The impact history and prolonged magmatism of the angrite parent body

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Abstract—As some of the oldest differentiated materials in our solar system, angrite meteorites can provide unique insights into the earliest stages of planetary evolution. However, the timing of planetary mixing, as evidenced by oxygen isotope variations in the quenched angrites, and the extent of magmatism on the angrite parent body (APB) remain poorly understood. Here, we report on microstructurally guided in situ geochemical and Pb–Pb isotopic measurements on angrites aimed at better understanding of the timing and nature of magmatic processes, as well as impact events, on the APB. The quenched angrite Northwest Africa (NWA) 12320 yielded a Pb–Pb date of 4571.2 ± 9.4 Ma, which we interpret as corresponding to the timing of planetary mixing. The only known shocked quenched angrite, NWA 7203, also yielded an ancient Pb–Pb date of 4562.9 ± 9.3 Ma, which is identical to the Pb–Pb date of 4563.6 ± 7.9 Ma obtained for the texturally intermediate angrite NWA 10463. Pb–Pb analyses in phosphates in the dunitic angrite NWA 8535 yielded a much younger date of 4514 ± 30 Ma, representing the youngest Pb–Pb date ever recorded for an angrite. Based on the evidence from the lack of shock deformation, olivine major and trace element compositions, and no apparent contamination in the oxygen isotope composition of NWA 8535, our findings are consistent with prolonged magmatism on the APB. This finding is consistent with a large size for the APB.

INTRODUCTION

Angrites constitute a group of alkali-depleted basaltic achondrite meteorites that are among the oldest igneous rocks in the solar system (Keil, 2012; Mittlefehldt et al., 2002; Zhu et al., 2019). Based on their isotopic systematics, such as ε50Ti, ε54Cr, and Δ17O, in addition to Fe-Mn ratios of pyroxene, it has been suggested that the angrite parent body (APB) originated from a similar planetary reservoir to the Earth–Moon system (Kruijer et al., 2020; Papike et al., 2017). Evidence from the Mn-Cr isotope characteristics of angrites also suggests that the APB was probably larger than the asteroid 4-Vesta (Zhu et al., 2019), although no individual asteroid has been identified as the source of angrites (Keil, 2012). Based on differing textures and mineralogy, angrites have been primarily divided into pluonic (slowly cooled) and quenched (rapidly cooled) subgroups (Keil, 2012). However, Northwest Africa (NWA) 10463 and NWA 8535 consist of similar mineralogical assemblages yet differing textures, which do not fit into either of these two categories. These are classified as intermediate and dunite type, respectively. Investigating these unique samples and their chronological histories can, therefore, provide insights into the evolution of the APB, and more generally of large planetesimals in the early inner solar system.
Pb–Pb dating studies demonstrate a dichotomy between the formation ages of plutonic angrites (4558.86 ± 0.30 to 4557.65 ± 0.13 Ma) and the quenched angrites (4564.18 ± 0.14 to 4563.8 ± 0.4 Ma; Keil, 2012). It has been consequently suggested that quenched angrites formed by extrusion of melt from their source reservoir onto the surface of the APB where they cooled rapidly, whereas the plutonic angrites represent melt pockets in the interior of the planetesimal, which cooled slowly, post APB differentiation (e.g., Keil, 2012; Sanborn & Wadhwa, 2021; Tissot et al., 2017; Zhu et al., 2019). It has been suggested that the bulk angrite $^{55}$Mn–$^{52}$Cr isochron represents the timing of mantle–crust differentiation (magma ocean crystallization) of the APB at 4563.2 ± 0.3 Ma, that is, ~5 Ma after the formation of calcium- and aluminum-rich inclusions (CAI), the oldest solar system solids (e.g., Desch et al., 2023; Piralla et al., 2023). The paleomagnetic records for angrites indicate that the core dynamo began ~4 Ma after CAI formation (Wang et al., 2017), which is identical to the mantle–crust differentiation age inferred by Zhu et al. (2019). This has led to the suggestion that crust and core formation occurred almost simultaneously in the APB. While it has been previously suggested that all angrites represent unshocked, unbrecciated, and unaltered primitive samples (Scott & Bottke, 2011), implying a simple crystallization history for the APB, recent petrological investigations on the quenched angrite NWA 7203 have revealed evidence for shock melting (Hayashi et al., 2022), and recent oxygen isotope investigations demonstrate evidence for early, large-scale planetary mixing (Rider-Stokes et al., 2023), implying a complex chronological history for the APB.

Angrites are medium- to coarse-grained basaltic igneous rocks consisting of variable proportions of calcic olivine, Al-Ti-bearing diopside–hedenbergite, and anorthite (Keil, 2012). Minor and accessory phases within angrites are kirschsteinite, spinel, ulvöspinel, metallic FeNi, troilite, titanomagnetite, whitlockite, ilmenite, celsian, rhönite, kurtite (the Fe$^{2+}$ analog of rhönite—Ca$_4$(FTi$_2$)[O$_4$Si$_8$Al$_4$O$_{36}$]) and silico-phosphates (Hwang et al., 2016, 2019; Keil, 2012). Most noticeably, angrites contain phosphates (silico-phosphate), which can host uranium and are thus key phases for in situ dating using the U to Pb radioactive decay system. The phosphates present in angrites are tsangpoite Ca$_9$(PO$_4$)$_2$[(SiO$_4$) (the hexagonal polymorph of silicocarnotite) and matyhite Ca$_9$(Ca$_{0.8}$,Na$_{0.2}$)$_3$Fe(PO$_4$)$_7$ (the Fe-bearing analog of Camellorrhithane) (Hwang et al., 2019), which are very similar in terms of chemistry and structure to apatite Ca$_9$(PO$_4$)$_2$(F, Cl, OH) and matyhite Ca$_9$Na(Fe,Mg)(PO$_4$)$_7$ (Hughes & Rakovan, 2002; Hughes et al., 2006; Hughes, 2015; Xie et al., 2015). Apatite and matyhite exhibit microstructures that progressively become more complex and deformed with increasing levels of shock-loading in terrestrial settings, lunar, Martian, and eucrite meteorites (e.g., Cernik et al., 2019; Cox et al., 2020; Darling et al., 2016, 2021; McGregor et al., 2021; White et al., 2021). In addition to mineral structure transformations, shock events can trigger chemical reactions and migration of volatile species through high-diffusivity pathways (e.g., Darling et al., 2021; Kizovski et al., 2019). Apatite is a sensitive impact chronometer, with a moderate closure temperature to solid-state Pb diffusion of approximately 350–570°C (Chew & Spikings, 2021). Pb diffusion and loss can be extreme depending on the microstructural complexity of the apatite grain, with shock deformation and recrystallization providing fast diffusion pathways that lead to a robust record of the impact age (McGregor et al., 2018). Shocked phosphates, including tsangpoite and matyhite, can, therefore, constrain the timing of impact events, while unshocked, undeformed, phosphates preserve chronological information about the timing of their cooling below 350–570°C.

