Supplementary Material accompanying

**Early degassing of lunar urKREEP by crust-breaching impact(s)**

by

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**1. Extended Methods**

During the first two analytical sessions, secondary ions of 19F- were not collected due to the very high count rates (being >1 million counts per second), which would have caused significant aging of the EM detector over the duration of a single analysis. During the final analytical session (August 2015), measurement of 19F on EM#4 was achieved by counting for ~30 s during each analysis using the baseline function of the NanoSIMS, which was enough to obtain a precision comparable to that obtained using electron probe microanalysis (EPMA)(Tartèse *et al*., 2013; Barnes *et al*., 2014; Tartèse *et al*., 2014a).

**2. Sample Descriptions**

*10044, 645*

Sample 10044 was collected in the area between the Apollo 11 Lunar Module (LM) and a double elongated crater to the southwest of the LM. Thin-section 10044,645 represents a medium to coarse-grained (grain size up to 2 mm) ophitic ilmenite mare basalt, with high-Ti and low-K contents(Beaty and Albee, 1978). This sample is relatively fresh and is not significantly affected by shock. 10044 is composed of pyroxene, plagioclase, ilmenite, silica, and interstitial areas filled with mesostasis(Beaty and Albee, 1978). This rock has a crystallisation age of ca. 3.72 Ga based on Rb-Sr and Ar-Ar systematics (Albee *et al*., 1970; Papanastassiou *et al.*, 1970; Guggisberg *et al*., 1979).

*10058,254*

Sample 10058 is a high-Ti, low-K type basalt, and belongs to the B1 group of Apollo 11 basalts(Beaty and Albee, 1970). It is a coarse-grained sub-ophitic ilmenite basalt mainly composed of pyroxene, plagioclase, ilmenite and interstitial silica. This rock has an Rb-Sr age of ca. 3.63 ± 0.20 Ga(Albee *et al.*, 1970) and an Ar-Ar age of 3.71 ± 0.04(Guggisberg *et al*., 1979).

*70035,195*

Apollo 17 sample 70035 is a medium-grained, vesicular, high-Ti basalt. It is a large, partially crystalline basalt with large (>1 mm) clinopyroxene crystals, plagioclase, ilmenite, spinel, armalcolite, olivine and mesostasis areas(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 (Nyquist *et al.*, 1977;Evensen *et al.*, 1973) and with an Ar-Ar date of 3.75 ± 0.07 Ga(Stettler *et al*., 1973).

*15555, 206*

15555 is a coarse-grained low-Ti olivine-normative basalt composed of olivine, pyroxene (clinopyroxene with pigeonite zonations and Fe-rich rims) and plagioclase with trace amounts of ilmenite and silica(Rhodes *et al.*, 1973). Crystallisation of this rock has been dated by Rb-Sr to be between 3.3-3.54 Ga (Chappell et al., 1972; Murthy et al., 1972; Birck et al., 1975) and 3.32 Ga by Ar-Ar (Podeosek et al., 1972).

*14304, 177*

14304, 177 is a thin-section of a very high-potassium (VHK) basalt. It is a coarse-grained sample with areas that have been granulated. Mineralogically it is composed of plagioclase, pyroxene (mostly clinopyroxene), olivine, K-feldspar, and K-rich glass (Neal *et al.*, 1989a,b). This sample contains interstitial K-rich areas and vein like structures running through pyroxene, plagioclase, and apatite grains (e.g., Figure 4A). This VHK basalt yielded a Rb-Sr age of 3.95 ± 0.04 Ga and a Sm-Nd age of 4.04 ± 0.11 Ga(Shih *et al.*, 1987). Both ages are within error and the crystallisation age is taken as ~4 Ga.

*15386, 46*

15386 is the largest sample of pristine KREEP basalt in the Apollo sample collection with a total mass of 7.5 grams. Mineralogically, sample 15386 is composed of plagioclase laths surrounded by interstitial pyroxene. The mesostasis has significant cristobalite (10%), ilmenite, and minor phosphate, iron and sulphide(Meyer *et al*., 2010). This sample has a crystallisation age of 3912 ± 25 Ma ago (weighted average age calculated by Tartèse *et al*., 2014a by combining Rb-Sr and Sm-Nd isochron dates from the literature). Note that the studied thin-section is different to the one analysed for apatite D/H-H2O by Tartèse *et al*.(2014a).

