Meteoritics & Planetary Science 49, Nr 12, 2241–2251 (2014)
doi: 10.1111/maps.12395

High resolution U-Pb ages of Ca-phosphates in Apollo 14 breccias: Implications for the age of the Imbrium impact

R. E. MERLE[1*], A. A. NEMCHIN[1,2], M. L. GRANGE[1], M. J. WHITEHOUSE[2], and R. T. PIDGEON[1]

[1]Department of Applied Geology, Curtin University, GPO Box U1987, Perth, WA 6845, Australia
[2]Swedish Museum of Natural History, S-104 05 Stockholm, Sweden
[*]Corresponding author. E-mail: r.merle@curtin.edu.au

(Received 03 July 2014; revision accepted 13 October 2014)

Abstract–Previous age estimates of the Imbrium impact range from 3770 to 3920 Ma, with the latter being the most commonly accepted age of this basin-forming event. The occurrence of Ca-phosphates in Apollo 14 breccias, interpreted to represent ejecta formed by this impact, provides a new opportunity to date the Imbrium event as well as refining the impact history of the Moon. We present new precise U-Pb analyses of Ca-phosphates from impact breccia sample 14311 that are concordant and give a reliable weighted average age of 3938 ± 4 Ma (2σ). Comparison with previously published U-Pb data on phosphate from Apollo 14 samples indicate that all ages are statistically similar and suggest phosphates could have been formed by the same impact at 3934 Ma ± 3 Ma (2σ). However, this age is older than the 3770 to 3920 Ma range determined for other samples and also interpreted as formed during the Imbrium impact. This suggests that several impacts occurred during a 20–30 Ma period around 3900 Ma and formed breccias sampled by the Apollo missions.

INTRODUCTION

The absence of plate tectonics and an atmosphere on the Moon as well as a progressively decreasing flux of impactors in the solar system resulted in an exceptional preservation of the early cratering record on the lunar surface. During the early stages of lunar evolution, the cratering process led to the formation of the major impact basins accompanied by the deposition of thick ejecta blankets composed of impact breccias. One of the latest, the Imbrium basin, has been included as a part of the Late Heavy Bombardment proposed by Tera et al. (1974) to have occurred at about 3900 Ma on the basis of early whole-rock and mineral Pb-Pb and Rb-Sr isochrons and plateau ^{40}Ar/^{39}Ar dating of lunar samples from the Apollo missions (e.g., Turner et al. 1971; De Laeter et al. 1973; Tera et al. 1974). These samples contain different amounts of rock and mineral clasts welded together by a matrix representing recrystallized impact melt. Several attempts to date the Imbrium impact have been made using impact melt breccias from Fra Mauro Formation sampled at the Apollo 14 landing site and interpreted as an ejecta blanket of the Imbrium impact (e.g., Wilshire and Jackson 1972; Swann et al. 1977). Different isotopic systems applied to various rocks and minerals yield a wide range of ages between about 3770 and 3920 Ma (Deutsch and Stöffler 1987; Stadermann et al. 1991; Dalrymple and Ryder 1993; Shih et al. 1993; Gnos et al. 2004; Liu et al. 2012). The most recent studies concentrated on determining age of the Imbrium impact using in situ secondary ion mass spectrometry (SIMS) U-Pb analysis on texturally unique zircon grains interpreted to have crystallized from impact melts (Gnos et al. 2004; Liu et al. 2012). The advantage of the in situ U-Pb dating technique is that individual grains (or parts of a grain) of a single U-bearing mineral can be dated, thereby obviating potential problems of analyzing mixtures of unrelated mineral phases. In addition to zircon, Ca-phosphates (apatite and merrillite) are valuable for determining ages of impact melt breccia samples and hence the impacts that formed these breccias (Nemchin et al. 2009; Joy et al. 2011a; Grange et al. 2013). These minerals have a lower

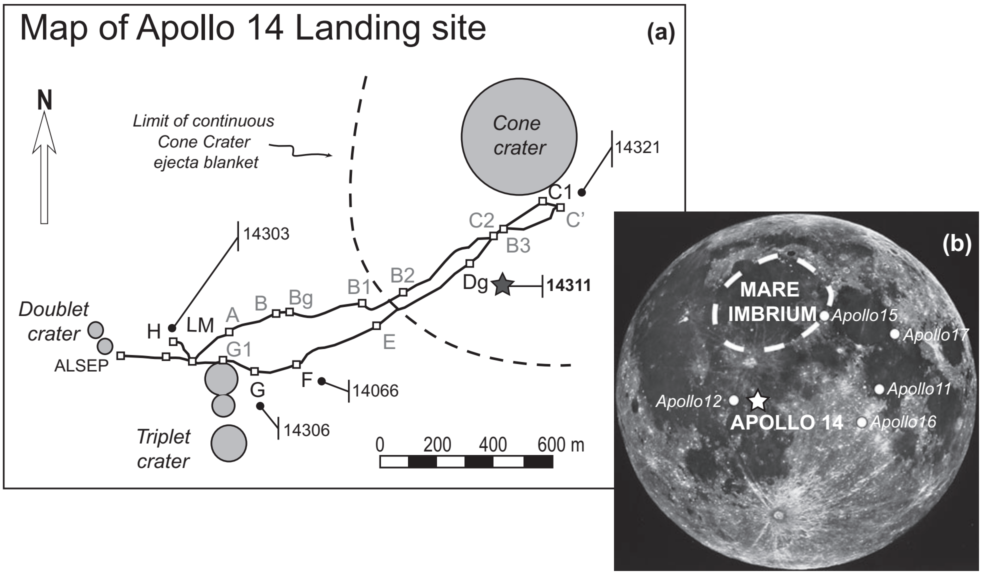

Fig. 1. a) Map of Apollo 14 landing site (after Stöffler 1989). The letters refer to the successive stations where samples were collected. The stations relevant to the samples from this study are shown in black. The station where the sample investigated in this study was collected is marked by a star and the number of the sample is indicated in bold. Numbers of samples with previously published apatite data are also given. The dashed line represents the limit of the continuous Cone crater ejecta blanket. LM = lunar module; ALSEP = Apollo Lunar surface experiments package. b) Locations of Mare Imbrium and Apollo 14 landing site on the near side of the Moon (after Lunar and Planetary Institute web site: http://www.lpi.usra.edu).

closure temperature for Pb diffusion (450–500 °C; Cherniak et al. 1991; Krogstad and Walker 1994; Chamberlain and Bowring 2000) compared to zircons and their U-Pb system is likely to be reset by the thermal pulse generated during a major impact or during relatively slow cooling in a thick ejecta blanket (e.g., Nemchin et al. 2009).

