Pb-Pb ages of feldspathic clasts in two Apollo 14 breccia samples.

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Abstract

Pb-Pb isochron ages of ca. 3.92 Ga for three K-feldspar-rich clasts from Apollo 14 breccias 14303 and 14083 were determined using Secondary Ion Mass Spectrometry (SIMS). They are interpreted to represent the resetting of the U-Pb system in the clasts as a result of brecciation during the Imbrium impact. One of the clasts contains zircon grains that record a significantly older crystallization age (ca. 4.33-4.35 Ga) for the rock represented by that clast. Initial Pb compositions determined for the clasts, combined with the previously measured Pb isotopic compositions of K-feldspar grains from several Apollo 14 breccia samples, constrain a range of initial Pb compositions in the ca. 3.9 Ga Fra Mauro formation at the Apollo 14 landing site. They also indicate that either the rocks represented by these clasts or the sources of these rocks evolved with a high $^{238}\text{U}/^{204}\text{Pb}$ (μ -value) for substantial periods of time, although the precise ages of the rocks represented by at least two investigated clasts are unknown.

1. Introduction

The U-Pb isotope system and its derivative Pb-Pb chronometer have been used with variable success to obtain ages of different lunar rocks ever since the first samples were delivered by the Apollo missions. In particular, the advent of ion probes at the time when the samples became available for study enabled *in situ*, small (few micrometres) scale and

relatively non-destructive analysis of zircon grains in lunar samples, placing important constraints on the magmatic and impact history of the Moon (e.g. Compston et al., 1984; Meyer et al., 1996). These earlier studies investigated zircon in matrix and lithic clasts from Apollo 12, 14, 15 and 17 breccia samples identifying multiple episodes of zircon formation between ca. 4.35 and 3.88 Ga. In particular Meyer et al. (1996) studied zircon grains found in the fragments of felsic rocks preserved in the impact breccia samples and noted that while most zircon grains allow estimates of their crystallisation ages, some experienced disturbance of U-Pb systems. In some clasts, this disturbance is accompanied by recrystallization of the host rock fragments, whereas others preserve their delicate K-feldspar – silica intergrowth texture.

More recently, this work has been extended to studies of other zircon samples, including detailed investigations of zircon internal structures and trace element distributions (Grange et al., 2009, 2013; Nemchin et al., 2008, 2009a; Timms et al., 2012; Hopkins and Mojzsis, 2015; Bellucci et al., 2016, Crow et al., 2017). Other U-bearing accessory minerals common in a range of lunar samples have also been studied recently, for example Zr-rich baddeleyite, zirconolite and tranquillityite (Rasmussen et al., 2008) as well as the Ca-phosphates, apatite and merrillite (Nemchin et al., 2009b; Snape et al., 2016a).

In contrast, minerals that are traditionally viewed as relatively low in U, which are mostly represented by major silicate phases in lunar samples, have been investigated as multigrain fractions using techniques that involve chemical separation of U and Pb and isotope analyses using Thermal Ionisation Mass Spectrometry (TIMS). A similar approach has been used in the studies of whole rock samples. This research has highlighted the extremely radiogenic nature of lunar Pb, indicating significant early loss of Pb from the Moon compared to Earth (e.g. Premo et al., 1999) and isotopic resetting of a large number of samples at ca. 3.9 Ga (e.g. Tera et al., 1974). In particular Premo et al. (1999) indicated that a significant number of lunar highlands rocks show high $^{207}\text{Pb}/^{206}\text{Pb}$ ratios around 1.45, which requires sources with extreme μ -values ($^{238}\text{U}/^{204}\text{Pb}$) in excess of 500 existing for prolonged periods of time since at least 4.36, but perhaps even since 4.46 Ga. They also suggested that ca. 3.9 Ga impacts contributed to the profound redistribution of Pb, probably resulting in substantial contamination of the rocks that formed from the sources with modest μ -values, such as for example Ferroan Anorthosite (FAN), by the highly radiogenic lunar Pb component. According to Premo et al. (1999), this mixing of Pb with different origins complicates extracting information about primary initial Pb isotope compositions in many

lunar rocks, especially because the composition and abundance of different mixing end members is often difficult to establish and can potentially vary between different grains in the same sample. The Pb deficit on the Moon, reflected in the low abundance of this element in many lunar samples, also makes analyses more difficult due to sample susceptibility to laboratory contamination. Contamination includes all of the Pb introduced to the samples during handling following their collection and delivery to the Earth, and diminishes the quality and reliability of chronological and other isotopic information.

Although the discussed nature of lunar Pb complicates the interpretation of obtained data, it also opens some possibilities that are not present themselves when studying less extreme Pb systems from the majority of planets and planetary bodies other than the Moon. Because of the low abundance of Pb on the Moon, many lunar rocks and minerals incorporated very little initial Pb during their formation. Importantly, sources of these rocks and minerals also appear to have low quantities of initial Pb, resulting in their Pb compositions being dominated by U decay and, therefore, being very radiogenic. As a consequence, Pb in lunar samples is dominated by a radiogenic component either formed from the *in situ* decay of U since the formation of the samples or, to a lesser degree, inherited from their sources. Even in minerals that are traditionally viewed as containing little to no U, isotopic compositions of Pb are often found to be radiogenic. This opens up an intriguing possibility to investigate lunar low-U minerals using ion probe-based techniques that, although significantly less precise than TIMS, have the advantage of high spatial resolution of analyses. They allow isotopic compositions measured on the scale of a few tens of micrometres within individual grains in thin sections of the rocks where the petrographic context of the analyses can be established and contamination minimised by restricting analyses to parts of the grains away from the grain boundaries and fractures.

The aim of this paper is to demonstrate the potential of such small scale studies by investigating Pb isotopes in three K-feldspar rich clasts found in lunar breccia samples 14083 and 14303. Only once before has the ion probe technique been used to analyse Pb in lunar feldspars found in zircon bearing clasts in order to assess lunar initial Pb compositions and use those for the correction of zircon data (Compston et al., 1991), but the full potential of ion probe analyses in low-U minerals was never fully utilised after this first study. Nevertheless, Compston et al. (1991) recognised high $^{207}\text{Pb}/^{206}\text{Pb}$ in feldspars (1.5 on average, but as high as 1.65 in one of the samples), similar to that identified by Premo et al (1999). They attributed this Pb to initial crystallisation of “granite” magma. The younger clasts with ages

<4.0 Ga, determined by either coexisting zircon analyses (described by Meyer et al., 1996), or Rb-Sr and ^{39}Ar - ^{40}Ar methods where zircon is not present, required a two stage Pb evolution model with at least one high μ stage, to explain this extreme $^{207}\text{Pb}/^{206}\text{Pb}$. The initial Pb composition of older clasts with >4.3 Ga ages were disturbed by addition of external Pb most likely during some overprinting thermal events (impacts). This initial study demonstrates that the Pb isotope investigation of lunar feldspars and other rock forming minerals clearly deserves further attention as it has a potential to become an additional tool in the studies of magmatic and impact history of the Moon.

The somewhat modified approach in the present study takes advantage of improvements in ion probe instrumentation during last three decades, which make it possible to increase precision of individual analyses and also utilises minerals other than feldspars. It also does not specifically seek to investigate only inclusion-free feldspars assuming that, within a relatively large pool of analyses, some will be randomly targeting areas that are inclusion-free and, therefore, will closely approximate initial Pb compositions in the samples. Combination of these modifications allows estimation of the time of Pb homogenisation in individual clasts with uncertainties ranging between a few tens of million and just a few million years without the need to rely on the independent chronometers, as well as to characterise the Pb composition of the clasts at this time. This extends the pool of lunar samples available for chronological studies using U-Pb system beyond those containing traditional chronometers such as zircon and phosphates.

2. Analytical technique

Thin sections 14303, 49 and 14083, 35 were prepared at NASA Johnson Space Center. They were cleaned with ethanol before being carbon coated for Scanning Electron Microscope (SEM) analysis. Backscattered Electron (BSE) imaging and Energy Dispersive Spectroscopy (EDS) element mapping of the thin sections was performed with a combination of a Tescan MIRA3 FEG-SEM fitted with an Oxford Instruments AZtec 2.2 EDS/EBSD acquisition system and an 80 mm² SDD detector at Curtin University, and a Quanta 650 FEG-SEM and accompanying Oxford Instruments EDS detector at Stockholm University. The EDS mapping and analysis of the samples was conducted with an electron beam accelerating voltage of 20 kV at a working distance of 10 mm. The BSE and element maps

were then used to identify phases such as plagioclase, K-Feldspar and pyroxene for SIMS analysis.