*76535, 51*

76535 was collected at the Apollo 17 Station 6 site in the Taurus-Littrow Valley, and is part of a rake sample. It is a remarkably pristine, coarse-grained plutonic rock which has not been altered by shock(Warren and Wasson, 1979). This sample is composed of plagioclase, olivine, orthopyroxene, plus accessory minerals and mesostasis(Gooley *et al*., 1974; Dymek *et al*, 1975; Warren, 1993; McCallum and Schwartz, 2001; Elardo et al., 2012). The mesostasis mineral assemblage consists of spinel, clinopyroxene, orthopyroxene, apatite, merrillite, baddeleyite, native Fe-metal, and K-feldspar. 76535 has a crystallisation age of ~ 4.373 ± 0.011 Ga (weighted average age from Papanastassiou and Wasserburg, 1976; Hinthorne *et al*., 1979; Premo and Tatsumoto, 1992; Nyquist *et al*., 2012; Carlson *et al*., 2014).

*78235,43*

78235 was chipped from a glass covered boulder at Station 8 on the Apollo 17 mission (Jackson *et al*., 1975). It is classified as a coarse-grained norite (grain size ~ 0.5 mm). This norite is heavily shocked and thin-section 78235,43 contains a sliver of the impact glass that covered the boulder at Station 8. Sample 78235 is mainly composed of orthopyroxene, plagioclase, and trace amounts of clinopyroxene, silica, apatite, merrillite, and glass (e.g., McCallum and Mathez, 1975). Recent age determinations seem to indicate a weighted average crystallisation age of 4.39 ± 0.04 Ga: Nyquist *et al.*, 1982; Edmunson *et al.*, 2009; Andreasen *et al*., 2013) making 78235 one of the oldest lunar samples in the Apollo collection.

*79215, 50*

79215 was collected at Station 9 on the Apollo 17 mission. It has been classified as a holocrystalline feldspathic granulitic impactite. 79215 is composed of ~ 72 % matrix and ~ 28 % relict lithic clasts of anorthosite and troctolite rocks (McGee *et al.*, 1978). The matrix portion is composed of plagioclase, olivine, high-Ca pyroxene, low-Ca pyroxene, and minor to trace amounts of oxides, metals and troilite (Bickel *et al.*, 1976; Treiman *et al.*, 2014). The troctolite portion is composed of plagioclase, olivine, orthopyroxene, clinopyroxene, and minor apatite, oxides, spinel and troilite(McGee *et al.*, 1978). Both matrix and a troctolitic clast are present in the studied thin-section, but apatite was only found in the troctolitic portion. This sample has a peak metamorphism age of ca. 3.9 Ga (Oberli *et al*., 1979; Hudgins *et al.*, 2009).

**3.** **Petrological histories of the lithologies studied**

1. Magnesian suite (MGS) samples

The MGS group includes the troctolite (76535) and norite (78235) studied in this work. The parent melts to these rocks are considered to have been formed by partial melting of early LMO Mg-rich olivine-dominated cumulates(Shearer *et al*., 2015) with melting likely initiated by mantle cumulate overturn. The Mg-rich melts are expected to have either assimilated urKREEP *en route* to the crust or have interacted with urKREEP at the base of the crust, before being intruded into the lunar crust where they experienced slow cooling likely in layered intrusions (reviewed in Shearer *et al*., 2015). In the case of these samples, the volatile signatures of the primitive melts have been overprinted by the KREEP contamination.

1. Metasomatised samples

Whilst troctolite 76535 is a pristine un-shocked sample (Warren, 1993) it is considered to have been affected by post-crystallisation metasomatism (e.g., Elardo *et al*., 2012). This alteration was likely facilitated by the infiltration of a KREEPy melt that was rich in Cl, Fe and Cr(Elardo *et al*., 2012). Likewise, granulite 79215 was annealed by impact and is thought to have been subsequently affected by metasomatism, probably of an agent (melt, vapour or fluid) derived from a KREEP component infiltrating the lunar crust that had been mobilised by impact (e.g., Treiman *et al*., 2014). Thus the volatiles in these samples can be directly related to the varying KREEP component added.

1. KREEP-rich basalts

KREEP basalts, inclusive of 15386 which is one of the most KREEP-rich basalts from the Moon, are considered to have formed from the partial melting of primitive olivine and pyroxene cumulates that either already contained an urKREEP component (incorporated during cumulate overturn) or assimilated urKREEP *en route* to the crust before being erupted onto the lunar surface(Warren and Wasson, 1979).

The very high potassium (VHK) basalts including 14304, are thought to be formed through the assimilation of lunar granite lithologies by a high-aluminium (HA) mare basaltic magma (Shervais *et al.*, 1985;Neal and Taylor, 1989). The variations in texture observed between VHK samples was attributed to different cooling rates within a single lava flow. Recently, Roberts *et al.* (2014), used textural and petrographic relationships of K-rich glass with host minerals and breccia matrix to invoke an impact origin. They suggested that following breccia formation the breccia was covered in a hot impact melt sheet that melted the low melting point components, such as granite, also present in Apollo 14 breccias, and infiltrated the breccia.