In this contribution we present new, precise U-Pb ages obtained for Ca-phosphate grains from breccia 14311 sampled during the Apollo 14 mission. We selected this rock as it was identified to be different from the typical Apollo 14 breccias and could originate from a different stratigraphic layer within the Fra Mauro Formation or entirely different impact (Stöffler 1989). We also compare the new ages with previously published U-Pb data, obtained for this and other landing sites and interpreted to date the Imbrium impact.

GEOLOGY OF THE FRA MAURO FORMATION

The Apollo 14 landing site is located 600–800 km from the rim of the Imbrium basin (Fig. 1). Pre-mission mapping and early studies of images of lunar surface indicated that the region at and around the Apollo 14 landing site is covered by ejecta from the Imbrium impact, identified as the Fra Mauro Formation (e.g., Swann et al. 1977). The landing site was selected for its proximity to the approximately 30 Ma Cone crater (Fig. 1) that is thought to have excavated rocks of the Fra Mauro Formation from beneath the surface regolith (Swann et al. 1977), hence giving the opportunity to investigate the deposits of one of the largest impacts on the Moon. The landing site can be subdivided into the Cone crater ejecta (the material excavated from the cavity created by the Cone crater impact) and a smooth older terrane around the site (Stöffler et al. 1989) which is formed mostly by regolith and regolith breccias. Two types of impact breccias have been identified. In the vicinity of the Cone crater, friable light matrix breccias (Meyer 2008) are the dominant type and supposedly form the continuous ejecta blanket of the Cone crater. Farther away, crystalline-matrix breccias (Meyer 2008) are very abundant and possibly represent the discontinuous ejecta blanket of the Cone crater event (Wilshire and Jackson 1972; Stöffler et al. 1989).

The existing textural variability in Apollo 14 breccia samples resulted in two conflicting interpretations of their origin. One suggests that the Fra Mauro Formation was not disturbed significantly by later impacts and all the breccias collected on the landing site are related to the formation of the Imbrium basin (Wilshire and Jackson 1972). This interpretation implies that the Fra Mauro Formation represents heterogeneous ejecta from the Imbrium basin and is in agreement with all collected samples being typically rich in KREEP. This enrichment and the chemical similarity of the samples support their formation in a single impact ejecta (Jolliff et al. 1991; Korotev et al. 2011). In contrast, Stöffler and coworkers (e.g., Stöffler et al. 1989; Stöffler 1989; Stadermann et al. 1991; and reference therein), suggested that only the crystalline-matrix breccias mostly collected farther from the Cone crater are representative of the Imbrium event (Fig. 1). These breccias are proposed to originate from a layer immediately underneath the regolith and named "subregolith basement" (Stöffler 1989). The light matrix breccias collected near the Cone crater could represent a deeper stratigraphic unit named the "Cone crater basement" that predates the Imbrium impact (Stöffler 1989) hence implying that old (local to Apollo 14) landing site material was reworked at the time of Fra Mauro Formation deposition (Stöffler et al. 1989). There is a general agreement that at least part of the sampled material represents genuine Imbrium ejecta. However, at the time of its deposition, this ejecta could also have been mixed with older local material of the landing site (Head and Hawke 1975; Hawke and Head 1978; Stöffler 1989).

AGE OF IMBRIUM IMPACT

The age of the Imbrium impact has been inferred from ages obtained from Apollo 12, 14, 15, and 16 samples which are interpreted to be genetically related to the impact.

The early Rb-Sr isochrons and ^{40}Ar/^{39}Ar analyses from these rocks yielded ages from 3800 Ma to 3850 Ma with the latter being related to Apollo 15 KREEP basalts from the Apennine Bench Formation located in the outermost ring of Imbrium (Basaltic Volcanism Study Project 1981; Wilhelms 1984; Spudis and Hawke 1986). As this formation was considered to be post-Imbrium but pre-Mare basalt in age, the age of Imbrium impact was established at approximately 3850 Ma. It thereafter became accepted as the canonical age of Imbrium (Spudis 1978; Wilhelms 1984; Spudis and Ryder 1985; Spudis and Hawke 1986; Ryder 1994; Hartmann et al. 2000).

Two subsequent studies challenged this canonical age. Rb-Sr analyses from Apollo 16 impact melt rocks related to the Fra Mauro Formation yielded ages as young as 3750 Ma suggesting that the Imbrium impact was not older than 3750 Ma (Deutsch and Stöffler 1987). This young Imbrium age was also indicated by ^{40}Ar/^{39}Ar ages of some Apollo 14 impact breccias (Stadermann et al. 1991), leading to an argument that the age of Imbrium impact is 3770 ± 20 Ma (2σ; Deutsch and Stöffler 1987; Stadermann et al. 1991; Stöffler et al. 2006). According to Stöffler et al. (2006), the originally accepted age of 3850 Ma was based on measured ages of lithologies that were supposedly reset by the Imbrium impact and that displayed a peak of their frequency distribution within the 3850–3900 Ma age range. This approach has been considered incorrect by these authors as the resulting mean age from the frequency distribution is not constrained by any geological evidence. Moreover, they argue that the Apennine Bench Formation is pre-Imbrium (Deutsch and Stöffler 1987). As a consequence, their preferred age of Imbrium is 3770 ± 20 Ma (2σ).

However, two following studies based on ^{40}Ar/^{39}Ar ages of plagioclase and melt from Apollo 15 impact melt breccias yielded ages in agreement with the canonical age of the Imbrium (Dalrymple and Ryder 1993; Shih et al. 1993). These authors dismissed the younger age of 3770 Ma as a local, post-Imbrium impact melt and preferred the accepted age of 3850 ± 20 Ma (2σ). Moreover, an anorthositic clast from the same landing site yielded an ^{40}Ar/^{39}Ar age of approximately 3830 Ma interpreted as reset by the Imbrium impact (Shih et al. 1993). This age is also supported by a recent study based on the trapped argon antiquity indicator used to semi-quantitatively calculate the age of lithification of the lunar regolith (see Wieler and Heber [2003] for more details) and suggesting that the Apollo 16 regolith breccias were formed between approximately 3800 and 3400 Ma (Joy et al. 2011b).

Recently, two independent studies determined U-Pb SIMS ages of zircon grains crystallized from the impact melt in lunar meteorite SaU169 and Apollo 12 samples. Zircon found in the lunar meteorite SaU169 yielded ages of 3909 ± 13 Ma (2σ; Gnos et al. 2004) and 3920 ± 13 Ma (2σ; Liu et al. 2012), while the age determined for zircon found in impact melt from the Apollo 12 breccias is 3914 ± 7 Ma (2σ; Liu et al. 2012). Considering these ages and their strong chemical affinity with KREEP, Gnos et al. (2004) and Liu et al. (2012) interpreted these melts as unambiguously representing Imbrium impact.

