41	3.49	5.28	20.6	6.42	6.65	810	299
Ti/Al	0.077	0.021	0.271	0.060	0.132	0.125	0.001	0.002
Mg/Al	0.006	0.000	1.97	1.82	0.659	1.076	0.005	0.005

*The devitrified HASP in 14076,5 contains the new lunar mineral yoshiokite (Vaniman and Bish, in prep.).

**n.a. = not analysed

Figure Captions

Fig.1: (a) Plot of Ti/Al versus Ca/Ti for all glasses and devitrified glasses analysed in this study. A semilog plot is used to accommodate the high Ca/Ti ratios (> 1000) found in plagioclase-like glasses. Two rhyolite glasses with >7% K_2O (columns 1 and 2 in Table 2) plot below the general mixing hyperbola. Expanded inset plots show that (1) the portion of the entire curve ranging from 50<(Ca/Ti)<3000 is not compressed into the x-axis and (2) the portion of the curve from 4<(Ca/Ti)<20 contains a high Ti/Al trend defined by low-Ti "pristine" mare glasses that are not part of the typical mixing hyperbola.

(b) Plot of Mg/Al versus Ca/Ti for all glasses and devitrified glasses. Absence of a common element between plotted ratios generates greater scatter than in Fig. 1a, but similar limits on mixing are observed. The high-K rhyolite and low-Ti "pristine" mare glasses still plot off of the range of main mixing hyperbolas.

Fig. 2: Plot of Al_2O_3 versus SiO_2; "x" symbols are used to distinguish the "pristine" mare glasses from all other glasses and devitrified glasses, and "*" symbols mark the odd range of high-Al and rhyolitic glasses in regolith breccia 14076,5. Circles are drawn around those glasses that occur as spheres or as fragments of spheres. All compositions with more than 16% Al_2O_3 and less than 40% SiO_2 are classified as "HASP-like" in this paper. The Apollo 14 HASP trend and the 14076,5 high-Al HASP trend are marked; the Apollo 16 anorthositic gabbro HASP trend is from Naney et al. (1976). Only one small (<0.001 mm^2) angular fragment of glass, in 14160,149, falls close to the Apollo 16 HASP trend.