1. Mare basalts

The source regions for the mare basalts (e.g., 10044, 10058, 70035, 15555) formed after cumulate overturn. This event is expected to have created the heterogeneous mixture of olivine, pyroxene, and ilmenite cumulates and small degrees of partial melting of these sources created the mare basalts (e.g., reviewed by Grove and Krawczynski, 2009 and Hallis *et al.*, 2014). Limited incorporation of KREEP component is expected in the source regions of the mare basalts, together with varying degrees of ilmenite contamination, and possibly small amounts of trapped instantaneous residual liquid in the mantle cumulates, all would have contributed to the volatile inventory of the source regions for the mare basalts.

**4. Electron Probe Microanalysis (EPMA) data**

EPMA data collected following the protocol of Barnes *et al*. (2014) is shown in Supplementary Table 1. Electron microprobe analyses were conducted on apatite in some of the studied samples (10058, 14304, 78235 and 79215) for which data were not available in the literature using the method outlined in Barnes *et al.* (2014) (Supplementary Table 1).

Supplementary Table 1. Chemical compositions of apatite in samples 10058, 14304, 78235, and 79215. Numbers in parentheses represent the number of analyses. S.d. is the standard deviation of each oxide.

|  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| Sample | 10058 (4) | s.d. | 14304 (6) | s.d. |  | 78235 (3) | s.d. | 79215 (4) | s.d. |
| P2O5 | 39.85 | 1.62 | 42.15 | 0.38 |  | 42.46 | 1.72 | 42.06 | 0.20 |
| SiO2 | 2.25 | 1.58 | 0.30 | 0.04 |  | 0.45 | 0.46 | 0.18 | 0.02 |
| Ce2O3 | 0.41 | 0.13 | 0.08 | 0.05 |  | 0.02 | 0.01 | 0.01 | 0.02 |
| Y2O3 | 1.20 | 0.55 | 0.12 | 0.06 |  | 0.01 | 0.02 | 0.07 | 0.01 |
| MgO | 0.03 | 0.00 | 0.35 | 0.07 |  | 0.11 | 0.02 | 0.18 | 0.01 |
| CaO | 52.38 | 1.32 | 55.49 | 0.25 |  | 54.50 | 0.97 | 56.05 | 0.41 |
| MnO | 0.02 | 0.01 | 0.01 | 0.01 |  | 0.00 | 0.01 | 0.00 | 0.01 |
| FeO | 0.68 | 0.19 | 0.36 | 0.07 |  | 0.26 | 0.19 | 0.22 | 0.07 |
| Na2O | 0.01 | 0.02 | 0.01 | 0.01 |  | 0.00 | 0.00 | 0.00 | 0.00 |
| SO2 | 0.09 | 0.17 | 0.01 | 0.01 |  | 0.07 | 0.04 | 0.03 | 0.02 |
| F | 3.46 | 0.29 | 3.65 | 0.24 |  | 3.14 | 0.53 | 3.94 | 0.11 |
| Cl | 0.06 | 0.03 | 0.44 | 0.11 |  | 0.78 | 0.06 | 0.66 | 0.02 |
| F=O | 1.46 |  | 1.54 |  |  | 1.32 |  | 1.66 |  |
| Cl=O | 0.01 |  | 0.10 |  |  | 0.18 |  | 0.15 |  |
| Total | 98.96 |  | 101.34 |  |  | 100.29 |  | 101.60 |  |
|  | *Stoichiometry based on 13 anions* |  |
| P | 2.87 |  | 2.97 |  |  | 3.00 |  | 2.96 |  |
| Si | 0.19 |  | 0.03 |  |  | 0.04 |  | 0.02 |  |
| Ce | 0.01 |  | 0.00 |  |  | 0.00 |  | 0.00 |  |
| Y | 0.05 |  | 0.01 |  |  | 0.00 |  | 0.00 |  |
| Mg | 0.00 |  | 0.04 |  |  | 0.01 |  | 0.02 |  |
| Ca | 4.78 |  | 4.95 |  |  | 4.88 |  | 5.01 |  |
| Mn | 0.00 |  | 0.00 |  |  | 0.00 |  | 0.00 |  |
| Fe | 0.05 |  | 0.02 |  |  | 0.02 |  | 0.02 |  |
| Na | 0.00 |  | 0.00 |  |  | 0.00 |  | 0.00 |  |
| S | 0.01 |  | 0.00 |  |  | 0.01 |  | 0.00 |  |
| F  | 0.93 |  | 0.96 |  |  | 0.83 |  | 1.04 |  |
| Cl | 0.01 |  | 0.06 |  |  | 0.11 |  | 0.09 |  |
| OH | 0.06 |  | 0.00 |  |  | 0.06 |  | 0.00 |  |
| Sum | 7.96 |  | 8.02 |  |  | 7.95 |  | 8.03 |  |
| P site | 3.06 |  | 2.99 |  |  | 3.04 |  | 2.98 |  |
| Ca site | 4.90 |  | 5.03 |  |  | 4.91 |  | 5.05 |  |

