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Characterization of mesostasis regions in lunar basalts: Understanding late-stage melt evolution and its influence on apatite formation

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ABSTRACT

Recent studies geared towards understanding the volatile abundances of the lunar interior have focused on the volatile-bearing accessory mineral apatite. Translating measurements of volatile abundances in lunar apatite into the volatile inventory of the silicate melts from which they crystallized, and ultimately of the mantle source regions of lunar magmas, however, has proved more difficult than initially thought. In this contribution, we report a detailed characterization of mesostasis regions in four Apollo mare basalts (10044, 12064, 15058, 70035) in order to ascertain the compositions of the melts from which apatite crystallized. The texture, modal mineralogy, and reconstructed bulk composition of these mesostasis regions vary greatly within and between samples. There is no clear relationship between bulk-rock basaltic composition and that of bulk-mesostasis regions, indicating that bulk-rock composition may have little influence on mesostasis compositions. The development of individual melt pockets, combined with the occurrence of silicate liquid immiscibility, exerts greater control on the composition and texture of mesostasis regions. In general, the reconstructed late-stage lunar melts have roughly andesitic to dacitic compositions with low alkali contents, displaying much higher SiO2 abundances than the bulk compositions of their host magmatic rocks. Relevant partition coefficients for apatite-melt volatile partitioning under lunar conditions should, therefore, be derived from experiments conducted using intermediate compositions instead of compositions representing mare basalts.
1. Introduction

In order to constrain the volatile inventory of the lunar interior many studies have focused on measuring structurally bound OH in apatite \([\text{Ca}_3(\text{PO}_4)_2(\text{F,Cl,OH})]\) from Apollo and lunar meteorite samples (e.g. Boyce et al. 2010; McCubbin et al. 2010a, 2010b, 2011; Barnes et al. 2013, 2014; Tartèse et al. 2013b, 2014a, 2014b). Yet, translating volatile measurements in apatite to volatile abundances in co-existing melt has proved troublesome, leading many studies to focus on improving understanding on the partitioning behavior of volatiles between apatite and melt (Boyce et al. 2014; McCubbin et al. 2015a). Few studies, however, have focused on constraining the petrographic context in which apatite forms in lunar melts. Apatite begins to crystallize after ~95 % melt solidification in typical mare magmas (McCubbin et al. 2010b), but is likely to start crystallizing earlier (~85 % melt solidification) in KREEP (enriched in incompatible elements such as K, REE and P) basalts (Tartèse et al. 2014a). Apatite, therefore, does not form from bulk basaltic melts but instead forms from differentiated late-stage melts, which are represented by mesostasis regions within lunar samples (Henderson 1970). Although mesostasis regions have been observed within many Apollo basalts and lunar basaltic meteorites, few studies have focused on constraining the silicate melt compositions from which they formed. To provide better understanding on the bulk composition of melts from which lunar apatite crystallized, we have characterized the mineralogy and geochemistry of apatite-bearing mesostasis areas in four Apollo mare basalts (samples 10044, 12064, 15058, and 70035) representative of the high-Ti and low-Ti mare basalts. Knowledge of the melt-compositions from which apatite crystallized will inform experimental studies aiding in the determination of appropriate apatite-melt partition coefficients of volatile elements in geochemical models of lunar magma evolution.

2. Samples

2.1. 10044

Lunar sample 10044 is a high-Ti ilmenite basalt with a low-K content (Beaty and Albee 1978). It is a subophitic basalt (James and Jackson 1970) that is sometimes described as a microgabbro (Anderson et al. 1970). A similarity between 10044, 10047, and 10058 has been noted (Beaty and Albee
1978) with a suggestion that these samples could be fragments of a larger block. Geochronological studies carried out on this sample yielded Rb-Sr dates of ~3.7 Ga (Papanastassiou et al. 1970), ^40\text{Ar}/^39\text{Ar} dates of 3.73 ± 0.04 Ga (Turner 1970; Guggisberg et al. 1979) and a tranquillityite ^207\text{Pb}/^206\text{Pb} date of 3.72 ± 0.01 Ga (Tartèse et al. 2013a). Cosmic-ray exposure (CRE) ages of ~70 Ma were determined using the abundance of cosmogenic ^81\text{Kr} (Hohenberg et al. 1970), ^126\text{Xe} (Srinivasan 1974) and ^38\text{Ar} (Guggisberg et al. 1979). 10044 contains subhedral to anhedral zoned pyroxene phenocrysts (~45% modal abundance) surrounded by a matrix of subophitic plagioclase (~35%), and ilmenite (~13%) (McGee et al. 1977). Mesostasis areas in this sample are composed of silica (~7%), troilite (~0.5%) associated with metallic iron, K-rich glass, and accessory minerals including apatite (~0.1%) and Zr-rich minerals such as baddeleyite and tranquillityite (McGee et al. 1977). We have examined mesostasis areas in thin section 10044,645, which is 6 × 10 mm in size. The mineralogy of this section is consistent with that of the main rock sample described above, containing anhedral pyroxene phenocrysts (~1 × 2 mm), plagioclase laths (~1 × 0.2 mm) and ilmenite (~3 × 0.5 mm). Multiple mesostasis regions are found throughout the 10044,645 section and are further described in section 4.1.

