Pb isotopes in the impact melt breccia 66095: Association with the Imbrium basin and the isotopic composition of lithologies at the Apollo 16 landing site

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Abstract

Recent *in situ* Secondary Ion Mass Spectrometry (SIMS) Pb isotope analyses of lunar basalts have provided precise crystallisation ages and initial Pb isotopic compositions for these samples. In this study, the same approach has been tested in the Apollo 16 impact melt breccia 66095, referred to as the “Rusty Rock” due to its enrichments in volatile elements, including Pb. Based on these analyses of the breccia, a Pb-Pb isochron age of 3909 ± 17 Ma (at the 95% confidence level) and an initial Pb composition for 66095 have been determined. This age is interpreted as representing the time of breccia formation that, when combined with recent studies of lunar breccias, can be linked to the Imbrium basin forming impact. The directly measured initial Pb composition of the breccia from this work is similar a modelled compositions presented previously, and likely reflects an average value for the lithologies present at the Apollo 16 landing site at the time that the Imbrium ejecta was emplaced. The 66095 initial Pb isotopic composition is compared with the compositions in other lunar samples and the nature of the endmember lithologies in this mixture has been discussed within the framework of a multiple stage model of Pb isotope evolution on the Moon. This study demonstrates the effectiveness of this technique beyond its application in crystalline basalts, opening up the possibility of obtaining precise geochronological and Pb isotopic compositions from a broader sample set than was previously recognised.

1. Introduction

The Pb isotope compositions of lunar samples indicate that μ -values (the ratio of $^{238}\text{U}/^{204}\text{Pb}$ extrapolated to the present) in many lunar lithologies and their mantle sources are significantly higher (~100-600; Tatsumoto 1970; Tera and Wasserburg 1974; Gaffney et al. 2007a; Nemchin et al. 2011; Snape et al. 2016) than those determined for the Earth (terrestrial mantle μ -values typically being ~8-10; Kramers and Tolstikhin 1997) and other planetary bodies (e.g. Mars with mantle μ -values of ~1-5; Gaffney et al. 2007b; Bellucci et al. 2015). Despite evidence of low- μ lunar mantle sources identified in several samples (e.g. Hanan and Tilton 1987; Misawa et al. 1993; Torigoye et al. 1995; Premo et al. 1999), the generally high- μ values determined for most lunar silicate reservoirs suggest a profound depletion of Pb in the Moon compared to the Earth, which has previously been attributed to early volatile loss (e.g. Tatsumoto 1970), potentially during the formation of the Moon during a giant impact between the proto-Earth and another planetary body (Hartmann and Davis 1975). As a consequence of the low Pb abundance in samples from the Moon, efforts to measure the isotopic composition of initial lunar Pb are typically hindered by the increased susceptibility to terrestrial contamination (Gaffney et al. 2007a; Nemchin et al. 2011). In addition, the highly radiogenic nature of lunar Pb isotope compositions makes it difficult to distinguish between Pb generated by *in situ* radiogenic decay of U after the rocks were formed and lunar initial Pb inherited from the source(s) of the samples during their formation (e.g. Nemchin et al. 2011).

Recent work by Snape et al. (2016) interpreted the Pb isotopic compositions measured in six lunar basalts as representing a combination of three main constituents: (1) initial Pb introduced to the samples when they crystallised, (2) radiogenic Pb formed by the decay of U in the sample after the introduction of the initial Pb, and (3) terrestrial contamination. For each sample, these three constituents define a triangular array of points on a plot of $^{207}\text{Pb}/^{206}\text{Pb}$ versus $^{204}\text{Pb}/^{206}\text{Pb}$ (Fig. 1), in which the analyses with the highest $^{204}\text{Pb}/^{206}\text{Pb}$ trend towards terrestrial Pb isotope compositions (Stacey and Kramers 1975). The addition of primitive meteoritic Pb would result in pulling the measured compositions towards the right side of this plot (Fig. 1), although this effect appears to be negligible in the samples analysed to date (Snape et al. 2016). The data along the bounding edge on

the left side of the triangle form an isochron defining the time when the sample crystallised, the variability in compositions along this line reflecting the different μ -values of the individual minerals. The analyses falling on this isochron with the highest $^{207}\text{Pb}/^{206}\text{Pb}$ ratios represent the best estimate for the initial Pb component that was incorporated into the rocks when they crystallised, while the analyses with the lowest $^{207}\text{Pb}/^{206}\text{Pb}$ ratios contain the maximum amount of the *in situ* radiogenic Pb component. Any analyses falling at intermediate locations between the apices of the triangle are interpreted as representing mixtures of these three endmember compositions. This approach was used to determine precise crystallisation ages for these basalts that correlated with previously published values (Snape et al. 2016 and references therein). In crystalline basalt samples, the existence of a well-defined initial Pb composition and a more radiogenic endmember resulting from the *in situ* decay of U is a logical consequence of how these samples formed. This study aims to test the applicability of this approach to non-basaltic lunar samples by investigating the Pb isotopic compositions of mineral phases in the Apollo 16 polymict impact melt breccia 66095, where a single well-defined initial Pb composition (and the resulting mixing relationship described above) would not necessarily be inevitable or expected.