By coupling quantified nanostructural analysis through electron backscatter diffraction (EBSD) with in situ phosphate Pb–Pb dating and trace element analyses of angrites, we empirically quantify the severity and timing of planetary processes on the APB, providing new insights into the magmatic evolution of the angrite meteorite suite and its shock metamorphic history.

**MATERIALS AND METHODS**

**Sample Petrography**

**NWA 7203**

NWA 7203 consists of fine- and coarse-grained regions, both consisting of 41 vol% olivine and kirschsteinite, 24 vol% Al-Ti-rich clinopyroxene, and 34 vol% pure anorthite (An 91), with accessory ulvöspinel, troilite, and silico-apatite (Hayashi et al., 2022; Figure 1a). Mg-rich zoned olivine xenocrysts occur as large (500 µm) subhedral grains embedded within the fine-grained areas. Pervasive shock-induced melt veins have been reported to crosscut both fine- and coarse-grained regions with amorphization in close proximity (Hayashi et al., 2022). Based on the oxygen isotope data of Rider-Stokes et al. (2023), NWA 7203 is characterized by a $\Delta^17$O value of $-0.052\%_{oo}$ plotting on the revised angrite fractionation line and, thus, clearly belongs to the angrite clan (Table 1).

**NWA 12320**

NWA 12320 is a recently identified quenched angrite, with a similar mineralogy to both Sahara 99555 and D’Orbigny (Keil, 2012). NWA 12320 consists of 45 vol% Al-Ti-bearing diopside, 24 vol% anorthite, 20 vol% olivine, 10 vol% hedenbergite, and accessory phosphates,
Fe-sulfides, and spinel (<1 vol%). The fine-grained texture of NWA 12320 is more similar to that of D’Orbigny in comparison to Sahara 99555, with clusters of olivine and anorthite being enclosed by large (500 μm) euhedral diopside crystals. Unlike Sahara 99555 and D’Orbigny, NWA 12320 contains large (1 mm) xenocrysts of Mg-rich olivine, one of which reveals irregular patchy zoning. Similar to other quenched angrites, hedenbergite appears to surround clusters of olivine and anorthite and as interstitial quenched melt between euhedral diopside. Fe-sulfides, phosphates, and spinel are often situated within the interstitial...
hedenbergite phase. Little to no evidence of shock deformation is observed in this sample (Figure 1b). NWA 12320 is characterized by an oxygen isotope disequilibrium, with matrix fractions having a $\Delta^{17}O$ value of $-0.024\%_o$ and relict olivine grains having a $\Delta^{17}O$ value of $-0.065\%_o$, which suggests an impact melt origin for this sample (Rider-Stokes et al., 2023; Table 1).

**NWA 10463**

NWA 10463 is distinct from the plutonic and quenched angrite meteorites due to the presence of two populations of olivine, those which are chemically zoned and those with kirschtenite exsolution lamellae. NWA 10463 comprises 29 vol% Mg-rich olivine, 36 vol% Al-Ti bearing diopside, 20 vol% anorthite, 10 vol% Ca-rich olivine, 2 vol% merrillite, and accessory spinel and Fe-sulfides (Figure 1c). Al-Ti-bearing diopside occurs as large 1 mm euhedral grains, with no chemical zoning or inclusions. Mg-rich olivine occurs as large 1.5 mm euhedral grains with obvious chemical zoning, while smaller (250 $\mu$m) Ca-rich olivine grains with Ca-poor exsolution lamellae are also present in the sample. Anorthite occurs as 500 $\mu$m wide rounded grains situated within the diopside groundmass (Figure 1c). NWA 10463 has a $\Delta^{17}O$ value of $-0.082\%_o$, plotting on the revised angrite fractionation line (Rider-Stokes et al., 2023; Table 1).

**Micro- and Nano-Structural Analysis**

To undertake initial microstructural characterizations, all samples were carbon-coated using an EMITECH K950 Turbo carbon sputter and examined with an FEI Quanta 200 3-D scanning electron microscope (SEM) fitted with an Oxford Instruments 80 mm$^2$ X-Max energy-dispersive X-ray (EDX) detector at The Open University. The beam conditions used for backscatter electron (BSE) imaging and smart-mapping comprised an incident beam of 0.6 nA current and a 20 kV accelerating voltage. Imaging and analyses were performed at a working distance of 15 mm. Whole-section elemental energy-dispersive spectroscopy (EDS) maps were acquired for each sample and hotspots of concentrated P and Ca were used to identify phosphate grains.