2.2. 12064

Sample 12064 is a coarse-grained low-Ti ilmenite basalt that displays a subophitic texture containing anhedral pyroxene crystals (~56% modal abundance) intergrown with anhedral plagioclase laths (~29%) (Klein et al. 1971). It is characterized by coarse-grained mesostasis areas (~9%) that contain fayalite, Fe-rich pyroxene, troilite, K-feldspar, K-rich glass, Zr-rich phases, merrillite and apatite (Kushiro and Haramura 1971). Plagioclase compositions range from An\textsubscript{93} to An\textsubscript{86} while pyroxene compositions are close to the Fe-rich end-member hedenbergite (Kushiro and Haramura 1971). The sample also contains coarse-grained laths of ilmenite (3.5%) associated with ulvöspinel (2%). Small, sporadic grains of pyroxferroite are observed coexisting with clinopyroxene (Klein et al. 1971). Rb-Sr (Papanastassiou and Wasserburg 1971) and ^40\text{Ar}/^39\text{Ar} (Horn et al. 1975) dating studies for sample 12064 yielded dates of 3.18 ± 0.09 Ga and 3.18 ± 0.01 Ga, respectively, which have been interpreted as crystallization ages. An exposure age of 255 Ma has been reported by Horn et al. (1975), while exposure ages determined from abundances of cosmogenic ^3\text{He}, ^21\text{Ne}, and ^38\text{Ar} cluster around
200 Ma (Hintenberger et al. 1970). We have examined mesostasis areas in thin section 12064,130, which is 8 × 4 mm in size. The mineralogy of the studied sample is consistent with modal abundances reported for the bulk rock, containing anhedral pyroxenes (> 2 × 2 mm), intergrown with anhedral plagioclase (~2 × 1 mm) and with minor ilmenite (~1 × 0.2 mm). Multiple mesostasis regions are found across the 12064,130 section and are further described in section 4.1.

2.3. 15058

Apollo 15 sample 15058 is one of the largest basalts returned from the Moon. It is a coarse-grained low-Ti pigeonite basalt (Ryder 1985). Olivine (~2% modal abundance) in this sample is found only in the cores of large pigeonite grains (~71%). This sample also contains radiating plagioclase (~24%) clusters (Butler 1971). Dates determined for sample 15058 range from 3.36 ± 0.03 Ga (40Ar/39Ar; Husain 1974) to 3.46 ± 0.04 Ga (Rb/Sr; Birck et al. 1975). 15058 is characterized by a multistage exposure history with increased 81Kr near the surface of the sample but constant at depth (Eugster et al. 1984). We have studied mesostasis areas in thin section 15058,20, which is 6 × 8 mm in size. The mineralogy of this section, consistent with that of the main rock sample, comprises anhedral pyroxene phenocrysts (> 2 × 2 mm), plagioclase (~1 × 0.5 mm) and minor ilmenite (< 0.5 × 0.2 mm). Mesostasis regions in 15058,20, which are further described in section 4.1, are observed mostly in a few clusters in the center of this thin section.

