Highlights

Unique felsite clast in an Apollo 14 breccia records multiple oxidation states

Represents pressure, temperature, and oxidation conditions not known for the Moon

Potentially the first evidence of a terrestrial meteorite
Title: Terrestrial-like zircon in a clast from an Apollo 14 breccia

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Abstract

A felsite clast in lunar breccia Apollo sample 14321, which has been interpreted as Imbrium ejecta, has petrographic and chemical features that are consistent with formation conditions commonly assigned to both lunar and terrestrial environments. A simple model of Imbrium impact ejecta presented here indicates a pre-impact depth of 30-70 km, i.e. near the base of the lunar crust. Results from Secondary Ion Mass Spectrometry trace element analyses indicate that zircon grains recovered from this clast have positive Ce/Ce* anomalies corresponding to an oxygen fugacity +2 to +4 log units higher than that of the lunar mantle, with crystallization temperatures of 771 ± 88 to 810 ± 37 °C (2σ) that are unusually low for lunar magmas. Additionally, Ti-in-quartz and zircon calculations indicate a pressure of crystallization of 6.9 ± 1.2 kbar, corresponding to a depth of crystallization of 167 ± 27 km on the Moon, contradicting ejecta modelling results. Such low-T, high-fO\textsubscript{2}, and high-P have not been observed for any other lunar clasts, are not known to exist on the Moon, and are broadly similar to those found in terrestrial magmas.

The terrestrial-like redox conditions inferred for the parental magma of these zircon grains and other accessory minerals in the felsite contrasts with the presence of Fe-metal, bulk clast geochemistry, and the Pb isotope composition of K-feldspar grains within the clast, all of which are consistent with a lunar origin. The dichotomy between redox conditions and the depth of origin inferred from the zircon compositions compared to the ejecta modelling necessitates a multi-stage petrogenesis. Two, currently unresolvable hypotheses for the origin and history of the clast are allowed by these data. The first postulates that the relatively oxidizing conditions were developed in a lunar
magma, possibly by fractional crystallization and enrichment of incompatible elements in a fluid-rich, phosphate-saturated magma, at the base of the lunar crust to form the zircon grains and their host felsite. Subsequent excavation by the Imbrium impact introduced more typical lunar features to the clast but preserved primary chemical characteristics in zircon and some other accessory minerals. However, this hypothesis fails to explain the high P of crystallization. Alternatively, the felsite and its zircon crystallized on Earth at a modest depth of 19 ± 3 km in the continental crust where oxidizing, low-T, fluid-rich conditions are common. Subsequently, the clast was ejected from the Earth during a large impact, entrained in the lunar regolith as a terrestrial meteorite with the evidence of reducing conditions introduced during its incorporation into the Imbrium ejecta and host breccia.

1. Introduction

No bedrock has been sampled from the Moon and any felsic magmatic rocks from the Moon currently available for study occur as small (millimeter to centimeter) clasts in lunar breccias and soils. As a result, most of the petrological context relevant to their origin and evolution is lost. Thus, all attempts to define the history of felsic magmatism on the Moon must rely on the investigations of the chemical and isotopic characteristics of these clasts and their constituents. However, chemical and isotopic information obtained from the analysis of different rock-forming and accessory minerals within single clasts, as well as bulk clast analyses, can result in conflicting evidence that is difficult to resolve within a single, coherent interpretation accurately describing the genesis and evolution of these felsic clasts.

The aim of this manuscript is to illustrate and attempt to reconcile some of these difficulties using the example of a felsite clast found in the Apollo 14 breccia sample 14321. The presence of zircon (ZrSiO₄) and quartz in this clast are particularly valuable for a comparative study between the different chemical and isotopic indicators of petrogenesis. Zircon is considered to be one of the most robust tools for absolute age determination, hosting U and Th, which decay into different Pb isotopes, potentially
enabling the use of three independent long-lived chronometers. Additionally, numerous studies of terrestrial and lunar zircon demonstrate that Hf and O isotope data, along with the concentration of trace elements, provide an opportunity to study the source characteristics of zircon host rocks and the conditions of zircon crystallization (e.g., Amelin et al., 1999, Crow et al., 2017, Ferry and Watson, 2007, Taylor et al., 2009, Trail et al., 2012, Valley et al., 2003; 2014). Specifically, Ti concentrations in zircon can be used to estimate the temperature of zircon crystallization (Ferry and Watson, 2007), whereas rare earth element (REE) concentrations reflect the composition of the parent magma. In particular, the Ce concentration relative to the adjacent light-REE can be used as a proxy of oxygen fugacity ($fO_2$) in the magma because Ce can exist as Ce$^{4+}$ and Ce$^{3+}$, in contrast to the solely trivalent state of the other LREE. Since Ce$^{4+}$ is more compatible within the zircon lattice, it will enter zircon preferentially compared to Ce$^{3+}$ and the other LREE, forming a positive Ce anomaly in chondrite-normalized diagrams (quantified as $\text{Ce/Ce}^* = [\text{Ce}]_n/([\text{La}]_n*\text{[Pr]}_n)^{0.5}$). The size of this anomaly is related to the Ce$^{4+}$/LREE$^{3+}$ of the melt from which the zircon crystallized and, therefore, is an indication of the redox conditions that existed in the melt during zircon crystallization (Burnham and Berry, 2012; 2014, Trail et al., 2012).

This manuscript combines previously obtained U-Pb zircon data, new zircon trace element analyses, and Ti-in-quartz measurements to constrain several important parameters characterizing the felsite melt during zircon crystallization. While these characteristics are supported by other, likely genetically related, accessory minerals present in the clast, they sharply contradict the chemical and isotope data obtained from some rock-forming minerals in the clast and whole-clast geochemistry. Similarly, results
from the zircon analyses here are inconsistent with the conditions inferred the host
breccia formation determined by modelling of Imbrium impact ejecta, which is believed
to be responsible for the delivery of the sample 14321 to the Apollo 14 landing site.
These contradictions result in conflicting interpretations of the origin of the felsite clast
that are explored in detail below.