To ensure the removal of surface defects, all samples were polished for approximately 20 min using 0.05 $\mu$m alumina powder using a Buehler Vibromet 2 vibratory polisher at the University of Portsmouth. This process removes the carbon coat and minimizes the scattering and shadowing of electrons caused by uneven surface interaction, which is critical for EBSD analyses. For NWA 7203 and NWA 8535, electron microscope observations were undertaken using a Zeiss EVO MA10 LaB$_6$ SEM at the University of Portsmouth, following the methodology of Darling et al. (2021). The samples were tilted to 70° and a
20 kV, 1.5–2 nA electron beam was used to generate EBSD “maps,” consisting of electron backscatter diffraction patterns (EBSP) acquired at step sizes of 0.1–1 µm and a working distance of 14 mm. Data were processed offline using Aztec Crystal, where a “wildspike” correction and noise reduction (level 8) were applied. Microstructural data were initially interpreted using band contrast (BC) images. BC describes the intensity of Kikuchi bands in relation to the overall EBSD, highlighting the crystallinity of the analyzed phosphates. Inverse pole figure (IPF) maps are colored according to the orientation of the studied phase relative to the crystal axes, allowing the differentiation of phase orientations. Finally, the degree of internal grain misorientation was visualized using grain reference orientation deviation (GROD) maps. Grains are defined by misorientation angles >10°, while subgrains are defined by orientations <10°. Olivine diffraction patterns were matched to an orthorhombic symmetry with parameters of \(a = 4.756\), \(b = 10.207\), \(c = 5.98\) and \(\alpha = 90°\), \(\beta = 90°\), \(\gamma = 90°\). The silico-phosphates’ diffraction patterns were matched to whitlockite, a trigonal symmetry with parameters of \(a = 10.4011\), \(b = 10.4011\), \(c = 37.3160\) and \(\alpha = 90°\), \(\beta = 90°\), \(\gamma = 120°\) (Inorganic crystal structure database no. 1490).

**Electron Probe Microanalysis**

Abundances of major elements were determined on major rock-forming minerals using a CAMECA SX100 electron probe microanalyzer (EPMA) instrument at the Open University, with a beam size of 1 µm, a beam current of 20 nA, and an accelerating voltage of 15 kV (see Table S1 for the analytical setup and standards). A minimum of five points on each silicate phase was obtained to improve the statistical significance of the results. The representative chemical compositions of olivine, pyroxene, and anorthite for NWA 10463, NWA 8535, and NWA 12320 are given in Table 2. NWA 4590 and NWA 4801 are also investigated for major element compositions in order to allow direct comparisons to the literature (Sanborn & Wadhwa, 2021). All major element data are presented in Table S2.

**SIMS Analysis**

Following SEM and EBSD characterization, NWA 12320, NWA 8535, and NWA 10463 were cut from their resin blocks using a wafering saw and the remaining resin was removed with tweezers prior to remounting in indium blocks. Due to the friability of NWA 7203, this sample remained in the original epoxy mount. The samples were then coated with 30 nm of gold using a Baltec SCD005 low vacuum sputter coater. The Pb isotopic composition of silico-phosphates in NWA 12320, NWA 10463, and NWA 8535, and the full U-Pb systematics in NWA 7203 silico-phosphates were measured in situ using a CAMECA IMS1280 large-geometry microprobe at the NordSIMS facility, Swedish Museum of Natural History. An Oregon Physics H201 RF Plasma source generated an O\(_{2-}\) Gaussian beam of approximately 2 nA with an impact energy of 23 kV, which was rastered over 5 × 5 µm areas. Prior to analysis, an ~15 × 15 µm rastered area was pre-sputtered for ~80 s to remove the gold coat and to minimize surface contamination. During analysis, the field aperture limited the field of view on the sample to a 7 µm square, further discriminating against surface and/or grain boundary-hosted contamination. In both routines, all four Pb isotopes (\(^{204}\text{Pb}, ^{206}\text{Pb}, ^{207}\text{Pb}, \text{and} ^{208}\text{Pb}\)) were measured simultaneously using low-noise (0.003 cps) multichannel ion counting detection, at a nominal mass resolution of 4860 (M/ΔM). In the Pb-Pb routine, the magnetic field was locked using an NMR field sensor in regulation mode and 18 cycles of 20-s integrations were performed; in the U–Pb routine, the Pb isotopes were integrated for 12 s per cycle, with peak jumping to U and UO species; most analyses comprised 18 cycles, but some four and eight cycle reconnaissance analyses were also undertaken. Inter-detector yields in both routines were determined using repeated analyses of the USGS BCR-2G reference glass (Woodhead & Hergt, 2000). Very low U contents and/or sometimes high common Pb affected most of the U–Pb analyses, and so these analyses, along with those on the other three samples, were processed for Pb isotopes only following protocols described by Merle et al. (2020), with data presented in Table S3. Age calculations were performed using Isoplot-Ex v. 4.15 (Ludwig, 2012) and assume the decay constant and \(^{238}\text{U}/^{235}\text{U}\) ratio recommendations of Goldmann et al. (2015); in inverse Pb/Pb space, error correlations are negligible and have been ignored. The source of nonradiogenic Pb in these early solar system samples is difficult to constrain accurately, so regression calculations are presented with two ages. The first assumes the nonradiogenic Pb is terrestrial contamination introduced during both post-fall residence on Earth as well as laboratory processing and represented by model modern terrestrial Pb (Stacey & Kramers, 1975); the second assumes an initial Pb component represented by initial solar system Pb (Canyon Diablo troilite, CDT; Tatsumoto et al., 1973), which is unlikely to have evolved to significantly more radiogenic compositions at the ages determined herein. Arbitrary 1σ uncertainties of 2% and 1% respectively have been assigned to these reference values in the calculations.