2.4. 70035

Apollo 17 sample 70035 is a medium-grained, vesicular, high-Ti basalt (Ridley and Brett 1973). It is a large crystalline basalt with large (>1mm) anhedral clinopyroxene crystals (~46% modal abundance) enclosing armalcolite, ilmenite, and spinel (~22%). Interstitial plagioclase (~26%) is found together with ilmenite and olivine (~2.5%) (Weigand 1973). The mesostasis regions (~2%) include silica, K-feldspar, tranquillityite, ilmenite, ulvospinel, troilite, K-rich glass and apatite (Papike et al. 1974; McGee et al. 1977). Metallic iron is found in the cracks and cleavage of opaque oxides and silicates in this sample (El Goresy and Ramdohr 1975). Plagioclase composition in sample 70035 varies from An88 to An83 (Weigand 1973). The Rb/Sr dates of 3.82 ± 0.06 Ga and 3.73 ± 0.11 Ga determined
for 70035 are consistent with each other (Evensen et al. 1973; Nyquist 1977) and with a $^{40}$Ar/$^{39}$Ar date of $3.75 \pm 0.07$ Ga (Stettler et al. 1973). Exposure ages determined from abundance of cosmogenic $^{38}$Ar (Stettler et al. 1973) and $^{81}$Kr (Drozd et al. 1977) are 95 to 100 Ma and $122 \pm 3$ Ma, respectively. We have studied mesostasis areas in thin section 70035,195. This section is $14 \times 3$ mm in size and has a mineralogy consistent with that of the main rock sample, comprising anhedral plagioclase phenocrysts ($> 2 \times 1$ mm), pyroxene ($\sim 1 \times 1$ mm) and ilmenite ($\sim 0.5 \times 0.2$ mm). Small mesostasis pockets are found throughout the studied section and are further described in section 4.1

3. Methods

3.1. Identifying mesostasis regions

The aim of this study was to characterize the regions in which apatite is found in lunar basalts, therefore, mesostasis regions containing apatite were primarily investigated. Using whole section element maps of the studied samples, mesostasis regions were identified by the presence of small (< 1 mm) anhedral and amorphous phases that crystallized between larger surrounding crystals. The presence of symplectite assemblages and/or silicate liquid immiscibility textures was also used to identify mesostasis regions. These regions are rich in fayalite, silica, and glass and host a wide variety of smaller phases (i.e. sulphides, phosphates) compared to the surrounding major minerals. Pernet-Fisher et al. (2014) suggested that coarse-grained silica in mare basalts (> 100 $\mu$m) is likely a pseudo-eutectic mineral and, therefore, should not be included as a mesostasis phase. For the majority of mesostasis regions investigated here this is not a concern as silica within the regions is fine-grained (<100 $\mu$m), and intergrown with other mesostasis phases. For mesostasis regions containing large (>100 $\mu$m), elongate silica grains, intergrown with other mesostasis phases, we have considered this as a product of crystallization of the late-stage melt and, therefore, as part of the mesostasis region. In the basalts studied here silica is only found associated with mesostasis regions.

A large variety of textures and mineral phases were observed in the different mesostasis regions. We determined the two-dimensional extents of the different regions in multiple ways. For silica-rich mesostasis regions the boundary was drawn around the area including silica. Pernet-Fisher et al. (2014)
proposed that up to 30 vol.% of mesostasis melt could have been equilibrated with larger surrounding phases. Re-equilibration of pre-existing plagioclase and pyroxene grains with mesostasis melt modified their chemistry and created chemical zonations. In some mesostasis regions clear modification of pre-existing pyroxene associated with overgrowth of mesostasis phases was observed on back-scattered electron (BSE) and false-color X-ray images, and later confirmed with electron probe microanalysis (EPMA). In regions with no clear modification of pre-existing phases, mesostasis boundaries were drawn around mesostasis phases only. Compositional differences between phases within and outside mesostasis regions are detailed in section 5. For modal abundance estimates, where possible, mesostasis regions were limited to areas that included late-stage phases with limited incorporation of surrounding pre-existing phases. It is worth noting that thin sections only provide 2D sections through 3D mesostasis regions, which likely implies a sampling bias. To try and mitigate the possible effects associated with this sampling bias, we analyzed multiple mesostasis regions > 50 × 50 µm.

3.2. Electron Microscopy

The BSE maps were collected using the FEI Quanta 3D dual beam scanning electron microscope (SEM) at The Open University. The instrument is fitted with an Oxford Instruments 80 mm X-MAX energy dispersive X-ray detector, which allowed X-ray maps of each sample to be obtained by using the SEM in Energy Dispersive Spectroscopy (EDS) mode. Elemental mapping was carried out using a 20 kV accelerating voltage and a 0.60 nA beam current. X-ray maps were acquired at resolutions of 512 × 448 and 1024 × 896 pixels with a magnification of 200 to 300.