There are two main reasons for testing this analytical approach in 66095, the first of which being the textural and petrologic nature of the sample. Previous studies describe 66095 as a clast-rich impact melt breccia with a subophitic to ophitic matrix making up about 80% of the rock (Bass 1972; Garrison and Taylor 1980; Ryder and Norman 1980). The Pb isotope compositions of phases in the crystalline melt matrix of the breccia can theoretically be treated in a similar manner to crystalline basalts, with the exception that the initial Pb component identified will represent a homogenised mixture of Pb that was mobilised in the impact melt, and the Pb-Pb isochron age will relate to the crystallisation of that impact melt.

The second reason for studying 66095 is that it exhibits a notable enrichment (relative to other lunar samples) in volatile elements, such as Cl, Zn and Pb (e.g. Krahenbuhl et al. 1973; El Goresy et al. 1973). Enrichments in volatiles were identified in other Apollo 16 breccias, but 66095 stands out as having the highest abundances of such elements (Krahenbuhl et al. 1973). Furthermore, it appears that

a significant amount of the Pb in the sample is not supported by the presence of U and cannot be explained by *in situ* radiogenic decay since the formation of the breccia, but instead represents an initial Pb component incorporated into the breccia (Nunes and Tatsumoto 1973; El Goresy et al. 1973). The volatile enrichments in the 66095 were previously identified as being associated with the akaganéite (a hydrated iron oxide; FeOOH) “rust” that is a characteristic feature of the breccia (Bass 1972; Taylor et al. 1974), with Pb being concentrated at the boundaries between akaganéite and troilite (El Goresy et al. 1973). In order to assess the validity of the Pb-Pb isochron approach in 66095, it will be necessary to establish whether the Pb was introduced to the sample as part of the breccia formation process or at a significantly later time.

2. Material and methods

2.1. Sample descriptions

Four sections of 66095 were analysed in this study (66095,77; 66095,85; 66095,222; 66095,322). Three of the sections (77; 222; 322) consist almost entirely of the subophitic to ophitic impact melt texture that makes up the breccia matrix. The melt matrix is characterised by plagioclase forming subhedral plagioclase laths between ~0.01-0.07 mm in length and occasional larger (~0.1-0.3 mm) subhedral to anhedral grains, partially enclosed in pyroxene (Fig. 2). This is consistent with previous studies of the breccia which described the matrix as containing plagioclase (50-60% by mode), pigeonite (up to 30%) and olivine (up to 10%), with accessory phases including cohenite, ilmenite, FeNi metal with intergrowths of schreibersite, as well as assemblages of troilite and sphalerite (Bass 1972; El Goresy et al. 1973; Taylor et al. 1974; Garrison and Taylor 1980). Highland “basalt” clasts previously identified in 66095 have been interpreted as impact melt and, given their mineralogical similarity to the breccia matrix, may be textural variants of the main melt matrix (Ryder and Norman 1980). Clasts resembling KREEP-rich (material enriched in K, Rare Earth Elements and P) Fra Mauro “basalt” material collected by other Apollo missions (e.g. Reid et al. 1977) were also identified in 66095 and considered to be part of a continuum of melt-rocks along with the highland basalts (Hunter and Taylor 1981).

The 66095,85 section is less homogeneous, and includes multiple large (<3.0 mm) anorthosite and troctolitic anorthosite clasts (Fig. 3a), consistent with the clast inventories reported previously (Garrison and Taylor 1980; Hunter and Taylor 1981). A large glass vein (0.1-0.5 mm thick) cross cuts the 66095,85 section and has, in places, entrained fragments of the subophitic matrix (Fig. 3b). Melt veins such as these were described in previous studies of the breccia, and have been attributed to both *in situ* melting and the injection of the breccia by superheated melt (Bass 1972; Roedder and Weiblen 1977; Garrison and Taylor 1980).

Examples of the FeNi metal and troilite assemblages are present in all four thin sections. The smallest of these assemblages occur as clusters of ~0.01 mm anhedral blebs in the matrix and in some of the clasts (Figs. 3-4). Larger assemblages (up to ~0.3 mm) are also present throughout the matrix in all four sections, these typically consist of a central FeNi metal grain with 0.01-0.03 mm troilite blebs occurring around the edges, and occasional 0.01 mm thick schreibersite grains within the metal and at the boundary between the metal and sulfide (Fig. 4). These schreibersite grains have textures similar to the vermicular morphologies in other occurrences of meteoritic schreibersite (e.g. Casanova et al. 1993; Lehner et al. 2010), which have explained as forming either via condensation as a separate phase during the formation of metal assemblages or as the result of subsolidus metal exsolution (Lehner et al. 2010).