Following SEM-based characterisation of the samples, and prior to the SIMS analyses, the samples were cleaned with ethanol before adding a 30 nm thick gold coat. The Pb isotopic compositions of various phases were determined over two analytical sessions using the CAMECA IMS 1280 ion microprobe housed at the Centre for Microscopy, Characterisation and Analysis (CMCA) at the University of Western Australia, using a methodology similar to that outlined in previous studies (Whitehouse et al. 2005; Nemchin et al. 2011; Bellucci et al. 2015). Apertures in the primary column were used to generate a slightly elliptical O_2^- spot of about 30 μm diameter (beam current of ca. 19-20 nA). Prior to each measurement, an area of 35 μm around the spot location was rastered by the ion beam for 60 seconds to remove the gold coating and minimise possible surface contamination. The instrument was operated in high-transmission mode, corresponding to a transfer magnification of 160 $\times$. In this mode, the field aperture size was chosen to limit the field of view on the sample surface (i.e. the area from which ions were admitted to the mass spectrometer) to be bigger than the unrastered spot but smaller than the rastered area, further minimising the possibility of surface contamination. Pb-isotopes (^{204}Pb , ^{206}Pb , ^{207}Pb , ^{208}Pb) were measured simultaneously in multi-collector mode using four low-noise (<0.01 counts per second) ion counting electron multipliers (Hamamatsu 416) with electronically gated deadtimes of 60 ns. Background counts for each channel were measured at the beginning and the end of each session. The average background counts for each of the two sessions were used to correct the sample analyses. The mass spectrometer was operated at a nominal mass resolution of 4860 ($M/\Delta M$), sufficient to resolve Pb from known molecular interferences. An NMR field sensor regulated the stability of the magnetic field.

Analyses of the USGS basaltic glass reference material, BCR-2G, were used to correct for mass fractionation and detector gain calibration (Table 1). The BCR-2G analyses were all within $\pm 5\%$ of the values determined by Woodhead and Hergt (2000), and these deviations were used to generate correction factors for the data. Data were then processed using in-house SIMS data reduction spreadsheets and the Excel add-in Isoplot (version 4.15; Ludwig 2008).

Obtaining accurate U/Pb in SIMS analysis requires correction for matrix effects using established standards characterised by independent techniques (usually TIMS). There are no U/Pb standards for rock forming minerals and for some, such as feldspars that typically do

not contain any U, finding and characterising standards would be impossible. Our initial Pb-Pb investigation of Apollo basalts (Snape et al., 2016) suggested that uncorrected U/Pb are correlated with the proportion of *in situ* accumulated Pb obtained from the analyses of different minerals in the samples. Based on this initial conclusion and taking into account difficulties with obtaining corrected U/Pb in rock forming minerals and mixtures of different minerals U analysis was not included in this new study. Nevertheless, BSE and EDS imaging of several areas within the clasts investigated in this study was conducted at Curtin University after SIMS analyses to determine potential hosts of *in situ* accumulated Pb in the analysed samples. Characterisation of mineral inclusions was done via high-resolution BSE images combined with EDS mapping collected using a beam acceleration voltage of between 5 and 10 kV to yield small enough beam activation volumes to facilitate phase identification of small grains. Analysis of EDS data collected in AZtec utilized TruMap, which is an algorithm for peak deconvolution and background removal that results in more accurate element maps.

3. Samples

3.1. Sample 14083

Breccia 14083 is paired with sample 14082. It was collected from the rim of Cone crater. 14083 is clast rich compared to 14082, but both are different from the main population of Apollo 14 breccias being enriched in plagioclase (An₇₀₋₉₆) and having light coloured matrices containing glass (McGee et al., 1977).

The two clasts investigated in the thin section 14083, 35 (Fig. 1 and 2) are less than 1 millimetre in size and different in composition and texture, although both contain K-feldspar. The first contains an assemblage of 100 to 500 micrometre grains of Ca-Fe-rich pyroxene, plagioclase, K-feldspar and silica. It also has a single phosphate grain (ca. 50 µm in size). The mineralogy of this clast is indicative of quartz-monzo-diorite (QMD) compositions. The second clast is composed mostly of fine intergrowths of K-feldspar and silica, although larger elongated crystals (200-500 µm in length) of silica, as well as similar sized crystals of ilmenite and plagioclase, are present on one side of the clast. In texture and mineralogy this clast is similar to felsite clasts found in other lunar breccias (e.g. Warren et al., 1987).

High resolution BSE images and EDS maps of small areas within both clasts reveal presence of more complex mineral assemblages than those visible in the overview images of the clasts. An area of about 80x80 µm imaged in the first clast, at the boundary of the large

plagioclase, silica and K-feldspar crystals (Fig.1) shows relatively small (ca. 20 μm) grains of Ca-Fe-rich-pyroxene, plagioclase and K-feldspar surrounded by silica (Fig.3). In addition, similarly sized (ca. 20 μm) aggregates composed of pyroxene, ilmenite, zircon and (to a lesser degree) Ca-phosphate are also present within the silica rich areas of the image (Fig.3a). Some of these aggregates appear to represent decomposition of pre-existing mineral phases, preserving their original elongated shape (Fig.3b). They contain granular masses less than 1 to a few μm of zircon and ilmenite grains, with some zircon also forming rims around ilmenite granules. In other aggregates zircon appear to form at the boundaries between slightly larger (5-10 μm) pyroxene and ilmenite crystals, forming a texture that could be viewed as evidence for recrystallization, but could be also interpreted as a primary crystallisation from the melt (Fig.3c).

Two areas of about 50x50 and 25x25 μm have been imaged in the second clast. The first one shows silica and K-feldspar intergrowths with three zircon, ilmenite, Ca-phosphate aggregates with ilmenite preserved as isolated islands surrounded by zircon, suggesting breakdown of pre-existing grains that were 10-15 μm in size (Fig.4a). The second image shows more a complex assemblage comprising silica, feldspar and pyroxene grains (Fig.4b). Unlike the first clast where pyroxene is Fe-rich, pyroxene in the second clast contains both Fe and Mg in addition to Ca and shows zonation with increasing Mg and Ca content towards the boundaries with other minerals. The image also shows a zircon rich granular aggregate (ca. 15 μm long and less than 5 μm wide) with some ilmenite and baddeleyite. The latter appears to form remnants inside a ca. 3 μm zircon grain.

3.2. Sample 14303

Breccia 14303 is an example of the clast rich crystalline matrix breccias typical of those at the Apollo 14 landing site. A large (more than 1 cm) “granite” clast, containing K-Ba-feldspar, plagioclase, olivine and K-rich glass, was reported in the sample by Warren et al. (1983). Shih et al. (1993; 1994) obtained a Rb-Sr age of 3.95 ± 0.38 Ga for this clast. Meyer et al. (1996) investigated another clast found in section 14303, 49, containing zircon grains with an age of about 4.3 Ga. Four large (more than 100 μm) zircon crystals in this clast were also studied by Nemchin et al. (2008) and Grange et al. (2013), confirming that the age of these grains are within uncertainty of the Rb-Sr age of the clast, which is also likely to be the crystallisation age of the rock represented by this clast. These studies found evidence for partial Pb loss from some parts of the grains resulting in dispersed U/Pb. Strong fracturing of

the sample (Fig.5) and zircon grains probably contributed to this Pb loss. In addition to zircon, this clast contains minor ilmenite, plagioclase and pyroxene. The latter is Fe-Mg pyroxene, but the grains have Ca-rich rims. The main constituent of the clast, however, is a mixture of silica, K-feldspar and K-rich glass. The latter is developed at the boundaries between silica and K-feldspar (Fig.6a).

High resolution imaging of several areas (100 to 200 μm in size), indicates the presence of small (few μm) zircon fragments and Ca-phosphate crystals. However, unlike two clasts in 14083 where these grains are very abundant and persist throughout the entire volume of the clasts, the distribution of zircon and Ca-phosphate in 14303 is very irregular. Small ($\sim 1 \mu\text{m}$) zircon fragments are mostly found near the large zircon grains identified in the sample, while Ca-phosphate grains ($\sim 1 \mu\text{m}$) form groups located irregularly in different parts of the clast. They are included by K-feldspar along with pyroxene hopper crystals of similar size and larger ilmenite grains (Fig.6b). Significant proportion of area of the thin section containing K-feldspar appears to be free of inclusions (Fig.6a), but the K-feldspar in this section is extremely inhomogeneous as evident from the BSE images (Fig.6a).

4. Assumptions related to the interpretation of lunar Pb

Snape et al. (2016b) obtained ages of several lunar basalt samples using SIMS, making an assumption that Pb isotope composition measured in any particular SIMS spot generally reflects a three component mixture. These components are represented by (i) Pb accumulated as a result of U decay in the sample after its formation, (ii) initial lunar Pb incorporated from the source into the sample during its formation and (iii) terrestrial (laboratory) contamination added to the sample during various stages of processing since its delivery by Apollo astronauts. The presence of these components in different proportions in the total Pb analysed in each spot results in the random distribution of analyses within a triangle when plotted on $^{207}\text{Pb}/^{206}\text{Pb}$ vs. $^{204}\text{Pb}/^{206}\text{Pb}$ diagram (Fig.7a). The pure in situ accumulated Pb is located at the vertical axis in the lower left corner of the triangle, while pure initial lunar Pb composition is represented by the top corner. Line between these two corners defines all possible lunar compositions unaffected by contamination. Addition of terrestrial contamination will shift analytical points to the right of the lunar Pb line towards the lower right corner of triangle (Fig.7a), which corresponds to the Stacey and Kramers model composition for modern terrestrial Pb (Stacy and Kramers, 1975). Naturally, the possible range of compositions

originating from contamination is not restricted to the single isotope composition reflected in the modern Stacey and Kramers Pb. However, all possible compositions of terrestrial Pb, including older Pb as illustrated with the Pb evolution curve in Figure 7a and those of some terrestrial basalts that can be more radiogenic than is permitted by a single stage evolution from the primitive meteoritic Pb (Canyon Diablo troilite, CDT), will all result in the deviation of analytical points to the right of the lunar Pb line. Consequently, the task of identifying lunar Pb compositions in any sample can be achieved by the filtering of obtained data set to identify the leftmost side of the triangle, i.e. finding analyses that define steepest leftmost line on the $^{207}\text{Pb}/^{206}\text{Pb}$ vs. $^{204}\text{Pb}/^{206}\text{Pb}$ diagram.