2. Felsite from breccia 14321

Saw cut residue containing two zircon grains was collected during the extraction
of a felsite clast from lunar breccia sample 14321 (Section 14321, 1613). Meyer et al.
(1996) obtained SHRIMP U-Pb data for these two zircon grains and pointed out that the
grains reside in “granitic glass” that also contains grains of quartz showing the same
texture as that in the fused portions of the clast, leaving little doubt that these two zircon
grains originated from the partially melted “granite” clast in section 14321,1027
described by Warren et al. (1983). The clast had an estimated mass of 1.8 g and consists
of 60% low-Ba alkali feldspar and 40% quartz with minor Fe-rich olivine and traces of
ferrohedenbergite, ilmenite, and FeNi-metal (Warren et al., 1983). However, the clast is
brecciated and contains close to 30% crystalline impact melt (Warren et al., 1983). Un-
melted areas are composed of quartz and alkali feldspar occurring as large (1.8 × 0.15
mm) inter-grown crystals (Warren et al., 1983). Oxycalciobetafite also occurs as
intergrowths with some of the feldspar grains within the un-melted areas (Meyer and
Yang, 1988). The crystalline impact melt consists of intergrowths of quartz and feldspar
less than a few micrometers in size with a significant proportion of pyroxene and small
blebs of Fe-metal (Figure 1, Figure 2, Supplementary Figure 1). Metallic FeNi is
indicative of low $f\text{O}_2$ conditions and is ubiquitous in lunar basalts and impact breccias. Bulk clast concentrations of Zn, Ge, Ga, Au, Ba, Ta, and REE, a single pyroxene analysis indicating relatively low Mn/Fe (Warren et al., 1983), and the highly radiogenic Pb isotope compositions of K-feldspar analyzed in one of the thin sections (Compston et al., 1991) also support a lunar origin of the clast. However, the presence of oxycalciobetafite in the same felsite clasts suggests this clast was formed under conditions that are not typically associated with the Moon. Oxycalciobetafite, a complex Ca, Y, Ti oxide that contains significant proportions of large lithophile elements, has been identified in one of the thin sections of the felsite clast (14321, 1494, Meyer and Yang, 1988). It contains significant amounts of Fe$^{3+}$ and W$^{6+}$, interpreted as an indication of its formation under relatively oxidizing conditions (Meyer and Yang, 1988). Likewise, the high concentration of Nb in the ilmenite in this clast was taken as supporting evidence for relatively oxidizing conditions because Nb can only be incorporated into ilmenite as Nb$^{5+}$ (Meyer and Yang, 1988). Additionally, a more recent investigation of the sample indicated that the REE pattern of oxycalciobetafite shows a split to four consecutive curved segments that were referred to as tetrads and interpreted to reflect formation in the presence of water or F-rich fluid (Monecke et al., 2011). This interpretation is also not fully consistent with lunar magmas that are normally considered to be relatively dry and reduced compared to terrestrial magmas.

2.1 Petrographic Description

The fragments analyzed here are about 0.5 and 1 mm in size (Figures 1 and 2) and contain 100-200 µm grains of quartz, K-feldspar, and zircon surrounded by a fine-grained
matrix consisting of K-rich impact melt (Figure 2). Texturally, these fragments are identical to more brecciated parts visible in thin sections of the felsite clast from the sample 14321 (e.g., section 14321,993, Supplementary Figure 1). Some of the quartz, K-feldspar, and zircon are also fragmented and mixed into the matrix (Figure 2). The analyzed zircon grains are subhedral, as are the smaller zircon crystals. Other small zircon grains are clearly angular fragments. K-feldspar is mostly euhedral, whereas quartz shows rounded boundaries and may have experienced a degree of abrasion or partial dissolution during the clast’s impact history. Direct contacts between the large zircon, quartz, and K-feldspar grains, are not clear and are either partially or completely obscured by some degree of brecciation and melting, preventing completely unambiguous interpretation of the origin of the zircon. However, the similar sizes of these grains and their euhedral to subhedral habit suggests that the simplest explanation of the observed texture is that all three minerals have formed together in a single igneous rock. The presence of smaller fragments of zircon, quartz, and K-feldspar in the impact melt also indicates their co-crystallization in the felsite, suggesting that they were dispersed and partially fragmented from the same original felsic rock during an impact that also included them into the high-K melt, probably formed mostly by partial melting of this original rock (Figure 2). The petrographic similarity between the saw cut residue fragments and thin sections (e.g., Figures 1, 2 and 3, Supplementary Figure 1) confirms the common history of all of the pieces analyzed in this study and indicates that the zircon grains analyzed are sourced from the felsite clast.

Internal structures of the two zircon grains visible in cathodoluminescence (CL) images are partly blurred by the high degree of radiation damage experienced by the
grains, but still show traces of broad zoning, especially visible in grain-1 (Figure 3). While not exclusive to magmatic zircon grains, these features are consistent with magmatic crystallization of the analyzed zircon. It is also apparent from scanning electron (SE) and X-ray images (particularly Si and K) that reaction rims have formed at the boundaries of the large quartz grains, indicating reaction and partial dissolution of grains originally formed in this clast into impact melt (Figure 3). Consequently, the most plausible interpretation is that zircon, quartz, and K-feldspar constituted the original felsic rock. As a result of impact, melt formed at the grain boundaries, obscuring the primary petrologic relationships between these three minerals.

