Impact glasses from the Apollo 14 landing site and implications for regional geology

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[1] Lunar impact glasses possess the unmodified refractory element ratios of the original fused target materials at the sites of impacts. These target materials are regolith developed on different terrains and local rock types. Almost 800 glasses from the Apollo 14 landing site have been analyzed by electron microprobe in this study. These glasses show significant variation and hint at the existence of multiple terrains of differing compositions near the landing site. To test this idea, we have used Clementine color image data to construct iron and titanium maps from which a petrologic map in an elemental system analogous to the sample database was made. This map shows the regional provenance of Apollo 14 samples and suggests that the highlands in the Fra Mauro region of the Moon consist of a potassium, rare Earth element, and phosphorus (KREEP)-rich, basaltic debris layer that overlies a more feldspathic terrain in some areas. This mapping effort demonstrates the efficacy of using Clementine image data to place lunar sample information into a regional, and ultimately global, context. Lunar impact glasses and orbital data can provide geochemical constraints on the local and regional geology of the Moon. *INDEX TERMS:* 0933 Exploration Geophysics: Remote sensing; 0994 Exploration Geophysics: Instruments and techniques; 5410 Planetology: Solid Surface Planets: Composition; 6250 Planetology: Solar System Objects: Moon (1221); *KEYWORDS:* impact glasses, Clementine, KREEP, Apollo 14, petrologic maps, highland basalt

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1. Introduction

[2] Impacts serve two purposes: they create geological products that can be analyzed for clues to the regional geology of planetary surfaces and they provide a window through which to view the bombardment history of the Earth and other planets. As the only body with both a well-preserved cratering record and samples of known provenance, the Moon has naturally become the touchstone of the terrestrial planets. The impact history of the Moon has been discussed in the context of the Earth, as the basis for evaluating the threat from sterilizing impacts to the origin and sustainability of life on Earth [e.g., *Maher and Stevenson*, 1988; *Sleep et al.*, 1989]. Important questions to be answered include the form of the large impact distribution with respect to time (e.g., smooth decline versus cataclysmic spike), whether there is periodicity in Earth–Moon cratering history, and the applicability of the lunar record to the Earth and other planets. Thus, it is important to test, develop, and refine our models for lunar impact history. Impact glasses also carry abundant information about the composition and structure of the Moon, if we can decipher their message. One way to do this is to study the samples returned by the Apollo missions, using modern microprobe techniques to investigate the composition and chronology of individual impact glasses.

[3] Lunar impact glasses are droplets of melt produced by energetic cratering events that quenched during ballistic flight and possess the refractory element ratios of the original fused target materials at the site of impact [*Delano*, 1991]. Glasses made by shock melting fuse and mix

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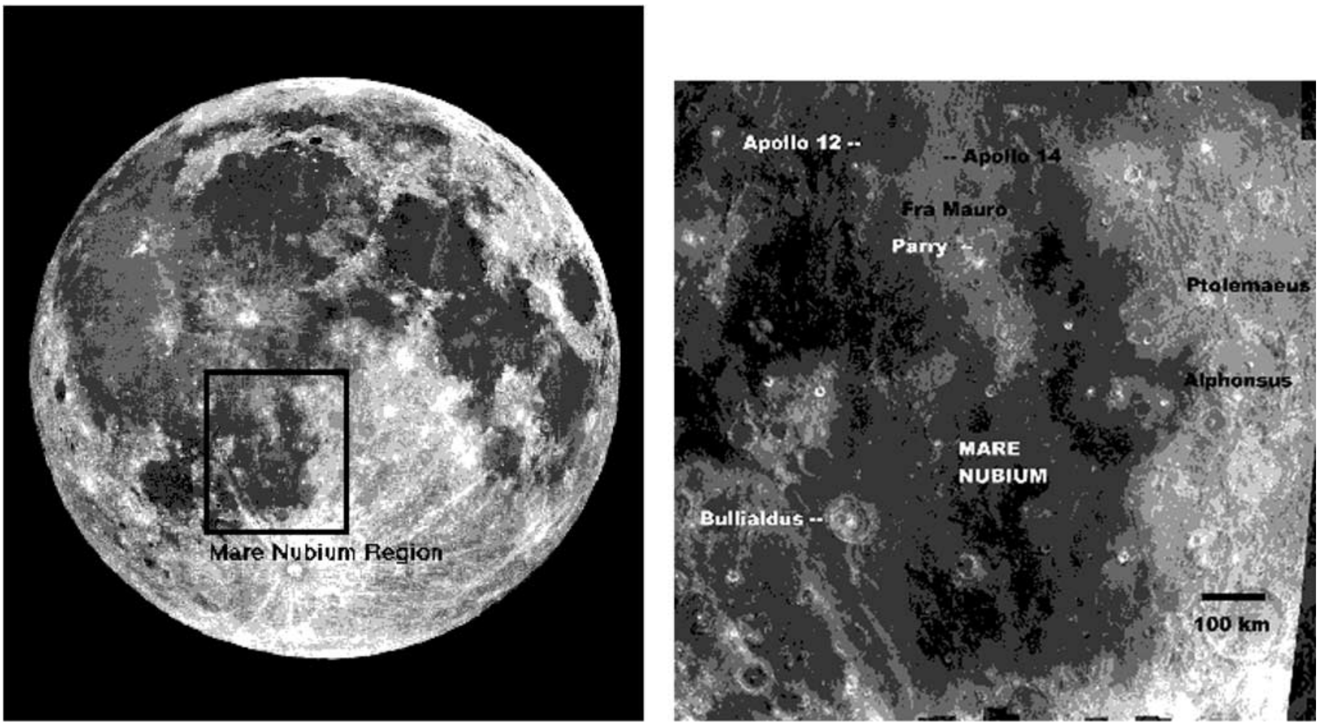


Figure 1. Index maps of area studied and discussed in text. The Apollo 14 landing site is in the north-central portion of Mare Nubium, just north of the pre-Imbrian crater Fra Mauro. Petrologic map of Figure 8 corresponds to the area shown at right.

existing lithologies and offer the potential of providing information for units and terrains distant from the sites they come from. *Reid et al.* [1972] used cluster analysis techniques on glasses from the Apollo 11, 12, and 14 and Luna 16 soils to define the compositional groups of those glasses. These groups were interpreted as representative of the composition of rock types at those collection sites. Well-known groups include "Highland Basalt," "Low-K Fra Mauro basalt," and "High-K Fra Mauro basalt." *Reid et al.* [1972] suggested that preferred compositions of glasses (determined by cluster analysis) could provide a guide to the composition of the rock types on the Moon. However, they noted that few glasses corresponded in composition to the large samples of rocks returned from the landing site and suggested that either the large rock samples were not representative of the regional population or that the glasses represented mixtures of various lithic components in the regolith [*Reid et al.*, 1972]. One of our goals is to evaluate competing models of impact glass generation and determine whether they represent unsampled rock types [*Horz*, 2000], ancient regoliths [*Reid et al.*, 1972], or combinations of both.

[4] Determining the provenance of samples from the Apollo sites is an important, ongoing task in lunar science. The global data provided by the Clementine [*Nozette et al.*, 1994] and Lunar Prospector (LP) [*Binder*, 1998] missions have greatly aided our attempts to place sample data into regional and global contexts. In particular, Clementine ultraviolet-visible camera images have been used to derive maps of the concentrations of Fe and Ti [*Lucey et al.*, 1995] at the full resolution of the camera (~200 m/pixel) [*Blewett et al.*, 1997]. These two elements are of great significance for lunar studies as the Fe content of both regions and samples tends to track the relative amounts of mare and highlands while the Ti content tracks the different types of mare basalt [e.g., *Heiken et al.*, 1991]. Both of these elements are easily measured in lunar impact glasses so we investigated the feasibility of combining data for impact glasses with orbital data from the Clementine mission to evaluate the regional setting of the Apollo landing sites.