The assumption of three component mixing appears to be valid for the mare and KREEP (from high K, REE and P) basalts (e.g. Snape et al., 2016b) as these basalts are fresh, crystallised relatively fast near the lunar surface and formed after the major period of lunar bombardment at about 3.9 Ga, i.e. have never been modified and/or reheated after their formation. The applicability of this assumption is less obvious for the impact breccia samples that represent a random mixture of fragments acquired in the target and are therefore expected to have different ages and post formation history. In addition these fragments would be variably reworked during the impacts that formed these breccias, mobilising but not necessarily homogenising Pb in the samples. Meteoritic Pb originating in the impactor can be also added to the samples. However, while there are groups of meteorites such as angrites characterised by high bulk μ -values that can deviate significantly from the Canyon Diablo troilite (CDT) Pb composition at the time of lunar impacts, the majority of most common meteorite types have primitive Pb compositions close to CDT. Therefore, unless Pb was completely homogenised in the breccia sample, addition of different proportions of meteoritic Pb would have a similar effect to that of terrestrial contamination, shifting individual analyses to the right of the lunar Pb line (Fig. 7a).

Regardless of issues highlighted above, analysing individual clasts helps to avoid at least some of the problems associated with the study of Pb isotope compositions in lunar breccias. Importantly a single lithic clast must represent a host rock that has a specific formation age and initial Pb composition, which even if unknown, removes uncertainty of dealing with the possibility of multiple lithologies of differing ages mixed in the breccia. The evolution of Pb in such clasts can be illustrated by a three stage model, describing accumulation of radiogenic Pb isotopes in the source of the rock (stage one), further growth in the rock represented by the clast (stage two) and final accumulation of Pb in the clast after it was incorporated into the

breccia (Fig.7b and c). In the particular case illustrated in Figure 7, model parameters are taken as follows:

- a) the source of the rock is evolving from CDT composition from the time of Solar System formation and has μ -value of 600;
- b) the age of the rock is taken as 4.35 Ga, based on the large number of zircon grains analysed in lunar samples giving this age, which probably reflects their crystallisation from magma enriched in incompatible elements (e.g. Nemchin et al., 2008; Crow et al., 2017);
- c) clast formation time is defined as 3.9 Ga, i.e. age determined for large number of breccia samples (e.g. Snape et al., 2016a).

This model is definitely a simplification. In particular, the first stage of the model can be split further into at least three separate steps: (i) evolution of Pb after Solar System condensation but before the formation of the Moon, (ii) evolution of Pb after lunar formation but prior to global differentiation of the Moon and (iii) evolution of Pb in the source of the rock represented by the clast. Nevertheless, exclusion of this additional complexity has no bearing on the observation that the isochron at the second stage is defined by Pb compositions of different (i.e. with distinct μ -values) constituents of the rock represented by the clast is steeper and falls above the line drawn between initial Pb composition measured in the clast and CDT composition in $^{207}\text{Pb}/^{206}\text{Pb}$ vs. $^{204}\text{Pb}/^{206}\text{Pb}$ plane, irrespective of parameters used to constrain the model (Fig.7 b and c). It also means that this isochron will plot outside (i.e. above) the triangle defined by the three component mixture discussed earlier and, if present, can be identified given a sufficient number of analyses plotting near the top end of the $^{207}\text{Pb}/^{206}\text{Pb}$ vs. $^{204}\text{Pb}/^{206}\text{Pb}$ diagram, indicating incomplete homogenisation of Pb in the clast during its formation. Importantly, filtering of analyses to identify a steepest leftmost boundary (line) of the region defined by the analytical points in the $^{207}\text{Pb}/^{206}\text{Pb}$ vs. $^{204}\text{Pb}/^{206}\text{Pb}$ plot, can still provide the time of the clast formation and the lower limit for the most radiogenic Pb attained in the clast's parent rock at the time of brecciation/impact, even if some analyses representing uncontaminated lunar Pb (grey triangle in Fig.7c) might be inadvertently rejected when located on the plot where it can be also interpreted as addition of terrestrial component.

The only apparent case where the proposed filtering approach might produce spurious results is when studied samples contain U-rich minerals that have incompletely reset U-Pb systems during the impact. Analysing these minerals, or partly overlapping them with the

analytical spots, will result in a scatter of the analyses along the vertical axis in the $^{207}\text{Pb}/^{206}\text{Pb}$ vs. $^{204}\text{Pb}/^{206}\text{Pb}$ plot (Fig. 7c) and intercept ages reflecting a random mix of the true age of the clast and the age of the rock represented by the clast. This problem is common for a range of chronometers. For example, the zircon U-Pb system is generally considered to be very resistant to any type of post-formational disturbance, but there are frequent examples of partial Pb loss from zircon in the literature (e.g. Grange et al., 2013, as related to the lunar zircon). Typically, the ability to reproduce the same age from multiple analyses of the same zircon grain or analyses of multiple grains increases confidence that the obtained age represents the true age of a real process. Similarly, finding a match between the ages of different clasts within a breccia sample and/or from different samples of a similar origin would improve confidence that partial resetting of U-bearing minerals does not contribute significantly to the obtained chronological data.

5. Pb-Pb results

The Pb isotope data obtained for all three clasts (Table 1) are distributed within a triangular field in $^{207}\text{Pb}/^{206}\text{Pb}$ vs. $^{204}\text{Pb}/^{206}\text{Pb}$ coordinate space (Fig. 8). The lower left corner of the triangle for all clasts is located on the vertical axis and corresponds to a $^{207}\text{Pb}/^{206}\text{Pb}$ ratio of about 0.4. It is defined by some analyses of K-feldspar as determined from the initial broad scale EDS imaging of all three samples (Fig. 1 to 3) in addition to several plagioclase analyses in the 14083 clasts 1 and 2, as well as pyroxene and Ca-phosphate analyses in the case of clast 1. The lower-right corner fits the modern terrestrial Pb model composition (Stacey and Kramers, 1975), but only represented by data from the clast from the sample 14303 where a majority of pyroxene and ilmenite analyses are shifted towards relatively non-radiogenic Pb compositions. The top corner for all three clasts is defined by the analyses with the highest $^{207}\text{Pb}/^{206}\text{Pb}$ (at about 1.5) and intermediate $^{204}\text{Pb}/^{206}\text{Pb}$ ratios. It is defined predominantly by plagioclase analyses in clast 1 of 14083, some K-feldspar analyses in the 14303 clast and both minerals in clast 2 of 14083. Importantly, all data obtained in this study, with the exception of one plagioclase analysis in clast 2 of sample 14083, 35 and three (one pyroxene, one K-feldspar and one ilmenite) analyses in the sample 14303, 49, lie within the triangles defined by the three components described above, suggesting efficient homogenisation of Pb on the scale of the analysed clasts. Consequently, the simplest interpretation of the observed distribution in the investigated clasts is mixing of these main components in different proportions.

When filtered to remove analyses that are presumably affected by terrestrial Pb contamination, the data (Table 1) for each sample define a statistically significant isochron (probability of fit >0.05) on a $^{207}\text{Pb}/^{206}\text{Pb}$ vs. $^{204}\text{Pb}/^{206}\text{Pb}$ plot (Fig. 9). These isochrons determine the best estimate for the equilibration age of each clast by projecting to the $^{207}\text{Pb}/^{206}\text{Pb}$ of the radiogenic end member at $^{204}\text{Pb}/^{206}\text{Pb} = 0$. The ages calculated using this approach for clasts 1 and 2 in 14083, 35 are 3.920 ± 0.005 Ga and 3.923 ± 0.028 Ga, respectively, while the clast in 14303, 49 has an age of 3.920 ± 0.013 Ga (uncertainties at 95% confidence level). The analytical points on the other end of the isochrons (i.e. with the highest $^{207}\text{Pb}/^{206}\text{Pb}$) place a lower limit on the $^{207}\text{Pb}/^{206}\text{Pb}$ of the initial Pb in the clasts, which represents the initial compositions for the post-impact ingrowth of Pb in the clasts. The $^{204}\text{Pb}/^{206}\text{Pb}$ and $^{208}\text{Pb}/^{206}\text{Pb}$ can be also estimated from the obtained $^{207}\text{Pb}/^{206}\text{Pb}$. The two clasts from the sample 14083 give very similar sets of values ($^{204}\text{Pb}/^{206}\text{Pb} = 0.0029 \pm 0.0006$ and 0.0027 ± 0.0003 , $^{207}\text{Pb}/^{206}\text{Pb} = 1.48 \pm 0.02$ and 1.48 ± 0.01 , $^{208}\text{Pb}/^{206}\text{Pb} = 0.86 \pm 0.03$ and 0.85 ± 0.01 for two clasts, respectively; uncertainties are 2σ). The values for the clast from the sample 14303, however, are slightly higher ($^{204}\text{Pb}/^{206}\text{Pb} = 0.0037 \pm 0.0002$, $^{207}\text{Pb}/^{206}\text{Pb} = 1.546 \pm 0.007$, $^{208}\text{Pb}/^{206}\text{Pb} = 0.90 \pm 0.07$).