3. Analytical methods

All imaging presented in this paper was performed using a FEI Quanta FEG 650 scanning electron microscope at Stockholm University, Sweden or the JEOL JXA-8530F electron microprobe at the Johnson Space Center. Chemical measurements were made using techniques described in the next three sub-sections.

3.1.1 Titanium in zircon

Titanium concentrations in the lunar zircon grains were measured using the large geometry CAMECA IMS1280 secondary ion mass spectrometer (SIMS) at the Swedish Museum of Natural History, Stockholm after Kenny et al. (2016). A primary O$_2^-$ beam of $\sim$ 4 nA was used to sample a 15 $\mu$m semicircular spot on the surface of the zircon. Secondary ions were measured at a mass resolution (M/ΔM) of 3000. Relative sensitivity factors for Ti were determined by repeat analysis (n=5) of NIST 610 (434 ± 15 μg/g,
The \textsuperscript{49}Ti/\textsuperscript{30}Si ratio was measured by peak-hopping in mono-collection mode using the axial ion-counting electron multiplier. Both species were measured with a -90 eV energy filter using a 30 eV bandpass. The accuracy of Ti measurements was monitored using two known reference zircon, 91500 and Temora 1. Crystallization temperatures for the zircon grains were determined by Ti-in-zircon thermometry (Ferry and Watson, 2007). Repeat measurements of 91500 (n=14) yielded Ti concentrations of 5.1 ± 0.4 µg/g (2σ, external uncertainty) and T of crystallization in of 686 ± 7 °C (2σ, external uncertainty) both of which are within uncertainty of previously published values of 5.2 ± 0.3 µg/g and 684 ± 42 °C (2σ, Fu et al., 2008). Repeat measurements of Temora zircon (n=7) yielded Ti concentrations of 11 ± 3 µg/g (2σ, external uncertainty) and T of crystallization of 751 ± 28 °C (2σ, external uncertainty), which are also within uncertainty of previously published values of 12.1 ± 4.8 µg/g and 757 ± 34 °C (2σ, Fu et al., 2008).

3.1.2 Ti in quartz

Three different silica grains in section 14321, 993 (Figure 4, Supplementary Figure 1) were identified as quartz by Raman spectroscopy with the Hawaii Institute of Geology and Geophysics’ Wi-Tec confocal Raman microscope with 532 nm (green) laser. Titanium concentrations were measured across five quartz grains in thin section 14321,993, including three grains where the Raman measurements were performed. Titanium analyses were performed using a JEOL JXA-8530F electron microprobe at the Johnson Space Center at an accelerating voltage of 15 kV and 200 nA current, with a spot size of 10 µm. The Ti peak was counted for 400 s (200 s off peak) on four spectrometers
simultaneously and the results were combined within the JEOL software. Silicon and Al were monitored using the fifth spectrometer (30 s on peak) to ensure analyses were limited to pure silica and uncontaminated by adjacent phases. The detection limit for Ti was ~8 μg/g.

3.2 Rare Earth Elements

Rare earth element concentrations were measured using the same SIMS instrument described in section 3.1.1 generally following the analytical method of Whitehouse (2004). A primary O$_2^-$ beam of ~ 4 nA was used to sample a 15 μm semicircular spot on the surface of the zircon. Light REE (La-Eu) were measured simultaneously using six ion counting electron multipliers on the multi-collector array at a mass resolution of (M/ΔM) of 4830. The abundant heavy REE (Gd, Dy, Er, Yb), $^{89}$Y, $^{180}$Hf, and the reference ion $^{30}$Si were measured by sequential switching into the axial EM at low mass resolution (M/ΔM > 1500). However, only the abundant, even atomic numbered heavy REE were measured. Isotopes $^{30}$Si, light REE ($^{140}$Ce, $^{139}$La, $^{141}$Pr, $^{144}$Nd, $^{152}$Sm, $^{153}$Eu), $^{89}$Y, and $^{180}$Hf were measured with a -45 eV energy filter, isotopes of $^{160}$Gd, $^{161}$Dy were measured with a -85 eV energy filter, and isotopes of $^{166}$Er, $^{172}$Yb were measured with a -65 eV energy filter. Relative sensitivity factors were calculated against repeat analyses (n = 8) of the NIST 610 reference glass, the matrix peak $^{30}$Si, and concentration values from Pearce et al. (1997). The accuracy of REE in zircon measurements was monitored using repeat analyses of secondary zircon 91500 (n=9). All measurements of the 91500 zircon were within uncertainty of REE concentrations determined in 91500 by Whitehouse (2004) (Supplementary Table 1).
4. Results

4.1 Zircon chemistry and age

The REE analyses of two zircon grains in the thin section 14321,1613 confirm the previous observation of pronounced positive Ce/Ce* anomalies of 7.6 ± 2.3 and 17.5 ± 8.2 (2σ), as calculated with the equation stated in the introduction (Figure 5A, Table 1) (Hinton and Meyer, 1991; Nemchin et al., 2010). In addition, the crystallization temperatures (T), based on Ti concentrations determined in the two grains range from 771 ± 88 to 810 ± 37 °C (2σ) (after Ferry and Watson, 2006) assuming α-TiO₂ >0.8 and α-SiO₂ = 1. The Hf, U, and Th concentrations in these two grains, range between 1.29-1.85 wt%, 298-986 µg/g, and 153-542 µg/g, respectively, and are the highest of any analyzed lunar zircon reported so far (Figure 5C,D, Table 1). In contrast, the total REE content is among the lowest in the lunar zircon population (Figure 5A). Importantly, the trace element and Ti concentration measurements were performed at different times, with different analytical routines, and no SIMS analytical spots intersect visible cracks in SEM or BSE imaging, which has been shown to disturb trace element concentration measurements in lunar zircon (Crow et al., 2017). Multiple analyses between two different analytical routines that have similar results gives extra credence to the REE and Ti-concentration data presented here.