[5] *The Apollo 14 Landing Site*: Apollo 14 was sent to sample the Fra Mauro Formation (Figure 1), interpreted to be the ejecta blanket of the Imbrium basin on the nearside of the Moon, a key event in lunar geological history [*Wilhelms*, 1987]. The Fra Mauro Formation itself is an extensive blanket-like deposit lying in a broad annulus around the Imbrium Basin. This ejecta blanket is now buried by younger rubble and by lunar soil that has been churned up by more recent meteoroid impacts and moonquakes. Much of the Apollo 14 landing site is densely covered with craters several tens of kilometers in diameter. Small craters, in large numbers down to sizes of a few meters, are also present. Ridges of the Fra Mauro Formation are roughly radial to the Imbrium Basin and were probably formed by material flowing along the ground during excavation of the basin. Cone Crater, which sits atop one of the ridges, penetrates below the lunar regolith into a bedrock substrate anticipated to be Imbrium Basin ejecta more or less in the original form [*Swann et al.*, 1977].

[6] Lunar orbital data from the Clementine and LP missions have provided a regional compositional setting in which to study Apollo 14 site geology. Gamma-ray spectrometer observations [*Lawrence et al.*, 2000] show a high concentration of potassium, rare Earth element, and phosphorus (KREEP) around and at the Apollo 14 landing site and both Clementine and LP iron data show that these highlands are more mafic than typical aluminous highland sites [*Blewett et al.*, 1997; *Elphic et al.*, 2000]. Together, these data show

that the Apollo 14 landing site is composed of KREEP-rich, basaltic material. However, we also find glasses at this site that are very low in KREEP, having a highland basalt composition. One of our goals in this study is to reconcile both sample and orbital observations in order to understand the provenance of glasses collected at the site and to decipher the regional composition and structure of the Moon.

[7] It is possible, then, to decipher the complex history and evolution of the lunar regolith by analyzing the impact and volcanic glasses found in the lunar soil samples. Just as *Delano* [1988] used volcanic glasses to obtain relative ages of five Apollo 14 breccias, impact glasses might also be able to provide constraints on the arrival of components to the surface. Additionally, the mixing of these surface components over time will be reflected in the compositions of the impact glasses.

2. Sample Analysis and Results

[8] Lunar impact glasses record the composition, in refractory element ratios, of the material from which they were formed. For this study, 151 glasses from Apollo 14 regolith 14259 have been analyzed by electron microprobe for all major elements, including Ti, Fe, and Al. We have compared these data with previous analyses of 627 glasses in regolith breccias from the Apollo 14 site (i.e., 14313, 14307, 14301, 14049, and 14047) [*Delano*, 1988], which represent ancient regoliths from the Apollo 14 region and, because they appear to have formed at different times [*Delano*, 1988], may be able to provide temporal constraints on the addition of compositional groups to the regolith. These sample data provide information on the composition of the local regolith and possibly, terrains distant from the site.

2.1. Analysis

[9] Fifteen grams of lunar regolith from the Apollo 14, 16, and 17 landing sites were provided by the Johnson Space Center curatorial facility. Nearly 180 glasses of impact and volcanic origin from lunar regolith 14259 (<1 mm) and 627 glasses from regolith breccias [*Delano*, 1988] were compositionally analyzed by electron microprobe in this study, and all data are available electronically. In addition to our compositional data, a subset of these impact glasses will be dated by $^{40}Ar/^{39}Ar$ isotope analysis in order to determine the chronology of impacts in the Earth–Moon system (N. E. B. Zellner et al., Impact events at the Apollo 14, 16, and 17 landing sites, in preparation). Glass data from the Apollo 14 landing site are discussed in this paper, and glass data from the Apollo 16 and 17 landing sites will be discussed in subsequent papers.

[10] Apollo 14 sample 14259,624 was part of the comprehensive sample collected during EVA 1. Of the glasses that were "large" ($\geq$90 μm in diameter), 180 (0.33 g) were handpicked from the sample, polished, photographed, and probed. All of the regolith breccias were originally larger than 50 g [*NASA*, 1971]. Subsequent to collection by the astronauts, thin sections were made and glasses in each were identified by microprobe analysis [*Delano*, 1988].

[11] Major element analyses of the lunar glasses were performed with on-line data reductions (dQuant and dQuant 32) using a JEOL 733 electron microprobe located in the Department of Earth and Environmental Sciences at Rensselaer. Five X-ray spectrometers on the electron microprobe were tuned and calibrated for each element that was being analyzed in the glass sample. An electron beam of 15 keV and 50 nA was focused onto the sample by a series of collimators and lenses, and when the sample was exposed to them, X-rays were released. Comparison of X-ray counts from instrument standards and lunar working standards (LWSs) were used in order to calibrate and account for instrumental effects.

[12] Glasses were analyzed for sodium (Na), calcium (Ca), aluminum (Al), potassium (K), iron (Fe), magnesium (Mg), titanium (Ti), chromium (Cr), manganese (Mn), and silicon (Si). A cup current of 50 nA was used during all analyses, and the beam diameter varied from 1 to 30 μm depending on the sample. Count times of 200 s were used for Na and K, while count times of 40 s were used for the other elements. Mobility of Na and K is a well-documented phenomenon in terrestrial glasses during electron microprobe analyses [e.g., *Nielsen and Sigurdsson*, 1981; *Jercinovic and Keil*, 1988], especially in hydrous siliceous compositions (e.g., rhyolites) [*Hanson et al.*, 1996]. However, alkali mobility in lunar glasses, which are anhydrous and mafic in composition, has not been observed to occur (within analytical uncertainties) at counting times of 300 s per element, and specimen currents of 75 nA at 15 keV [*Delano*, 1996]. Consequently, the Na,K-abundances reported in this manuscript are considered accurate within the stated uncertainties. Backgrounds were collected for 20 s on each side of the peak for every element on every analysis. Minimum detection limits (MDLs) under these conditions are SiO_2 (75 ppm), TiO_2 (175 ppm), Al_2O_3 (66 ppm), Cr_2O_3 (237 ppm), FeO (224 ppm), MnO (243 ppm), MgO (96 ppm), CaO (154 ppm), Na_2O (37 ppm), and K_2O (37 ppm). LWSs consisted of glasses, volcanic and impact, which were repeatedly analyzed during each probe session in order to assess the analytical precision of the instrument. Further precision analyses were carried out on standard glasses, both basaltic glasses with known compositions.

[13] A total of 1,194 glasses from polished thin sections of Apollo 14 regolith breccias (14047, 14049, 14301, 14307, and 14313) were analyzed by Delano in the 1980s during his initial search for picritic volcanic glasses. A photographic mosaic of each polished thin section was constructed, and the locations of all glasses were noted. The search strategy involved doing four-oxide *reconnaissance* analyses (SiO_2, TiO_2, Al_2O_3, and FeO) simultaneous with a visual inspection of an energy-dispersive spectrum of the sample to identify those glasses having picritic compositions. Most of the picritic glasses (259) were later analyzed for their abundances of 10 major element oxides, and the results were reported [*Delano*, 1986, 1988]. Except for nine nonpicritic glasses, complete analyses were not performed on the other nonpicritic glasses. In the current study, 627 glasses with $Al_2O_3 \geq 12$ wt.% (i.e., nonmare compositions) have been plotted on a ternary diagram to provide compositional information about the compositional range and variety of glasses at the Apollo 14 site. However, since the accuracy and precision of these 627 four-oxide analyses are not comparable to the recent analyses of glasses from 14259 described previously, we have compared the results of four-oxide analyses and complete 10-oxide analyses on the 268 Apollo 14 glasses that were analyzed by both methods. This comparison has been done by plotting the