Quantitative mineral compositions were determined using a CAMECA SX-100 Electron Probe Micro Analyzer (EPMA) at The Open University. An accelerating voltage of 20 kV and a beam current of 20 nA were used except for plagioclase and glass analyses where the beam current was reduced to 10 nA. The beam diameter varied from 1 µm to 10 µm, depending on the dimensions of the analyzed phase. Standard count rates of 20 to 40 s per element were used, with a background counting time of half the peak counting time before and after peak analysis. A selection of natural standards were used for calibration, including feldspar (Si, Al, K), jadeite (Na), forsterite (Mg), hematite (Fe), rutile (Ti),
and apatite (P). The apatite compositions used here for bulk mesostasis composition calculations are those reported by Tartèse et al. (2013b) for apatite grains located in the same thin sections but not necessarily in the same mesostasis regions. For 70035, the average apatite composition of those analyzed in the other samples by Tartèse et al. (2013b) was used as these authors did not analyze apatite in this sample. The modal mineralogy and the quench glass abundances, for each mesostasis area, were calculated using pixel histograms from BSE-images in the ImageJ® software. For each mesostasis region a bulk composition was calculated using average EPMA compositions for each phase and the modal mineralogy within individual regions.

4. Results

4.1. Mesostasis textural descriptions

The BSE images and false-color compositional maps of representative mesostasis regions for the four samples are shown in Figures 1 to 8, and the modal mineral abundances in Table 1.

In sample 10044,645, eight mesostasis regions were analyzed, and representative BSE images of some of these regions are shown in Figure 1, while Figure 2 displays false-color X-ray elemental maps combining Si, Ca and Fe. These regions are ~200 × 200 µm and are located between pre-existing plagioclase laths (Figs. 1B & 1C) and pyroxene phenocrysts (Figs. 1A, 1C, & 1D). All of the regions contain apatite, pyroxene and ilmenite, while silica, plagioclase, K-glass, and K-feldspar were found in the majority of areas. Two mesostasis regions contained fayalite grains large enough (i.e. >10 µm) for multiple microprobe spot analyses (Figs. 1A & 1D). Symplectite texture (labelled as ‘pxf’ in accompanying figures), formed from the breakdown of pyroxferroite into fayalite, silica, and hedenbergite, was observed in two regions within 10044,645 (Figs. 1D/2C & 2F). Two regions within this sample contained coarse-grained silica (Figs. 1B & 2D). Spheroidal textures comprising of Si-K-Ba-rich glass (hereafter referred to as K-glass) enclosed by fayalite, characteristic of silicate-liquid immiscibility (SLI) (Pernet-Fisher et al. 2014), were observed in five of the regions and shown in Figure 1D. Such textures were described by Pernet-Fisher et al. (2014) as ‘sieve’ textures and classified as mature (large glass droplets) or immature (small glass droplets). The mesostasis region in Figure 1D displays immature ‘sieve’ texture, with fine-grained droplets of K-glass trapped within host fayalite.
Seven mesostasis regions within basalt 12064/130 were analyzed. These regions are ~100 × 100 μm and found mostly between pyroxene phenocrysts (Figs. 3A, 3C, & 3D) and plagioclase laths (Fig. 3B). Mesostasis regions contain varying amounts of apatite, silica, pyroxene, K-feldspar, fayalite, and ilmenite (Figs. 3 & 4). Pyroxferroite breakdown products are present in some regions (Figs. 3B, 4B, 4C, 4D & 4F). Both mature (Fig. 3A) and immature (Figs. 3B & 3D) ‘sieve’ textures, indicative of SLI, were observed in all but two mesostasis region of 12064 (Figs. 3C & 4D). One region within 12064 contained both mature and immature SLI textures (Fig. 3A & 4A).

In sample 15058/20, six mesostasis regions were analyzed. These regions are ~300 × 300 μm and found between pre-existing plagioclase (Fig. 5B) and pyroxene (Figs. 5A & 5C). Most of these regions contain a high abundance of silica (Figs. 5A, 5B, 6A, 6C, 6E & 6F). Five of the regions contained apatite, pyroxene, plagioclase, and ilmenite, while one area did not contain apatite. K-glass was found in some of these regions. Textures indicative of SLI or pyroxferroite breakdown products were not observed in this sample.