The previously reported ²⁰⁷Pb/²⁰⁶Pb ages of zircon grains from the clast range from 3958 ± 18 to 4011 ± 10 Ma (2σ, Supplementary Table 2, Grange et al., 2013; Meyer et al., 1996). This range in ages suggests partial resetting of the U-Pb system (Figure 6)
during an impact that incorporated the felsite material into the host breccia. Therefore, the oldest $^{207}\text{Pb}/^{206}\text{Pb}$ ages are interpreted to define the minimum age of crystallization of the clast ca. 4011 Ma. This age is coincident with whole rock-clast $^{147}\text{Sm}-^{143}\text{Nd}$ and $^{87}\text{Rb}-^{87}\text{Sr}$ isochrons, which yielded ages of $4110 \pm 200$ Ma and $4090 \pm 110$ Ma, respectively (Shih et al., 1985; $\lambda^{(87}\text{Rb}) = 0.0139$ AE$^{-1}$).

4.2 Quartz chemistry

Weighted average of Ti concentrations across five grains in 14321, 933 yield a statistically identical composition of $200 \pm 2$ μg/g ($2\sigma$, n=31, MSWD= 1.3, p = 0.14, Figure 7). Analytical spots were taken across each grain from rim to rim. No variation in Ti concentration was measured in any of the grains analyzed. This is an important result highlighting the robustness of the measurements and quartz itself. Since there are no concentration gradients, there was no apparent diffusion in or out of these grains during the impact history of the sample.

4.3 Ejecta modelling to constrain maximum depth of felsite clast formation

Apollo 14 breccia samples are typically assumed to represent Imbrium impact ejecta (Swann et al., 1971, 1977). The Imbrium impact basin on the lunar nearside is large enough to have had material excavated from significant depth. Ejection depth is correlated to the diameter of the transient crater. However, the exact size of Imbrium’s transient crater diameter is uncertain because transient-to-final crater scaling laws based
on surface features are not well constrained for the lunar impact basins. A more robust
approach for relating final basin structure to transient crater diameter is to use the
diameter of the central mantle uplift (crustal thinning) or surrounding annulus of
thickened crust, which are clearly imaged by gravity measurements and well reproduced
by numerical simulations (Potter et al., 2013, 2015; Miljkovic et al., 2013, 2016; Johnson
et al., 2016). Depending on the assumed pre-impact thermal profile and exact scaling
equation adopted, this approach gives a range of 500-750 km for Imbrium’s transient
crater diameter. The upper limit of this range is similar to an earlier estimate of 744 km
for Imbrium’s transient crater diameter using a simple geometrical reconstruction model
(Wieczorek and Philips, 1999). To cover the full range of sizes, two end-member
scenarios are considered: $D_t = 500$ km (Potter et al., 2015) and $D_t = 750$ km (Wieczorek
and Philips, 1999; Miljkovic et al. 2016).

The size of the transient crater depends on both the impactor size and velocity for
a given planetary surface. To illustrate the sensitivity of the model here to impactor speed
in a vertical impact, two speeds, $U$, are considered that can be viewed as representative
end-members for impacts on the Moon, $U = 10$ km/s and $U = 20$ km/s. Assuming the
impactor and target materials are of similar density and adopting the widely used
transient crater scaling law (Schmidt and Housen, 1987):

$$D_t = 1.16L^{0.78}U^{0.43}g^{-0.22},$$

these two speeds give impactor diameters $L = 106$ km and 72 km, respectively, for a 500
km diameter transient crater and $L = 179$ and 121 km, respectively, for a 750 km diameter
transient crater.
Neglecting the curvature of the Moon and assuming an ejection angle of 45 degrees, an initial ejection speed (at the time the ejecta emerges above the surface) of approximately 1.3 km/s is required to transport material from Imbrium to the Apollo 14 landing site. The corresponding radial launch position within the Imbrium transient crater of this ejecta can be estimated using ejecta scaling equations based on laboratory experiments and numerical simulations of vertical impacts (Housen and Holsapple, 2011). Approximate launch radii of 155-175 km are derived for a 500 km diameter transient crater and 260-290 km, for a 750 km transient crater diameter. Ejecta launched from the transient crater at these speeds derives from within excavation streamtubes that project back from the launch position to the impact point. The so-called Z-model (Maxwell, 1977) provides a simple geometrical approximation of these excavation streamtubes that is broadly consistent with numerical simulations of crater growth and ejection. Streamtubes bounded by streamlines were calculated that intersect the surface at the relevant launch radii using a Z-value of 3 and an origin at the impact point.

Finally, the peak shock pressure of Imbrium ejecta was determined using the results from numerical impact simulations (Pierazzo et al., 1997). Pierazzo et al. (1997) constrained the rate of shock pressure decay with depth as a function of impact speed and target material. For vertical impacts, the shock pressure contours are approximately spherical and tangent to the surface at the impact point. Using this geometry, scaling equations for the dimensions of the zone of complete melting, and the shock pressure attenuation exponent for granite (Pierazzo et al., 1997), shock pressure contours (56 GPa, complete melting; 20 GPa; 10 GPa; and 1 GPa) for each of the four Imbrium impact scenarios were calculated (Figure 8).
5. Discussion