The discrepancy between the ^{40}Ar/^{39}Ar and U-Pb ages interpreted to represent the Imbrium impact is explained by the use of old monitor ages and decay constant when calculating ^{40}Ar/^{39}Ar ages. Correcting for the more recent monitor ages and decay constant (Renne et al. 2010) makes these ages close to 3900 Ma hence similar within error to those obtained using U-Pb zircon systematics (Gnos et al. 2004; Liu et al. 2012).

Previous Ca-phosphate SIMS analyses made on four Apollo 14 samples (14066, 14303, 14306, and 14321) yielded ages ranging from 3858 to 3950 Ma potentially bracketing the age of Imbrium impact (Nemchin et al. 2009). The analyzed minerals are phosphates, but specific mineral phases (such as apatite or merrillite) or their mixtures have not been determined. This lack of clear identification of analyzed phases has no influence on the age pattern (Nemchin et al. 2009). One possible source of uncertainty in this earlier study is related to the initial Pb correction. In particular, two samples (14303 and 14321) displayed significant amounts of initial Pb yielding unreliable ages. Samples 14066 and 14306 have a higher proportion of radiogenic Pb, making the data less susceptible to the uncertainties associated with the initial Pb correction and give a tighter age range between 3922 ± 16 Ma and 3926 ± 8 Ma, which is comparable to the SaU169 and Apollo 12 zircon ages.

STUDIED SAMPLE

Phosphates found in two thin sections of the impact melt breccia 14311 (14311-4 and 14311-5) have been investigated by SIMS U-Pb dating.

Sample 14311 was collected close to a small crater at Station Dg (Fig. 1). It is a very coherent polymict impact melt breccia composed of 75–95% of crystalline matrix formed by a mosaic of pyroxene and plagioclase crystals or crystal fragments and Fe-Ti oxides (Fig. 2) and 5–25% of mineral and lithic clasts, represented by igneous rocks and older generations of breccias (Simonds et al. 1977; Swann et al. 1977; Carlson and Walton 1978). Rare olivine clasts with reaction coronas have been identified by Wilshire and Jackson (1972). Accessory minerals include zircons and Ca-phosphates (Fig. 2).

This sample is chemically similar to other impact breccias from this landing site (Scoon 1972). However, textural differences and exposure age estimates of 14311 older than many other Apollo 14 breccias (approximately 600 Ma; Stadermann et al. 1991; Crozaz et al. 1972) led Stöffler and coworkers (e.g., Stöffler et al. 1989; Stöffler 1989; Stadermann et al. 1991) to suggest that this sample might originate from a different part of the Fra Mauro Formation.

ANALYTICAL PROCEDURES

Polished thin sections of breccia samples were prepared by and at NASA's Johnson Space Center. Ca-phosphate grains were identified in thin sections using an optical microscope. They were then investigated by backscattered electron (BSE) imaging and their chemical composition confirmed semi-quantitatively using an energy-dispersive X-ray spectroscopy (EDS) system attached to a Zeiss EVO scanning electron microscope at Curtin University. The acceleration voltage applied during several sessions was set at 20 kV and the working distance at 8.5–9 mm.

In earlier Ca-phosphates analyses, we applied a cleaning procedure that was designed to remove contaminant Pb. However, this was not successful as common Pb was relatively high in these early measurements, significantly affecting the analytical precision. In the present procedures, we have omitted several previously applied cleaning steps and we have used an ultrasonic bath with ethanol and distilled water to remove surface contamination. As a result ^{206}Pb/^{204}Pb ratios were higher by up to a factor of 10, and the analytical precision was correspondingly higher. Ca-phosphate U-Pb systems were analyzed with a high-resolution ion microprobe (SHRIMP II instrument) at Curtin University. The analytical conditions were identical to those described by Compston et al. (1984) and Williams (1998). The samples were analyzed with the intensity of the O^{2-} primary beam set between 1.1 and 2.3 nA and a spot size of 10 × 10 μm. The Ca-phosphates data were calibrated against the BR2 2058 Ma apatite standard (Grange et al. 2009) with a uranium concentration of 67 ppm.

SHRIMP II raw data were reduced using Squid2 (Ludwig 2009). Common Pb was corrected using the present-day terrestrial ratios from Stacey and Kramers (1975). All the analytical results are shown in Table 1. Concordia and weighted average ages were plotted and calculated using Excel add-in Isoplot3 (Ludwig 2008). Individual ages and weighted average ages are given at 2σ level throughout text and tables unless specified otherwise. All the weighted average ages were calculated using the ^{207}Pb/^{206}Pb ages. Ellipses in the concordia plot and box height in the weighted average age plot are drawn at 2σ level.

RESULTS

A total of fourteen analyses have been made on twelve Ca-phosphate grains in sample 14311-4 and one grain in sample 14311-5. Among the thirteen grains analyzed, nine were merrillite, two were apatite and the last two, a mixture of both phases (Fig. 2).

Their average size is about 30 μm but two grains are 70 μm (grains 14311-5, ap5 and 14311-4d, ap3; Fig. 2). The grains are subhedral and usually show straight boundaries with the other grains in the matrix (Fig. 2), but some are embayed or rounded (Fig. 2), indicating that the phosphate grains are clasts predating the impact but may have partly recrystallized during the breccia formation.

All the data yield ^{207}Pb/^{206}Pb ages ranging from 3921 ± 17 Ma to 3950 ± 16 Ma and are similar within uncertainties regardless of the analyzed phosphate phase (Table 1). Two analyses were done within a single grain from sample 14311-5 and are identical within