**LA-ICP-MS Analysis**

Trace element abundances were determined in plagioclase, pyroxene, and olivine at the University of
<table>
<thead>
<tr>
<th></th>
<th>NWA 4590</th>
<th>NWA 4801</th>
<th>NWA 8535</th>
<th>NWA 10463</th>
<th>NWA 12320</th>
</tr>
</thead>
<tbody>
<tr>
<td>MgO</td>
<td>3.9 ± 1.5</td>
<td>7.1 ± 0.6</td>
<td>bdl</td>
<td>0.6 ± 0.1</td>
<td>0.2 ± 0.1</td>
</tr>
<tr>
<td>CaO</td>
<td>24.4 ± 5.9</td>
<td>23.1 ± 0.6</td>
<td>19.1 ± 3.5</td>
<td>25.3 ± 2.8</td>
<td>24.6 ± 2.8</td>
</tr>
<tr>
<td>MnO</td>
<td>0.5 ± 0.1</td>
<td>0.1</td>
<td>bdl</td>
<td>0.2 ± 0.1</td>
<td>0.2 ± 0.1</td>
</tr>
<tr>
<td>FeO</td>
<td>37.2 ± 5.2</td>
<td>13.1 ± 0.7</td>
<td>4.2 ± 0.1</td>
<td>149 ± 3.2</td>
<td>149 ± 3.2</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>8.2 ± 0.6</td>
<td>34.7 ± 6.4</td>
<td>bdl</td>
<td>39.9 ± 9.0</td>
<td>39.9 ± 9.0</td>
</tr>
<tr>
<td>Cr₂O₃</td>
<td>bdl</td>
<td>0.1</td>
<td>bdl</td>
<td>0.3 ± 0.1</td>
<td>0.3 ± 0.1</td>
</tr>
<tr>
<td>SiO₂</td>
<td>32.1 ± 6.0</td>
<td>44.5 ± 0.7</td>
<td>41.6 ± 7.7</td>
<td>40.0 ± 0.7</td>
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<tr>
<td>TiO₂</td>
<td>0.1</td>
<td>0.1</td>
<td>1.5 ± 0.9</td>
<td>0.3 ± 0.1</td>
<td>0.3 ± 0.1</td>
</tr>
<tr>
<td>Total</td>
<td>98.2 ± 2.1</td>
<td>98.6 ± 0.4</td>
<td>97.7 ± 4.4</td>
<td>100.3 ± 0.4</td>
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</table>

Table 2. Representative major element compositions of silicate phases.

Note: Errors are 1SD. Number of analyses for NWA 4590: olivine (30), clinopyroxene (30), and plagioclase (30). Number of analyses for NWA 4801: olivine (30), clinopyroxene (30), and plagioclase (30). Number of analyses for NWA 8535: olivine (45), clinopyroxene (25), and plagioclase (19). Number of analyses for NWA 10463: olivine (30), clinopyroxene (30), and plagioclase (30). Number of analyses NWA 12320: olivine (30), clinopyroxene (30), and plagioclase (30). Abbreviation: bdl, below detection limit.
Manchester, using a Teledyne Photon Machines Analyte Excite®+193 nm ArF Excimer laser ablation system with a HelEx II active 2-volume ablation cell, coupled to an Agilent 8900 ICP-MS (see Table S4 for the analytical setup and data processing procedure).

Silicates were analyzed using a spot size of 85 μm, a fluence of 5 J cm⁻², and a repetition rate of 5 Hz. Each analysis lasted 40 s and was preceded by a 20 s 20-counting time of the gas blank (background). We analyzed masses 23Na, 27Al, 29Si, 39K, 44Ca, 45Sc, 47Ti, 51V, 52Cr, 55Mn, 59Co, 60Ni, 63Cu, 66Zn, 71Ga, 85Rb, 88Sr, 89Y, 90Zr, 95Nb, 105Rh, 112Sn, 127I, 133Cs, 137Ba, 141Pr, 146Nd, 147Sm, 153Eu, 157Gd, 159Tb, 163Dy, 165Ho, 166Er, 169Tm, 172Yb, 175Lu, 176Hf, 178Lu, 181Ta, 187Os, 188Re, 189W, 194Pt, and 197Au (see Table S4 for 89Y, 90Zr, 93Nb, 133Cs, 137Ba, 139La, 140Ce, 141Pr, 146Nd, 147Sm, 153Eu, 157Gd, 159Tb, 163Dy, 165Ho, 166Er, 169Tm, 172Yb, 175Lu, 208Pb, 232Th, and 238U. Analyzed masses 23Na, 27Al, 29Si, 39K, 44Ca, 45Sc, 47Ti, 51V, 52Cr, 55Mn, 59Co, 60Ni, 63Cu, 66Zn, 71Ga, 85Rb, 88Sr, 89Y, 90Zr, 93Nb, 133Cs, 137Ba, 140Ce, 141Pr, 146Nd, 147Sm, 153Eu, 157Gd, 159Tb, 163Dy, 165Ho, 166Er, 169Tm, 172Yb, 175Lu, 208Pb, 232Th, and 238U (see Table S4 for dwell times used). Signal intensities were corrected from background contributions by subtracting the gas blank.

The trace elements data reduction scheme of the Iolite 4 software (Paton et al., 2011) was used for data reduction, using known Si abundances for reference materials (Jochum et al., 2005; Woodhead et al., 2007) and those measured by EPMA for angrite plagioclase, pyroxene, and olivine for internal standardization. Angrite silicate analyses were bracketed by analyzing USGS reference glasses BHVO-2G, BIR-1G, and BCR-2G every 10–15 unknown analyses. USGS glass BIR-1G was used as the primary reference material, while glasses BHVO-2G and BCR-2G were treated as unknowns and used as quality control reference materials. For all the trace elements analyzed, accuracy is typically within ±10% of recommended values for the BHVO-2G and BCR-2G USGS reference glasses (see Table S5 and Figure S1). The combination of a large spot size of 85 μm, a moderate fluence of 5 J cm⁻², and total laser shot counts of <250 was used to minimize fractionation effects between silicate minerals and silicate glass calibration materials (Bussweiler et al., 2019). All data are given in Table S6, together with their associated two standard error uncertainties and detection limits calculated using the method of Howell et al. (2013).

RESULTS

Electron Backscatter Diffraction

NWA 7203

Electron backscatter diffraction analysis on olivine within the groundmass of NWA 7203 reveals degraded crystallinity in band contrast images with complex fractures cross-cutting the entire sample (Figure 3). One of the larger fractures runs horizontally through the lower portion of the analyzed area, offsetting the surrounding mineralogy. Olivine present in the groundmass demonstrates variable degrees of shock-induced deformation. While some grains appear undeformed, grains in close proximity with the fracture network comprise of complex microstructures and ~12° of cumulative misorientation (Figure S3). IPF maps reveal shock twins in two clinopyroxene grains in close proximity to the large offsetting fracture (Figure 3 and Figure S4). It is also noted that xenocrysts, here termed “relict olivine” grains are present within NWA 7203 similar to previous studies by Rider-Stokes et al. (2023) on NWA 12320 and Asuka (A) 12209. However, in NWA 7203, there is a lack of evidence for any recrystallization with only minor fragmentation observed in olivine grains (Figure S5).