5.1 Excavation of the felsite clast and its delivery to the Apollo 14 landing site

If the felsite clast did originate as Imbrium ejecta, the simple model presented here indicates that the streamtubes responsible for delivering the ejecta to the Apollo 14 landing site cut across the shock pressure contours illustrated by solid black lines in Figure 8 and radial position(s) within the Imbrium basin. This is supported by the lithological complexity of the breccia 14321, which contains a range of variably modified lithic and mineral clasts surrounded by some crystalline matrix and a significant portion of impact melt. Nevertheless, zircon and quartz in this clast lack petrographic evidence for shock features, with an exception of possible linear contrast variations observable in the BSE images of the latter (Figure 1). Ideally, electron backscatter diffraction (EBSD) imaging would be done on these zircon grains to further investigate any shock features that are or may have been present (e.g., Timms et al., 2012). However, the $\alpha$-dose experienced by these zircon grains since 4.01 Ga is $1.46 \times 10^{16}$ $\alpha$/mg and full metamictization is known to occur during $1-8 \times 10^{15}$ $\alpha$/mg events (Murakami et al., 1991). As such, EBSD would not be a viable analytical technique because the grains will not index as crystalline zircon. The lack of identifiable shock textures indicates relatively low shock pressure, unlikely to have exceeded 20 GPa, experienced by the 14321 felsite. If correct, the felsite is likely to have originated from a radial position of 100 to 250 km from the center of Imbrium and about 30-40 km deep within the lunar crust prior to impact, with both estimates being dependent on the size of the Imbrium transient crater.
Regardless of the shock pressure experienced by the felsite, the modelled streamtubes of ejecta (Figure 8) provide maximum possible estimate of depth for any material, which can be transported to the Apollo landing site, as 50 to 70 km, depending on the size of the Imbrium transient crater. If the Imbrium basin was created by an oblique impact (e.g., Schultz and Crawford, 2016), impactor size and shock pressure estimates presented here would change considerably, but the transient crater diameter and maximum excavation depth will not be radically different.

### 5.2 Crystallization conditions recorded by zircon

Based on Ce/Ce* ratios and calculated crystallization temperatures, the estimated oxygen fugacity for the magma(s) that crystallized these two zircon grains are $+1.3 \pm 0.5$ and $+3.4 \pm 5.6$ (2σ) log units above the Iron-Wüstite (IW) buffer (Table 1, after Trail et al., 2012). The combination of low abundances of REE and high concentrations of U, Th and Hf in the zircon grains (Figure 5A, C and D) suggests prior crystallization of phosphate, apatite in particular. Rare earth elements are highly compatible in phosphate minerals and early phosphate saturation would reduce REE abundances in the coexisting melt, which would be reflected in the REE composition of any later-crystallizing zircon. In contrast, Hf is incompatible in phosphates, while U and Th have partition coefficients close to unity in apatite (Prowatke and Klemme, 2006). Consequently, the concentrations of these elements will continue to increase in the evolving magma irrespective of phosphate crystallization, resulting in the elevated abundances of these elements in the two zircon grains from the 14321 felsite (Figure 5C,D). Thus, the trace element characteristics of oxycalciobetafite and the zircon grains in the 14321 felsite clast are
consistent with a phosphate (apatite) saturated, possibly fluid-enriched parental magma.

While the temperature of zircon crystallization can be determined independently from their Ti concentrations, given that TiO$_2$ activity is known or can be inferred from the mineral assemblage present in the host rock (Ferry and Watson, 2008), it is also possible to define crystallization temperature using Ti concentrations in quartz (e.g., Thomas et al., 2010). The latter is also pressure ($P$) dependent and such that both $P$ and $T$ information can be extracted from the combined Ti in zircon and quartz data. Both sets of experimental data linking $P$ and $T$ to the Ti concentrations suggest dependence on SiO$_2$ and TiO$_2$ activities in the crystallizing melt (Ferry and Watson, 2008; Thomas et al., 2010). The abundance of quartz in the felsite clast studied here indicates that SiO$_2$ activity is equal to 1. The presence of ilmenite that appears to have co-crystallized with the zircon (Meyer and Yang, 1988) is expected to buffer TiO$_2$ activity of the melt. The TiO$_2$ activity of the felsite melt at the time the zircon crystallization of $\geq 0.8$ was adopted for the model P-T calculations, following the study of Ashley and Law (2015).

Importantly, the phase measured here is quartz (Figure 4) with no evidence of formation from tridymite or cristobalite. Titanium concentrations of $200 \pm 2$ $\mu$g/g were determined in quartz from the clast in thin sections 14321, 993 (Figure 7). Thus, the petrographic context suggests quartz and zircon are primary phases, such that the felsite formed at a high enough pressure to be in the quartz field. Using the felsite liquidus temperature, this translates to formation at a pressure of at least 1 kb corresponding to a depth of formation of at least 24 km deep on the Moon (assuming an average lunar crust density of 2550 kg/m$^3$ and gravity of 1.622 m/s$^2$, Wieczorek et al. 2013). A more robust approach uses Ti concentrations measured in zircon and quartz and yields an average crystallization $P$ of
6.9 ± 1.2 kbar (2σ, Table 2), which on the Moon indicates a formation depth of 167 ± 27 km (2σ). This would place the crystallization of the felsite at a significant depth within the lunar mantle.

These estimates of crystallization temperature (771 ± 88 to 810 ± 37 °C), oxygen fugacity (IW +1.3 ± 0.5 to +3.4 ± 5.6), and pressure (6.9 ± 1.2 kbar) for the zircon grains measured here are unique to the lunar zircon record and the Moon. Lunar zircon typically lacks Ce/Ce* anomalies and crystallization temperatures based on Ti-in-zircon thermometry range between about 900 and 1300 °C (Figure 5B, Crow et al., 2017; Taylor et al., 2009; Valley et al., 2014). The high T estimated from other lunar zircon compared to the terrestrial record suggests that they crystallized from relatively dry magmas and the lack of Ce anomalies in lunar zircon suggests relatively reducing conditions during magmatic crystallization. Similarly, the lunar mantle is estimated to be ~one log unit below the IW buffer (Crow et al., 2017, Nemchin et al., 2010, Taylor et al., 2009, Wadhwa, 2008). Lunar basalts record relatively reducing conditions as indicated by common occurrence of metallic Fe and very low levels of ferric iron (Fe³⁺) in rock-forming minerals (Wadhwa, 2008). In summary, all redox proxies indicate that the Moon is overwhelmingly dominated by reducing conditions as compared to the Earth, with two exceptions. One is the discovery of magnetite in a clast from lunar regolith breccia 60016 (Joy et al., 2015). The other exception, which is in stark contrast to the overall lunar zircon record, are the lunar zircon grains and felsite clast investigated here.