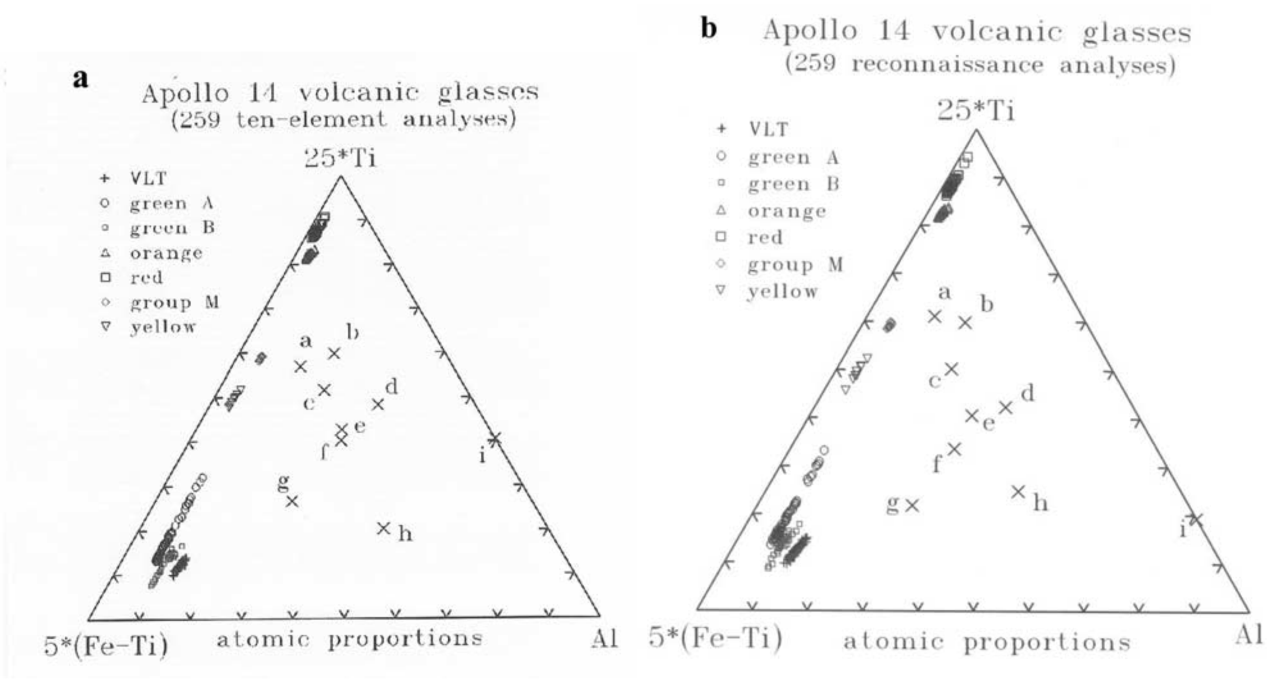


Figure 2. Ternary diagrams showing the analyses for 268 picritic volcanic glasses analyzed by *Delano* [1986, 1988]. (a) The 10-element analysis for each glass. (b) The four-element analysis for each glass. Visual comparison of both figures shows that the four-element analyses compare favorably with the 10-element analyses and therefore provide a useful description of the Apollo 14 glass compositions on these ternary diagrams. Glasses a–i are nonmare glasses that also show strong similarities in their relative locations on the two ternary diagrams. One sample (i), which shows the largest difference, is a heterogeneous granitic glass having a low TiO_2 abundance (0.5 wt.%).

kinds of analyses in separate ternary diagrams (Figures 2a and 2b) for the same 268 glasses. Analyses of the 259 picritic glasses plot near the left side of both ternary diagrams and define trends in both figures that are largely indistinguishable. In addition, the nine nonmare glasses (glasses "a–i" in Figures 2a and 2b) also show strong similarities in their relative locations on the two ternary diagrams. One sample (i), which shows the largest difference, is a heterogeneous granitic glass having a low TiO_2 abundance (0.5 wt.%). Visual comparison of Figures 2a and 2b shows that the four-element analyses compare favorably with the complete 10-element analyses and therefore provide a useful description of the Apollo 14 glass compositions on this ternary diagram.

2.2. Properties of Lunar Impact Glasses

[14] The compositions of glasses collected at a specific site reflect the geologic, as well as stratigraphic, character of that site, while glasses with compositions not representative of the collection site may be exotic to the surface of that site. Although the location of impact ejection may not be known, the combination of widespread, random sampling makes impact glasses a potentially useful tool for the geochemical exploration of the Moon's crustal composition [*Delano*, 1991]. Analysis of compositionally unusual glasses collected at a landing site may provide information about the geological character of sites not visited by the astronauts.

[15] Geologically simple areas (i.e., those with one compositional unit only) should have impact glasses that reflect that compositional monotony. In contrast, areas with multiple compositionally distinct units will have impact glasses whose compositions reflect that geochemical complexity. For example, the western nearside of the Moon contains many KREEP-rich areas (areas rich in potassium (K), rare Earth elements (REE), and phosphorous (P)), and so those glasses should be rich in these elements as well. The far side of the Moon, however, contains few KREEP-rich areas [*Elphic et al.*, 2000], and glasses in highland meteorites (which may be derived from the far side) [*Warren and Kallemeyn*, 1991] are indeed low in KREEP [*Delano*, 1991]. By compositionally analyzing lunar impact glasses and by comparing their compositions with lunar orbital data of their collection sites, the geology and compositional structure of the Moon can be determined on a global scale.

[16] Figure 3 shows the compositions of the highland regoliths from the Apollo 14, 16, and 17 landing sites, as well as the Luna 20 site and lunar meteorites. The coordinates of Figure 3 (and of all of the other ternary diagram figures in this study) represent the atomic proportions of the nonvolatile elements analyzed in the lunar impact glasses: aluminum (Al), associated with plagioclase feldspar (e.g., $CaAl_2Si_2O_8$) in lunar rocks and regoliths, iron (Fe), a measure of the mafic content of soils, and titanium (Ti), associated with ilmenite (e.g., $FeTiO_3$) in lunar rocks and regoliths. We express iron as the parameter (Fe-Ti), which defines the atomic proportion of iron (Fe) in the glass that was not present in ilmenite ($FeTiO_3$). These three atomic parameters can be used to describe the chemical and mineralogical nature of the original target materials

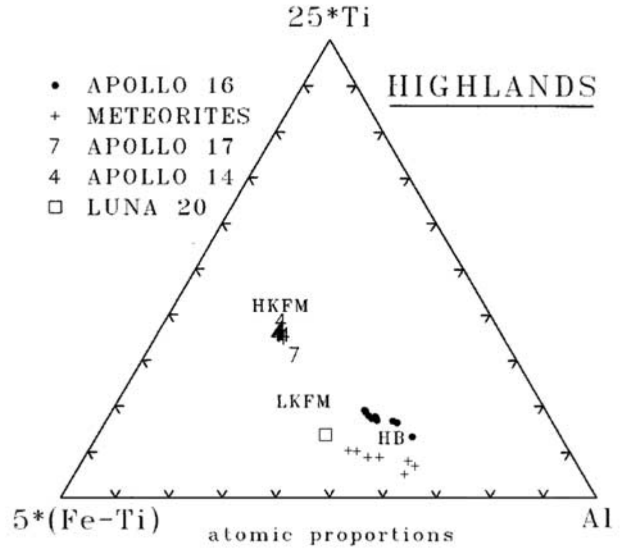


Figure 3. Ternary diagram showing the compositions of regolith from the Apollo 14 (“4”), Apollo 16 (filled circles), and Apollo 17 (“7”) sites. The lunar meteorite compositions are also denoted (“+”) as well as the Luna 20 soil composition (square). These data are taken from the works of *Koeberl et al.* [1989], *Korotev* [1981], *Lindstrom et al.* [1991], *Palme et al.* [1991], and *Warren and Kallemeyn* [1987, 1991]. Three groups of highland glasses that are spread out over the Moon are also plotted: HB (Highland Basalt), LKFM (Low-K Fra Mauro Basalt), and HKFM (High-K Fra Mauro Basalt). These data are taken from the works of *Reid et al.* [1972, 1973] and *Ridley et al.* [1973].