Band contrast images of phosphates in NWA 7203 reveal sub-micron scale complexity, with networks of fractures and boundaries separating micron to sub-micron scale domains of more strongly diffracting phosphate. IPF and GROD maps reveal the presence of high-angle (>10°) grain boundaries with multiple grains demonstrating differences in orientation. Interestingly, low degrees of cumulative misorientation (~4°) are present within phosphate grains (Figure 4). Pole figures for both phosphate grains clearly indicate the randomly orientated spread of crystallites, indicative of recrystallization (Figure S6).

NWA 8535

The large (200 μm) olivine grains in NWA 8535 occur as subhedral, lobate grains. Olivine grains yield simple microstructures with a lack of evidence for extreme shock-induced deformation, as highlighted by the GROD maps. Olivine grains are free of fractures and show no evidence of deformation twinning, subgrain formation, or dynamic recrystallization. Band contrast images demonstrate strong diffraction with little degradation. In concert, low degrees of cumulative misorientation (~2°) are observed in the sample with little to no deviation across olivine grains (Figure 3).

Pb–Pb Dating Results

In total, 35 in situ Pb–Pb isotopic analyses of silicophosphates were carried out, including targets in NWA 7203 (n = 11), NWA 12320 (n = 14), NWA 10463 (n = 6), and NWA 8535 (n = 4). All uncertainties below are reported at the 2σ confidence level. Based on regression through CDT Pb isotope composition (which assumes that phosphates incorporated primordial Pb akin to that in the protosolar nebula), NWA 12320 silicophosphates yield a Pb–Pb isochron date of 4571.2 ± 9.4 Ma, with a mean squared weighted deviation (MSWD) of 1.07, while regression through Stacey & Kramers (S & K) modern terrestrial Pb isotope composition (which assumes that common Pb in the analyzed phosphates is terrestrial contamination) yields a
similar date of 4574.3 ± 9.7 Ma, with an MSWD of 1.3 (Figure 5a), both regressions omitting a single outlier. The date acquired through regression through CDT is within error of the oldest quenched angrite formation age obtained for NWA 1670 (4564.39 ± 0.20 Ma; Zhu et al., 2019). However, regression through S & K returns a value marginally outside the error of the oldest quenched angrites. Based on regression through CDT Pb isotope composition, NWA 10463 silico phosphates yield a Pb–Pb isochron date of 4563.6 ± 7.9 Ma, with an MSWD of 0.81, while regression through S & K modern terrestrial Pb isotope composition indicates a near identical date of
4563.7 ± 7.9 Ma, with an MSWD of 0.84 (Figure 5b). Again, both dates are within error of the oldest quenched angrites formation ages. Based on regression through CDT Pb isotope composition, NWA 8535 silico-phosphates yield a Pb–Pb isochron date of 4514 ± 30 Ma, with an MSWD of 0.111, while regression through S & K modern terrestrial Pb isotope composition indicates an identical date of 4516 ± 31 Ma, with an MSWD of 0.16 (Figure 5c). These Pb–Pb isochron dates obtained for phosphates in NWA 8535 are approximately 40 Ma younger than the formation ages of angrites investigated previously. Finally, based on regression through CDT Pb isotope composition, NWA 7203 silico-phosphates yield a Pb–Pb isochron date of 4562 ± 9.3 Ma, with an MSWD of 0.54, while regression through S & K modern terrestrial Pb isotope composition indicates an identical date of 4562.7 ± 9.4 Ma, with an MSWD of 0.56 (Figure 5d). Both dates for NWA 7203 silico-phosphates overlap with the oldest quenched angrite (Zhu et al., 2019) and the Pb–Pb isochron date of 4543 ± 19 Ma obtained on silico-phosphates in NWA 7203 by Hayashi et al. (2022).

Trace Element Chemistry

Representative rare earth element (REE) concentrations in olivine, pyroxene, and anorthite in NWA 4590, NWA 4801, and NWA 8535 are provided in Table 3. The ranges of olivine REE abundances in NWA 4590, NWA 4801, and NWA 8535 are shown in Figure 6a. Olivine in all three samples displays the heavy rare earth enrichment (HREE) over light REE (LREE) that is characteristic of this mineral, as well as slight negative Eu anomalies in NWA 4590 and NWA 4801. Olivine in NWA 8535 has the lowest absolute REE abundances (LREE ∼0.003–0.01 and HREE ∼0.1–0.5 times CI chondrites) of all samples investigated.