For the other samples, apatite compositions are given by Tartèse *et al*. (2013) for 10044 and 15555, Tartèse et al. (2014a) for 15386, McCubbin *et al*. (2011), Elardo *et al.* (2012) and Barnes *et al*. (2014) for 76535, and Treiman *et al*. (2014) for 79215. EMPA data has not yet been collected for apatite in 70035. Stoichiometry was calculated on the basis of thirteen anions (see McCubbin *et al*., 2011 for a discussion of the various stoichiometric normalisation methods specific to apatite). The analytical reproducibility of fluorine values on apatite standards was better than 0.3 wt.%, except for analysis of apatite in 79215, which all exhibited anomalously high F contents. All other analyses resulted in satisfactory stoichiometric totals. As already recognised in previous studies, one of the main characteristics of lunar apatite is their F-rich nature (McCubbin *et al*., 2011; Tartèse *et al*., 2013; McCubbin *et al*., 2015). In all the studied samples excluding mare basalt 15555, all of the apatite crystals have >3 wt.% fluorine, corresponding to > ~80 mol.% F in the apatite volatile site.

**5. Relating the heavy Cl-isotopic composition of lunar apatite to a KREEP component**

Supplementary Table 2 provides the data and literature references used to assess whether variable KREEP contamination might be responsible for the unique Cl-isotopic compositions of lunar samples (Figure 8).

Supplementary Table 2. Bulk-rock La and Sm concentrations and bulk-rock ε143Nd initial values of the samples studied in this work and 12039\* and 12040\* (studied by Boyce *et al.,* 2015).

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
| Sample | La (ppm) | Reference(s) | Sm (ppm) | Reference(s) | ε143 Nd initial | Reference(s) |
| 10044 | 10.22 ± 1.23† | Wänke *et al*., 1970Wakita *et al*., 1970Kharkar *et al*, 1971Rhodes and Blanchard, 1980Neal 2001 | 17.73 ± 3.95† | Wänke *et al*., 1970Wakita *et al*., 1970Kharkar *et al*, 1971Philpotts and Schnetzler,1970 | +7.10 ± 0.4 | Snyder *et al.*, 1994 |
| 10058 | 10.2 ± 0.20 | Hallis *et al*., 2014 | 15.6 ± 0.30 | Hallis *et al*., 2014 | +7.6 ± 0.4 | Snyder *et al*., 1994 |
| 15555 | 1.79 ± 0.03 | Hallis *et al*., 2014 | 1.34 ± 0.02 | Hallis *et al*., 2014 | +2.80 ± 0.3† | McCleod *et al*., 2014Sprung *et al*., 2013Rankenburg *et al*., 2006Brandon *et al*., 2009 |
| 70035 | 7.97 ± 0.12 | Hallis *et al*., 2014 | 12.6 ± 0.20 | Hallis *et al*., 2014 | +6.60 ± 1.6 | Sprung *et al.,* 2013 |
| 14304 | 25.2 ± 0.30 | Neal *et al*., 1989b | 12.1 ± 0.20 | Neal *et al*., 1989b | +0.27 ± 0.3 | Shih *et al*., 1987 |
| 15386 | 78.3 ± 1.20 | Hallis *et al*., 2014 | 34.1 ± 0.6 | Hallis *et al*., 2014 | -1.98 ± 0.5† | McCleod *et al*., 2014Rankenburg *et al*., 2006Brandon *et al.,* 2009 |
| 76535 | 1.51 | Haskin *et al*., 1974 | 0.61 | Haskin *et al*., 1974 | -0.64 ± 0.5† | Borg *et al*., 2014Premo and Tatsumoto, 1992 |
| 78235 | 4.47 | Blanchard and McKay, 1981 | 1.93 | Blanchard and McKay, 1981 | -0.27 ± 0.7 | Edmunson *et al*., 2009 ‡ |
| 79215 | 3.23 ± 0.21† | Hudgins *et al*., 2008 | 1.46 ± 0.19† | Hudgins *et al*., 2008 | - | - |
| 12039\* | 7.25 | Nyquist *et al*., 1977 | 4.8 | Nyquist *et al*., 1977 | +5.00 ± 0.3 | Sprung *et al*., 2013 |
| 12040\* | 4.04 ± 0.06 | Hallis *et al.,* 2014 | 3.18 ± 0.06 | Hallis *et al.,* 2014 | +3.78 | McCleod *et al*., 2014 |