2.2. Analytical protocol

The four 66095 thin sections analysed were prepared at NASA Johnson Space Center. Each section was cleaned with ethanol before being carbon coated. Backscattered electron (BSE) images and elemental maps of each section were acquired using a Quanta 650 FEGSEM and accompanying Oxford Instruments Energy Dispersive Spectroscopy (EDS) detector at Stockholm University, operating with an accelerating voltage of 20 kV at a working distance of 10 mm.

Following the SEM documentation of the samples and prior to the SIMS analyses, the samples were cleaned with a fine (1 µm) diamond paste and ethanol to remove the carbon coating before adding a 30 nm gold coating. The Pb isotopic compositions of the phases were determined over three analytical

sessions using a CAMECA IMS 1280 ion microprobe at the NordSIMS facility in the Swedish Museum of Natural History, Stockholm, using a methodology similar to that outlined in previous studies (Whitehouse et al. 2005; Bellucci et al. 2015). Apertures in the primary column were used to generate a slightly elliptical O_2^- sample probe with dimensions appropriate to the target. The smaller accessory phases (including sulfides and schreibersite) were analysed using a $\sim 10\ \mu m$ spot (beam current 2-4 nA), whereas plagioclase grains were analysed with either a $\sim 20\ \mu m$ spot (beam current 10-12 nA), or a $\sim 30\ \mu m$ spot (19-20 nA). Prior to each measurement, an area of 20-35 μm around the spot location was rastered for 120 seconds in order 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 will be 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. The mass spectrometer was operated with a nominal mass resolution of 4860 ($M/\Delta M$), sufficient to resolve Pb from known molecular interferences. A Nuclear Magnetic Resonance (NMR) field sensor regulated the stability of the magnetic field to high precision. The Pb isotopes 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 65 ns. Background counts for each channel were measured at regular intervals during each session. The average background counts were used to correct the sample analyses in instances where statistically significant background noise levels were detected (i.e. where the standard deviation of the background measurements for a given session was lower than the average background values for that session). The average background values are reported in Table B.2. Individual analyses were filtered out of the final dataset if the count rates for any masses were lower than 3 $\times$ the background count rates during that session.

Analyses of the USGS basaltic glass reference material, BCR-2G, were used to generate a correction factor to account for mass fractionation and detector relative gain calibration in the unknown analyses, assuming the values of Woodhead and Hergt (2000). The reproducibility of the BCR-2G analyses for

the three sessions were as follows: $^{208}\text{Pb}/^{206}\text{Pb} = 0.35\%$, 0.42% and 0.80% ; $^{207}\text{Pb}/^{206}\text{Pb} = 0.46\%$, 0.23% and 0.78% ; $^{208}\text{Pb}/^{204}\text{Pb} = 1.19\%$, 0.82% and 1.06% ; $^{207}\text{Pb}/^{204}\text{Pb} = 1.22\%$, 0.66% and 2.06% ; $^{206}\text{Pb}/^{204}\text{Pb} = 1.09\%$, 0.46% and 1.42% (reported as 2σ standard deviations from the average values for each session). Data were then processed using in-house SIMS data reduction spreadsheets and the Excel add-in Isoplot (version 4.15; Ludwig 2008).

3. Results

The data were filtered following the logic detailed in the introduction to obtain the steepest possible statistically valid trend on the $^{207}\text{Pb}/^{206}\text{Pb}$ versus $^{204}\text{Pb}/^{206}\text{Pb}$ plot (Fig. 5). This trend corresponds to an “isochron” with an age of 3909 ± 17 Ma (error is at the 95% confidence level; MSWD = 1.04; probability of fit = 0.4). Notably, the data filtered out from this trend as being subject to terrestrial contamination include those with the lowest counts of Pb largest and some of the largest analytical uncertainties (Table B.1; Figs. 5a; A.2). Although this relationship is not clear enough to be used as a means to filter the data in itself, it further substantiates the view that the right hand apex of the mixing triangle in Fig. 5a is populated by analyses where the concentration of lunar Pb is lower, making the analyses more susceptible to terrestrial contamination. This “isochron” trend is generated primarily from analyses of plagioclase grains in the melt matrices of the 66095,222 and 66095,322 thin sections, which yielded results with the least terrestrial contamination. Three analyses from 66095,85, including one analysis of the glass melt vein, were within error of the overall trend and, as such, used to further constrain the age. The remaining data from the four thin sections (including all of the measurements made in 66095,77) plotted closer to terrestrial Pb compositions.