By comparison, the terrestrial zircon record indicates a much lower T of crystallization and a substantial range of apparent oxidation states for parental magmas (Figure 5B). An almost ubiquitous characteristic of terrestrial zircon chemistry is that
they have Ti concentrations ranging from 1-100 µg/g Ti, corresponding to crystallization temperatures of 500-1000 °C and generally positive Ce/Ce* anomalies (Figure 5B, Carley et al., 2014 and references therein). Similarly, the oxidation state of the terrestrial mantle is above the IW buffer and within ± 2 log units of the fayalite-magnetite-quartz buffer (FMQ, Frost and McCammon, 2008, Gaillard et al. 2015) and significantly more oxidized than the lunar mantle. The two zircon grains studied here record fO₂ of +2 to +4 log units above the lunar mantle, more similar to the terrestrial mantle and have crystallization temperatures more consistent with terrestrial zircon (Figure 5B). Thus, the chemistry of the zircon grains reported here record crystallization conditions similar to those of terrestrial zircon and that contrast sharply with the high-T, reduced, and anhydrous magmas that produced the entire population of previously studied lunar zircon (Figure 5B, Crow et al., 2017, Taylor et al., 2009, and Valley et al. 2014).

5.3 Conflict between zircon-quartz data, other chemical features of the felsite clast, and ejecta modelling.

Several contradictions exist between the chemical data from this felsite clast the modelling of Imbrium ejecta presented here. First, the chemical characteristics shown by the zircon and quartz grains from the felsite clast in this study are more compatible with the crystallization of felsic melts on the Earth rather than from lunar magmas, despite their recovery from a lunar breccia. Further complications exist when considering all information provided by other minerals previously investigated in the clast. Accessory minerals, such as ilmenite and oxycalciobetafite, are consistent with the zircon data presented here, indicating a relatively oxidized, low-T, incompatible element rich, and
possibly fluid rich melt. However, the presence of Fe-metal and bulk concentrations of trace elements, such as Zn, Ge, Ga, Au, Ba, Ta, and REE (Warren et al., 1983), in particular low concentrations of volatile metals in the felsite, indicate an origin consistent with crystallization conditions typically ascribed to lunar melts. A lunar origin for the 14321 felsite is further supported by the highly-radiogenic Pb isotopic composition of its K-feldspar (Compston et al., 1991), which is similar to that found in other clasts of felsic rocks identified in different lunar breccias (Nemchin et al., 2017, Premo et al., 1999).

Another contradiction becomes evident when comparing the impact modelling results, which limit the depth of excavation for Imbrium ejecta to 30-70 km below the lunar surface (Figure 8), and P-T estimates obtained using Ti in quartz and zircon thermobarometry. The latter suggests that a lunar formation depth of the felsite clast was 167 ± 27 km, significantly deeper than that indicated by the Imbrium impact model and likely too deep to both crystallize a felsic melt and allow excavation of the felsite ample even by an impact large enough to form the Imbrium basin.

It is evident that irrespective of the true origin of the felsite, the disparate oxidation conditions recorded by this clast explicitly implies a multi-stage petrogenesis. Thus, part of the mineral assemblage must represent primary magmatic characteristics of the rock whereas other parts were acquired during some form of secondary modification. Zircon is highly stable with the ability to resist chemical, thermal, and mechanical modifications. Therefore, it is the mineral most difficult to modify among the assemblage that comprises the felsite clast, hence the zircon is anticipated to best reflect primary magmatic conditions of the crystallizing felsite melt.

The partial Pb loss, which resulted in the variation of the U-Pb ages of the
analyzed zircon grains may indicate that grains have experienced some degree of secondary modification and by inference, their chemical trace element compositions may have also been affected by secondary processes. However, according to experimental data, the diffusivity of LREE and Ti are three and four orders of magnitude slower in zircon, respectively, than that of Pb (Cherniak et al., 1997, Cherniak and Watson, 2001, Cherniak and Watson, 2007). Therefore, while Pb loss from a zircon grain can occur at the 5-10 micrometers margin within a time frame of about 1 Ma at 900°C (excursions to higher temperatures during an impact would probably result in a complete melting of the clast), it would require close to 10 Ma to have a similar effect on the REE and even longer for a measurable Ti change to occur in the grain. It is also possible that mobilization of different elements from zircon during the impact is not governed by volume diffusion. However, while Ti and REE represent lattice substitutions in zircon, Pb is accumulated in defects associated with radiation damage, which should enhance preferential Pb loss as compared to other chemical constituents. Consequently, it is plausible that zircon grains investigated here preserved their primary REE and Ti concentrations while losing some of radiogenic Pb during the impact.