Where: ‡ data is for sample 78238. † indicate averages and standard deviations of multiple analyses, all other uncertainties represent the respective analytical uncertainties where available.

**6. Additional methods accompanying the modelling calculations**

We have applied a Rayleigh distillation model to calculate the degree of Cl isotope fractionation caused by degassing of metal chlorides. In this model the fractionation factor ** is related to the mass difference between the two isotopologue species constituting of the vapour phase (e.g., Zn35Cl2 and Zn37Cl2) and is given by ** = √(*m1*/*m2*), where *m1* and *m2* are the masses of the light and heavy isotopologues, respectively. This gives ** values of 0.987 for NaCl, 0.989 for ZnCl2 and 0.988 for FeCl2. Using these ** values, we calculated that >85% volatilisation of Cl as NaCl, or >90 % volatilisation of Cl as either FeCl2 or ZnCl2, would increase the δ37Cl value of Cl remaining in the melt to ~+30 ‰, starting from an Earth-like initial δ37Cl of 0 ‰.



Supplementary Figure 1. Degassing curves for the loss of various metal chlorides from urKREEP. The model uses the different ** values for the various metal chloride species (details in the text) and the various post-degassing Cl contents estimated for urKREEP (reviewed in McCubbin *et al*., 2015a). The % of degassing are relevant to the loss of ZnCl2.

Estimates for the Cl content of urKREEP (~1350 ppm, McCubbin *et al*., 2015) indicate that the un-degassed urKREEP magmatic liquid would have contained ~2 wt. % Cl (Supplementary Figure 1)

In the main manuscript, scenarios involving the contemporaneous degassing of H, either as H2 or HCl, are considered. Supplementary Figure 2 details these degassing models. The curves use the fractionation factors of Richet *et al*. (1999) calculated for temperatures in the range of 900 to 1300 °C. Two starting H-isotopic compositions are assumed A) -400 ‰ (representing the lowest measured δD value from a KREEP-rich lunar sample; Barnes *et al*., 2014) and B) -200 ‰, representing approximately the average δD value for water in KREEP-rich lithologies.

Supplementary Figure 2. Hydrogen degassing models for loss of H from urKREEP, assuming an un-degassed H-isotopic composition for urKREEP of A) -400 ‰ and B) -200 ‰, and assuming H is lost as H2, HCl, or HF. The grey bars indicate the current range of H-isotopic compositions measured in KREEP-rich lithologies (Barnes *et al*., 2014; Tartèse *et al*., 2014).

In some scenarios, as outlined in the main manuscript, there may be a requirement for post-accretion addition of volatiles to the Moon. For the addition of chondritic material to the Moon, a LMO depth of 400 km and a density of 3300 kg m-3 were assumed after Barnes *et al*.(2015). Using constraints from Day *et al*.(2007), Barnes *et al.*(2015) calculated that a maximum amount of 52 ppm water could have been delivered to the Moon during the lifetime of the LMO, which equates to the addition of 1.46×1019 kg of CI-type carbonaceous chondrite material(assuming the bulk water contents for carbonaceous chondrites from Alexander *et al*. (2012)). Note that the addition of water by carbonaceous chondrites during and particularly after the event that degassed urKREEP, means that water in urKREEP should be characterised by the same H-isotopic composition (between -200 and +200 ‰) as water found in the carbonaceous chondrites (Alexander *et al*., 2012). Assuming that the bulk chlorine content of CI-type carbonaceous chondrites is 0.1 wt.%, associated with a δ37Cl value of ~0 ± 1 ‰(Sharp *et al*., 2013), then the maximum Cl that is added to the lunar interior during late accretion is 1.46×1016 kg Cl. If the BSM Cl value is assumed to be of the lower estimate ~3.94×1018 kg (~100 ppm, McCubbin *et al*., 2015) then late accretion adds <0.5 % of the total BSM Cl abundance. Therefore, the maximum amount of Cl added during late accretion is insignificant, and will result in negligible change in the post-degassing Cl isotopic composition of urKREEP by <0.15 ‰, which is within current analytical uncertainty.

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