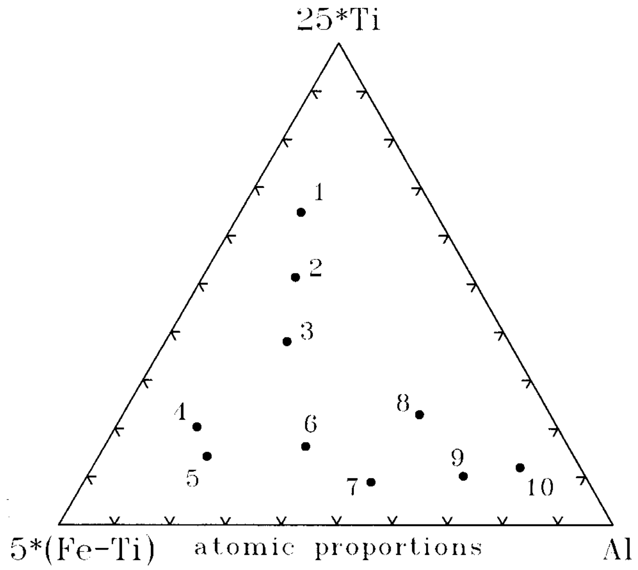


Figure 4. Ternary diagram showing the unique locations of the 10 glasses listed in Table 1. Glasses 1 (E3) and 2 (Z2) contain a lot of KREEP. Glass 3 (X2) is representative of the HKFM composition, while glass 6 (S5) is representative of the LKFM composition. Glasses 4 (V3) and 5 (C3) possess mare compositions. Glass 7 (T4) has a highland basalt composition, while glasses 8 (N3), 9 (I2), and 10 (J5) have high-Al compositions. Uncertainties in the data are not much greater than the points themselves.

[*Delano*, 1991], as illustrated by Table 1, which lists the chemical properties of 10 glasses, and by Figure 4, which places these glasses in unique locations on the ternary diagram.

[17] It is evident from Figure 3 that there is a chemical distinction between the lunar meteorites, which may have originated on the far side of the Moon [*Pieters et al.*, 1983; *Ostertag et al.*, 1985], and the regolith from the Apollo and Luna landing sites on the lunar nearside. The lunar meteorite compositions tend to be more feldspathic and less rich in mafic components and KREEP [*Warren and Kallemeyn*, 1991]. Further, there is a distinction among the regolith compositions of the Apollo landing sites; the compositions of the Apollo 14 and 17 regoliths are both less feldspathic and more KREEP rich than the composition of the Apollo 16 regolith.

[18] These compositional differences correspond with similar differences observed in the global, remote sensing data. Maps of iron, titanium, and thorium from Clementine [*Blewett et al.*, 1997] and LP [*Lawrence et al.*, 2000] show that the nearside highlands contains mafic and KREEP-rich zones in the west and more feldspathic terrains toward the east, while far side compositions tend to be very feldspathic and KREEP poor, except on the floor of SPA basin. To a first order, these orbital observations support the notion that the lunar meteorites come from the far side of the Moon. Understanding lunar orbital data of the Apollo and Luna sites can provide ground truth for building a hypothesis for interpreting compositions of impact glasses sampled there. Compositional boundaries on the Moon exist both on and below the lunar surface and analysis and interpretation of

Table 1. Representative Compositions of 10 Impact Glasses from Apollo 14 Soil Sample 14259,624

	E3	Z2	X2	V3	C3	S5	T4	N3	I2	J5
SiO_2	46.29	49.73	46.52	49.38	40.60	45.11	44.65	42.57	44.49	42.96
TiO_2	4.79	2.83	0.21	1.06	0.81	0.66	0.27	0.84	0.26	0.30
Al_2O_3	12.9	14.79	16.71	12.19	17.81	23.55	25.25	31.31	28.01	30.57
Cr_2O_3	0.25	0.19	0.21	0.30	0.44	0.16	0.11	0.06	0.11	0.09
FeO	12.38	10.49	10.26	16.21	17.76	9.29	5.66	4.66	2.80	1.48
MnO	0.17	0.14	0.14	0.23	0.27	0.13	0.08	0.07	0.04	0.03
MgO	12.38	8.01	9.73	8.67	13.67	5.84	9.02	5.27	6.33	6.89
CaO	7.77	9.49	10.97	11.49	8.22	14.93	14.94	14.84	17.45	17.64
Na_2O	0.60	0.98	0.66	0.34	0.19	0.30	0.17	0.32	0.30	0.06
K_2O	0.54	0.99	0.45	0.15	0.16	0.04	0.02	0.06	0.10	0.01

Their locations on the ternary diagram can be seen in Figure 4.

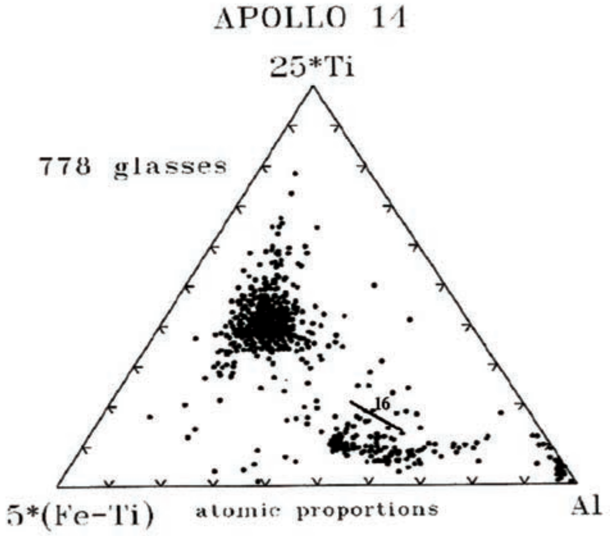


Figure 5. Ternary diagram showing the compositional distribution of 778 Apollo 14 impact glasses from regolith (this study) and regolith breccias [*Delano*, 1988]. The low-KREEP highland basalt glasses are tightly clustered and located near the middle of the Al/(Fe-Ti) join of the diagram. The line marked "16" shows the compositions of the highland basalt glasses found at the Apollo 16 site. It should be obvious that the highland basalt glasses found at Apollo 14 differ in composition from those found at Apollo 16. Uncertainties in the data are not much greater than the points themselves.

glass compositions may be able to help us interpret the history and evolution of lunar regolith over time.

2.3. Results

[19] Results of our analyses are shown in Figure 5. This plot shows that impact glasses from the Apollo 14 site comprise three principal compositional groups. By far the most populous group is a diffuse cluster of glasses that plot in the middle of the ternary, around the average soil composition (cf. Table 1 and Figure 4, glass 3 (X2); Figures 3 and 5). This cluster, which has compositional tails that trend toward all thee axes, apparently represents the average composition of the Apollo 14 site, as shown by its similarity with the Apollo 14 soil composition (Figure 3). Compared to most of the lunar highlands, this composition is relatively mafic and elevated in KREEP; such a composition was called "high-K Fra Mauro basalt" (HKFM) by *Reid et al.* [1972] and typifies much of the Imbrium ejecta blanket around the western nearside of the Moon [*Wilhelms*, 1987]. This HKFM composition also corresponds to that of the average Apollo 14 crystalline breccias, thought to represent the Imbrium basin component at the site [*Swann et al.*, 1977].

[20] The second most populous cluster of glass compositions is both less KREEP rich and more aluminous than the most populous HKFM group (Table 1 and Figure 4, glass 7 (T4); Table 2 and Figure 5). These glasses have the composition of "highland basalt" and appear to be distinct from the local, Fra Mauro Formation bedrock. The highland basalt glasses appear to closely resemble feldspathic material from the Apollo 16 site and compositional trends in this group show mixing toward even more feldspathic components, probably due to glass formation in plagioclase grains, as evidenced by a cluster of glasses that occur at the Al apex of the ternary (Figure 5), which clearly represent melts of almost pure plagioclase. Such glasses must have formed during regolith formation on feldspathic rocks.

[21] The highland basalt glasses found in the Apollo 14 soil also have counterparts in the Apollo 14 regolith breccias (Figure 6), previously analyzed by *Delano* [1988]. The distribution of compositional glass groups in these regolith breccias mimic the pattern seen in the current regolith (cf. Figures 5 and 6), although different proportions of glass groups are evident. These differences probably reflect both temporal and spatial variations in the compositions of the site. The very tight cluster of highland basalt glasses (arrow; Figure 6f) is particularly prominent in breccia 14047 (Figure 6e), deemed the youngest regolith breccia on the basis of the volcanic glasses found in this sample [*Delano*, 1988]. This may be telling us that the highland basalt composition is a relatively recent addition to the site.