The isotopic composition of the initial Pb component was calculated from three plagioclase analyses and three sulfide analyses in the 66095,222 and ,322 thin sections that have the highest $^{207}\text{Pb}/^{206}\text{Pb}$ compositions of all the analyses (Table B.1). Three analyses of the schreibersite in the 66095,222 thin section (Fig. 4a) also yielded $^{204}\text{Pb}/^{206}\text{Pb}$ and $^{207}\text{Pb}/^{206}\text{Pb}$ ratios close to those obtained in the plagioclase and sulfide grains, although they are slightly shifted to the right of the trend defining the leftmost side of the triangular array, most likely indicating the presence of some terrestrial

contamination. Taking a weighted average of the plagioclase and sulfide analyses results in a composition of $^{204}\text{Pb}/^{206}\text{Pb} = 0.00642 \pm 0.00005$, $^{207}\text{Pb}/^{206}\text{Pb} = 1.461 \pm 0.005$ and $^{208}\text{Pb}/^{206}\text{Pb} = 0.930 \pm 0.005$ (errors at the 95% confidence level). This initial Pb composition is very similar to those calculated previously for 66095 on the basis of whole-rock analyses and corrected using measured $^{238}\text{U}/^{204}\text{Pb}$ ratios (Nunes and Tatsumoto 1973; Fig. 5b).

4. Discussion

4.1. Introduction of Pb to the breccia

If the Pb measured in 66095 was present in the rock when the breccia formed, then the trend identified in the data (Fig. 5b) would be an isochron with the 3909 ± 17 Ma age representing the time of breccia formation. Conversely, if the formation of the breccia and introduction of the Pb occurred at significantly different times, then the trend formed by the data in Fig. 5b would not represent an isochron, but a mixing line between the isotopic composition of the Pb that was introduced to the breccia after its formation, and Pb produced by the *in situ* decay of U after the breccia was formed.

Several explanations for the unusual characteristics and high volatile content (including Pb) of 66095 have been put forward, including: (1) exogenous source models, in which the vaporization of a comet or carbonaceous chondrite led to the volatile enrichment of the Apollo 16 soil (Gibson and Moore 1973; El Goresy et al. 1973); and (2) lunar source models, either with some form of fumarolic activity resulting in the mobilization and injection of volatiles to the breccia after its formation (Krahenbuhl et al. 1973; Nunes and Tatsumoto 1973), or with the volatiles being hosted in igneous lithologies that were subsequently incorporated into the breccia (Allen et al. 1975). In addition to these models, it was also proposed that the akaganéite rust could have resulted from alteration of lawrencite and Fe-Ni metal following exposure to water vapour after the sample was collected (i.e. as a result of terrestrial contamination; Taylor et al. 1974). Reviewing the work of previous studies, in combination with new Cl isotope data, Shearer et al. (2014) came to the conclusion that the high volatile content of 66095 is indigenous to the Moon, and potentially due to the degassing of an impact ejecta blanket, exposing the sample to fumarolic activity. The Cl isotope studies of the breccia also indicated that some portion of

the rust alteration may have a lunar origin, with the fumarolic activity having an oxidising effect on the phases in the rock, while a further stage of oxidation could have occurred after the sample was returned to Earth (Shearer et al. 2014).

The fact that measured initial Pb composition identified in this study is so similar to the model compositions from Nunes and Tatsumoto (1973), which were calculated using measured $^{238}\text{U}/^{204}\text{Pb}$ ratios and bulk Pb isotope compositions, provides one argument that the trend in data is a true isochron, and not a mixing trend. Furthermore, a majority (90 %) of the SIMS analyses forming the trend in Fig. 5b were obtained from plagioclase crystals within the melt matrix (Fig. 2; Table B.1). This indicates that the Pb was present during the breccia formation process in order for it to have been incorporated into the crystallising impact melt matrix. The identification of the same Pb component in the glass of the melt veins in the 66095,85 section is consistent with formation of the veins by *in situ* melting, as was described previously (Bass 1972; Garrison and Taylor 1980). Alternatively, if these veins were formed by subsequent injection of melt into the breccia, this must have happened immediately after crystallisation of the breccia matrix, such that the same Pb component could have been incorporated into the melt.

The consistency of the Pb isotope compositions throughout the separate 66095 thin-sections mirrors an observation of previous studies that the breccia exhibits “constant volatile trace element ratios, in the diverse range of petrologic types” (Hunter and Taylor 1981). This observation was considered to imply an overprinting of the trace elements in the rock by an external source. In the case of the Pb isotope data presented in this study, it supports the interpretation that the isotope composition of the non-radiogenic end-member represents a single Pb component, and the validity of combining the data from all four thin sections to constrain both an initial Pb composition for this component and the time at which it was introduced to the breccia. However, the low concentration of Pb in some phases (indicated by low count rates in Table B.1.) indicates that the Pb in the sample is less likely explained by the introduction of volatile material after the impact melt crystallised. Notably, the Pb concentrations are particularly low in the FeNi metal grains analysed, consistent with the incompatibility of Pb in such phases. Equally, smaller plagioclase grains in the melt matrix that appear

to have been completely recrystallized (Figs. 2a and 2c; Table B.1.) have higher count rates than the larger grains, which may represent incompletely melted plagioclase/anorthosite clasts from the precursor material where only limited amounts of Pb were incorporated, potentially by diffusion from the surrounding melt (Fig. 2d; Table B.1.). These observations imply that if the Pb in 66095 is associated with fumarolic activity (as proposed by Shearer et al. 2014), this occurred in conjunction with the breccia formation.