It appears that the oxycalciobetafite and ilmenite have also preserved their original characteristics. Quartz is almost as chemically and mechanically resistant as zircon and could be expected to survive the changes that accompanied the secondary processes that have affected the rock. Although, Ti diffuses faster in quartz than zircon (Cherniak et al., 2007), it would still require a few millions of years to completely re-equilibrate 100-200 micrometers quartz grains at earlier used 900°C, without leaving any traces of inhomogeneity. This appears not to be the case based on the multiple Ti
analyses of quartz grains. Consequently, it is likely that quartz preserved its primary chemical characteristics, similar to zircon and other accessory phases. Texturally, these minerals appear to constitute the un-brecciated part of the clast, also supporting preservation of their primary characteristics. In contrast, the Fe-metal is confined to the crystalline shock melt and likely formed by post-crystallization heating during incorporation of the felsite into the breccia (Figures 1 and 2). Metallic Fe could have been created and added through the \textit{in situ} reduction of Fe from the pyroxenes or ilmenite. Similarly, the shock melt contains a significant amount of pyroxene that has a lunar Mn/Fe ratio (Figures 1 and 2) but no pyroxene occurs within the un-brecciated coarser-grained intergrowths of quartz and K-feldspar.

K-feldspar in this felsite shows a highly radiogenic Pb isotopic composition similar to K-feldspar grains in other clasts found in Apollo 14 breccias (Compston et al., 1991, Nemchin et al., 2017). These compositions have been interpreted to represent radiogenic Pb that accumulated in the samples prior to the impact that formed the breccia. During the last impact event that formed the breccia, the radiogenic Pb was distributed throughout the sample. This process homogenized the Pb isotope composition of the minerals on a grain scale (Nemchin et al., 2017). It is, therefore, likely that the K-feldspar in the felsite clast from 14321 has also acquired its radiogenic Pb as a secondary component resulting from relatively low-temperature diffusion of mobile, highly radiogenic Pb (Premo et al., 1999) during the impact that resulted in breccia formation, in this case Imbrium.
5.4 Formation of the felsite clast

Previous studies proposed that the felsite clast in 14321 formed by extensive fractional crystallization, which concentrated highly-charged cations in the residual liquid, also resulting in an increasingly oxidized melt, perhaps due to the presence of a fluid or gas (Burgisser and Scaillet, 2007, Meyer and Yang, 1988, Monecke et al., 2011). Low crystallization temperatures estimated from the Ti concentrations in zircon and quartz, the low abundances of REE as a result of apatite saturation, as well as the tetrad effect in the REE pattern of oxycaliobetafite (Monecke et al., 2011) suggests that the residual liquid may also have been enriched in F or even water. While these conditions have not been previously recorded anywhere on the Moon, the data obtained for the felsite clast suggest that they could have been heterogeneously distributed within the lunar crust. One possibility is that slow cooling and fractionation of an initially basaltic melt within the lower crust or near the crust-mantle boundary, in a manner similar to fractionation of some layered intrusions on the Earth and similar to the KREEP formation process, just on a smaller scale. The minimum time of this fractionation is defined as 4011 ± 10 Ma by the U-Pb system in the investigated zircon grains. After crystallization at a depth of 30-70 km, the felsite was excavated during the Imbrium impact and the characteristics indicative of more reducing conditions were introduced to the clast during incorporation of the clast into the host breccia at ca. 3.9 Ga. At the same time the Pb isotope composition was homogenized across main minerals, such as K-feldspar, but excluding zircon, which nevertheless, could have experienced partial Pb loss. The only observation that cannot be explained directly by a lunar origin of the sample is Quartz/Zircon Ti-based pressure estimate for the felsite formation that places it at 167 ±
This depth estimate is difficult to accept from the perspective of both crystallisation of the felsite, as it places it significantly below the mantle-crust boundary where felsite likely cannot crystalize, and the predicted depth of excavation even when large, basin forming impacts are considered.

An alternative interpretation that can reconcile all observations including the high P of crystallization, is a terrestrial origin for the felsite clast. Although this explanation may seem unlikely, current estimates suggest that between $10^7$ and several times $10^8$ kg/km$^3$ of Earth may have been delivered to the lunar surface as terrestrial meteorites (Armstrong et al., 2012), corresponding to about 0.05 to 0.5% by volume of a 10 m thick lunar regolith (Crawford et al., 2008). Additionally, on Earth, the depth corresponding to 6.9 ± 1.2 kbar is 19 ± 3 km and places the sample comfortably within the middle crust where it could have formed at ca. 4.01 Ga under oxidizing, low-T, fluid rich conditions common for terrestrial magmas. In this scenario, zircon, other accessory minerals, and quartz would have preserved the record of primary crystallization. The subsequent history of the felsite would include excavation by a large impact from the depth of 19 ± 3 km and its delivery to the Moon as a terrestrial meteorite. This would have been followed by its incorporation into Imbrium impact ejecta and ultimately the 14321 breccia. Thus, the combined effect of both impact events would have introduced all of the secondary ‘lunar’ features, including (i) mixing with impact melt or partial re-melting of the clast, (ii) introduction of Fe-metal, (iii) profound loss of volatiles making the chemical signature of the whole rock indistinguishable from all other lunar samples and (iv) introduction of highly radiogenic Pb into K-feldspar grains.
6. Conclusions