Seven mesostasis regions within sample 70035/195 were analyzed. The mesostasis regions in this sample are ~100 × 100 μm, and found between pre-existing pyroxene and plagioclase grains, and they generally contain silica, pyroxene, plagioclase, ilmenite, and K-glass (Figs. 7 & 8). These regions contain small (< 2 to 10 μm) apatite crystals co-existing with merrillite grains (e.g., Fig. 8A). Out of the nineteen areas initially investigated we found that most of the regions contained merrillite. Apatite was not widespread but instead found concentrated within a few of the mesostasis regions.

4.2. Composition of mesostasis phases

For all four samples plagioclase compositions vary from An$_{93}$ to An$_{68}$ (Fig. 9A). The K-rich plagioclase feldspars are those firmly within mesostasis regions (Fig. 9A). Most of the pyroxene analyses in samples 10044 and 12064 plot close to the Hd – Fs binary (Fig. 9B). In contrast, all pyroxene analyses for 70035 are more Mg-rich, plotting towards the En and Di regions (Fig. 9B). The few analyses of pyroxene compositions in 15058 range between those in 70035 and in samples 10044/12064(Fig. 9B).
Glass compositions from mesostasis regions are displayed in a Total-Alkali-Silica (TAS) diagram in Figure 10, together with compositions of the bulk-rock mare basalts studied and of lunar granites (Kushiro and Haramura 1971; Rhodes and Hubbard 1973; Rhodes et al. 1976; Beaty and Albee 1978; Seddio et al. 2013). In general, the glass compositions plot in a similar region of the diagram to the lunar granites (~4 - 10 wt.% alkali and ~68 wt.% to 78 wt.% SiO₂).

4.3 Reconstructed bulk mesostasis compositions

Average modal abundances for mesostasis regions in the four studied samples are given in Table 1, while average compositions of mesostasis mineral and glass phases are given in Tables 2 - 5. These data were combined to calculate the bulk mesostasis compositions, and average compositions for the latter are given in Table 6. Compositional variations between different mesostasis regions within individual samples are generally larger than variations between different samples. Bulk SiO₂ contents within 10044 mesostasis regions, for example, varied from 57 wt.% to 83 wt.%, while SiO₂ contents varied by about 12 wt.% across the different mesostasis regions in 70035. Large variations between bulk compositions of mesostasis regions were also observed for TiO₂ in sample 70035 for example, which varied by 14 wt.%. Significant variations in CaO (6.2 wt.% difference) contents in sample 12064 were also observed between different mesostasis regions. Very little variation within regions was observed for MnO, Na₂O, K₂O, and P₂O₅ contents, which is related to the lower abundance of these oxides in the calculated mesostasis compositions.

The reconstructed bulk mesostasis compositions display large variations between each sample. The largest variation is observed for SiO₂, which varies from 70 wt.% (10044) to 56.2 wt.% (70035). There is no correlation between the reconstructed SiO₂ content of the mesostasis regions and the SiO₂ content of the bulk sample. Sample 70035 does have the lowest bulk-rock SiO₂ content (37.8 wt.%; Rhodes et al., 1976) out of the four samples studied here, but 10044 has a lower bulk-rock SiO₂ content (42.2 wt.%; Beaty and Albee 1978) than both 12064 (46.0 wt.%; Scoon, 1971) and 15058 (47.8 wt.%; Rhodes and Hubbard, 1973) and, yet, the highest bulk-mesostasis SiO₂ content. The reconstructed mesostasis compositions for the four samples also display large variations in TiO₂ content. Sample 70035, a high-Ti basalt, has the highest mesostasis TiO₂ content (7.0 wt.%), however, high-Ti basalt 10044 has a
relatively low mesostasis TiO$_2$ content (1.5 wt.%). TiO$_2$ contents of mesostasis regions in low-Ti basalts 12064 and 15058 are 0.9 wt.% and 3.6 wt.%, respectively. FeO contents of mesostasis regions in samples 10044 (10.8 wt.%), 15058 (11.1 wt.%) and 70035 (11.2 wt.%) are fairly similar, while it is much higher in 12064 (23.0 wt.%). The CaO contents of bulk mesostasis are similar in samples 10044 and 15058 (6.4 wt.% CaO), while bulk mesostasis in 12064 and 70035 have varying CaO contents (5.7 – 8.8 wt.% CaO). The Al$_2$O$_3$ contents of mesostasis regions in 10044, 15058, and 70035 are similar (9.3, 9.2, and 10.1 wt.%), while 12064 has a lower Al$_2$O$_3$ content of 4.1 wt.%. The MgO contents of the mesostasis regions appear to be more dependent on the composition of surrounding pre-existing grains than on bulk-rock composition, which is consistent with the observations of Pernet-Fisher et al. (2014). The similarity of Al$_2$O$_3$, CaO, and K$_2$O concentrations of the mesostasis regions of 10044 and 15058 on one hand, and of 12064 and 70035 on the other hand, is a reflection of surrounding pre-existing grains. The majority of mesostasis regions within 10044 and 15058 are mostly surrounded by pre-existing pyroxenes and smaller plagioclase grains, while mesostasis regions in 12064 are found between pre-existing plagioclase and pyroxene grains, and those in 70035 are commonly observed between pre-existing plagioclase grains. Phase boundaries in contact with mesostasis melt are thought to re-equilibrate with this melt. However, precisely quantifying the extent of diffusion into pre-existing phenocrysts is not possible from our dataset. It is worth noting, however, that mesostasis areas