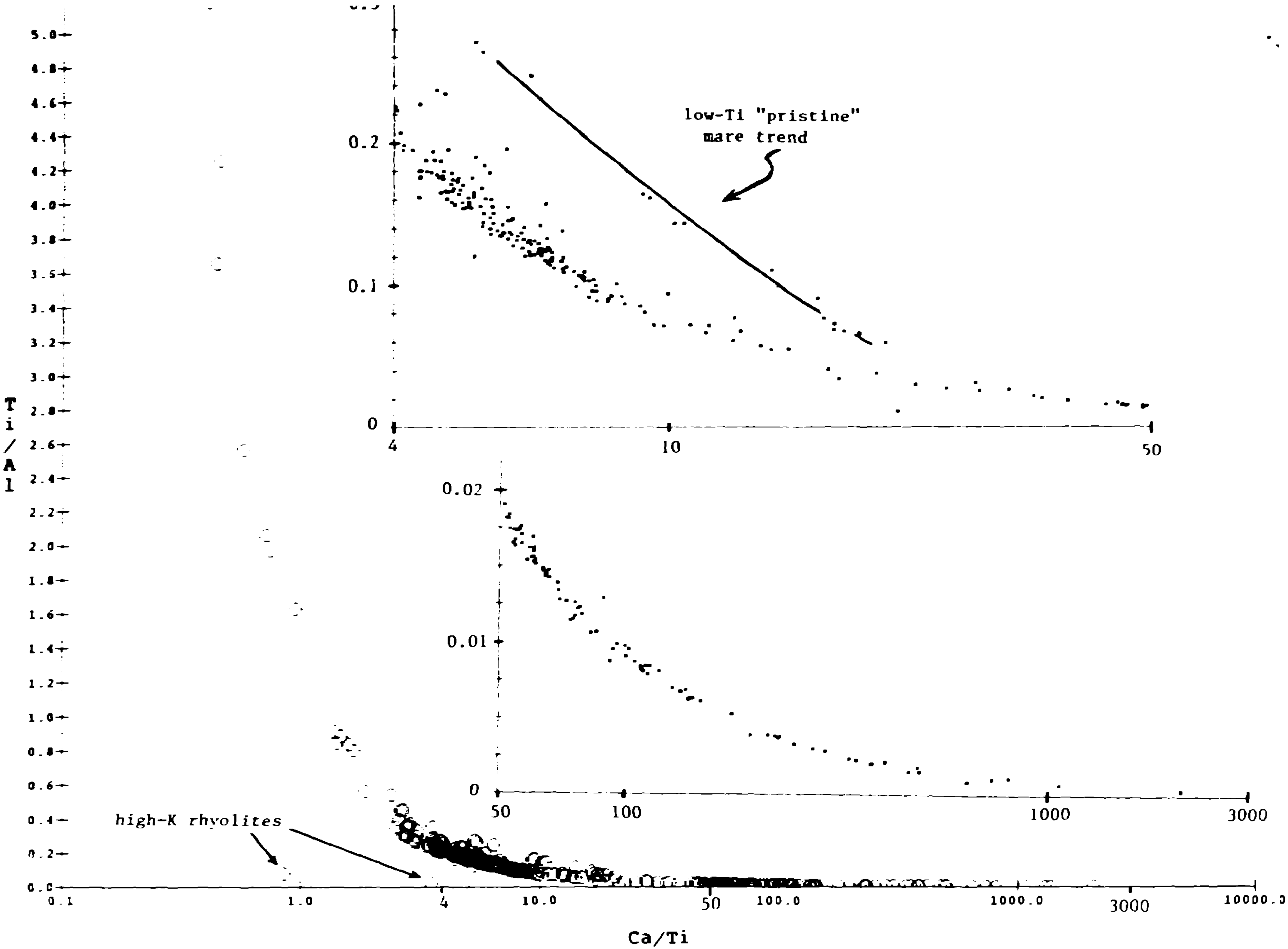
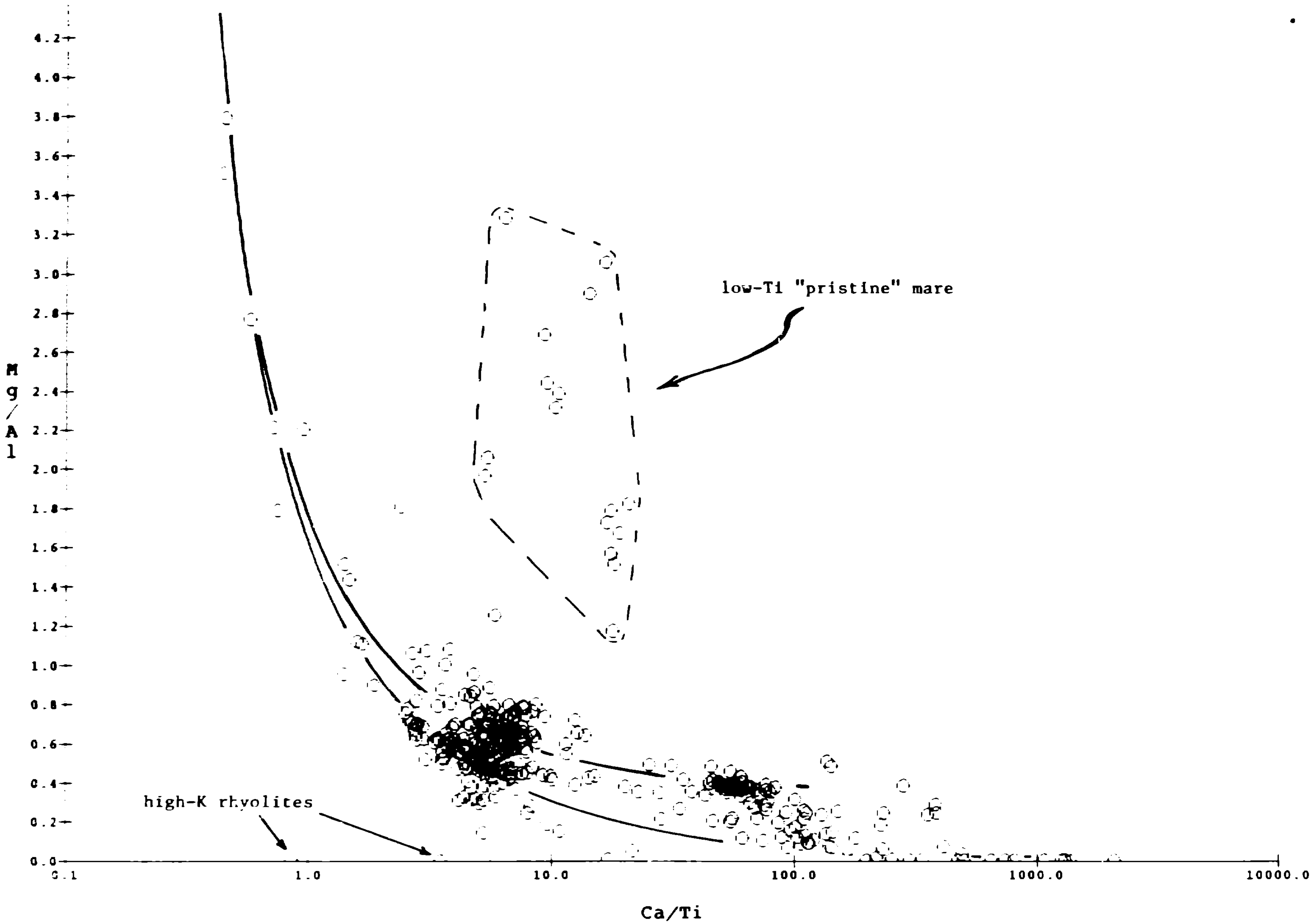

low-Ti "pristine"
mare trend
high-K rhyolites
Ti/Al
Ca/Ti
0.2
0.1
0
4
10
50
0.02
0.01
0
50
100
1000
3000
5.0
4.8
4.6
4.4
4.2
4.0
3.8
3.6
3.4
3.2
3.0
2.8
2.6
2.4
2.2
2.0
1.8
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
0.1
1.0
4
10.0
50
100.0
1000.0
3000
10000.0