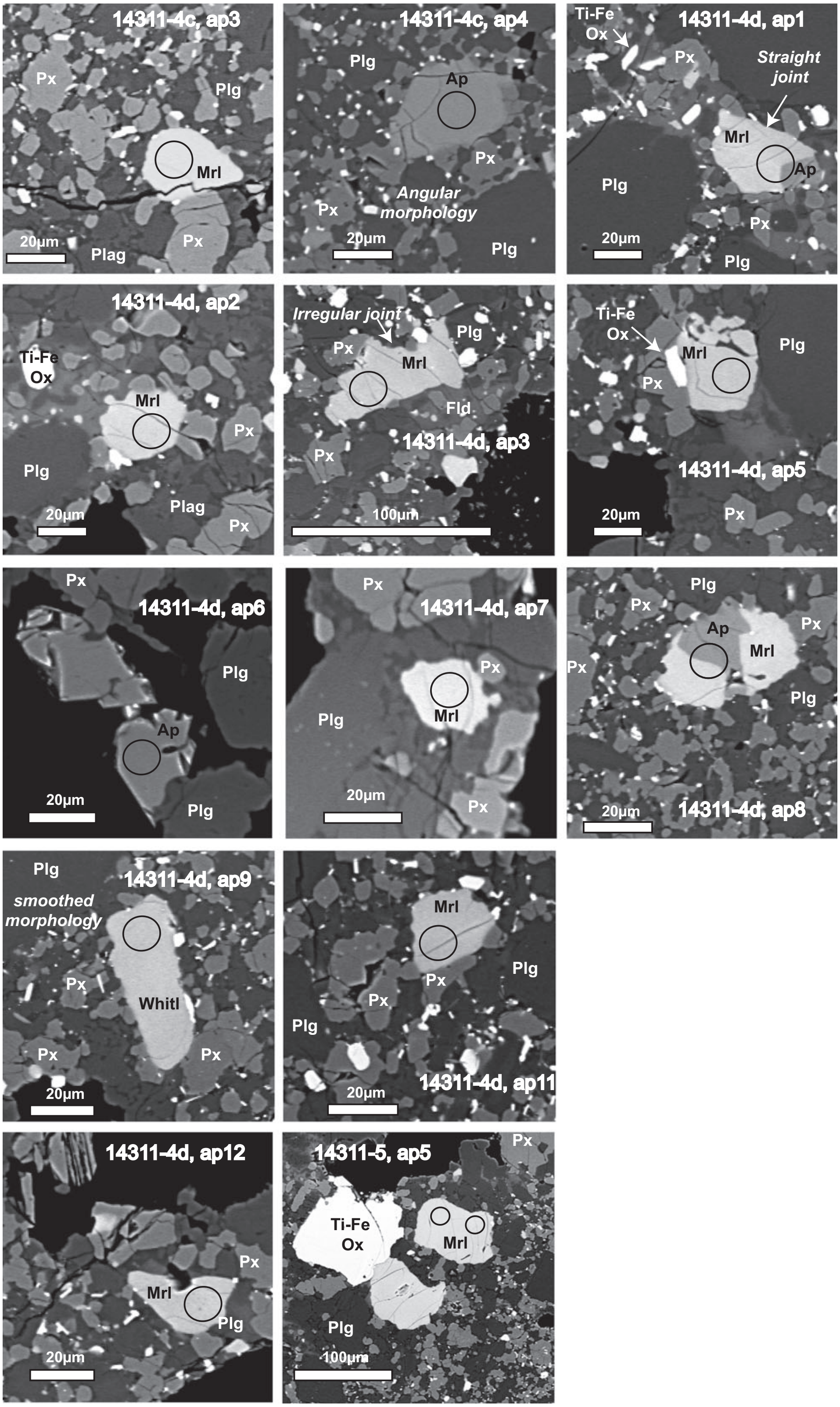

Fig. 2. BSE images of Ca-phosphate grains in breccia 14311. Ca-phosphates with rounded morphology, straight and irregular boundaries with the other grains in the matrix are represented. The principal mineral phases present in the thin sections are also identified. Mrl: merrillite, Ap: apatite; Px: pyroxene; Plg: plagioclase; Fld: feldspar; Ti-Fe Ox: titanium-iron oxides.

Table 1. SIMS U-Pb data for Ca-phosphate grains from sample 14311.

Sample name Spot name	Analyzed Mineral phase	[U] ppm	[Th] ppm	Th/U	$^{206}Pb/^{204}Pb$ Measured[a]	$^{207}Pb^*/^{206}Pb^*$	±2σ %	$^{207}Pb^*/^{235}U$	±2σ %	$^{206}Pb^*/^{238}U$	±2σ %	ρ	$^{207}Pb/^{206}Pb$ age (Ma)	±2σ (Ma)
14611,4 (one analysis per grain)														
311-4d-1	ap+mrl	4.28	50	11.8	3127	0.4061	1.09	53.209	8.75	0.9571	8.67	0.991	3921	17
311-4d-2	mrl	6.18	75	12.1	2092	0.4087	0.75	49.739	9.20	0.8921	9.16	0.996	3925	12
311-4d-3b	mrl	0.82	11	12.9	154516	0.4090	0.77	47.838	9.48	0.8484	9.45	0.996	3942	12
311-4d-5	mrl	0.99	13	12.8	[a]	0.4084	1.03	48.385	8.64	0.8535	8.58	0.993	3950	16
311-4d-6b	ap	106	38	0.36	19469	0.4079	0.69	53.012	7.61	0.9437	7.58	0.996	3937	11
311-4d-7	mrl	1.14	14	12.3	[a]	0.4089	0.64	46.960	8.06	0.8308	8.03	0.997	3946	10
311-4d-8	ap+mrl	3.22	23	7.2	[a]	0.4064	0.86	47.857	9.50	0.8442	9.46	0.995	3950	14
311-4d-9a	mrl	1.30	14	10.4	[a]	0.4080	1.05	44.184	7.66	0.7848	7.57	0.988	3940	17
311-4d-11	mrl	0.89	12	13.1	[a]	0.4060	0.72	44.757	7.65	0.7958	7.61	0.995	3938	11
311-4d-12	mrl	1.28	16	12.4	[a]	0.4047	0.74	44.728	9.49	0.8006	9.46	0.997	3928	11
311-4c-3	mrl	1.29	12	9.6	[a]	0.4064	0.61	47.211	11.24	0.8406	11.22	0.998	3936	10
311-4c-4	ap	77.1	57	0.74	[a]	0.4070	0.99	51.785	7.59	0.9197	7.51	0.990	3940	16
14311-5, apatite 5														
311-5-5a	mrl	1.00	11.01	10.96	[a]	0.4076	0.63	48.341	7.69	0.8594	7.63	0.992	3939	15
311-5-5c	mrl	0.86	9.64	11.18	17317	0.4082	1.41	48.446	7.68	0.8619	7.55	0.983	3938	21

*Indicates radiogenic Pb, i.e., corrected from common Pb (after Stacey and Kramers 1975). mrl = merrillite; ap = apatite.

[a] Indicates that the amount of ^{204}Pb is too small to give a significant ratio.