6. Discussion

6.1. Nature of *in situ* Pb in K-feldspar

K-Feldspar in many rocks in general and in lunar samples in particular is considered to be a host of Pb, while not concentrating any significant quantities of U (e.g. Compston et al, 1991 for lunar feldspars). However, significant number of analyses of K-feldspar in three investigated clasts show high proportion of Pb accumulated *in situ* after the formation of breccia samples. For the clast in the sample 14303, the entire range of lunar Pb compositions, after filtering analyses affected by contamination, is defined by K-rich phases (presumably K-feldspar) as identified by EDS (Fig.3). These analyses are most likely mixtures of K-feldspar, silica intergrown with the feldspar and K-rich glass formed at the boundaries between the feldspar and silica, as evident from the detailed imaging of the samples (Fig.6). In any case, the presence of *in situ* accumulated Pb also implies the presence of various, but significant quantities of U within the areas targeted by analyses in all clasts, suggesting the presence of phases other than K-feldspar within the analytical spots. Persistence of micro-inclusions of U-bearing minerals in two clasts from the sample 14083 explains variability of observed Pb compositions in K-feldspar grains and other major minerals present in these

clasts. However, while these U-rich accessory phases are also present in the clast from 14303, they are less abundant throughout the investigated thin section. Therefore, K-rich glass is likely to be an important carrier of U in this clast. Importantly, relationships within Th-U-Pb system, indicated by ^{208}Pb - ^{207}Pb - ^{206}Pb (Fig. 10) suggest more than one U and Th carrier in each of the studied clasts. Plotting Pb-Pb data filtered for contamination on $^{208}\text{Pb}/^{206}\text{Pb}$ vs $^{207}\text{Pb}/^{206}\text{Pb}$ diagram shows tight group of analyses at high $^{207}\text{Pb}/^{206}\text{Pb}$ at about 1.5 with the corresponding $^{208}\text{Pb}/^{206}\text{Pb}$ at about 0.8-0.9. This $^{207}\text{Pb}/^{206}\text{Pb}$ corresponds to the upper end of the isochrons in the $^{207}\text{Pb}/^{206}\text{Pb}$ vs $^{204}\text{Pb}/^{206}\text{Pb}$ coordinates and characterises initial Pb composition at the time of the clasts incorporation into the breccias. The limited range of $^{208}\text{Pb}/^{206}\text{Pb}$ values for these analyses indicates an efficient Pb homogenisation at the time of breccia formation. Analyses with lower $^{207}\text{Pb}/^{206}\text{Pb}$ containing more *in situ* accumulated Pb show divergence of $^{208}\text{Pb}/^{206}\text{Pb}$ towards higher and lower values as compared to the initial Pb compositions (Fig.10). This indicates presence of phases with both high and low Th/U ratios. Taking 3.9 Ga as the period of time necessary to acquire the observed compositions, the phase enriched in Th relative to U should have a Th/U ratio in excess of 5, whereas in the low Th/U mineral this ratio must be lower than 1. Both Zr-rich phases and Ca-phosphates identified in the analysed samples include minerals that can provide the required range of Th/U to explain the measured values. Goreva and Burnett (2001) investigated Th and U variations in the samples of ordinary chondrites and found that coexisting apatite and merrillite have diverse Th/U (around 1 and 11 respectively). Similar observations have been made for Apollo 14 breccia samples by Snape et al. (2016a). Zircon is usually depleted in Th relative to U, although Th/U in excess of 1 are also found in some grains (e.g. Hoskin and Schaltegger, 2003). In contrast zirconolite and to some degree tranquillityite are Th-rich (Rasmussen et al., 2008).

6.2. Significance of Pb-Pb ages

The presence of U-bearing phases, especially highly diffusion-resistant zircon, among the assemblage of largely U-poor minerals in the breccia samples can be detrimental for the age determinations using the Pb-Pb isochron approach, if the Pb isotope compositions in these phases have been not homogenised completely with the rest of the mineral assemblage. If this is the case, constraining lines using different minerals might at best highlight mixing of Pb ratios with different evolution paths and no age significance, rather than define true isochrons. The problem can be illustrated using the clast investigated in sample 14303, which

also contains zircon that appears to be older than the age determined from the Pb-Pb data (Fig.11, Table 2). The $^{238}\text{U}/^{206}\text{Pb}$ obtained from multiple analyses of three large (>100 μm) zircon grains and corrected for the non-radiogenic Pb contribution using modern Stacy and Kramers (1975) Pb composition (assuming that the source is laboratory contamination) show variation resulting in a scatter of analytical points from slightly reverse discordant to slightly discordant when plotted on the concordia diagram (Fig.11a). It is difficult to determine if this scatter is real and a reflection of relatively young (>3.9 Ga) Pb loss from the grains, or a result of analytical issues associated with the need for using external standards to correct for matrix effects when calculating $^{238}\text{U}/^{206}\text{Pb}$. In contrast, the variation of $^{207}\text{Pb}/^{206}\text{Pb}$ ages beyond the analytical uncertainty suggests that a genuine age heterogeneity is present in the analysed zircon grains (Fig.11a, b). The distribution of ^{204}Pb uncorrected analyses on a $^{207}\text{Pb}/^{206}\text{Pb}$ vs $^{204}\text{Pb}/^{206}\text{Pb}$ plot (Fig.11b) indicates that some analyses (with high $^{204}\text{Pb}/^{206}\text{Pb}$) have been affected by laboratory contamination, whereas scatter in $^{207}\text{Pb}/^{206}\text{Pb}$ observed within the low $^{204}\text{Pb}/^{206}\text{Pb}$ analyses suggests partial Pb loss from zircon grains. However, there is no indication in the data distribution that supports addition of lunar initial Pb to the zircon grains at 3.9 Ga. The maximum $^{207}\text{Pb}/^{206}\text{Pb}$ ages (corrected using the Stacey and Kramers (1975) Pb composition) are close to 4.33-4.35 Ga and define the minimum time of formation of the granite represented by this clast, whereas the minimum $^{207}\text{Pb}/^{206}\text{Pb}$ ages at about 4.23-4.26 Ga define the upper limit for the time when the U-Pb system in the zircon grains was reset. Importantly, including these zircon analyses when calculating a Pb-Pb isochron would rotate the best fit line towards higher intercept of the vertical axis in $^{207}\text{Pb}/^{206}\text{Pb}$ vs $^{204}\text{Pb}/^{206}\text{Pb}$ plot, resulting in the older age estimate obtained from such a fit. Nevertheless, taking into account the uneven distribution of zircon throughout the clast in 14303, where it is confined to three large grains and smaller fragments near these three grains, it is highly unlikely that zircon was sampled in the Pb-Pb analyses presented here. It is possible that small Ca-phosphate grains that are more abundant in the investigated thin section were partly incorporated in these analyses, but independent studies of Ca-phosphates in Apollo 14 breccias (Snape et al. 2016a) indicate their profound resetting during a 3.9 Ga impact and their Pb isotope system is considered to be a part of Pb homogenisation experienced by the clast during this impact. Consequently, the age of 3.920 ± 0.013 Ga obtained from Pb-Pb isochron is interpreted as the best estimate of the time of impact that resulted in incorporation of the “granite” clast into the breccia sample. The minimum age of

the “granite” precursor is determined by the maximum $^{207}\text{Pb}/^{206}\text{Pb}$ ages of zircon at about 4.33-4.35 Ga.

In contrast to 14303, some analyses of the two clasts in 14083 clearly overlap with those of U-bearing minerals. However, these minerals in 14083 are represented by relatively small (few μm in size) grains that also show textures compatible with the decomposition or recrystallization of pre-existing crystals. Consequently, they are likely to either have formed during the impact event that brought these clasts together in the breccia, or had their U-Pb systems profoundly reset during this impact. This conclusion is also supported by the similarity of the Pb-Pb ages obtained for these clasts, which indicates possible Pb homogenisation across the thin section and perhaps throughout the entire sample. These ages are also similar to that determined for the clast from 14303 and to the U-Pb ages obtained for the phosphates from a number of Apollo 14 breccia samples. The latter are interpreted as representing resetting of the U-Pb system during the impact that formed those breccias (Snape et al. 2016a). Consequently the Pb-Pb ages of the clasts are also likely to reflect mobilisation and re-equilibration of Pb isotopes in the rock fragments as a result of this impact.

A 3.92 Ga impact event is, therefore, interpreted as being responsible for the formation of the clasts by the fragmentation of the source granites in the target region and incorporation of this material into the breccia samples, as well as for mobilising Pb and resulting in what appears to be a complete resetting of the Pb-Pb system in all minerals, with the exception of the large zircon grains in the sample 14303. These zircon grains have experienced only partial Pb loss and it is possible that the lost radiogenic component has been mixed and effectively homogenised with the rest of Pb present in the sample. Although there is no similarly unambiguous evidence (i.e. older zircon grains) for the pre 3.92 Ga formation of the two clasts investigated in sample 14083, their origin in the target region prior to breccia assembly follows from textural evidence (i.e. they are clasts in an impact melt breccia).