The ranges of REE abundances in clinopyroxene in NWA 4590, NWA 4801, and NWA 8535 are shown in Figure 6b. All three samples display subparallel LREE-depleted patterns with moderate negative Eu anomalies. Overall, the clinopyroxene REE abundance increases from NWA 8535 to NWA 4590 to NWA 4801.
<table>
<thead>
<tr>
<th></th>
<th>NWA 4590</th>
<th>NWA 4801</th>
<th>NWA 8535</th>
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<tr>
<td>La</td>
<td>0.131 ± 0.119</td>
<td>0.164 ± 0.07</td>
<td>1.205 ± 0.172</td>
</tr>
<tr>
<td>Ce</td>
<td>0.673 ± 0.609</td>
<td>0.287 ± 0.124</td>
<td>1.516 ± 0.164</td>
</tr>
<tr>
<td>Pr</td>
<td>0.16 ± 0.14</td>
<td>0.037 ± 0.016</td>
<td>0.144 ± 0.016</td>
</tr>
<tr>
<td>Nd</td>
<td>1.138 ± 0.942</td>
<td>1.58 ± 0.061</td>
<td>0.465 ± 0.051</td>
</tr>
<tr>
<td>Sm</td>
<td>0.807 ± 0.577</td>
<td>0.031 ± 0.016</td>
<td>0.003 ± 0.013</td>
</tr>
<tr>
<td>Eu</td>
<td>0.214 ± 0.146</td>
<td>1.167 ± 0.435</td>
<td>0.232 ± 0.128</td>
</tr>
<tr>
<td>Gd</td>
<td>2.096 ± 1.214</td>
<td>0.033 ± 0.011</td>
<td>0.004 ± 0.001</td>
</tr>
<tr>
<td>Tb</td>
<td>0.545 ± 0.278</td>
<td>0.004 ± 0.002</td>
<td>0.004 ± 0.001</td>
</tr>
<tr>
<td>Dy</td>
<td>4.994 ± 2.106</td>
<td>0.022 ± 0.011</td>
<td>0.005 ± 0.001</td>
</tr>
<tr>
<td>Ho</td>
<td>1.328 ± 0.469</td>
<td>0.004 ± 0.002</td>
<td>0.005 ± 0.001</td>
</tr>
<tr>
<td>Er</td>
<td>4.731 ± 1.33</td>
<td>0.008 ± 0.004</td>
<td>0.006 ± 0.003</td>
</tr>
<tr>
<td>Tm</td>
<td>0.747 ± 0.154</td>
<td>0.001 ± 0.0003</td>
<td>0.006 ± 0.004</td>
</tr>
<tr>
<td>Yb</td>
<td>5.054 ± 0.714</td>
<td>0.006 ± 0.002</td>
<td>0.209 ± 0.126</td>
</tr>
<tr>
<td>Lu</td>
<td>0.736 ± 0.066</td>
<td>0.001</td>
<td>0.006 ± 0.004</td>
</tr>
<tr>
<td>Sc</td>
<td>3.52 ± 2.55</td>
<td>5.14 ± 2.06</td>
<td>5.14 ± 2.06</td>
</tr>
<tr>
<td>Ti</td>
<td>413.48 ± 36.06</td>
<td>272.57 ± 27.88</td>
<td>22.69 ± 13.88</td>
</tr>
<tr>
<td>V</td>
<td>2.03 ± 1.16</td>
<td>2.98 ± 0.59</td>
<td>31.21 ± 8.76</td>
</tr>
<tr>
<td>Cr</td>
<td>7.16 ± 4.82</td>
<td>26.04 ± 5.85</td>
<td>2370.76 ± 973.15</td>
</tr>
<tr>
<td>Mn</td>
<td>3052.54 ± 289.4</td>
<td>2452.63 ± 48.82</td>
<td>1644.53 ± 201.94</td>
</tr>
<tr>
<td>Co</td>
<td>30.73 ± 7.26</td>
<td>36.63 ± 1.57</td>
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</tr>
<tr>
<td>Ni</td>
<td>4.01 ± 0.56</td>
<td>15.83 ± 3.27</td>
<td>160.56 ± 38</td>
</tr>
</tbody>
</table>

**Note:** Errors are 1SD. Number of analyses for NWA 4590: olivine (19), clinopyroxene (20), and plagioclase (19). Number of analyses for NWA 4801: olivine (10), clinopyroxene (23), and plagioclase (27). Number of analyses NWA 8535: olivine (33) and clinopyroxene (2). Abbreviation: bdl, below detection limit.
DISCUSSION

The Timing of Mixing and Impacts on the APB

An oxygen isotope disequilibrium and evidence of high-temperature processing of olivine “xenocrysts” in the quenched angrites NWA 12320, Asuka 12209, and Asuka 881371 have led to the suggestion that these samples record evidence of large-scale planetary mixing (Rider-Stokes et al., 2023). Rider-Stokes et al. (2023) further suggest that these samples are in fact impact melt rocks, with the olivine representing remnant material of the APB and the groundmass representing recrystallized melt. Any in situ ages from the groundmass would, therefore, record the timing of crystallization of the impact melt. The ancient Pb–Pb date of 4571.2 ± 9.4 Ma obtained for phosphates in NWA 12320 supports the hypothesis that the mixing event recorded by the angrite meteorites occurred very early in the inner solar system. This is consistent with recent high-precision Pb isotope data on NWA 12320 that yielded an old Pb–Pb isochron date of 4563.03 ± 0.45 Ma (Datta et al., 2020). This implies that the crystallization of NWA 12320, followed by a subsequent mixing event, occurred within 4–5 Ma after the formation of CAIs (Desch et al., 2023; Piralla et al., 2023). The cause of this mixing is still a matter of debate; however, it could be a result of impact mixing in the early solar system as a result of Jupiter’s migration (Kruijer et al., 2017; Rider-Stokes et al., 2023; Walsh et al., 2011).

From EBSD analysis, it is clear that NWA 7203 as a whole (both groundmass and relict olivines), and the phosphates situated within have experienced moderate levels of microstructural response to shock-induced deformation (Figures 3 and 4). If the groundmass of quenched angrites does indeed represent impact melt, as suggested by Rider-Stokes et al. (2023), it would be expected that the minerals would be annealed and undeformed due to fresh growth. Shock deformation in NWA 7203 would therefore have occurred postimpact melting. The high-angle grain boundaries present in phosphates within NWA 7203 are indicative of recrystallization, implying that phosphates have undergone Pb loss and diffusion, resulting in the phosphate 206Pb/204Pb date recording the timing of impact, rather than the original crystallization. It is noted, however, that these phosphates may not experience Pb diffusion identical to apatite and merrillite due to their chemical and structural differences (Hwang et al., 2019). The ancient date of 4562 ± 9.3 Ma obtained on NWA 7203 phosphates is very similar to the crystallization ages of other quenched angrites, suggesting that these phosphates have retained radiogenic Pb, or that the phosphates record an ancient impact event, within uncertainties of the crystallization of the quenched angrites. While not resolvable within uncertainty, Hayashi et al. (2022) may have observed slightly younger phosphate Pb–Pb dates close to melt veins (4555 ± 32 Ma) which suggests that partial resetting of the Pb isotope system may have occurred in phosphates in close proximity to melt veins. Due to NWA 12320 revealing more ancient ages in comparison to the shocked phosphates in NWA 7203 and evidence of shock-induced deformation within the groundmass of NWA 7203, the mixing event that induced the oxygen isotopic disequilibrium must occurred prior to the event recorded by NWA 7203. It is therefore suggested that the ages recorded by the shocked phosphates in NWA 7203 record an impact event on the APB unrelated to the mixing events recorded in NWA 12320, Asuka 12209, and Asuka 881371.