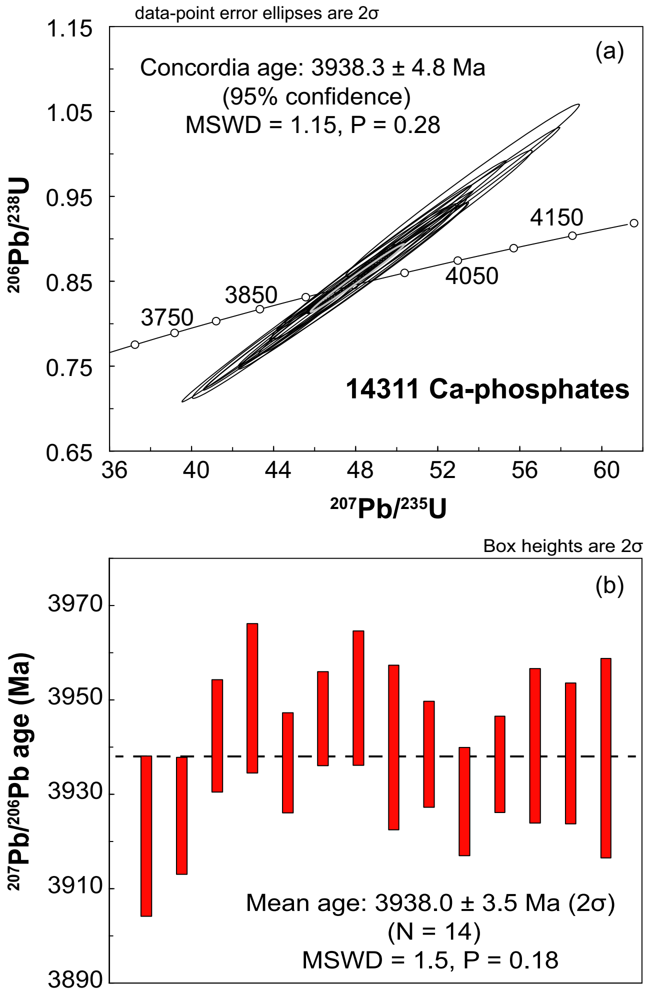

Fig. 3. a) Concordia diagram showing ^{204}Pb-corrected Ca-phosphate data obtained for sample 14311. Error ellipses are shown at 2σ level. b) Weighted average plot of ^{207}Pb/^{206} Pb ages. Error bars are shown at 2σ level.

uncertainties (Table 1) giving a weighted average age of 3938 ± 12 Ma (2σ, MSWD = 0.06, *P* = 0.94).

The entire data set forms a cluster near the concordia curve (Fig. 3a) and defines a concordia age (Ludwig 1998) of 3938 ± 5 Ma (95% confidence, MSWD = 1.15, *P* = 0.28). All ^{207}Pb/^{206}Pb ages combined as a weighted average yield an age of 3938 ± 4 Ma (2 σ, MSWD = 1.5, *P* = 0.11, Fig 3b).

DISCUSSION

Ca-Phosphate Ages in Apollo 14 Impact Breccias

The coexistence of merrillite and apatite in the same sample is widely documented in lunar rocks (Nemchin et al. 2009; Joy et al. 2011a; Grange et al. 2013; this study) and is interpreted to be a result of crystallization of a common phosphorus-saturated melt (Neal and Taylor 1991; Jolliff et al. 1993).

The size and morphology of Ca-phosphate grains in breccia 14311 suggests that these grains are mineral clasts inherited from the target rock, although some recrystallization or new crystallization from the impact melt is possible.

Regardless of the origin of Ca-phosphate crystals in 14311, their ^{207}Pb/^{206}Pb ages show a very narrow range and are indistinguishable within error. This indicates a complete resetting of their U-Pb systems (Table 1). Such observation is clearly different from partial resetting of apatite in the lunar sample 67955 as recorded by Norman and Nemchin (2014), which is expressed in highly variable ^{207}Pb/^{206}Pb ages between different grains analyzed and easy to recognize.

Our new results on Ca-phosphates from impact melt breccia 14311 show an extremely low proportion of initial Pb with ^{206}Pb/^{204}Pb ranging between several thousands and several millions hence eliminating any doubts in accuracy of the obtained mean age of 3938 ± 4 Ma. This age can be compared with ages of phosphates in other samples from the Apollo 14 landing site, although a significant number of these ages determined on Ca-phosphates from samples 14306, 14303, and 14321 suffer from substantial addition of non-radiogenic Pb (Nemchin et al. 2009). In Nemchin et al. (2009), Ca-phosphates from samples 14303 and 14321 have a majority of ^{206}Pb/^{204}Pb ratios lower than 100. However, 21 analyses of phosphates from sample 14306 have ^{206}Pb/^{204}Pb that range between about 100 and 600 and six grains analyzed in sample 14066 show comparatively radiogenic Pb with ^{206}Pb/^{204}Pb ranging from about 1000 to about 10,000 making the ^{207}Pb/^{206}Pb ages relatively insensitive to the initial Pb correction (Nemchin et al. 2009). The generally higher common Pb content of previously analyzed Ca-phosphates translates to significantly larger uncertainties sometimes as much as ten times which, in turn, increases the calculated uncertainties of the average ages obtained for these samples. This reduces the ability to resolve small age differences between samples. The statistical approach of Galbraith (1988, 1990) developed for data sets governed by Poisson processes helps to overcome some of these issues. This approach uses a maximum-likelihood procedure to find a best-fit solution assuming binomially distributed components (Galbraith 1988). Galbraith's approach is visualized by the Radial Plot algorithm (Galbraith 1990) which is specifically designed to assess the homogeneity and calculation of a combined estimate of a set of age data with different precision (Galbraith 1988, 1990). This plot is a bivariate (x,y) radial scatter plot with a circular scale. The age data set is log-transformed and standardized relative to