The 3.92 Ga ages on the Moon in general, and when associated with the samples from the Apollo 14 landing site in particular, have been interpreted as being related to the formation of the Imbrium basin (e.g. Liu et al., 2012, Snape et al., 2016a and references therein). Consequently, the small set of data presented here hints that in the aftermath of the Imbrium impact the Pb-Pb systems of the impact breccias were profoundly homogenised across multiple components with different origins. This is especially evident at the sample scale

where two clasts from the same thin section of 14083 have both ages and estimated initial Pb compositions that are indistinguishable within the uncertainties. It appears to be more complex when the different samples analysed here are compared (i.e. 14303 and 14083). While the ages of the clast homogenisation in these two samples are similar, the initial Pb values determined for two samples differ, suggesting possible variability of initial Pb on the scale of the landing site, probably related to the range of lithologies being present at the target area of impact.

6.3. Initial Pb compositions

The initial Pb compositions determined from the lines fitted through the filtered Pb data obtained for the 14303 and 14083 samples have the highest $^{207}\text{Pb}/^{206}\text{Pb}$ observed in lunar samples (e.g. Tera et al, 1974; Premo et al., 1999). They are also highest obtained so far for Apollo 14 breccias, with the exception of data acquired by Compston et al. (1991) for K-feldspars found in some Apollo 14 samples and often associated with zircon grains, similar to those described here in the clast from the section 14303, 49. Compston et al. (1991) did not attempt to construct mineral Pb-Pb isochrons for their data, concentrating their effort on the best, large K-feldspars that are free of inclusions. As a result, their analyses show low to non-existent U and Th and represent pure initial Pb compositions. Compston et al. (1991) assumed that highly radiogenic Pb in the K-feldspars reflects primary magmatic compositions at the time of zircon (in the rocks represented by the clasts) crystallisation. While this conclusion can be re-evaluated based on the new data presented here, the Pb compositions of those K-feldspars can be used as estimates of initial values to compare with the initial values obtained for 14303, 49 and 14083, 35, with the view that all these compositions probably reflect homogenisation that took place in the samples at about 3.92 Ga (note that only samples included in the further discussion are those where mean initial values were provided by Compston et al, 1991). A limitation on this comparison follows from the $^{204}\text{Pb}/^{206}\text{Pb}$ values being listed by Compston et al. (1991) only to the third decimal place, although some compositions can be estimated with higher precision retrospectively from their plots.

Pb compositions obtained here and by Compston et al. (1991) show range significantly larger than analytical uncertainty (Fig.12). There is also visible correlation between $^{204}\text{Pb}/^{206}\text{Pb}$, $^{207}\text{Pb}/^{206}\text{Pb}$ and to some degree $^{208}\text{Pb}/^{206}\text{Pb}$, resulting in the trends with positive slopes in $^{207}\text{Pb}/^{206}\text{Pb}$ vs. $^{204}\text{Pb}/^{206}\text{Pb}$ and $^{208}\text{Pb}/^{206}\text{Pb}$ vs. $^{204}\text{Pb}/^{206}\text{Pb}$ coordinates,

although there is also some scatter of compositions mostly defined by analyses derived from four different sections of 14303, which might indicate incomplete homogenisation of Pb isotope composition across the sample or incomplete filtering of the data sets to remove contamination. Nevertheless, all of these analyses from 14303 have the highest measured Pb isotope ratios amongst the Apollo 14 samples, while the Pb composition determined for 14321, 1027 is characterised by the lowest, with all other clasts having intermediate $^{204}\text{Pb}/^{206}\text{Pb}$, $^{207}\text{Pb}/^{206}\text{Pb}$ and $^{208}\text{Pb}/^{206}\text{Pb}$ values (Fig.12).

The observed correlated variation in isotope compositions can potentially reflect some Pb accumulated from *in situ* U decay after 3.9 Ga homogenisation of the clasts in the breccia samples, although analyses of feldspar from the sample 14321, 1027 which would have the largest contribution of this *in situ* Pb, if this explanation is correct, do not show U or Th signals in excess of just a few counts per second (as compared to 10 to 30 thousand counts per second for ^{206}Pb , Compston et al. 1991). Consequently, a better explanation is that the observed variation reflects a real range of initial compositions in the Apollo 14 breccia samples. Regardless of the exact interpretation of the initial Pb compositions obtained for Apollo 14 breccias, they make the best currently available estimate of the range of Pb compositions of Fra-Mauro formation (Imbrium impact ejecta, exposed at the landing site) at about 3.92 Ga. It also defines an average composition of source of this ejecta (i.e. the impact target rock) at the time.

6.4. Apollo 14 breccias and the evolution of lunar Pb

The estimated range of Pb isotope compositions in Apollo 14 breccias could be exaggerated by incomplete filtering of the datasets, resulting in some of the remaining analyses included in the initial Pb calculation containing a small proportion of Pb derived from either laboratory contamination or *in situ* U decay after the clasts have been incorporated into the breccia samples. Nevertheless, assuming that most of the observed features, such as the variability of the compositions outside of the analytical uncertainties and the steep trend shown by the data in $^{207}\text{Pb}/^{206}\text{Pb}$ vs $^{204}\text{Pb}/^{206}\text{Pb}$ coordinates, reflect real differences between the samples, some limits can be placed on the Pb isotope evolution of the samples and their sources.

Compston et al (1991) were able to explain most of their Pb data using two stage Pb evolution models with the first stage starting at CDT composition. In some cases, even one

stage was sufficient to explain observed Pb isotope values. For some samples the first stage can involve low μ -reservoir, while the second stage must be always high μ , mostly in excess of 1000. Compston et al (1991) also noted that for several investigated samples second stage must start no later than at about 4.35 Ga and for a number of other samples this age can also be used as the time separating two stages in Pb evolution. While highlighting the possibility, they were careful not to imply explicitly that this age might represent the time of a significant differentiation event on the Moon. However, new isotope data obtained during the last several years strongly support 4.36-4.38 Ga as a time of major differentiation (Borg et al., 2011; McLeod et al., 2014; Gaffney and Borg, 2014; Snape et al., 2016b), in line with the original observation of Compston et al. (1991). In particular, ^{142}Nd - ^{143}Nd , Lu-Hf and Pb isotope studies of both mare basalts and KREEP rich rocks suggest that this age is likely to be the time of the voluminous appearance of the enriched (KREEP) materials on the Moon. Snape et al. (2016b) also modelled initial Pb composition and obtained a range of μ -values for this reservoir between approximately 2500 and 3500. Using these values, Pb isotope compositions obtained here and by Compston et al. (1991) can be explained as originating from enriched sources with the μ -values ranging from about 1500 to 5500 (Fig.13a). The $^{207}\text{Pb}/^{206}\text{Pb}$ variation shown by the samples would be then a reflection of the time of formation of felsic rocks represented by different clasts (model ages of these rocks). These constraints, however, follow an assumption that the obtained initial Pb values are acquired during the crystallisation of the rocks, similar to that made by Compston et al. (1991), while the interpretation advocated here involves re-homogenisation of Pb in the rocks during a ca. 3.92 Ga impact (or impacts) that brecciated the original rocks forming the clasts investigated in this study. If the assumption of an enriched reservoir forming on the Moon at about 4.36-4.38 Ga with the evolved initial Pb composition determined by Snape et al. (2016b) is correct, the model ages of the clasts from at least two samples (14303 and 14321) are younger than the zircon ages obtained independently for the same samples (**REFS**). The maximum $^{207}\text{Pb}/^{206}\text{Pb}$ ages of zircon at about 4.33-4.35 Ga in one of the clasts from 14303, described earlier, is interpreted as the minimum age of “granite” that is now represented by the clast. However, the model Pb age of this clast is estimated as ca. 4.08 Ga, whereas the model ages of three other clasts from the same sample, studied by Compston et al (1991), range from about 3.99 to 4.15 Ga (Fig.13a). The model Pb age of the clast from 14321 studied by Compston et al (1991) is near 3.88 Ga (Fig.13a), but these authors also refer to a 3.96 ± 0.02 Ga age obtained for zircon in this clast.

This age discrepancy can be reconciled and μ -values of the sources of the rocks represented by the clasts estimated within the interpretation that involves Pb homogenisation in the samples at about 3.92 Ga. The history of Pb accumulation in this case would include:

- (i) enriched source(s) of the rocks evolving from the model Pb composition determined by Snape et al. (2016b) between 4.36-4.38 Ga (time of KREEP formation on the Moon - t_0) and the zircon ages (t_1) of the respective samples (3.96 and 4.33-4.35 Ga) representing crystallisation of felsic rocks found as clasts in the studied samples. Possible Pb isotope compositions at the time of crystallisation would fall on a chord between the model Pb composition of Snape et al. (2016b) and purely radiogenic Pb formed between t_0 and t_1 (Fig.13b). These compositions can be expressed using the equation:

$$\left(\frac{^{207}\text{Pb}}{^{206}\text{Pb}}\right) = \frac{\left(\frac{^{207}\text{Pb}}{^{206}\text{Pb}}\right)_{t_0} - \frac{1}{137.88} \cdot \frac{e^{\lambda_{235} \cdot t_0} - e^{\lambda_{235} \cdot t_1}}{e^{\lambda_{238} \cdot t_0} - e^{\lambda_{238} \cdot t_1}}}{\left(\frac{^{204}\text{Pb}}{^{206}\text{Pb}}\right)_{t_0}} \cdot \left(\frac{^{204}\text{Pb}}{^{206}\text{Pb}}\right) + \frac{1}{137.88} \cdot \frac{e^{\lambda_{235} \cdot t_0} - e^{\lambda_{235} \cdot t_1}}{e^{\lambda_{238} \cdot t_0} - e^{\lambda_{238} \cdot t_1}}$$