5. Discussion

5.1. Relationships between bulk-rock chemistry and mesostasis composition

Analysis of mesostasis regions in samples from this study and those studied by Pernet-Fisher et al. (2014) show that these regions have distinct mineralogy and textures, which vary greatly across a single sample, and display both mature (Figs. 3A & Fig. 4A) and immature (Figs. 4B, 4C, & 4E) SLI-related ‘sieve’ textures. Mesostasis compositions appear to be more dependent on the composition of surrounding mineral phases than on bulk-rock composition, which is consistent with the observations of Pernet-Fisher et al. (2014). The similarity of Al$_2$O$_3$, CaO, and K$_2$O concentrations of the mesostasis regions of 10044 and 15058 on one hand, and of 12064 and 70035 on the other hand, is a reflection of surrounding pre-existing grains. The majority of mesostasis regions within 10044 and 15058 are mostly surrounded by pre-existing pyroxenes and smaller plagioclase grains, while mesostasis regions in 12064 are found between pre-existing plagioclase and pyroxene grains, and those in 70035 are commonly observed between pre-existing plagioclase grains. Phase boundaries in contact with mesostasis melt are thought to re-equilibrate with this melt. However, precisely quantifying the extent of diffusion into pre-existing phenocrysts is not possible from our dataset. It is worth noting, however, that mesostasis areas
surrounded by pre-existing plagioclase that was not included in melt reconstructions may lead to modeled melts having lower Al$_2$O$_3$ contents for example, assuming some of the melt Al$_2$O$_3$ is lost as diffusion into pre-existing grains.

Mineral compositional variations between different mesostasis regions within a sample also support fractional crystallization as an important process in controlling mesostasis bulk compositions and explaining differences for different mesostasis regions. For example, Figure 11 highlights how feldspar and pyroxene compositions within different mesostasis regions in sample 10044 vary. It is important to note that in addition, sampling bias, notably due to the 2D nature of mesostasis regions observed in thin sections while they are in fact 3D objects, can also be responsible for part of the variations observed between different mesostasis regions in individual samples.

The bulk-rock samples from this study are all relatively enriched in Fe (Mg# = 37 for 12064, 38 for 10044 and 44 for 15058), the less differentiated being sample 70035 (Mg# = 48). Sample 12064 has the lowest Mg# and the highest mesostasis FeO content. Sample 10044 has a similar Mg# but a lower bulk mesostasis FeO content compared to 12064. Pernet-Fisher et al. (2014) have suggested that lunar basalts with low Mg# (<50) are more likely to undergo SLI than those with higher Mg# (>50). Even though all the studied samples have low-Mg#, the two samples that do not display evidence of SLI, 15058 and 70035, have the highest Mg#, which supports the observation of Pernet-Fisher et al. (2014). Also, Pernet-Fisher et al. (2014) found that their low Mg# basalts displayed the largest range in pyroxene compositions. In the studied samples, pyroxene have more restricted compositions. Pyroxene in samples 70035 and 15058 displays the largest range in compositions (Fig. 9b), which is opposite to the observation of Pernet-Fisher et al. (2014) since these two samples have the highest Mg#.

The SiO$_2$ contents of K-rich glass for all samples cluster together at around 74-78 wt.%, while the Na$_2$O+K$_2$O contents of glass in 70035 (~7.0-7.5 wt.%) are slightly lower than in basalts 10044, 12064 and 15058 (>8 wt.%; Fig. 10). This may suggest that mesostasis regions in 70035 generally crystallized earlier than in other mare basalts, having slightly less evolved chemical compositions (Table 6), which is also reflected in the more Mg-rich nature of pyroxene in 70035 mesostasis regions. In general there is no relationship between SiO$_2$ in the bulk-rock, bulk-mesostasis, and mesostasis
glasses, supporting the hypothesis that fractional crystallization of major silicate minerals may not be the main process controlling the compositional characteristics of mesostasis regions.