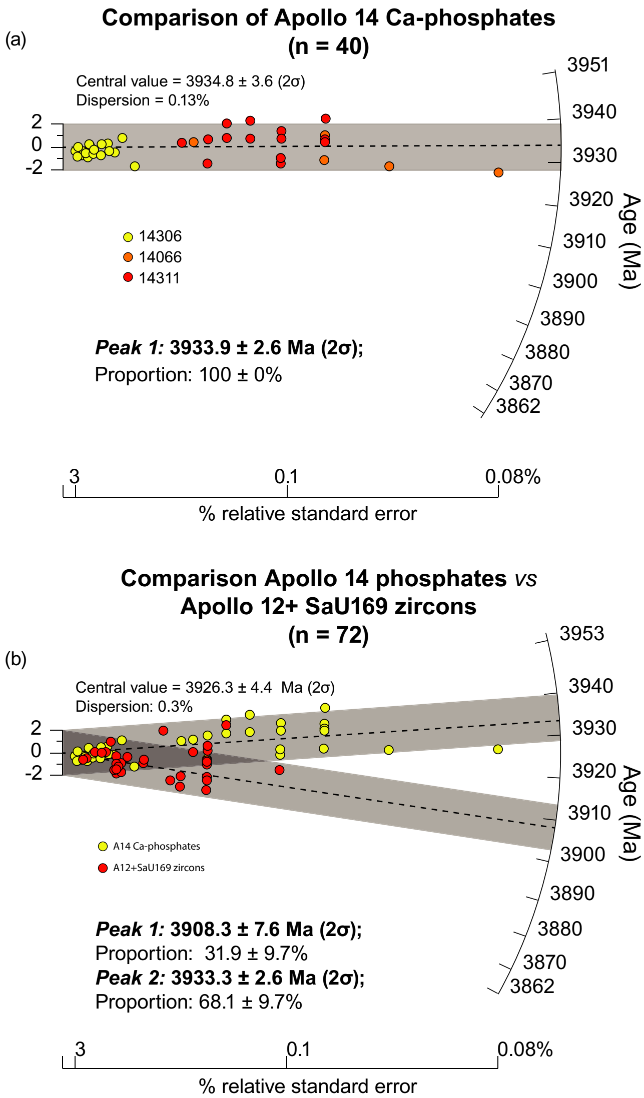

Fig. 4. Radial plots for Apollo 14 Ca-phosphate data and impact melt zircons from SaU 169 and Apollo 12 sample. The dashed lines represent the calculated values for the age distribution peaks. The gray bands represent the 2σ error interval. Note that one age obtained from sample 14066 is significantly younger than the other ages acquired from this sample (see Nemchin et al. 2009) and was considered an outlier and not included in the calculations or represented in the figure. a) Comparison of Apollo 14 Ca-phosphate data from samples 14311, 14306, and 14066 (Nemchin et al. 2009). b) Comparison of Apollo 14 Ca-phosphates data *and* SaU 169—Apollo 12 impact melt zircons (Gnos et al. 2004; Liu et al. 2012).

a central value calculated by weighted average of the transformed data. The standardized values are reported on the *y*-axis, and the inverse value of uncertainty of this log-transformed value on the *x*-axis (Fig. 4). Therefore, it helps to visualize the scatter of individual analyses and their uncertainties. The advantage of this procedure is that it uses the relative errors that generally show less grain-to-grain variability than the absolute errors, as the analytical precision is proportional to the age. In order to check the homogeneity of the data set, we applied the mixture modeling algorithm of Galbraith (2005) implemented in Radial Plot or radial plot. In this modeling, the algorithm selected the optimal number of age components.

Applying this approach to the pool of early phosphate analyses from samples 14066 and 14306 (with ^{206}Pb/^{204}Pb ratio greater than 100) and the new data from 14311 results in a dispersion of 0.13% and a central value of 3935 ± 4 Ma (2σ; Fig. 4). The mixture modeling yielded one single peak at 3934 ± 3 Ma (2σ; Fig. 4). The modeling suggests that the data distribution is best explained by a unimodal distribution centered at 3934 ± 3 Ma. This result is identical to the weighted average age of 3938 ± 4 Ma determined from the new analyses of Ca-phosphate from breccia 14311. As a consequence, this statistical approach suggests that all analyses are similar within the errors regardless of the analyzed phosphate phase. We consider the age of 3934 ± 3 Ma as the best estimate of the age of resetting of Ca-phosphate in the studied Apollo 14 impact breccias.

Age of Imbrium Impact

Gnos et al. (2004) suggested that the 3909 ± 13 Ma age of zircon grains in lunar meteorite SaU169 dates the Imbrium impact. A similar zircon age of 3920 ± 13 Ma was obtained for the same sample by Liu et al. (2012). Liu et al. (2012) also analyzed zircon formed in Apollo 12 impact melts at 3914 ± 7 Ma and interpreted it as the age of the Imbrium impact. Combining all the zircon data from SaU169 (Gnos et al. 2004; Liu et al. 2012) gives a weighted average age of 3915 ± 6 Ma (2σ, $N = 20$; MSWD = 1.1, $P = 0.33$). These ages are similar within uncertainties to the recalculated ^{40}Ar/^{39}Ar ages obtained from the other Apollo impact breccia samples that have been interpreted to date formation of the Imbrium basin (Jourdan, personal communication).

In order to compare the ages of the impact melt zircons from Apollo 12 and SaU169 with the Apollo 14 Ca-phosphate ages, the same statistical approach used for Ca-phosphate data earlier was also applied to the combined published zircon and our Ca-phosphate U-Pb data sets. The algorithm selects the optimal number of age components. While the data show a dispersion of 0.30% and the calculated central value is 3926 ± 4 Ma (2σ), two peaks are identified by the mixture modeling (Fig. 4b). One at 3933 ± 3 Ma (2σ) represents

68 ± 10% of the combined zircon-phosphate population and is defined almost exclusively by the phosphate data (with an exception of two zircon analyses from Apollo 12 sample, which could be viewed as outliers representing inherited grains in the analyzed breccia rather than those crystallized in the impact melt). The other at 3908 ± 8 Ma (2σ) representing 32 ± 10% of the data is defined entirely by the zircon data. Consequently, this latter age is the age of an impact as recorded by the impact melt zircons while the former being the age of an older impact recorded by the Ca-phosphates.

It is clear though that both ages and groups of samples discussed above cannot be attributed to the Imbrium event. We interpret the two ages to represent two closely spaced in time but separate impacts. In addition, all discussed Apollo 14 breccias containing investigated Ca-phosphate as well as Apollo 12 and SaU169 samples show high concentration of incompatible elements (KREEP component), which suggests that a high proportion of KREEP in a breccia sample does not automatically prove that the breccia originates from the Imbrium impact.

CONCLUSIONS

We have obtained a new high-precision age of 3938 ± 4 Ma for Ca-phosphates from lunar breccia sample 14311. That is older than reported ages between 3770 Ma and 3920 Ma for the Imbrium impact.

Previous less precise Ca-phosphate data from Apollo 14 breccias, with ^{206}Pb/^{204}Pb ratio > 100, are shown by statistical analysis to be identical in age to the new data, suggesting that all the Ca-phosphates from Apollo 14 breccias were completely reset during an impact at 3934 ± 3 Ma.

Statistical comparison of Ca-phosphate data from the Apollo 14 breccias with the ages of zircon from Apollo 12 samples and SaU169 suggests that they have been formed by different impacts. It also highlights a possibility that the breccias from the Apollo sample collection may belong to a number of different groups with a small differences in age detectable only by dating techniques with a few million years analytical precision. Whether these breccias are formed by several basin-forming events or reflect smaller local impacts remains to be seen.

Acknowledgments—The authors thank A. Cavosie and E. Gnos for their constructive reviews. C. Koeberl is also thanked for handling this article as associate editor. The SEM imaging and EDS data and the SHRIMP work were made with the technical support of the John De Laeter Centre. This work was funded by the Australian Research Council Discovery Project DP120102457.

Editorial Handling—Dr. Christian Koeberl.