Figure 1a



low-Ti "pristine" mare
high-K rhyolites
Mg/Al
Ca/Ti
4.2
4.0
3.8
3.6
3.4
3.2
3.0
2.8
2.6
2.4
2.2
2.0
1.8
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
0.1
1.0
10.0
100.0
1000.0
10000.0

Figure 1b

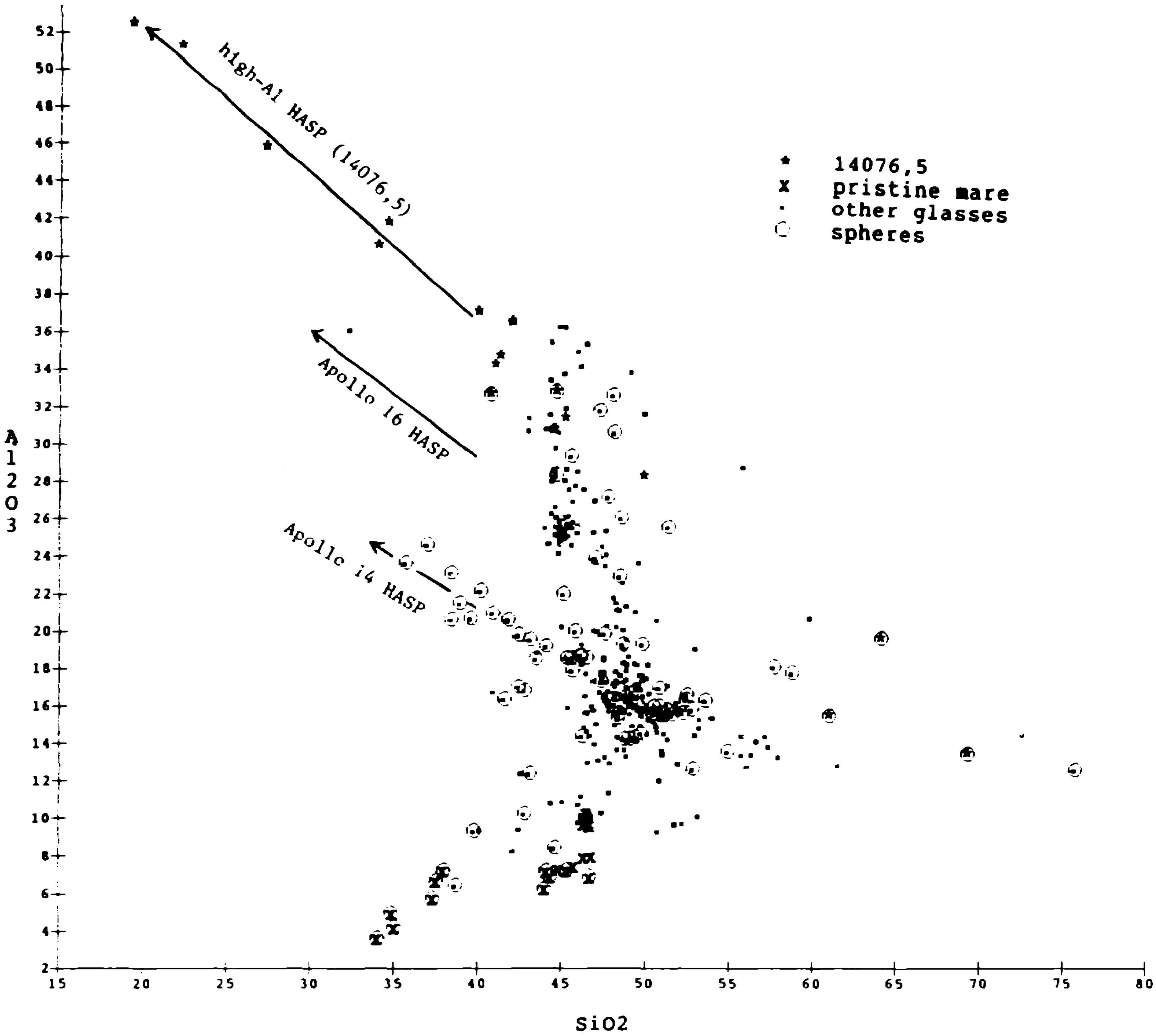

high-Al HASP (14076,5)
Apollo 16 HASP
Apollo 14 HASP
14076,5
pristine mare
other glasses
spheres
Al2O3
SiO2
52
50
48
46
44
42
40
38
36
34
32
30
28
26
24
22
20
18
16
14
12
10
8
6
4
2
15
20
25
30
35
40
45
50
55
60
65
70
75
80

Figure 2