Prolonged Magmatism on the APB

It has been previously argued that the youngest plutonic angrite, Angra Dos Reis (4556.60 ± 0.26 Ma; Amelin, 2008), records the timing of disruption of the APB producing smaller APB-like asteroids >10 km in

<table>
<thead>
<tr>
<th>REE</th>
<th>NWA 4801</th>
<th>NWA 4590</th>
<th>NWA 8535</th>
</tr>
</thead>
<tbody>
<tr>
<td>La</td>
<td>0.8</td>
<td>0.9</td>
<td>1.0</td>
</tr>
<tr>
<td>Ce</td>
<td>1.2</td>
<td>1.3</td>
<td>1.4</td>
</tr>
<tr>
<td>Pr</td>
<td>2.0</td>
<td>2.2</td>
<td>2.3</td>
</tr>
<tr>
<td>Nd</td>
<td>3.0</td>
<td>3.2</td>
<td>3.4</td>
</tr>
<tr>
<td>Sm</td>
<td>4.0</td>
<td>4.2</td>
<td>4.4</td>
</tr>
<tr>
<td>Eu</td>
<td>5.0</td>
<td>5.2</td>
<td>5.4</td>
</tr>
<tr>
<td>Gd</td>
<td>6.0</td>
<td>6.2</td>
<td>6.4</td>
</tr>
<tr>
<td>Tb</td>
<td>7.0</td>
<td>7.2</td>
<td>7.4</td>
</tr>
<tr>
<td>Dy</td>
<td>8.0</td>
<td>8.2</td>
<td>8.4</td>
</tr>
<tr>
<td>Ho</td>
<td>9.0</td>
<td>9.2</td>
<td>9.4</td>
</tr>
<tr>
<td>Er</td>
<td>10.0</td>
<td>10.2</td>
<td>10.4</td>
</tr>
<tr>
<td>Tm</td>
<td>11.0</td>
<td>11.2</td>
<td>11.4</td>
</tr>
<tr>
<td>Yb</td>
<td>12.0</td>
<td>12.2</td>
<td>12.4</td>
</tr>
<tr>
<td>Lu</td>
<td>13.0</td>
<td>13.2</td>
<td>13.4</td>
</tr>
</tbody>
</table>

FIGURE 6. Representative chondrite-normalized REE abundances in olivine (a) and clinopyroxene (b) in NWA 4801, NWA 4590, and NWA 8535. CI chondrite REE abundances are from Barrat et al. (2012).
FIGURE 7. Major element chemistry of olivine within angrite meteorites, depicting the increasing fractionation through differing subgroups. Major element chemistry of quenched angrites is indicated by the green field (Keil, 2012; Papike et al., 2017; Sanborn, 2012), the intermediate angrite by the yellow fields (Papike et al., 2017), the plutonic angrites by the orange fields (Baghdadi et al., 2015; Keil, 2012; Papike et al., 2017; Riches et al., 2012; Sanborn, 2012), and the dunitic angrite by the blue field (Santos, 2016).

diameter, preventing any further magmatic crystallization and avoiding any further impact-induced deformation (Scott & Bottke, 2011). However, here we obtained a much younger phosphate Pb–Pb date of 4514 ± 30 Ma for NWA 8535, suggesting that the APB survived for a longer period of time than previously expected.

At present, there is no consensus on the origin of NWA 8535. It has been suggested that the sample is closely related to the quenched angrites based on the presence of vesicles and the zoning of olivine (Agee et al., 2015; Santos, 2016). However, here we obtained a much younger phosphate Pb–Pb date of 4514 ± 30 Ma for NWA 8535, suggesting that the APB survived for a longer period of time than previously expected.

Papike et al. (2017) illustrated the increasing levels of magmatic fractionation recorded between the quenched, intermediate, and plutonic angrite meteorites by comparing CaO versus MgO and MnO versus MgO abundances in olivine (Figure 7). Both Ti and Mn behave incompatibly in olivine and thus can be used as an indicator for fractional crystallization (Kanner et al., 2003). Olivine in NWA 8535 contains less Ti (~10–100 µg g⁻¹) and Mn (~1300–2000 µg g⁻¹) compared to the plutonic angrites (~220–470 µg g⁻¹ Ti and ~2400–3500 µg g⁻¹ Mn; Table S6). However, on a Ti versus Zr abundances diagram, NWA 8535 olivine plots outside the field of the quenched angrites and appears closer to the plutonic angrites (Figure S8). Furthermore, NWA 8535 uniquely contains Cr-bearing symplectites within olivine grains (Santos, 2016). These features are similar to those identified in the Apollo 17 dunite, 72415–72418, which have been suggested to be derived through phase reversion of garnets that formed at depth (e.g., Bell et al., 1975; Bhanot & Downes, 2021; Bhanot et al., 2023).

While Santos (2016) suggests that this deep-seated origin of Cr-spinels is unlikely due to the proposed size of the APB. Instead, they consider a more likely scenario of diffusion of minor elements out of the olivine. However, more recent studies have suggested that the APB was similar if not larger than the Moon (Tissot et al., 2022), which would lend support for the deeper origin of Cr-spinel in NWA 8535. In any case, chemical compositions, textural variations, and the distinct Pb–Pb date recorded by phosphates in NWA 8535 suggest that the relationship between NWA 8535 and the quenched angrites is unlikely. Based on the textures observed, it is suggested that NWA 8535 represents an olivine cumulate, yet the presence of vesicles and zoning in this sample is perplexing and is unexpected in deep mantle settings or in magma chambers where olivine settling has occurred.