[22] The glass data from Apollo 14 soil 14259,624 show that the bulk composition of the deposit at the site is dominated by high-K Fra Mauro "basalt." The wide scatter of glasses around this composition indicates both mixing with other lithologies and the impact of micrometeorites on individual mineral grains within larger rocks. In addition to that dominant group of glasses, we find smaller groups of more feldspathic glasses, in particular a tight cluster of "highland basalt" glasses, similar to glasses and soils found at the Apollo 16 site and in lunar meteorites (Figure 5 and Table 2). These glasses represent some significant geological unit, perhaps under or near the landing site. To better assess the provenance of such material, we need to examine the regional data provided by remote sensing in a context that allows direct comparison to the data obtained from sample analysis.

2.4. Petrologic Mapping of the Apollo 14 Landing Site and Surrounding Environs

[23] The Apollo 14 site was the first highland site to be explored and occurs within the Mare Nubium region on the nearside of the Moon (Figure 1) [*Wilhelms*, 1987]. This area has been covered in the global data obtained by Clementine and LP, which mapped the region in the visible, infrared,

Table 2. Average Composition (wt.%) of the 27 Highland Basalt Impact Glasses from 14259,624 Compared to Glasses (8,8, 8,13, 8,26, and 82,8) Found in Lunar Meteorites ALHA81005 and MAC88105

	14259,624	ALHA,8,8	ALHA,8,13	ALHA,8,26	MAC,82,8
SiO_2	44.98	44.7	44.9	44.8	44.1
TiO_2	0.30	0.3	0.32	0.29	0.32
Al_2O_3	24.91	25.5	25.5	25.2	25.2
Cr_2O_3	0.14	0.15	0.14	0.18	0.22
FeO	5.97	5.81	5.63	5.77	7.59
MnO	0.08	0.10	0.11	0.08	0.19
MgO	8.42	8.91	8.58	8.67	6.29
CaO	14.81	14.4	14.7	14.6	15.6
Na_2O	0.15	0.16	0.10	0.31	0.38
K_2O	0.02	<0.03	<0.03	0.04	0.07

Na and K are subject to volatilization and should not be used when comparing the glass compositions. Glass compositions in the meteorites are from the work of *Delano* [1991].

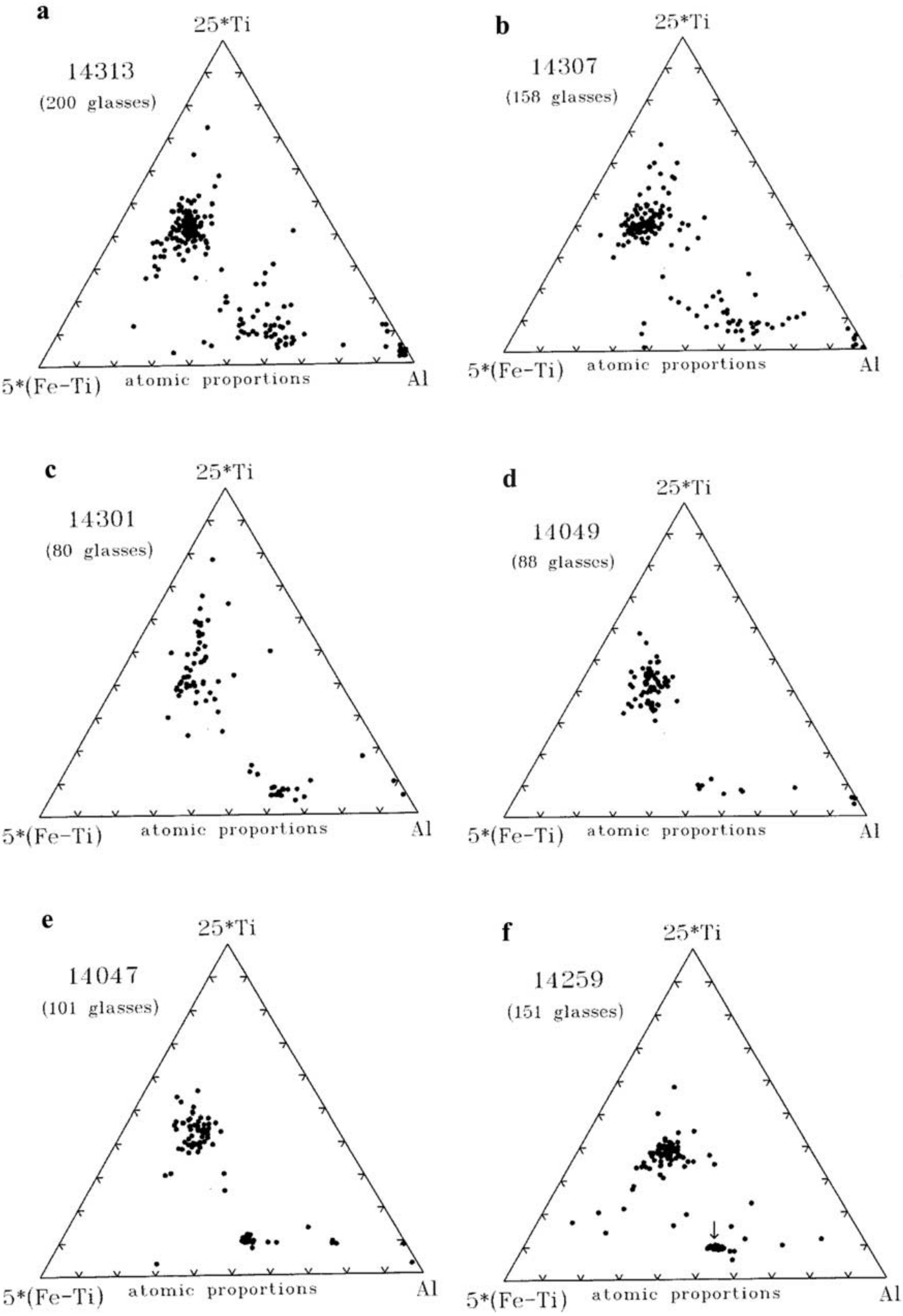


Figure 6. Apollo 14 breccias 14313, 14307, 14301, 14049, and 14047 in order from oldest (a) to youngest (e) (as inferred by their components of volcanic glass), with the impact glasses for each breccia denoted by filled circles (data from the work of *Delano* [1988]). (f) The compositional distribution of the Apollo 14 14259,624 impact glasses (this study). The incorporation of the highland basalt glasses into the youngest breccia, 14047, shows that these glasses appeared recently. These glasses are identified in (f) by the arrow. Uncertainties in the data are not much greater than the points themselves.