REFERENCES

Basaltic Volcanism Study Project 1981. *Basaltic volcanism on the terrestrial planets*. New York: Pergamon Press. 1286 p.

Carlson I. C. and Walton W. J. A. 1978. *Apollo 14 rock samples*. Houston, Texas: Johnson Space Center Publication #14240.

Chamberlain K. R. and Bowring S. A. 2000. Apatite-feldspar U-Pb thermochronometer: A reliable, mid-range (~450 °C), diffusion controlled system. *Chemical Geology* 172:73–200.

Cherniak D. J., Lanford W. A., and Ryerson F. J. 1991. Lead diffusion in apatite and zircon using ion implantation and Rutherford backscattering techniques. *Geochimica et Cosmochimica Acta* 55:1663–1673.

Compston W., Williams I. S., and Meyer C. 1984. U-Pb, geochronology of zircons from lunar breccia 73217, using a sensitive high mass-resolution ion microprobe. Proceedings, 14th Lunar and Planetary Science Conference, Part 2. *Journal of Geophysical Research* 89 (suppl.):525–534.

Crozaz G., Drozd R., Hohenberg C. M., Hoyt H. P., Ragan D., Walker R. M., and Yuhas D. 1972. Solar hare and galactic cosmic ray studies of Apollo 14 and 15 samples. Proceedings, 3rd Lunar Science Conference. *Geochimica et Cosmochimica Acta* 3 (suppl.):2917–2931.

Dalrymple G. B. and Ryder G. 1993. ^{40}Ar/^{39}Ar age spectra of Apollo 15 impact melt rocks by laser step-heating and their bearing on the history of the lunar basin formation. *Journal of Geophysical Research* 98:13085–13095.

De Laeter J. R., Vernon M. J., and Compston W. 1973. Revision of lunar Rb-Sr ages. *Geochimica et Cosmichimica Acta* 37:700–702.

Deutsch A. and Stöffler D. 1987. Rb-Sr-analyses of Apollo 16 melt rocks and a new age estimate for the Imbrium basin: Lunar basin chronology and the early heavy bombardment of the Moon. *Geochimica et Cosmochimica Acta* 51:951–1964.

Galbraith R. F. 1988. Graphical display of estimates having differing standard errors. *Technometrics* 30:271–281.

Galbraith R. F. 1990. The radial plot: Graphical assessment of spread in ages. *Nuclear Tracks and Radiation Measurements* 17:207–214.

Galbraith R. F. 2005. *Statistics for fission track analysis*. Boca Raton, Florida: Chapman and Hall. 224 p.

Gnos E., Hofmann B. A., Al-Kathiri A., Lorenzetti S., Eugster O., Whitehouse M. J., Villa I. M., Jull A. J. T., Eikenberg J., Spettel B., Krähenbühl U., Franchi I. A., and Greenwood R. C. 2004. Pinpointing the source of a lunar meteorite: Implications for the evolution of the Moon. *Science* 305:657–659.

Grange M. L., Nemchin A. A., Pidgeon R. T., Timms N., Muhling J. R., and Kennedy A. K. 2009. Thermal history recorded by the Apollo 17 impact melt breccia 73217. *Geochimica et Cosmochimica Acta* 73:3093–3107.

Grange M. L., Nemchin A. A., and Pidgeon R. T. 2013. The effect of 1.9 and 1.4 Ga impact events on 4.3 Ga zircon and phosphate from an Apollo 15 melt breccia. *Journal of Geophysical Research Planets* 118:2180–2197.

Hartmann W. K., Ryder G., Dones L., and Grinspoon D. H. 2000. The time-dependent intense bombardment of the primordial Earth-Moon system. In *Origin of the Earth and Moon*, edited by Righter R. M. and Canup R. Tucson, Arizona: The University of Arizona Press. pp. 493–512.

Hawke B. R. and Head J. W. 1978. Lunar KREEP volcanism: Geologic evidence for history and mode of emplacement. Proceedings, 9th Lunar and Planetary Science Conference. pp. 3285–3309.

Head J. W. and Hawke B. R. 1975. Geology of the Apollo 14 region (Fra Mauro): Stratigraphic history and sample provenance. Proceedings, 6th Lunar Science Conference. pp. 2483–2501.

Jolliff B. L., Korotev R. L., and Haskin L. A. 1991. Geochemistry of 2-4-mm particles from Apollo 14 soil (14161) and implications regarding igneous components and soil-forming processes. Proceedings, 21st Lunar and Planetary Science Conference. pp. 193–219.

Jolliff B. L., Haskin L. A., Colson R. O., and Wadhwa M. 1993. Partitioning in REE-saturating minerals: Theory, experiment, and modelling of whitlockite, apatite, and evolution of lunar residual magmas. *Geochimica et Cosmochimica Acta* 57:4069–4094.

Joy K. H., Burgess R., Hinton R., Fernandes V. A., Crawford I. A., Kearsley A. T., Irving A. J., and EIMF. 2011a. Petrogenesis and chronology of lunar meteorite Northwest Africa 4472: A KREEPy regolith breccia from the Moon. *Geochimica et Cosmochimica Acta* 75:2420–2452.

Joy K. H., Kring D. A., Bogard D. D., McKay D. S., and Zolensky M. E. 2011b. Re-examination of the formation ages of the Apollo 16 regolith breccias. *Geochimica et Cosmochimica Acta* 75:7208–7225.

Korotev R. L., Jolliff B. L., Zeigler R. A., Seddio S. M., and Haskin L. A. 2011. Apollo 12 revisited. *Geochimica et Cosmochimica Acta* 75:1540–1573.

Krogstad E. J. and Walker R. J. 1994. Higher closure temperatures of the U-Pb system in large apatites from the Tin Mountain pegmatite, Black Hills, South Dakota, USA. *Geochimica et Cosmochimica Acta* 58:3845–3853.

Liu D., Jolliff B. L., Zeigler R. A., Korotev R. L., Yushan Wan Y., Xie H., Zhang Yuhai, Dong C., and Wang W. 2012. Comparative zircon U-Pb geochronology of impact melt breccias from Apollo 12 and lunar meteorite SaU 169, and implications for the age of the Imbrium impact. *Earth and Planetary Science Letters* 319–320:277–286.

Ludwig K. R. 1998. On the treatment of concordant uranium-lead ages. *Geochimica et Cosmochimica Acta* 62:665–676.

Ludwig K. R. 2008. *User's manual for Isoplot 3.60, A geochronological toolkit for Microsoft Excel, rev. 8*. Berkeley Geochronological Center Special Publication 4. Berkeley, California: Berkeley Geochronological Center. 77 p.