4.2. Significance of Pb-Pb isochron age

A variety of impact breccias and melts were returned by the Apollo 16 mission from the Cayley Plains and Descartes Mountains, demonstrating that these terrains comprise crustal lithologies modified by impacts, and are not volcanic features, as had been suspected prior to the mission (Milton 1972; Muehlberger et al. 1972). Studies attempting to connect the Cayley Plains and Descartes Mountains to particular impact structures have resulted in two main interpretations regarding the emplacement of these geologic units: (1) the Cayley Plains unit represents ejecta from the Imbrium basin forming event, and was emplaced ballistically on top of the older Descartes material, which was introduced to the region by an earlier impact event, such as the formation of the Nectaris basin (e.g. Head 1974); (2) the Cayley Plains and Descartes Mountains represent different ejecta facies from the Imbrium basin (e.g. Norman et al. 2010). A more detailed review of these two interpretations can be found in Joy et al. (2011). The 66095 sample was chipped from a 0.5 m boulder on the rim of a 10 m crater at Station 6. This was one of the southernmost points of the Apollo 16 traverse, located close to the boundary between the Cayley Plains and Descartes Mountains units, at the foot of Stone Mountain (the southern outcrop of the Descartes unit).

The 3909 ± 17 Ma age obtained from the Pb component in 66095 is broadly consistent with the Rb–Sr model ages, ^{40}Ar – ^{39}Ar age, and previous U–Pb isochron, which indicated that the excess Pb in the sample was introduced to the rock between ~3800–4000 Ma (Nyquist et al. 1973; Turner et al. 1973; Nunes and Tatsumoto 1973). Perhaps more importantly, this age is indistinguishable from recent estimates for the age of the Imbrium basin forming impact, based on U–Pb analyses of zircons and

phosphates in Apollo 12 and Apollo 14 impact melt breccias, as well as the lunar meteorite SaU (3926±2 Ma; Gnos et al. 2004; Liu et al. 2012; Snape et al. 2016). Norman et al. (2010) determined ^{40}Ar – ^{39}Ar plateau ages of 3866±9 Ma for a range of clasts from two separate Apollo 16 feldspathic breccias, which they interpret as the age of the emplacement for the Descartes formation. Furthermore, they note that, when corrected for recalibrations of the ^{40}Ar – ^{39}Ar flux monitor ages, these ages would be consistent with the older ~3925 Ma U–Pb ages determined for the Imbrium basin.

In addition to the similarity in ages between the introduction of Pb to 66095 and the proposed timing of the Imbrium basin forming event, several compositional traits of the sample indicate the inclusion of material originating from the Procellarum KREEP Terrane (PKT; Jolliff et al. 2000), being incorporated as ejecta during the Imbrium impact. The range of major and minor element compositions determined for the 66095 matrix and glass components was interpreted to represent a mixture of highland and KREEP-rich lithologies, such as the anorthosite and Fra Mauro “basalt” that are present in the clast inventory of the breccia (Garrison and Taylor 1980; Hunter and Taylor 1981). This interpretation is supported by the “KREEPy” trace element characteristics identified in 66095 and other polymict Apollo 16 rocks (e.g. Jovanovic and Reed 1983; Ebihara et al. 1992). Finally, high $\delta^{37}\text{Cl}$ values such as those obtained by Shearer et al. (2014) in 66095 are proposed to represent a fundamental characteristic of KREEP (Barnes et al. 2016). Taking all these factors into consideration, the 66095 breccia probably formed during the emplacement of Imbrium ejecta, incorporating a range of lithologies from both the Imbrium region and the nearside lunar highlands. This interpretation is in keeping with the classification of 66095 as part of the Apollo 16 Mafic Impact-Melt Breccias (MIMBs; Korotev et al. 1997), which have also been demonstrated as most likely representing ejecta from the Imbrium basin (Korotev 1997).