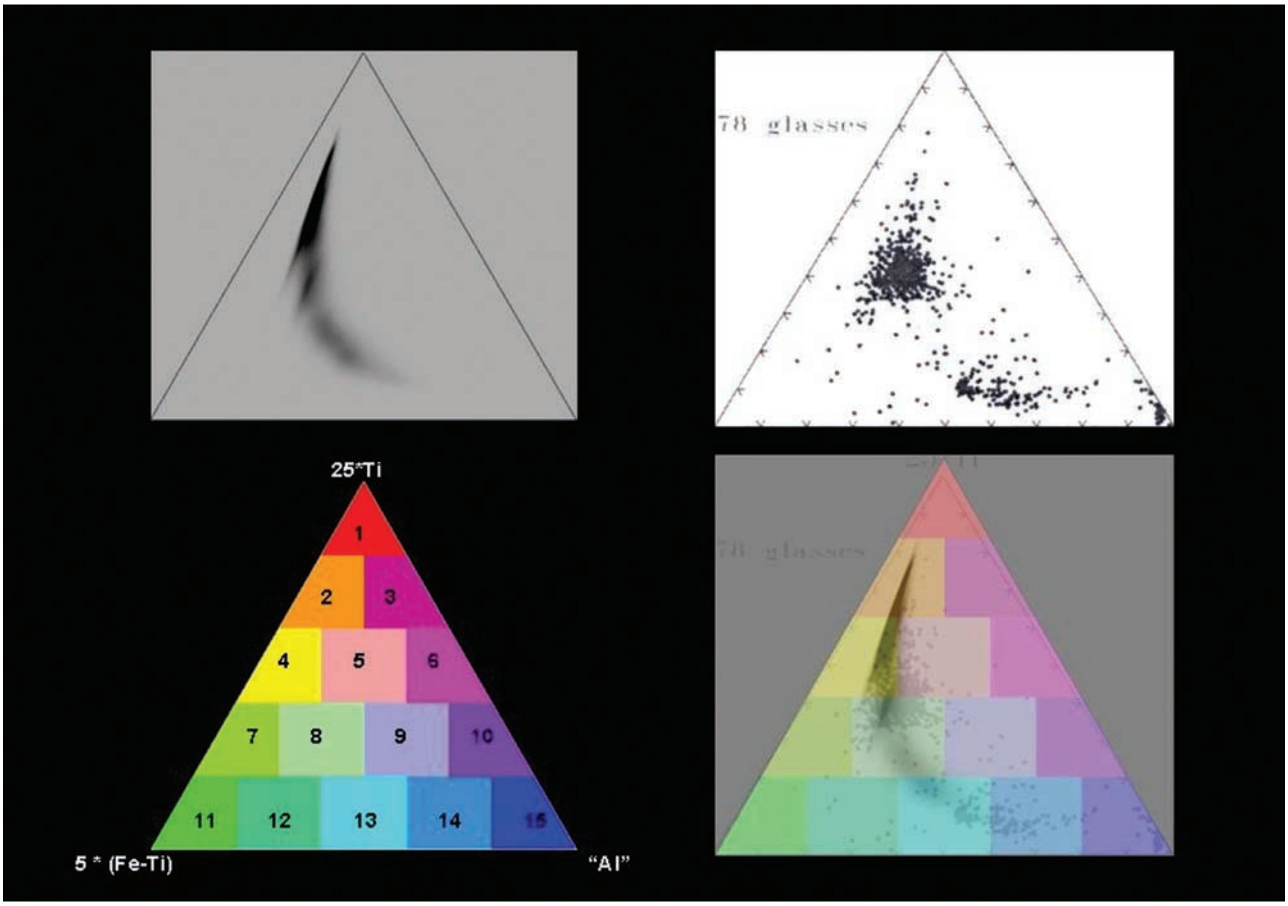


Figure 7. Ternary diagrams showing how the regional petrologic units correspond to chemical compositions. Ternary at top right shows the Apollo 14 glass data of Figure 5. The ternary at top left is a scattergram of calculated Fe, Ti, and “pseudo-Al” (see text) values for each pixel in the Nubium image mosaic. Note that the trend of these pixel values mimic and extend the measured glass compositions from the site. The ternary at bottom right superposes the glass data (circles) and the pixel data (fine points) on a ternary space, arbitrarily divided into 15 compositional “units” (ternary at bottom left). The assigned colors are represented on the petrologic unit map of Figure 8. Red represents regions high in Ti, blue represents regions high in Al, and green represents area high in mare (Fe-Ti) compositions.

and gamma-ray portions of the spectrum. These data can be expressed in terms of chemical composition; specifically, using the information provided by the Apollo and Lunar samples, the Clementine color data can be analyzed in terms of iron and titanium content [*Lucey et al.*, 1995, 2000; *Blewett et al.*, 1997]. Quantitative maps of Fe and Ti content are possible at the full resolution of the Clementine sensors, about 200 m/pixel [*Blewett et al.*, 1997; *Lucey et al.*, 2000].

[24] Although detailed mapping of the Moon by X-ray has not yet been done globally and hence, there is no global coverage of aluminum concentrations, lunar soils display a remarkable congruence of composition in terms of iron and aluminum content. Specifically, iron and aluminum are (nearly perfectly) inversely correlated [*Janghorbani et al.*, 1973; *Miller et al.*, 1974; *Spudis et al.*, 1988], such that for a given Fe content, a soil’s aluminum content may be inferred to an accuracy of 1–2 wt.%, a value similar to the inherent precision of the Fe and Ti mapping technique itself [*Blewett et al.*, 1997]. Given this method of estimation, we can then analyze the Clementine data in a manner identical to that used to analyze the composition of impact glasses from the site, i.e., by plotting values on the Ti-(Fe-Ti)-Al ternary diagram (Figure 5).

[25] For this analysis, we have made Clementine image mosaics that cover the Mare Nubium region from the equator to 30°S latitude and from 0° to 30°W longitude. We have used the equations of *Lucey et al.* [2000] to derive maps of the Fe and Ti concentration of this region. Each elemental map consists of pixels that have unique calculated Fe and Ti values. From the Clementine iron image, we used a simple linear relationship between Fe and Al observed in lunar soils [*Spudis et al.*, 1988] to compute an estimate of the amount of Al in each pixel. Thus, each pixel in the Clementine image mosaic has an associated Fe, Ti, and “Al” value. These values were recalculated to atomic proportions, rescaled according to the same procedures done for the impact glasses (Figure 5), and plotted in ternary space (Figure 7). This new ternary plot is analogous to the plot done for the impact glasses, but instead shows the distribution of pixel compositions on the Clementine image maps. After each pixel’s value in Ti-(Fe-Ti)-“Al” space is computed, it is assigned an (arbitrary) color and shown in