5.2. Fractional crystallization modeling and the influence of bulk-rock composition on late-stage melts.

To provide further understanding on the evolution of these lunar basalts, crystallization modeling was undertaken using whole-rock major element compositions for each of the four samples. Liquid lines of descent were calculated using the ‘Simulating Planetary Igneous Crystallization Environments’ package (SPICEs; Davenport et al. 2014), which incorporates the FXMOTR, MAGFOX, and MAGPOX programs (Longhi 1991). The use of MELTS for modeling basaltic systems is well demonstrated in the literature (Ghiorso and Sack 1995; Ghiorso et al. 2002; Gualda et al. 2012) and has been used for extraterrestrial applications (e.g. Anand et al. 2003; Day et al. 2006; Liu et al. 2009; Fagan et al. 2014). However, the SPICEs program has the unique advantage of being calibrated for extraterrestrial systems. Here, the MAGFOX program was used to model fractional crystallization of the four Apollo samples under lunar relevant conditions. The MAGFOX program has been widely utilized for modeling Apollo basalt evolution (Neal et al. 1994a, 1994b) and more recently to investigate SLI in late-stage melts (Pernet-Fisher et al. 2014). Results from the MAGFOX algorithm are plotted on the AFM 2D pseudo-ternary (Na$_2$O + K$_2$O – FeO – MgO; Fig. 12).

For each sample, all available bulk compositions were input into the MAGFOX algorithm. The liquid line of descent (LLD) for each sample varies with composition indicating the sensitivity of the model to relatively minor changes in bulk composition (Fig. 12). To investigate the possible effect of pressure, we used the bulk composition from Engel and Engel (1970) for sample 10044 and varied the pressure between 1 kb, 5 kb, and 10 kb, which had very little effect on the until the final stages of crystallization (Fig. 12A). When MgO becomes exhausted in the system, the 1 kb LLD moves towards lower FeO contents while the 10 kb moves in the opposite direction on the AFM (the run at 5 kb did not crystallize to the point of MgO exhaustion (Fig. 12A). Based on modeling for sample 10044, we considered the effect of pressure much less significant than the effect of the bulk rock composition, and runs were only performed at a pressure of 1 kb for the remaining samples.
MAGFOX was unable to model crystallization up to 100% fractionation for any of the samples. The volume of crystals fractionated for 10044 was 64 % using the bulk composition from Wänke et al. (1970), 98 % using that of Engel and Engel (1970) and Beaty and Albee (1978), and 99 % using those from Agrid et al. (1970), Wakita et al. (1970) and Dymek et al. (1975) (Fig. 12B). For sample 12064, the volume of crystals fractionated ranged from 88 % using the composition from LSPET (1970) to 99 % with those from Kushiro and Haramura (1971) and Scoon (1971) (Fig. 12C). Finally, the volume of crystals fractionated for sample 15058 varied from 97 % using the composition of Rhodes and Hubbard (1973) to 99 % with that of Willis et al. (1972) (Fig. 12D) while the crystallization of 70035 reached 96 % (Rhodes et al. 1976).

For all the samples the LLD’s plot within the mare basaltic field on the AFM (Fagan et al. 2014). The LLD’s for 10044 are in good agreement with some of the compositions of late-stage melts calculated in this study (Fig. 12B). The bulk-rock composition from Beaty and Albee (1978) has a low initial bulk alkali content (Na$_2$O + K$_2$O = 0.02 wt.%), resulting in a LLD which is too depleted in Na$_2$O and K$_2$O to correspond with any of the late-stage melt calculated compositions. The LLD calculated using the bulk-rock composition of Wänke et al. (1970), which has an initial alkali content much higher than the other compositions, also has alkali contents which are higher than the majority of the mesostasis region calculated compositions. There is good agreement for the majority of calculated mesostasis regions and the compositions of Dymek et al (1975), Engel and Engel (1970), and Wakita et al. (1970). The LLD’s for 12064 plot closely together and show fairly good agreement with the calculated late-stage melt compositions (Fig. 12C). For samples 15058 and 70035, the LLD’s do not correspond with calculated mesostasis region compositions (Fig. 12D)