- (ii) evolution of Pb in the rocks prior to homogenisation, culminating in the mixing of Pb from U-bearing and U-poor phases at 3.92 Ga and resulting in the initial Pb compositions determined in the clasts from the lines constrained in $^{207}\text{Pb}/^{206}\text{Pb}$ vs. $^{204}\text{Pb}/^{206}\text{Pb}$ coordinates using filtered analyses. All possible Pb compositions in the sample prior to mixing can be defined as a line between initial Pb estimated from analyses of each clast and purely radiogenic Pb formed between t_1 and the time of homogenisation t_2 (Fig.13b). This can be expressed using equation:

$$\left(\frac{{}^{207}\text{Pb}}{{}^{206}\text{Pb}}\right) = \frac{\left(\frac{{}^{207}\text{Pb}}{{}^{206}\text{Pb}}\right)_{t_2} - \frac{1}{137.88} \cdot \frac{e^{\lambda_{235} \cdot t_1} - e^{\lambda_{235} \cdot t_2}}{e^{\lambda_{238} \cdot t_1} - e^{\lambda_{238} \cdot t_2}}}{\left(\frac{{}^{204}\text{Pb}}{{}^{206}\text{Pb}}\right)_{t_2}} \cdot \left(\frac{{}^{204}\text{Pb}}{{}^{206}\text{Pb}}\right) + \frac{1}{137.88} \cdot \frac{e^{\lambda_{235} \cdot t_1} - e^{\lambda_{235} \cdot t_2}}{e^{\lambda_{238} \cdot t_1} - e^{\lambda_{238} \cdot t_2}}$$

606

607 The intersection of the two lines defined by these two equations constrained for each sample
 608 determines the ${}^{207}\text{Pb}/{}^{206}\text{Pb}$ and ${}^{204}\text{Pb}/{}^{206}\text{Pb}$ ratios that correspond to the initial Pb
 609 compositions of the rocks represented by investigated clasts, and can be used to estimate μ of
 610 their sources. Even though the propagated errors result in large and highly nonlinear
 611 uncertainties in the estimated μ -values, applying this calculation to two clasts from the
 612 samples 14321 and 14303 places the lower limit on the μ of their sources as ca. 6000 and
 613 6500, respectively. It is not possible to reach the observed Pb isotope compositions in these
 614 clasts if the μ -values are lower than 6000 and 6500. Similar constraints are difficult to make
 615 for other clasts because there is no independent estimate for the ages of the rocks represented
 616 by these clasts. Nevertheless, the initial Pb isotope compositions determined for these clasts
 617 from linear arrays constrained using the filtered analyses are characterised by higher
 618 ${}^{204}\text{Pb}/{}^{206}\text{Pb}$ ratios than those observed in 14321 and 14303. These higher ${}^{204}\text{Pb}/{}^{206}\text{Pb}$ ratios
 619 reflect lower μ -values in the sources of the rocks represented by these clasts. For example, if
 620 the two rocks preserved in the clasts from the sample 14083, investigated here, are as old as
 621 one in the sample 14303, then the μ of their source would be around 3000 and will decrease if
 622 the rocks are younger (e.g. μ of about 2000, if the age is around 3950 Ma). While the values
 623 of 2000 to 3000 appear to be similar to those determined for the enriched reservoir by Snape
 624 et al. (2016b) based on analysis of KREEP basalts, μ -values of 6000 and above are
 625 significantly different. This suggests that a range of compositions existed in the enriched
 626 (KREEP) reservoir, and a possibility that at least some plutonic rocks containing K-feldspar-
 627 rich differentiates could have originated from enriched sources distinctly different from those
 628 responsible for the formation of younger KREEP basalts.

629

630 7. Conclusions

Major minerals in the K-feldspar rich clasts in lunar breccias can be used to constrain Pb-Pb impact ages of the breccia samples and initial Pb compositions of these clasts at the time of impacts. Pb-Pb analyses of three such clasts in two Apollo 14 impact melt breccias indicate a profound resetting of the U-Pb system and homogenisation of Pb during a 3.92 Ga event, at least on the scale of a thin section, which is interpreted to be the impact event that formed the Imbrium basin. Initial Pb compositions determined for the three analysed clasts combined with Pb isotope compositions measured in K-feldspars from clasts in other Apollo 14 breccias define a range of very radiogenic compositions that characterise the variability of the Fra Mauro formation at the Apollo 14 landing site. The scatter in the analyses of the investigated clasts that extends beyond the analytical uncertainty can be explained by accumulation of Pb in the K-feldspar-rich rocks prior to 3.92 Ga and remixing of this Pb during the impact. These rocks crystallised from the melts derived from an enriched (KREEP) reservoir with μ -values of at least several thousand. Some of the studied samples indicate μ -values in the KREEP source as high as 6000-6500, significantly higher than those determined from the study of younger KREEP basalts (Snape et al. 2016b). This indicates substantial compositional variability of the lunar KREEP reservoir, and a possibility that further studies of Pb-Pb systems in the clasts of evolved rocks from lunar breccias can help to identify compositionally distinct reservoirs within the enriched part of lunar mantle. Importantly, the ability to obtain SIMS Pb-Pb ages of lunar rocks and even small fragments of these rocks that do not contain accessory phases traditionally used as U-Pb chronometers increases pool of lunar samples available for dating with precision better than a few tens of million years.

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Figure captions

Figure 1: BSE image and element maps of “QMD” (quartz-monzo-diorite) clast in the thin section 14083, 35 (clast 1). The clast comprises plagioclase (Pl), pyroxene (Px), K-feldspar (Kfsp), silica (SiO₂), and apatite (Ap).

Figure 2: BSE image and element maps of felsite clast in the thin section 14083, 35 (clast 2), and comprises intergrown K-feldspar (Kfsp) and silica (SiO₂) with minor plagioclase (Pl) and ilmenite (Ilm).

Figure 3: Post-SIMS BSE images of three areas within the clast 1 in the thin section 14083, 35, showing aggregates composed of zircon (Zirc), ilmenite (Ilm) and Ca-phosphate (Ap) grains.

Figure 4: Post SIMS BSE images of three areas within the clast 2 in the thin section 14083, 35, showing zircon (Zirc) – ilmenite (Ilm) – Ca-phosphate (Ap) aggregates.

Figure 5: BSE image and element maps of “granite” clast in the thin section 14303, 49

Figure 6: Post-SIMS BSE images of two areas within the clast in the thin section 14303, 49: a) K-feldspar (K-fsp) – silica (SiO_2) intergrowths with K-rich glass developing at the boundaries between these two phases, also shows internal inhomogeneity of K-feldspar; b) sulphide (Sulph), ilmenite (Ilm), Ca-phosphate (Ap) and pyroxene (Px) inclusions in K-feldspar (K-fsp) grains.

Figure 7: Lunar Pb isotope systematics: a) simple three component mixing, also shown is a terrestrial Pb evolution curve as defined by Stacey and Kramers (1975) model between 3700 and 0 Ma, SK-modern Stacey and Kramers Pb composition, CDT-Canyon Diabolo Troilite composition; b) illustration of incomplete Pb homogenisation in the clasts during the impact, which would result in some analyses plotting above the main mixing triangle; c) insert of figure 7b showing area of permitted Pb compositions free of terrestrial contamination and resulting from incomplete homogenisation during an impact (grey triangle) and also compositions resulting from including U bearing phases that have been incompletely reset during the impact (pink triangle).

Figure 8: $^{207}\text{Pb}/^{206}\text{Pb}$ vs. $^{204}\text{Pb}/^{206}\text{Pb}$ plots showing complete data sets for three investigated clasts. CDT – Canyon Diabolo Troilite; SK - modern terrestrial model composition (Stacey and Kramers, 1975); Kfsp – K-feldspar; Px – pyroxene; Pl – plagioclase; Ap – apatite; Ilm – ilmenite.

Figure 9: $^{207}\text{Pb}/^{206}\text{Pb}$ vs. $^{204}\text{Pb}/^{206}\text{Pb}$ plots showing filtered data used to define isochrons for three investigated clasts. Kfsp – K-feldspar; Px – pyroxene; Pl – plagioclase; Ap – apatite. Uncertainties on ages are quoted at the 95% confidence level.

Figure 10: $^{208}\text{Pb}/^{206}\text{Pb}$ vs. $^{207}\text{Pb}/^{206}\text{Pb}$ plot of data obtained for three clasts and filtered to eliminate laboratory contamination.

Figure 11: U-Pb data obtained for zircon from the “granite” clast found in the section 14303, 49: a) concordia diagrams showing analyses of three large zircon grains; b) $^{207}\text{Pb}/^{206}\text{Pb}$ vs.

$^{204}\text{Pb}/^{206}\text{Pb}$ plot, also showing filtered analyses of K-feldspar in the clast, defining lunar Pb line; insert shows variability of $^{207}\text{Pb}/^{206}\text{Pb}$ interpreted to reflect incomplete resetting of U-Pb system.

Figure 12: Initial Pb compositions of feldspar rich clasts from Apollo 14 breccias (red crosses represent samples analysed here; black crosses are from Compston et al., 1991).