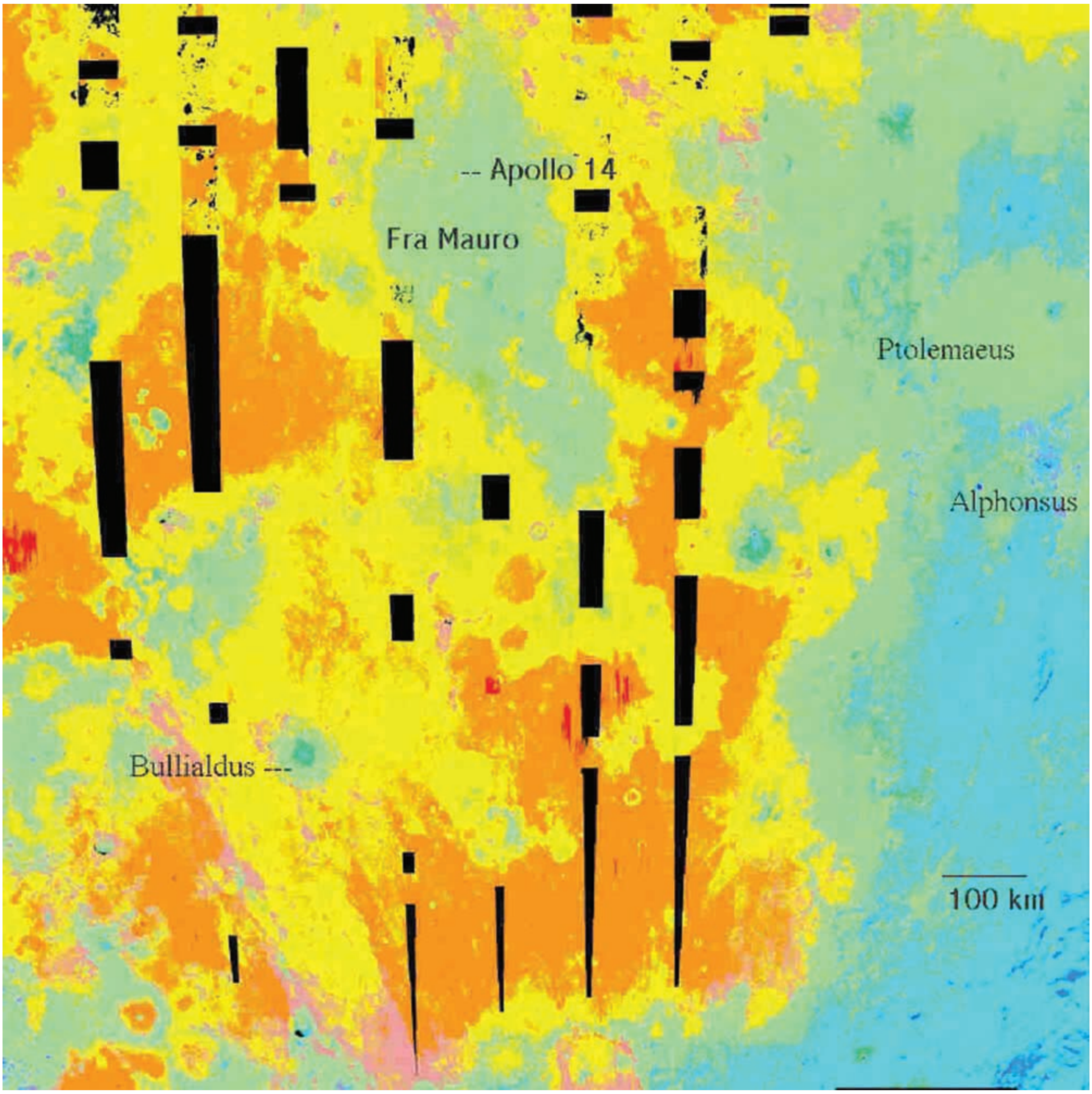
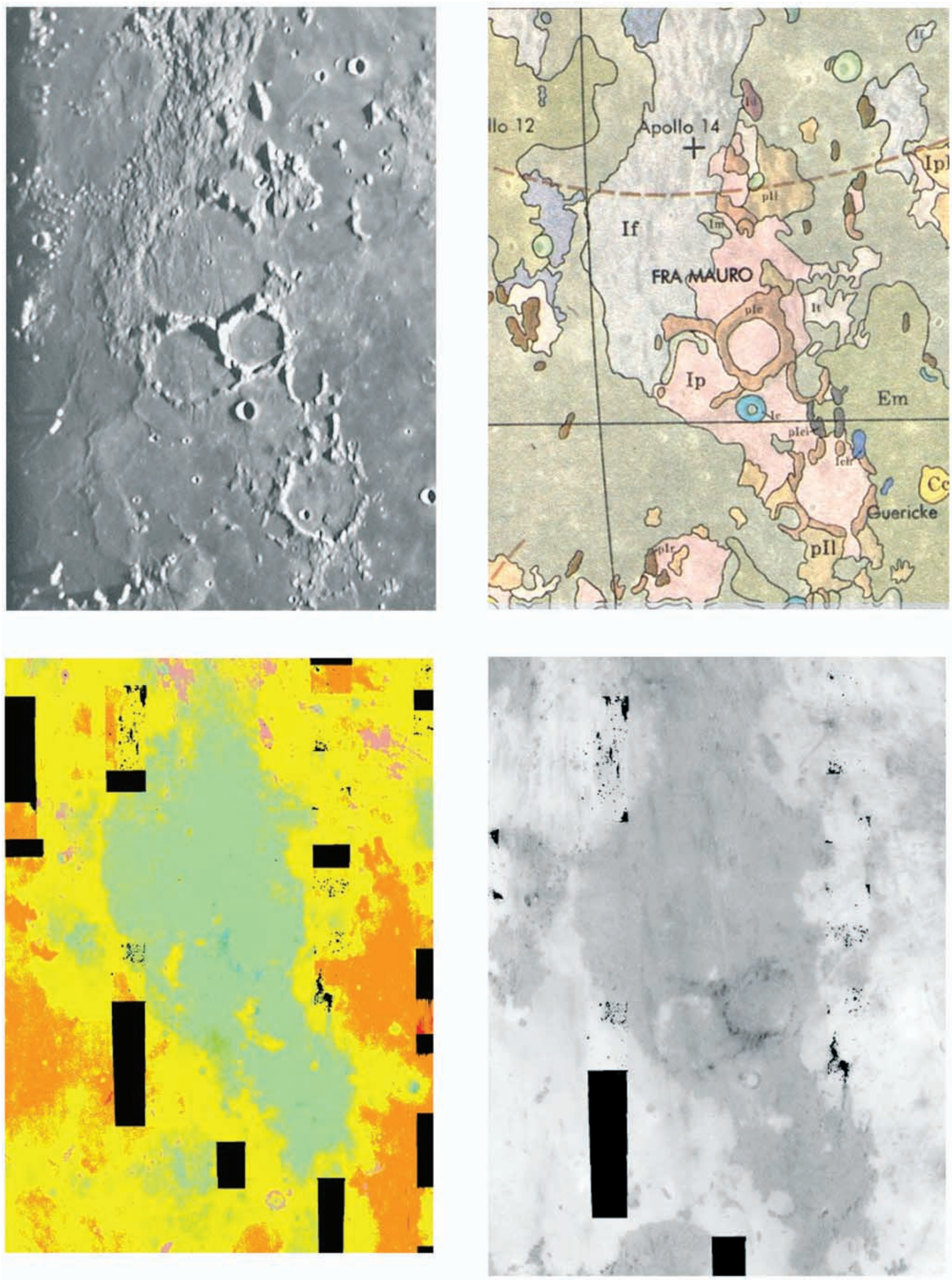


Figure 8. Petrologic map of the Mare Nubium region and the Apollo 14 landing site (near the top center of the map; compare with same area shown in Figure 1). Each color corresponds to a unit in the ternary diagram (Figure 7). The Apollo 14 site occurs in unit 8 (Figure 7), which agrees with soil and glass data from the site (Figures 3 and 5). The black strips represent an absence of Clementine data. Resolution is about 200 m/pixel.

image format. For this mapping effort, we chose to allow the primary colors red, green, and blue to represent the principal components Ti, (Fe-Ti), and pseudo-Al, respectively. Pure end-members have these colors, while mixtures have colors intermediate between these primary values, and all are based on equal areas of the ternary diagram, in a manner analogous to the ternary technique of petrologic mapping in the Fe-Th-Ti system of *Davis and Spudis* [1987] and *Spudis et al.* [2000]. This method allows us to examine the regional distribution of chemically defined, petrologic units (Figure 8).

[26] An examination and comparison of this pixel plot and that of the Apollo 14 impact glasses reveals some interesting properties (Figure 7). First, the compositional fields on both diagrams (top, Figure 7) show significant overlap. Many of the pixels fall along a mixing line between the Ti and the (Fe-Ti) apexes; this is largely because the area includes much of Mare Nubium (Figure 1) and these pixels reflect mixing between high-Ti and low-Ti mare basalts. However, there is admixture of some highland component, shown by the displacement of pixels toward the bottom right (Al) apex (Figure 7). A curved trend line points toward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this same corner; these compositions represent both the adjacent Al-rich, Ptolemaeus highlands on the eastern edge of the study area (Figures 1 and 8) and the occasional island of highlands material that stands out above the mare basalt within Mare Nubium (Figure 1). Both of the major compositional trends evident in the pixel plot are also evident on the impact glass plot (Figure 7).

[27] A close comparison of the plot of orbital pixels and the regional petrologic unit map shows that this map accurately reflects the composition not only of the Apollo 14 site (unit 8; "high-K Fra Mauro basalt"), but also the mare basaltic composition (unit 4) of the nearby Apollo 12 landing site (cf. Figures 1 and 8). These results from both a highlands and mare Apollo landing site give confidence that the petrologic map accurately reflects the regional geology of the Mare Nubium region.

[28] The petrologic map shows several interesting relations. First, the dominance of units 4 and 2 within Mare Nubium corresponds to previous work showing that both low- and high-Ti mare flows occur there [*Rose and Spudis*, 2000]. The regional composition of the Fra Mauro peninsula is that of unit 8 (Figure 8), similar to that of Apollo 14 soils and the biggest cluster of impact glasses (Figures 3 and 5). The widespread distribution of this composition suggests that much of the Fra Mauro Formation is remarkably uniform in bulk composition and is made up of "basaltic" lithologies similar to HKFM. We can also see that more feldspathic highland lithologies (units 13 and 14) are also present, largely in the eastern half of the map area, along the margins of Mare Nubium in the Ptolemaeus highlands.

[29] Such feldspathic components are not limited to that area, as shown by the composition of the rim of the crater Parry, a pre-Imbrian crater south of the Apollo 14 landing site at Fra Mauro (Figure 9). Parry occurs at the very distal end of the Imbrium basin continuous debris blanket, where the basin ejecta thins to a feather edge. Its prominent rim displays outcrops of unit 13, the "highland basalt" composition typical of Apollo 16 and a small group of our analyzed glasses. These feldspathic outcrops occur only on the rim crest of Parry (Figure 9), where Fra Mauro material is either absent or thinned by mass wasting. Its presence on this crater rim demonstrates that feldspathic material here underlies the more mafic Fra Mauro "basaltic" composition (unit 8) that is present elsewhere on the Fra Mauro peninsula. We interpret the relations in Figure 9 as evidence for the pervasive presence of a more "anorthositic" zone at depth, a pre-Imbrian feldspathic basement that is probably a western extension of the aluminous highlands province shown near the crater Ptolemaeus (Figure 8). The outcrop of feldspathic material at the surface here suggests that it may be present at depth at the Apollo 14 site.