Geochemical data from a felsite clast in lunar breccia 14321, interpreted to be Imbrium ejecta, are internally inconsistent and estimates of its crystallization depth obtained from mineral compositions are in disagreement with constraints provided by impact modelling. Disparate oxidation states recorded in the clast require a multistage formation process. Similarly, the calculated pressure of crystallization based on quartz and zircon compositions indicates a depth of origin on the Moon of 167 ± 27 km, likely far too deep for a felsic melt to crystallize, while the impact model presented here restricts its depth of excavation by the Imbrium basin to between 30-70 km. Zircon, oxycalciobetafite, and ilmenite in the clast record a low temperature, oxidized, possibly F- or even water-enriched melt that appears to be unique to the Moon, yet common to Earth. In contrast, the presence of Fe-metal in the felsite, its bulk rock geochemistry, and Pb isotope compositions in alkali feldspar grains indicate formation in a reduced environment and a more typical lunar geochemistry. Thus, two origins for the clast are possible. The first possibility is that the felsite formed on the Moon at 30-70 km depth in an unusually oxidizing magmatic environment with a $fO_2$ that was +2 to +4 log units above that of the lunar mantle at ca. 4011 ± 10 Ma. Such relatively oxidized conditions might have been achieved through an enrichment of incompatible elements during a fractional crystallization process at the base of the lunar crust, similar to layered intrusions on Earth. The clast was then excavated by the Imbrium impact from its original location. During its excavation, transport, and eventual incorporation in lunar breccia 14321, the Fe-metal was introduced to the clast or formed in situ through reduction of Fe from the pyroxenes or ilmenite. In addition, other secondary features, such as radiogenic
Pb isotope compositions of alkali feldspars, general depletion of the sample in volatile elements could have been also acquired during breccia formation. The second possibility for the origin of the clast, which explains all of the geochemical features examined by this study, is crystallization on Earth at a depth of 19 ± 3 km, where low temperature, oxidizing, fluid-enriched conditions are common. The clast was then ejected from the Earth by a large impact, which did not cause any notable effects. Subsequent, it was entrained in the lunar regolith as a terrestrial meteorite and subsequently thermally and chemically processed by the Imbrium impact. In this scenario, all Moon-like chemical and isotopic features were introduced when the breccia 14321 was assembled and the clast was incorporated into the sample.

7. Acknowledgements

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microprobe facility operates as a Nordic infrastructure. This is NordSIMS publication #584.

8. References:


Figure Captions

**Figure 1.** Backscatter electron images of clasts from saw cuts containing the two zircon grains, which are surrounded by K-Feldspar, quenched melt glass containing Fe-metal (smaller than 10 μm), and quartz (Qtz). Bright material in cracks or divots is the remnant of gold from coating for SIMS analyses.

**Figure 2.** Backscatter electron image of the broader textural context for one of the zircon grains analyzed here. While there is no direct contact between the large zircon, quartz and
K-feldspar grains, the similar sizes and their euhedral to subhedral habit suggests that
they are cogenetic and partially fragmented during an impact.

**Figure 3.** Cl, SEM, and EDS maps of certain elements surrounding the two zircon grains
analysed here. When contrast and brightness are increased substantially compared to
more commonly applied analytical conditions CL patterns show traces of broad zoning,
especially visible in Grain-1.

**Figure 4.** Raman spectra for 4 quartz grains in section 14321, 993 and reference spectra
for other silica polymorphs.

**Figure 5A.** REE in lunar zircon normalized to CI chondrites (McDonough and Sun, 1995). blue - zircon grains from (Crow et al., 2017 and Taylor et al., 2009); red – zircon
from saw cuts of felsite clast found in breccia 14321 from this study and Hinton and
Meyer, 1991. **Figure 5B** Ce/Ce* vs. crystallization T determined from Ti concentrations
in zircon. Fields are from literature spanning most geological settings where zircon
crystallizes (Carley et al., 2014 and references therein). The data representing the Jack
Hills population are from the most recent compilation of Bell et al., (2016). Lunar data is
from Crow et al., (2017) and Taylor et al., (2009). **Figure 5C** Hf concentrations vs. Y.
All lunar zircon data are from Crow et al., (2017). **Figure 5D** Th concentrations vs. U.
All lunar zircon data are compiled from Crow et al., (2017) and Taylor et al., (2009).
Figure 6. U-Pb data for two zircon grains from felsite clast in 14321 a) Terra-Wasserburg plot; b) $^{207}\text{Pb}/^{206}\text{Pb}$ ages. Red and black ellipses/error bars represent two different zircon grains. The lack of a statistically identical age group suggests these grains may have been partially reset. Therefore, the ca. 4011 Ma age is interpreted to be the minimum age of crystallization.

Figure 7. A) BSE images of measured quartz grains in thin section 14321,993 with Ti analysis spots and corresponding weighted average for all grains measured. Each color or pattern corresponds to a different grain in 14321,993.

Figure 8. Shock pressure provenance diagrams of Imbrium ejecta for different plausible impact scenarios (transient crater diameter $D_t$, impactor speed $U$, impactor diameter $L$): (a) $D_t = 750$ km, $U = 20$ km/s, $L = 101$ km; (b) $D_t = 500$ km, $U = 20$ km, $L = 72$ km; (c) $D_t = 750$ km, $U = 10$ km/s, $L = 149$ km; (d) $D_t = 500$ km, $U = 10$ km, $L = 106$ km. The colour shading indicates the estimated peak shock pressure $P_{sh}$ experienced by the ejecta: red – $P_{sh} > 56$ GPa (melt); dark blue $P_{sh} = 20-56$ GPa; light blue – $P_{sh} = 10-20$ GPa; green – $P_{sh} = 1-10$ GPa. The solid black curves delineate the approximate source of ejecta transported to the Apollo 14 landing site, relative to the center of Imbrium.
Figure 3
Click here to download Figure: Bellucci et al., 2018 EPSL Lunar Zircon Reboot 2 revised Figure 3
Figure 6
Click here to download Figure: Bellucci et al., 2018 EPSL Lunar Zircon Reboot 2 Figure 6.pdf
Mean = 200 ± 2 [83%] 95% conf. MSWD = 1.3, probability = 0.14
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14321-1613-2       Sample/CI
14321-1613         Hinton and Meyer, 1991   Sample/CI

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1) Calculated using Ferry and Watson 2007
2) $\alpha$SiO$_2$ of 1
3) $\alpha$TiO$_2$ of 0.8
4) Calculated using Thomas et al., 2010
5) Figure 7
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