Figure 13: Pb evolution prior to formation of the clasts and inclusion into the breccia samples: a) using a single stage model starting at 4.37 Ga from the Pb composition defined by Snape et al. (2016b); b) assuming two stage Pb evolution for two clasts with the known zircon ages and mixing during a 3.92 Ga impact, intersection of grey segments represents modelling of initial Pb in the clast from 14321, 1027 (investigated by Compston et al, 1991), intersection of blue segments represents modelling of initial Pb in the clast from 14303, 49 described here, also shown are Pb growth curves defined by μ -values that are compatible with the observed Pb compositions.

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

Figure 7

Figure 8

Figure 9

Figure 10

Figure 11

Figure 12

Figure 13

Spot	²⁰⁴ Pb (cps)	²⁰⁶ Pb (cps)	²⁰⁴ Pb/ ²⁰⁶ Pb	% err (1s)	²⁰⁷ Pb/ ²⁰⁶ Pb	% err (1s)	²⁰⁸ Pb/ ²⁰⁶ Pb	% err (1s)
Sample 14083, 35								
Clast 1, used to constrain isochron								
Px-1	0.182	1682.3	0.000103	7.1	0.4392	0.13	0.9394	0.11
Px-3	0.041	260.5	0.000135	15.5	0.4386	0.34	1.0591	0.26
Px-7	0.032	9.8	0.002827	17.1	1.4645	1.26	0.8435	1.43
Pl-1	0.025	209.5	0.000091	21.0	0.4308	0.38	0.3174	0.43
Pl-3	0.030	9.4	0.002607	18.5	1.4817	1.28	0.8688	1.45
Pl-5	0.020	3.9	0.003758	24.2	1.4899	1.98	0.8873	2.24
Pl-7	0.023	5.0	0.003485	22.1	1.5174	1.75	0.8888	1.98
Kfsp-1	0.051	472.7	0.000095	13.7	0.4288	0.25	0.8857	0.20
Kfsp-2	0.032	783.5	0.000034	17.9	0.4107	0.20	0.8292	0.16
Ap-1	0.187	1919.2	0.000013	7.0	0.4075	0.13	0.3971	0.13
Px-2	0.136	112.8	0.001130	8.3	0.7795	0.43	0.7873	0.43
Pl-9	0.021	24.0	0.000648	23.4	0.5393	1.04	1.3320	0.82
Clast 1, filtered out								
Px-2	0.491	632.2	0.000765	4.3	0.4499	0.22	1.2609	0.16
Px-5	0.385	54.0	0.006882	4.9	0.9854	0.58	0.9741	0.59
Px-4	0.047	20.6	0.001973	14.5	0.7399	1.02	0.7280	1.03
Px-6	0.582	258.5	0.002181	4.0	0.7677	0.29	0.5696	0.31
Pl-8	0.072	21.4	0.003154	11.3	0.9489	0.94	1.0569	0.91
Pl-2	0.057	35.7	0.001461	12.7	1.4678	0.66	0.8528	0.74
Pl-4	0.024	3.8	0.004818	21.5	1.4704	2.02	0.8793	2.28
Pl-6	0.030	3.6	0.006719	18.6	1.5110	2.04	0.9037	2.31
Kfsp-9	0.352	1404.1	0.000246	5.1	0.4189	0.15	1.0491	0.11
Kfsp-10	0.837	388.2	0.002129	3.3	0.6016	0.25	1.4917	0.20
Kfsp-4	0.053	59.2	0.000793	13.5	0.4636	0.70	2.3601	0.47
Kfsp-5	0.146	86.0	0.001597	8.0	0.4366	0.59	1.9861	0.40
Kfsp-8	0.552	175.2	0.003050	4.1	0.5065	0.39	2.9833	0.27
Kfsp-7	0.404	1200.6	0.000325	4.8	0.4156	0.16	1.1832	0.12
Kfsp-3	0.071	217.6	0.000294	11.6	0.4369	0.37	2.3665	0.25
Kfsp-6	0.260	3851.6	0.000065	6.0	0.4074	0.09	1.2448	0.07
Clast 2, used to constrain isochron								
Pl-1	0.034	15.1	0.001861	23.3	1.4728	1.01	0.8507	1.15
Pl-2	0.030	12.2	0.002010	18.5	1.4713	1.12	0.8577	1.28
Pl-3	0.037	10.5	0.002939	16.6	1.4883	1.21	0.8474	1.39
Kfsp-11	0.286	1238.9	0.000122	5.7	0.4509	0.15	1.3827	0.11
Kfsp-20	0.040	10.4	0.003315	15.7	1.4558	1.22	0.8795	1.38
Kfsp-5	0.108	35.1	0.002937	9.2	1.4840	0.66	0.8519	0.75
Kfsp-3	0.072	23.2	0.002913	11.3	1.4896	0.81	0.8422	0.93
Pl-4	0.031	85.7	0.000313	17.4	0.5288	0.56	1.0815	0.45
Pl-5	0.246	509.0	0.000472	6.1	0.5637	0.22	1.7905	0.17
Clast 2, filtered out								
Kfsp-1	0.235	70.5	0.003253	6.2	1.1495	0.49	0.8507	0.53
Kfsp-4	0.320	49.2	0.006380	5.4	1.2823	0.58	1.0047	0.61
Kfsp-6	0.243	21.5	0.011045	6.2	1.1242	0.90	0.8826	0.95
Kfsp-2	0.625	31.3	0.019648	3.9	1.3795	0.71	1.0761	0.75
Kfsp-7	0.161	19.8	0.007722	7.6	1.2610	0.91	0.9765	0.97
Kfsp-8	0.237	23.1	0.009807	6.3	1.1707	0.86	0.9577	0.90
Kfsp-9	0.966	42.9	0.021896	3.1	0.6369	0.74	0.4665	0.82
Kfsp-10	0.392	97.1	0.003898	4.9	0.5679	0.51	1.2310	0.41
Kfsp-12	0.149	12.3	0.011430	8.0	1.3147	1.15	1.0075	1.22
Kfsp-13	0.083	7.2	0.010457	10.8	1.2564	1.51	1.0447	1.58
Kfsp-14	0.091	15.4	0.005428	10.2	0.7278	1.19	0.7864	1.17
Kfsp-15	0.107	29.5	0.003382	9.4	0.4716	0.98	0.8231	0.83
Kfsp-16	0.290	16.7	0.016655	5.7	0.5215	1.26	1.4310	0.97
Kfsp-17	0.194	203.2	0.000910	6.9	0.4304	0.39	0.8634	0.31
Kfsp-18	0.138	12.4	0.010410	8.3	0.8416	1.27	1.2734	1.15
Kfsp-19	0.106	29.1	0.003397	9.4	0.8292	0.83	0.9750	0.80

Sample 14303, 49
used to constrain isochron

Kfsp-34	0.419	107.8	0.003752	4.7	1.5528	0.37	0.9020	0.42
Kfsp-35	0.398	122.5	0.003133	4.8	1.4450	0.36	0.8296	0.41
Kfsp-35	0.426	120.4	0.003418	4.7	1.4381	0.36	0.8208	0.41
Kfsp-40	0.679	723.5	0.000911	3.7	0.7131	0.17	0.8034	0.17
Kfsp-27	8.953	5420.1	0.001638	1.0	0.9173	0.06	0.9561	0.06
Kfsp-26	8.851	5326.8	0.001648	1.0	0.9172	0.06	0.9515	0.06
Kfsp-24	8.071	4978.6	0.001608	1.1	0.9209	0.06	0.9169	0.06
Kfsp-23	8.216	4953.9	0.001645	1.1	0.9161	0.06	0.9414	0.06
Kfsp-22	8.535	5223.6	0.001621	1.0	0.9141	0.06	0.9354	0.06
Kfsp-21	8.578	4846.8	0.001756	1.0	0.9631	0.06	0.8962	0.06
Kfsp-20	8.457	4798.3	0.001748	1.0	0.9552	0.06	0.8950	0.06
Kfsp-19	8.357	4832.0	0.001715	1.0	0.9439	0.06	0.8888	0.06
Kfsp-18	7.487	4429.2	0.001677	1.1	0.9325	0.07	0.8771	0.07
Kfsp-14	3.351	2191.9	0.001515	1.7	0.8839	0.09	0.8225	0.10
Kfsp-10	4.586	3764.2	0.001208	1.4	0.7855	0.07	0.6573	0.08
Kfsp-9	5.941	2971.5	0.001982	1.2	1.0232	0.08	0.7437	0.08
Kfsp-8	3.229	11407.3	0.000281	1.7	0.4912	0.05	0.5445	0.05
Kfsp-6	0.702	189.6	0.003650	3.6	1.5427	0.28	0.8911	0.32