4.3. Nature of the initial Pb component in 66095

The initial Pb isotope composition of 66095 is extremely radiogenic ($^{204}\text{Pb}/^{206}\text{Pb} = 0.00642 \pm 0.00005$, $^{207}\text{Pb}/^{206}\text{Pb} = 1.461 \pm 0.005$ and $^{208}\text{Pb}/^{206}\text{Pb} = 0.930 \pm 0.004$), and can only be explained by Pb isotope evolution in a source reservoir with a high μ -value ($\mu \sim 900$ – 1000) or, more likely a mixture of Pb from

different source reservoirs, including some with μ -values >1000 . Such high μ -values have been determined for a range of lunar samples, but are not observed in other planetary materials (Kramers and Tolstikhin 1997; Gaffney et al. 2007b; Amelin 2008; Bellucci et al. 2015). As such, the Pb isotope data provide an additional argument against an exogenous source for at least the Pb component of the volatile elements in 66095 and the Apollo 16 soils (e.g. Gibson and Moore 1973; El Goresy et al. 1973).

This initial Pb isotope composition likely represents a mixture of multiple Pb components derived from the lithologies at the Apollo 16 landing site at ~ 3900 Ma, immediately after the Imbrium basin formed and the ejecta were emplaced at the landing site. On the scale of this individual sample, this mixture appears to be effectively homogenous, although some of the scatter in the unfiltered analytical data to the right of initial Pb composition (Fig. 5a) could feasibly be the result of an imperfect mixture of these components in addition to the effects of terrestrial contamination. When compared with the initial Pb isotopic compositions determined by Snape et al. (2016) for lunar basalts, the initial Pb isotopic composition of 66095 lies to the right of the KREEP-rich basalts implying input of one or more less radiogenic Pb components from lower- μ sources (Fig. 6). Taking the KREEP-rich nature of the Imbrium basin into consideration, it is likely that some proportion of the initial Pb component in 66095 originated from a similarly KREEP-rich component, whereas the other main source of Pb would have been the pre-existing anorthositic highland rocks, including ferroan anorthosite (FAN), in the region of the Apollo 16 landing site.

Although quantitative modelling of the mixing relationships is difficult with the currently available data set, a simple depiction of the main components of the mixture is possible on a qualitative level utilising the basalt Pb isotope evolution model presented by Snape et al. (2016). The enriched (KREEP) component of the mixture is represented by the products from melting of the “urKREEP” layer (Warren and Wasson 1979) that formed during the final stages of the Lunar Magma Ocean (LMO) crystallisation at 4376 ± 18 Ma, and is expected to have had very high μ -values on the order of several thousands (Nemchin et al. 2011). Such high μ -values are supported by analyses of KREEP-rich basalts 14072 and 15386, which indicate that the samples originated from source reservoirs with

μ -values of ~2500-4000 (Snape et al. 2016). In Fig. 6 the evolution of the Bulk Silicate Moon (BSM) is calculated as originating from Canyon Diablo Troilite compositions (Göpel et al. 1985) at 4500 Ma with a μ -value of 462 ± 46 until 4376 Ma, at which point the high- μ urKREEP reservoir begins to evolve (model values taken from Snape et al. 2016). At the time of formation of 66095 (3909 Ma), the Pb composition evolved in such reservoirs would plot, in the $^{207}\text{Pb}/^{206}\text{Pb}$ versus $^{204}\text{Pb}/^{206}\text{Pb}$ coordinates, slightly below and to the left of that estimated to be the initial Pb composition for the breccia (Fig. 6). This would represent the best estimate of the composition of the KREEP-rich mixing component, determined with the assumption that no significant fractionation between U and Pb took place during the formation of the KREEP-rich lithologies compared to their urKREEP source. This assumption is consistent with the measured initial Pb compositions of the KREEP-rich 14072 and 15386 samples, which have similar ages (~3900 Ma) to that of the 66095 breccia (Fig. 6).

The Pb isotope composition of anorthositic crust at 3909 ± 17 Ma representing the other mixing component is expected to be located to the right of 66095 on the $^{207}\text{Pb}/^{206}\text{Pb}$ versus $^{204}\text{Pb}/^{206}\text{Pb}$ diagram, having higher $^{207}\text{Pb}/^{206}\text{Pb}$ and $^{204}\text{Pb}/^{206}\text{Pb}$ ratios, reflecting the lower μ -values of the crust. Although direct Pb isotope analyses of the samples representative of this crust are likely to have incorporated laboratory contamination and, therefore, cannot be viewed as defining entirely accurate initial Pb compositions and/or ages of these rocks, they give approximate upper limit estimates of the μ -values in FAN samples as ~35-100 (Premo et al. 1999). With that in mind, possible mixing relationships between KREEP-rich material delivered as the Imbrium ejecta and the local anorthositic crust to form the isotopic composition observed in the 66095 are illustrated schematically in Figure 6.