The complete lack of shock-induced deformation in NWA 8535, as revealed by EBSD (Figure 3), could suggest a pristine cumulate origin that formed at depth in the APB which avoided any shock-induced deformation, or a crystalline impact melt origin, that formed several tens of millions years after formation of the APB. NWA 8535 is characterized by a bulk Δ¹⁷O value of ~0.70‰, plotting directly on the revised angrite fractionation line (Rider-Stokes et al., 2023). Whereas the groundmass of NWA 12320, Asuka 12209, and Asuka 881371, on the other hand, have more positive Δ¹⁷O values of ~0.024‰, ~0.001‰, and ~0.003‰, respectively, which have been interpreted as indicating that these rocks are impact melt, and include contribution from impactor(s) with more positive Δ¹⁷O values (Rider-Stokes et al., 2023). The lack of Δ¹⁷O contamination in NWA 8535 therefore argues against a total impact melt origin and provides supporting evidence that NWA 8535 represents a pristine cumulate that formed at depth on the APB. As seen in Figure 2, the phosphates within NWA 8535 show a close textural magmatic relationship with other mesostasis phases (diopside, anorthite, and Fe-sulfides). This suggests that the crystallization of phosphates should be recording the timing of crystallization of the residual melt.
in NWA 8535. The date recorded by silico-phosphates in NWA 8535 thus implies magmatism on APB occurred at least 40 Ma after the crystallization of plutonic angrites (Figure 8). Alternatively, if the NWA 8535 and plutonic angrites are consanguineous, the age retained by the phosphates measured here could represent the period of mantle cooling through the phosphate closure temperature. While the temperature of closure to solid-state Pb diffusion in silico-phosphates is unknown, apatite has a well-defined temperature of closure ~450°C (Cherniak et al., 1991). For the APB to retain internal temperatures of >450°C over a period of ~50 Ma, the planetesimal must have accreted early, to capture enough 26Al for the internal heat production necessary to maintain this long time interval of melt crystallization, similar to the propositions for 4 Vesta (Roszjar et al., 2016).

**The Size of the APB**

Initial discussions based on the degree of shock deformation in angrite meteorites, cosmic ray exposure ages, and mineralogy led to the conclusion that the APB had a radius of ~100 km (Keil, 2012). However, volatile abundances in D’Orbigny and Sahara 99555 have led to estimations that the APB radius could have been at least ≥270 km and possibly ≥340 km, larger than 4-Vesta (e.g., McCubbin & Barnes, 2019; Sarafian et al., 2017). Furthermore, based on recent high-pressure experiments, Tissot et al. (2022) suggested that the lower limit for the size of the APB must have been at least 600–770 km and more likely greater than 1085–1405 km in radius. The asteroid 4-Vesta exhibits prolonged magmatism, with mantle-generated basaltic melts forming until 4532±11/±6 Ma (Roszjar et al., 2016). As for the APB, prior to this study, Angra Dos Reis recorded the youngest angrite formation age at 4556.60±6 Ma (Amelin, 2008), suggesting short-lived magmatism and arguing against a large parent body. The chronological age of NWA 8535 (4514±30 Ma), however, brings evidence for prolonged heating on the APB, supporting the propositions of Tissot et al. (2022) and suggesting that the interior of the APB must have been thermally well insulated by an early-formed crust that prevented heat loss, similar to 4-Vesta (Roszjar et al., 2016).

**A REVIEW OF ANGRITE CHRONOLOGY**

The initial evolution of the APB appears to be swift, and Bizzarro et al. (2005) and Kleine et al. (2012) infer from Al-Mg chronometry that accretion of the APB was largely completed by ~4565 Ma, only <3 Ma after CAI...
formation. Mantle–crust differentiation and core formation likely occurred simultaneously shortly after accretion at 4563.2 ± 0.3 Ma based on the bulk angrite $^{55}$Mn–$^{52}$Cr isochron (Zhu et al., 2019) and paleomagnetic records for angrites (Wang et al., 2017). Interestingly, the quenched angrite NWA 12320, which demonstrates evidence for planetary mixing (Rider-Stokes et al., 2022), yielded ancient dates of 4571.2 ± 9.4 Ma and 4563.0 ± 0.4 Ma (Datta et al., 2020). These ancient dates constrain the timing of mixing recorded by the oxygen isotope disequilibrium. Therefore, planetary mixing, mantle–crust differentiation, and core formation all occurred in an exceptionally brief timeframe on the APB.

The recently identified intermediate angrite, NWA 10463, is thought to represent an intermediate stage between the quenched and plutonic angrites based on the presence of both zoned olivine and olivine with exsolution lamellae (Santos, 2016). Reger et al. (2021) calculated a Pb–Pb age of 4560.25 ± 0.18 Ma, consistent with the hypothesis that NWA 10463 represents an intermediate sample. Based on trace element affinities between NWA 2999 and the quenched angrites (Sahara 99555 and D’Orbigny), it has been suggested that the magmatic reservoir that produced the quenched angrites persisted until 4560.74 ± 0.47 Ma (Sanborn & Wadhwa, 2021). Following this, other magmatic reservoirs that resulted in the magmatic crystallization of NWA 4590, NWA 4801, and LEW 86010 ceased to be active at approximately 4557–4558 Ma (Zhu et al., 2019). Angra Dos Reis crystallized approximately 1 Ma later, at 4556.6 ± 0.26 Ma (Amelin, 2008). Subsequent bombardment of the APB crust continued, resulting in impact-reset ages for NWA 7203 (4555 ± 32 Ma; Hayashi et al., 2022).

Mantle-driven magmatism or progressive mantle cooling endured for a further ~30 Ma, resulting in the formation of the dunitic angrite, NWA 8535. While it is not known when the APB was catastrophically disrupted, the solar system during this period is regarded as hostile (Figure 9).

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Conflict of Interest Statement—The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data Availability Statement—All data generated or analyzed during this study are either included in the article or its Supplementary Information.

Editorial Handling—Dr. Cyrena A. Goodrich

REFERENCES


Bhanot, K. K., and Downes, H. 2021. Multiple Origins of Spinel Symplectite textures in Lunar Dunites 72415 and 72417. 84th Meeting of the Meteoritical Society, abstract #2609.


Data S1. Supplementary Tables S1–S5 and Figure S1. Data S2. Supplementary Figures S2–S8.

SUPPORTING INFORMATION

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