filtered out

Kfsp-38	2.153	954.8	0.002198	2.1	1.0202	0.14	0.6935	0.15
Kfsp-39	2.612	1321.7	0.001928	1.9	0.9747	0.12	0.8227	0.12
Kfsp-16	3.499	2040.0	0.001700	1.6	0.8823	0.10	0.7679	0.10
Kfsp-13	4.890	2571.6	0.001885	1.4	0.9323	0.09	0.7799	0.09
Kfsp-30	1.757	1844.8	0.000928	2.3	0.6188	0.11	0.6687	0.11
Kfsp-25	11.113	4975.1	0.002216	0.9	0.9281	0.06	0.9422	0.06
Kfsp-15	2.519	1541.9	0.001618	1.9	0.7880	0.12	0.8493	0.11
Kfsp-5	3.665	2609.9	0.001392	1.6	0.7700	0.09	0.8918	0.09
Kfsp-4	1.655	1278.8	0.001281	2.4	0.7328	0.13	0.7458	0.13
Kfsp-2	4.677	4630.0	0.001002	1.4	0.5924	0.07	0.9074	0.06
Kfsp-12	8.356	2554.6	0.003244	1.0	0.9505	0.09	0.6657	0.09
Kfsp-7	7.843	2548.8	0.003052	1.1	0.8558	0.09	0.7502	0.09
Kfsp-3	1.858	884.6	0.002079	2.2	0.7545	0.16	0.8886	0.15
Kfsp-29	6.141	905.6	0.006621	1.2	0.8911	0.15	1.5623	0.13
Kfsp-36	4.197	957.5	0.004278	1.5	1.1956	0.13	0.7850	0.15
Kfsp-37	6.296	1333.9	0.004609	1.2	0.8976	0.12	0.7139	0.13
Kfsp-41	4.095	858.1	0.004658	1.5	1.2820	0.14	0.8667	0.15
Px-9	7.101	631.9	0.010973	1.1	1.0560	0.17	1.0127	0.17
Kfsp-28	30.538	6242.1	0.004854	0.5	0.8966	0.06	1.0407	0.05
Kfsp-11	45.641	2919.7	0.015511	0.5	0.8728	0.08	1.1579	0.08
Kfsp-1	30.843	3612.0	0.008472	0.5	0.6964	0.08	1.3404	0.07
Kfsp-31	1.642	50.4	0.031747	2.4	1.1160	0.59	1.4880	0.55
Kfsp-32	16.408	289.0	0.055462	0.8	0.8622	0.26	2.0959	0.22
Kfsp-33	4.148	181.3	0.022333	1.5	1.2676	0.30	1.3632	0.30
Ilm-1	1.390	61.2	0.022100	2.6	0.7841	0.58	1.0872	0.54
Ilm-2	15.407	303.8	0.049543	0.8	0.8553	0.26	1.9345	0.21
Ilm-3	1.550	30.8	0.049062	2.5	0.9709	0.78	1.9586	0.67
Px-1	0.690	21.5	0.031040	3.7	0.7826	0.98	1.2695	0.87
Px-2	0.501	14.5	0.033297	4.4	0.8367	1.18	1.3906	1.04
Px-3	1.228	25.0	0.047762	2.8	0.7466	0.93	1.6564	0.77
Px-4	3.830	70.4	0.053108	1.6	0.8438	0.53	2.0218	0.44
Px-5	1.645	32.8	0.048857	2.4	0.8989	0.77	1.9354	0.65
Px-6	9.312	241.4	0.037673	1.0	0.9930	0.28	1.6722	0.25
Px-7	39.985	775.0	0.050416	0.5	0.8909	0.16	1.9800	0.13
Px-8	20.172	884.9	0.022273	0.7	1.0116	0.14	1.2871	0.14

BCR

March 2016 session

Average	0.0537	0.8338	2.124
SD	0.0002	0.0012	0.006
RSD %	0.35	0.14	0.29
Woodhead & Hergt, 2000	0.05332	0.83305	2.0644
correction factor	0.9923	0.9991	0.9718

December 2015 session

Average	0.0546	0.8405	2.076
SD	0.0006	0.0028	0.007
RSD %	1.06	0.34	0.33
Woodhead & Hergt, 2000	0.05332	0.83305	2.0644
correction factor	0.9773	0.9912	0.9942

Common Pb corrected (using modern Stacey and Kramers Pb composition)																			²⁰⁷ Pb/ ²⁰⁶ Pb			
Spot	U (ppm)	Th (ppm)	²³² Th/ ²³⁸ U	²⁰⁶ Pb/ ²³⁸ U % err (1s)	²⁰⁷ Pb/ ²³⁵ U % err (1s)	²⁰⁶ Pb/ ²³⁸ U % err (1s)	²⁰⁶ Pb/ ²³⁸ U % err (1s)	²⁰⁶ Pb/ ²³⁸ U % err (1s)	²⁰⁶ Pb/ ²³⁸ U % err (1s)	²⁰⁶ Pb/ ²³⁸ U % err (1s)	²⁰⁶ Pb/ ²³⁸ U % err (1s)	²⁰⁶ Pb/ ²³⁸ U % err (1s)	²⁰⁶ Pb/ ²³⁸ U % err (1s)	²⁰⁶ Pb/ ²³⁸ U % err (1s)	²⁰⁶ Pb/ ²³⁸ U % err (1s)	²⁰⁶ Pb/ ²³⁸ U % err (1s)	²⁰⁶ Pb/ ²³⁸ U % err (1s)	²⁰⁶ Pb/ ²³⁸ U % err (1s)	rho	Age	+/- (2s)	
grain 4																						
1	479	300	0.65	0.00005	19	0.5264	0.10	0.1528	0.26	0.937	0.94	1.067817	0.94	0.5261583	0.10	67.9	0.95	0.937	0.94	0.994	4316	1
2	377	228	0.63	0.00037	6	0.5228	0.31	0.1603	0.87	0.899	0.83	1.119473	0.83	0.5206039	0.32	64.1	0.89	0.894	0.83	0.935	4301	5
3	618	396	0.66	0.00004	14	0.5287	0.20	0.1558	0.22	0.950	0.82	1.053094	0.82	0.5285092	0.20	69.2	0.84	0.950	0.82	0.972	4323	3
4	574	350	0.61	0.00008	8	0.5373	0.14	0.1660	0.36	0.992	1.19	1.009761	1.19	0.5368904	0.14	73.5	1.19	0.992	1.19	0.993	4346	2
grain 2																						
1	108	53	0.50	0.00009	29	0.5190	0.68	0.1368	5.88	0.916	0.92	1.094113	0.92	0.5184946	0.68	65.3	1.15	0.914	0.92	0.802	4295	10
2	153	69	0.47	0.00026	18	0.5101	0.18	0.1187	0.52	0.912	0.89	1.10132	0.89	0.5084794	0.19	63.7	0.91	0.908	0.89	0.978	4266	3
3	148	74	0.52	0.00664	5	0.5632	0.46	0.3469	2.23	1.030	0.89	1.108469	1.08	0.5245253	0.70	65.3	1.29	0.908	1.08	0.840	4312	10
4	149	64	0.43	0.00116	19	0.5258	0.41	0.1600	4.45	0.996	1.33	1.02613	1.33	0.5189456	0.41	72.2	1.40	0.996	1.33	0.955	4296	6
5	199	135	0.68	0.00135	5	0.5376	0.31	0.2400	0.46	1.034	1.21	0.991914	1.21	0.5298729	0.31	76.7	1.25	1.034	1.21	0.969	4327	5
grain 1																						
1	88	31	0.37	0.00015	20	0.5157	0.24	0.0925	0.80	0.955	0.96	1.049981	0.96	0.5148287	0.25	67.6	0.99	0.953	0.96	0.968	4284	4
2	112	48	0.44	0.00106	6	0.5286	0.20	0.1454	1.30	0.944	0.91	1.080898	0.92	0.5224076	0.22	66.6	0.94	0.926	0.92	0.972	4306	3
3	128	58	0.47	0.00004	31	0.5346	0.19	0.1105	0.58	0.950	0.91	1.053812	0.91	0.5343591	0.19	69.9	0.93	0.949	0.91	0.978	4339	3
4	70	25	0.37	0.00058	11	0.5303	0.25	0.1099	0.76	0.954	0.98	1.0603	0.99	0.5269658	0.27	68.5	1.03	0.944	0.99	0.966	4318	4
5	70	25	0.37	0.00118	8	0.5033	0.38	0.1254	1.55	0.900	0.98	1.136599	1.00	0.4958565	0.41	60.2	1.08	0.881	1.00	0.923	4229	6
6	61	21	0.35	0.00032	15	0.5312	0.27	0.1002	1.91	0.982	1.00	1.024385	1.01	0.5293213	0.28	71.2	1.04	0.976	1.01	0.964	4325	4
7	81	30	0.39	0.00015	30	0.5289	0.23	0.0981	0.74	0.952	0.96	1.053592	0.96	0.5280109	0.24	69.1	0.99	0.949	0.96	0.970	4321	4
8	65	24	0.38	0.00012	27	0.5298	0.27	0.0926	0.87	0.941	0.99	1.06469	0.99	0.5291038	0.27	68.5	1.03	0.939	0.99	0.965	4324	4
9	82	33	0.42	0.00002	376	0.5063	0.24	0.1037	0.73	0.900	1.01	1.111319	1.02	0.5061619	0.26	62.8	1.05	0.900	1.02	0.968	4259	4
10	74	27	0.36	0.00138	4	0.5417	0.29	0.1404	1.23	1.026	1.21	1.000478	1.21	0.5338789	0.29	76.6	1.25	1.026	1.21	0.973	4338	4
11	74	24	0.33	0.00009	14	0.5201	0.30	0.0847	0.83	0.981	1.26	1.020536	1.26	0.5195787	0.30	70.4	1.30	0.981	1.26	0.973	4298	4