Owing to the uncertainties in the initial Pb isotopic composition measured in 66095 and that predicted for the KREEP-rich lithologies, a range of mixing trends can be constructed between the potential Pb components. At one extreme end of this range, where the gradient of the mixing trend is steepest (labelled “A” in Fig. 6), the point at which the mixing trend intercepts the BSM curve implies that the reservoir of the highland Pb component (with a μ -value of ~80) would have formed from approximately the same Pb composition as the urKREEP reservoir did at 4376 Ma, as defined by the Snape et al. (2016) model. This would also imply that both the urKREEP reservoir and that of the

highland Pb component diverged from the BSM at a similar time, in order for there to have been minimal evolution of the BSM Pb isotope compositions between the formation of the two reservoirs. Given that the urKREEP reservoir is hypothesised as the final product formed during LMO crystallisation, and the anorthositic highlands have been interpreted as the remnants of a flotation crust formed earlier in the LMO crystallisation sequence, this would indicate very rapid crystallisation during these final stages of the LMO. Such a scenario may fit with suggestions of a late formation of the Moon (<4426 Ma; Borg et al. 2011; Carlson et al. 2014; McLeod et al. 2014; Gaffney and Borg 2014; Connelly and Bizzarro 2016), but would be harder to reconcile with the older canonical age for the Moon of ~ 4500 Ma. Conversely, a mixing trend with a shallower gradient (labelled “B” in Fig. 6) would indicate a larger difference between the Pb compositions at the time of FAN formation and the 4376 Ma time when the urKREEP reservoir formed. This would imply a longer period of time between the formation of urKREEP and FAN, although the exact length of time is hard to constrain, since the μ -value of the BSM in the Snape et al. (2016) model is highly variable and depends on when the Moon is considered to have formed (with BSM μ -values of 274 ± 50 if the Moon formed at 4567 Ma, and 1063 ± 184 if it formed at 4425 Ma).

Further work may help to quantitatively define the mixing trend of Pb components at the Apollo 16 landing site by analysing the other rocks returned by the mission in which volatile enrichments have been observed (Krahenbuhl et al. 1973). If the hypothesis put forward here for the origin of Pb in 66095 is correct, other samples from the same landing site are expected to contain initial Pb isotope compositions that vary along this mixing trend. Therefore, measuring these compositions would make it possible to better constrain the compositions of the KREEP-rich and FAN mixing endmembers, and provide an external check of our hypothesis. Importantly, new constraints on the Pb isotopic composition of the FAN suite would help determine the point at which the FAN suite separated from the BSM and whether the final stages of LMO crystallisation were very rapid or more protracted.

5. Conclusions

In situ SIMS measurements of Pb isotope compositions in four thin sections of the Apollo 16 impact melt breccia 66095 indicate the presence of a single initial Pb component distributed throughout the breccia. The presence of this Pb component in plagioclase grains making up the crystalline melt matrix of the breccia indicates that the Pb was incorporated into the samples at the time of breccia formation. Based on the isochron determined from these measurements the breccia is interpreted as forming in connection with a meteorite impact on the lunar nearside at 3909 ± 17 Ma. This age correlates with the timing of the Imbrium impact proposed by several previous studies (Gnos et al. 2004; Liu et al. 2012; Snape et al. 2016) and, given the compositions of the various lithologies in the breccia, it is proposed that the rock can be most simply explained as having formed during the Imbrium event. Previous studies have linked the Pb and other volatiles in the 66095 breccia with fumarolic activity, potentially occurring during the degassing of an impact ejecta blanket (Krahenbuhl et al. 1973; Nunes and Tatsumoto 1973; Shearer et al. 2014). The data presented here is consistent with this model, provided that this process occurred immediately after the formation of the breccia in order for the same Pb component to be present in the crystalline melt matrix as well as the accessory phases and melt veins in the sample.

The initial Pb isotope composition, obtained from the data presented here, is very similar to the values calculated by Nunes and Tatsumoto (1973) for the 66095 breccia. The radiogenic nature of this Pb isotope composition provides further evidence that the volatile enrichments in 66095 are indigenous to the Moon, and most likely represents a homogenised mixture of Pb from KREEP-rich Imbrium ejecta and lower- μ anorthositic highland lithologies. Taking this assumption into account, then a mixing trend defined by likely Pb-isotope compositions of KREEP-rich lithologies and that measured in 66095 provides a way to investigate the Pb isotope composition of the lower- μ highland component, although there are currently several uncertainties that make it hard to constrain this mixing relationship.

These data demonstrate the effectiveness of this Pb-Pb isochron technique for lunar samples beyond its application in crystalline basalts. Additionally, this approach provides an alternative way to obtain precise ages of lunar samples where there is an absence of the minerals traditionally used in U-Pb

geochronology (i.e. zircon and phosphate phases). Continued development of this method may provide new ways to test models for both the impact history and early magmatic evolution of the Moon.