The overall broad agreement between petrological and modeling estimates of mesostasis melt compositions in sample 12064, and to a lesser extent 10044, suggests that SPICEs may be an efficient tool for calculating the composition of late-stage melts (Fig. 12). However, SPICE modeling was unable to reconcile compositions in samples 15058 and 70035. Additionally, AFM diagrams only considers Na$_2$O + K$_2$O, FeO, and MgO contents modeled using SPICEs, and other chemical parameters may differ in their reconciliation. Petrological estimates of mesostasis regions compositions for 15058 appear to slightly overestimate MgO and Na$_2$O + K$_2$O contents (Fig. 12D). This is similar for 70035, which shows
a large discrepancy between the reconstructed bulk mesostasis compositions and those modeled by SPICEs, as the reconstructed bulk mesostasis compositions are Mg-rich and would plot near the beginning of the LLD, when SPICEs modeling suggests that mesostasis compositions should be similar to those in sample 10044. The high MgO content calculated for the bulk mesostasis regions in 70035 (Table 6) presumably results from the high proportion of pyroxene relative to plagioclase surrounding mesostasis regions in this sample. The pyroxene grains in 70035 have also higher Mg contents than those of the other samples (Fig. 9B). As highlighted by the other samples, however, the bulk-rock composition inputted in SPICE can have a significant influence on the calculated LLDs and with only one available composition for 70035 it is difficult to make strong conclusions. Overall the outcome of MAGFOX modeling indicates that fractional crystallization can produce the compositions seen for some late-stage melts but not all. This suggests, therefore, that other processes such as equilibrium crystallization and/or alteration of early-crystallized pyroxene and/or plagioclase phenocrysts are also affecting late-stage melt compositions. The variability of late-stage melts also highlights that apatite within lunar mare basalts does not crystallize from a fixed melt composition.

5.3. Silicate liquid immiscibility

We have argued that the composition of phases between which mesostasis regions become trapped and crystallize have a large influence on these late-stage melt compositions. After these late-stage melts become trapped, SLI is thought to exert additional control on the compositions of these melts (Pernet-Fisher et al., 2014). It is not known, however, if SLI commonly operates in all late-stage melts. There are many regions, in the samples studied here, where SLI has obviously occurred. Where present, however, the extent of SLI appears limited and has no influence on the bulk composition of these regions as both fractions remain. It should be noted, however, that the absence of SLI-related textures, such as sieve textures, does not indicate that SLI did not occur, only that it was not followed by immediate quenching if it occurs. In the sections studied here, apatite was not found in direct contact with textures directly related to SLI within mesostasis regions, preventing a thorough investigation of whether apatite crystallized before, during or after SLI. Volatiles, such as F, Cl and OH, can be
fractionated during SLI (Lester et al. 2013), which, therefore, could add further uncertainty into reconstructing volatile abundances in silicate melts based on analysis of volatiles in apatite.

6. Summary

The lack of relationship between bulk-rock chemistry and reconstructed mesostasis melt composition argues for distinct chemical evolution of the different mesostasis regions within a single crystallizing basalt. Mesostasis regions within a single sample can vary in composition and textural maturity, which suggests that volatile contents could also vary within these regions. Our study also shows that mesostasis regions have bulk compositions that differ significantly from those of the initial basaltic melts that formed the bulk sample. As such, partition coefficients derived from experimental studies of apatite-melt partitioning designed for basaltic melts may not be fully applicable. Future experiments on apatite-melt volatile partitioning should, therefore, be conducted with more silicic starting compositions given the strong dependence that melt composition has on partitioning in this system (Mathez and Webster 2005).

The mineralogy and petrology of mare basalts are well characterized in the literature, yet detailed analyses of mesostasis regions in Apollo samples have been largely overlooked. This study has highlighted the variability of mesostasis regions in lunar basalts. Once a mesostasis melt is trapped between pre-existing grains, its evolution becomes distinct and separated from the evolution of melts trapped in other mesostasis regions. It is expected that volatile evolution in these mesostasis regions is equally distinct, and as such, detailed petrographic information of apatite surroundings should be collected when conducting apatite analysis. In general, the mesostasis melts are elevated in SiO$_2$, slightly enriched in alkali elements, and contain varying amounts of TiO$_2$ and FeO. The bulk-mesostasis compositions calculated here may also be used to guide future experimental work on apatite-melt volatile partitioning under lunar conditions.

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