Ludwig K. R. 2009. *SQUID 2: A User's manual, rev. 12*. Berkeley Geochronological Center Special Publication 5. Berkeley, California: Berkeley Geochronological Center. 110 p.

Meyer C. 2008. Lunar sample compendium 14311. http://curator.jsc.nasa.gov/lunar/lsc/14311.pdf

Neal C. R. and Taylor L. A. 1991. Evidence for metasomatism of the lunar highlands and the origin of whitlockite. *Geochimica et Cosmochimica Acta* 55:2965–2980.

Nemchin A. A., Pidgeon R. T., Healy D., Grange M. L., Whitehouse M. J., and Vaughan J. 2009. The comparative behavior of apatite-zircon U-Pb systems in Apollo 14 breccias: Implications for the thermal history of the Fra Mauro formation. *Meteoritics & Planetary Science* 44:1717–1734.

Norman M. D. and Nemchin A. A. 2014. A 4.2 billion year old impact basin on the Moon: U-Pb dating of zirconolite and apatite in lunar melt rock 67955. *Earth and Planetary Science Letters* 388:387–398.

Renne P. R., Mundil R., Balco G., Min K., and Ludwig K. R. 2010. Joint determination of ^{40}K decay constants and ^{40}Ar*/^{40}K for the Fish Canyon sanidine standard, and improved accuracy for ^{40}Ar/^{39}Ar geochronology. *Geochimica et Cosmochimica Acta* 74:5349–5367.

Ryder G. 1994. Coincidence in time of the Imbrium basin impact and the Apollo 15 volcanic flows: The case for impact induced melting. *Geological Society of America Special Paper* 293:11–18.

Scoon J. H. 1972. Chemical analyses of lunar samples 14003, 14311 and 14321. Proceedings, 3rd Lunar Science Conference. pp. 1335–1336.

Shih C.-Y., Nyquist L. E., Dasch E. J., Bogard D. D., Bansal B. M., and Wiesmann H. 1993. Age of pristine noritic clasts from lunar breccias 15445 and 15455. *Geochimica et Cosmochimica Acta* 57:915–931.

Simonds C. H., Phinney W. C., Warner J. L., McGee P. E., Geeslin J., Brown R. W., and Rhodes J. M. 1977. Apollo 14 revisited, or breccias aren't so bad after all. Proceedings, 8th Lunar Science Conference. pp. 1869–1893.

Spudis P. D. 1978. Composition and origin of the Apennine Bench Formation. Proceedings, 9th Lunar Planetary Science Conference. pp. 3379–3394.

Spudis P. D. and Hawke B. R. 1986. The Apennine Bench Formation revisited. In *Apollo 15 Workshop*, edited by Spudis P. D. and Ryder G. LPI Technical Report 86-03. Houston, Texas: Lunar and Planetary Institute. pp. 5–107.

Spudis P. D. and Ryder G. 1985. Geology and petrology of the Apollo 15 landing site: Past, present and future understanding. *Transactions America Geophysical Union* 66:724–726.

Stacey J. S. and Kramers J. D. 1975. Approximation of terrestrial lead isotope evolution by a two-stage model. *Earth Planetary Sciences Letters* 26:207–221.

Stadermann F. J., Heusser E., Jessberger E. K., Lingner S., and Stöffler D. 1991. The case for a younger Imbrium basin: New ^{40}Ar-^{39}Ar ages of Apollo 14 rocks. *Geochimica et Cosmochimica Acta* 55:2339–2349.

Stöffler D. 1989. Brecciated nature of the Apollo 14 lunar sample suite: A review. In *Workshop on Moon in Transition: Apollo 14, KREEP, and Evolved Lunar Rocks (November 14-16, 1988, Houston, Texas)*, edited by Taylor G. J. and Warren P. H.. Lunar and Planetary Institute Technical Report 89-03. Houston, Texas: Lunar and Planetary Institute. pp. 138–144.

Stöffler D., Bobe K. D., Jessberger E. K., Lingner S., Palme H., Spettel B., Stadermann F., and Wänke H. 1989. Fra Mauro Formation, Apollo 14: IV. Synopsis and synthesis of consortium studies. In *Workshop on Moon in Transition: Apollo 14, KREEP, and Evolved Lunar Rocks (November 14-16, 1988, Houston, Texas)*, edited by Taylor G. J. and Warren P. H., Lunar and Planetary Institute Technical report 89-03, pp. 145–148.

Stöffler D., Ryder G., Ivanov B. A., Artemieva N. A., Cintala M. J., and Grieve R. A. F. 2006. Cratering history and lunar chronology. In *New views of the Moon*, edited by Jolliff B. L., Wieczorek M. A., Shearer C. K., and Neal C. R. Reviews in Mineralogy and Geochemistry, vol. 60.

Washington, D.C.: Mineralogical Society of America and Geochemical Society. pp. 519–596.

Swann G. A., Bailey N. G., Batson R. M., Eggleton R. E., Hait M. H., Holt H. E., Larson K. B., Reed V. S., Schaber G. G., Sutton R. L., Trask N. J., Ulrich G. E., and Wilshire H. G. 1977. Geology of the Apollo 14 landing site in the Fra Mauro Highlands. *Geological Survey Professional Paper* 880:103.

Tera F., Papanastassiou D. A., and Wasserburg G. J. 1974. Isotopic evidence for a terminal lunar cataclysm. *Earth and Planetary Science Letters* 22:1–21.

Turner G., Huneke J. C., Podosek F. A., and Wasserburg G. J. 1971. ^{40}Ar-^{39}Ar ages and cosmic-ray exposure ages of Apollo 14 samples. *Earth and Planetary Science Letters* 12:19–35.

Wieler R. and Heber V. S. 2003. Noble gas isotopes on the Moon. *Space Science Reviews* 106:197–210.

Wilhelms D. E. 1984. The Moon. In *The geology of terrestrial planets*, edited by Carr M. H. NASA SP 469. Washington, D.C.: National Aeronautics and Space Administration. pp. 107–206.

Williams I. S. 1998. U-Th-Pb geochronology by ion microprobe. In *Applications of microanalytical techniques to understanding mineralising processes*, edited by McKibben M. A., Shanks W. C., and Riley W. I. *Reviews in Economic Geology* 7:1–35.

Wilshire H. G. and Jackson E. D. 1972. Petrology and stratigraphy of the Fra Mauro formation at the Apollo 14 site. U.S. Geological Survey Professional Paper 785. Washington, D.C.: U.S. Geological Survey. 30 p.

SUPPORTING INFORMATION

Additional supporting information may be found in the online version of this article:

Figure S1: EDS spectra from Ca-phosphates found in impact breccia 14311. The black circles indicate where the EDS analyses were made in the grains.