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Figure captions

Figure 1. – Schematic illustration of the three component mixture of Pb isotope compositions when plotted as $^{207}\text{Pb}/^{206}\text{Pb}$ versus $^{204}\text{Pb}/^{206}\text{Pb}$. Figure adapted from Snape et al. (2016).

Figure 2. – Back Scattered Electron (BSE) images showing the crystalline melt matrix textures in the 66095,222 and 66095,322 sections. Also indicated are the locations of several SIMS analyses that were used to construct the Pb-Pb isochron for the sample, including two points (indicated with yellow spots) that were used to calculate the initial Pb composition. The numbers in the SIMS spots correspond to the analysis numbers that are included in Supplementary Table B.1.

Figure 3. – Back Scattered Electron (BSE) images textures in 66095,85. (a) Cataclastic troctolitic anorthosite clast, composed primarily of heavily fractured grains of plagioclase (Pl; ~83% by mode) with anhedral olivine (Ol; ~16%), and some accessory FeNi-metal (~1%); (b) melt vein containing entrained clast of the crystalline breccia matrix; (c) a large (~1 mm) cataclastic anorthosite clast adjacent to a melt vein.

Figure 4. – Back Scattered Electron (BSE) images and element maps (Fe, Ni, P, S, Al) of the FeNi metal assemblages in thin sections (a) 66095,222 and (b) 66095,322. Occurrences of associated accessory phases have been indicated, including sulfide (likely troilite), schreibersite and phosphate grains.

Figure 5. – (a) $^{207}\text{Pb}/^{206}\text{Pb}$ versus $^{204}\text{Pb}/^{206}\text{Pb}$ plot of the complete datasets acquired from all four 66095 thin sections. The modelled composition of modern day terrestrial Pb (S+K) has been plotted for comparison (Stacey and Kramers 1975), as well as the measured composition of Canyon Diablo Troilite (CDT; Göpel et al. 1985). The filtered data used to define the isochron (see main text for details of filtering process) are indicated with opaque symbols. The unfiltered data not used to define the isochron are indicated with semi-transparent symbols. (b) $^{207}\text{Pb}/^{206}\text{Pb}$ versus $^{204}\text{Pb}/^{206}\text{Pb}$ plot illustrating the filtered dataset and isochron for the Pb component within 66095. The initial compositions for the 66095 Pb component obtained from this dataset are compared with the “2-stage”

and “3-stage” models calculated by Nunes and Tatsumoto (1973) in the inset panel. The error bars represent 2σ uncertainties.

Figure 6. – $^{207}\text{Pb}/^{206}\text{Pb}$ versus $^{204}\text{Pb}/^{206}\text{Pb}$ plot illustrating multiple stage evolution of the Pb component in 66095 within the context of the model presented by Snape et al. (2016) to explain the Pb isotope evolution of lunar basalts. The Pb component in 66095 most likely represents a mixture of Pb derived from separate lithologies, including that derived from high- μ KREEP-rich material and lower- μ anorthositic highland rocks. The blue curve illustrates evolution of the urKREEP source with range of μ -values between 2500-4000, ending at the time at which the Pb was introduced to the breccia (3909 Ma). Such μ -values are indicated by the compositions of the KREEP-rich samples (14072 and 15386) determined by Snape et al. (2016). The potential range of mixing trends between the KREEP-rich and FAN components has been indicated with dashed grey arrows labelled as “A” and “B” (see main text for discussion of the implications of these two endmember cases), an intermediate example is illustrated with a dashed black arrow. Similarly, potential Pb isotope growth curves for the FAN component are shown (assuming a μ -value of ~ 80), and the approximate area where these curves would intersect with the Apollo 16 mixing trend (assuming Pb growth until 3909 Ma) is indicated in grey, with an intermediate FAN composition represented by a star. In this diagram the Bulk Silicate Moon curve is calculated as originating from Canyon Diablo Troilite compositions (Göpel et al. 1985) at 4500 Ma with a μ -value of 462 ± 46 , although the μ -value and resulting trajectory of this curve will be highly dependent on the time at which the Moon is considered to have formed. The error bars for the initial Pb isotope compositions and the model t_1 composition represent 2σ uncertainties.

Supplementary material

Appendix A – Supplementary Figures

Figure A.1. – Back Scattered Electron (BSE) maps of the four thin sections analysed in this study. (a) 66095,222; (b) 66095,322; (c) 66095,77; (d) 66095,85.

Figure. A.2. – Plots of (a) ^{206}Pb count rates vs. the 1σ % errors on the $^{206}\text{Pb}/^{204}\text{Pb}$ ratios and (b) ^{207}Pb count rates vs. the 1σ % errors on the $^{207}\text{Pb}/^{204}\text{Pb}$ ratios.

620 **Appendix B – Supplementary Tables**

621 Table B.1 – Complete SIMS dataset.

622 Table B.2. – Average electron multiplier background levels for each analytical session.

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5