[30] Although we cannot be certain, we suggest that the "feldspathic" highland basalt glasses found at the Apollo 14 landing site (Figure 5) are derived from the pre-Imbrian, subejecta blanket basement. Such material could be formed in several ways. During the deposition of basin ejecta by ballistic sedimentation, vigorous mixing of local substrate and primary ejecta result in the creation of a petrologically "mixed" deposit [*Oberbeck*, 1975]. Such a mixed deposit would consist of a coarsely variable megabreccia, in which clasts of feldspathic substrate are intimately mixed with the more mafic, HKFM primary ejecta deposited by the Imbrium basin. In such a scenario, the feldspathic glasses could form by normal, regolith processes within a few hundred meters of its present location. On the other hand, it is also possible that the total thickness of Fra Mauro ejecta is relatively thin at this ballistic range from the Imbrium basin (about 600 km) [*Wilhelms*, 1987]. In this case, it is possible that the feldspathic component was added by a single, large cratering event, such as the impact that created Cone crater [*Swann et al.*, 1977]. In this scenario, Cone penetrated the KREEP-rich Fra Mauro Formation and excavated feldspathic, highland basalt from beneath the Imbrium basin ejecta.

[31] Cone Crater penetrates below the lunar regolith into a bedrock substrate anticipated to be Imbrium Basin ejecta more or less in the original form. In fact, boulders ejected from this crater record a complex history and include breccias that may represent pre-Imbrian cratering in this region [*Swann et al.*, 1977]. Therefore, the compositions of the low-KREEP, highland basalt glasses, which may have been brought to the surface during the impact event that formed Cone Crater $\leq$30 Ma ago [*Schurmann and Hafner*, 1972; *Turner et al.*, 1971], may reflect the composition of pre-Imbrian regolith at the Apollo 14 site. If an impact occurred near Cone Crater, but in an area that is not deeply covered with Imbrium ejecta, the glasses could have been excavated from below this depth by smaller craters and not necessarily by Cone Crater itself. We estimate the maximum depth of excavation of Cone Crater to be between 27 and 34 m (using the equation of *Melosh* [1989]). The Fra Mauro Formation at this location is a few to several tens of meters thick [*Swann et al.*, 1977], so our hypothesis is consistent with both cratering mechanics and regional geology.

[32] Finally, it must be acknowledged that large impacts may throw small amounts of material great distances from the impact site, as evidenced in the map area by the prominent rays of the crater Tycho near the southern border of the map area (Figure 8). Thus, it is possible that the exotic glasses at the Apollo 14 site were thrown there by a distant, singular impact event and do not represent a local unit of any significance. Because of the presence of feld-

Figure 9. (opposite) Fra Mauro and its immediate vicinity. The rugged blanket of material called the Fra Mauro Formation [*Wilhelms*, 1987] covers the rims of the pre-Imbrian craters Fra Mauro, Bonpland, and Parry (top left and right). The composition of the Fra Mauro deposit appears remarkably uniform as almost entirely unit 8 (bottom left; see Figure 7 for position in ternary plot). Note that the rim of Parry (arrows) shows small occurrences of the more feldspathic units 13 and 14, which are also evident by outcrops of low Fe material on the crater rim crest (Clementine Fe map, shown at bottom right), where the Fra Mauro Formation deposits are very thin. These relations suggest that the basaltic, KREEP-rich Fra Mauro Formation may overlie a relatively feldspathic, lower-Fe highland basement. This basement complex may be the ultimate source of feldspathic impact glasses found at the site (Figure 5).

spathic material on the rim of Parry discussed above, we tend not to favor this explanation, but it cannot be ruled out completely for this deposit or indeed, any sample in the Apollo collections.

2.5. Timing of the Addition of Feldspathic Glass

[33] *Delano* [1988] determined a timeline for five Apollo 14 regolith breccias (14313, 14307, 14301, 14049, and 14047) by showing that they contained different populations of pristine, *volcanic* glasses. *Delano* [1988] concluded that the variations in volcanic glasses among the breccias appeared to reflect not only different source regoliths but also different closure ages for the breccias, after which they became closed to the incorporation of new material. Breccia 14301 was found to have formed sometime *during* the epoch of high-Ti, mare volcanism, while breccias 14307, 14313, 14049, and 14047 formed *after* the termination of low-Ti, mare volcanism, making them younger, with 14047 being the youngest [*Delano*, 1988]. In looking at the ternary diagrams (Figures 6a–6e), which plot the impact glasses from the oldest to the youngest breccias as distinct points, it is interesting to note that 14047 (Figure 6e) is the only breccia to show a substantial population of highland basalt glasses, which can be seen distinctly in Figure 6f, a ternary diagram of the impact glasses from regolith sample 14259,624. Since 14047 is the youngest breccia [*Delano*, 1988], this suggests that the highland basalt glasses arrived at the Apollo 14 surface relatively recently.

[34] Comparison of Figures 5, 7, and 8 show that feldspathic, highland basalt glasses are not representative of the local Apollo 14 regolith. We suggest that they may represent pre-Imbrian material, brought to the surface during an impact event, possibly the event that produced Cone Crater. Alternatively, they may have been ballistically transported from a crater made by an impact in a low-KREEP, highland basalt site. Whatever the cause, Figure 6e shows that these glasses arrived recently. These glasses may provide insights into the evolutionary history of the lunar regolith, providing evidence for the composition of the lunar surface before 3.85 Ga, the time before Imbrium ejecta covered any nearside surface existing at that time. Analysis of the other Apollo 14 glasses, those rich in KREEP, provides evidence for the appearance of KREEP, which may be the limiting factor in dating lunar impact glasses and the reason for the lack of evidence of impact events before 3.9 Ga found by *Cohen et al.* [2000] and *Dalrymple and Ryder* [1993, 1996]. The ages of these highland basalt glasses will tell the story (Zellner et al., in preparation).

3. Conclusions

[35] Lunar impact glasses from the Apollo 14 landing site reflect the refractory element ratios of the target materials from which they were formed and possess a wide range of rock and regolith compositions sampled on the Moon. The orbital compositional data resemble the glass data on a regional scale. Impact glasses with compositions different from those of the local surface regoliths are interpreted as being either (1) ballistically transported to the site from a distant impact [*Delano*, 1991] or (2) excavated locally from underlying units at the site [*Rhodes*, 1977]. In either case, the glasses reflect the composition of the target. Since most of the Moon consists of a regolith of varying thickness, impact glasses reflect the composition(s) of the regolith(s), in contrast to earlier reports [*Horz*, 2000; *Reid et al.*, 1972]. All of these glasses provide general geochemical information about lunar surface and subsurface layers and provide geochemical constraints on the full range of lunar regolith compositions [*Delano*, 1991] over time.

[36] The compositions of lunar impact glasses can be used to constrain the history and evolution of the Moon, both geologically and stratigraphically, and can serve as regional probes for estimating the range of compositions present in large areas. Additionally, we suggest that while compositional data alone cannot identify glasses as transported or excavated, they do imply that Imbrium ejecta covered the Apollo 14 area.

[37] Analysis and interpretation of the chemical compositions of almost 800 impact glasses from the Apollo 14 landing site lead to the following conclusions for this study:

1. Impact glasses represent the composition(s) of the local regolith(s) via their refractory element ratios.
2. Compositions of impact glasses, together with an understanding of lunar orbital data of the site of sample collection, can provide geological and evolutionary information about that site.
3. Impact glasses whose compositions are different from the local regolith are exotic to the surface of the site and may be the result of ballistic transport or exhumation from subsurface soils, both a consequence of impact events.
4. Compositions of impact glasses may provide constraints on the arrival of components to a surface.

[38] We further suggest that the technique of petrologic mapping using Clementine Fe and Ti maps derived for this study may be profitably applied to other Apollo and Luna landing sites and may also provide insight into the global geology of the Moon, in particular, by allowing us to interpret the geology of sites unvisited through the powerful lens of the Apollo and Luna sample database.

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