Multiple impact events on the L-chondritic parent body: Insights from SIMS U-Pb dating of Ca-phosphates in the NWA 7251 L-melt breccia

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Abstract—Here we report in situ secondary ionization mass spectrometry Ca-phosphate U-Pb ages for an L-impact melt breccia (NWA 7251), which are integrated with petrological and mineral chemical studies of this meteorite. NWA 7251 is a heavily shocked rock that is composed mainly of the chondrite host, impact melt portion, and melt veins (crosscutting and pervasive type). The host is an L4 chondrite that has been shocked to S4. The impact melt portion has a fine-grained igneous texture, and is composed mainly of olivine, low-Ca pyroxene, high-Ca pyroxene, and albitic glass. The impact melt was generated at pressure of >30–35 GPa and temperature of >1300–1500 °C during an impact event. The Ca-phosphate grains in the host were affected by a shock heating event. Most of the Ca-phosphate grains in the melt were neocrystallized, but relatively large grains enclosed by or adjacent to metal veins or melt globules are likely inherited. The U-Pb isotopic systematics of Ca-phosphates in NWA 7251 yield an upper intercept age of 4457 ± 56 Ma and a lower intercept age of 574 ± 82 Ma on the normal U-Pb concordia diagram. The age of 4457 ± 56 Ma is interpreted to be related to an early shocking event rather than the thermal metamorphism of the parent body. The impact melt and veins in NWA 7251 were generated at 574 ± 82 Ma, resulting from disruption of the L chondrite parent body.

INTRODUCTION

Impact is one of the primary processes during the formation and evolution of the solar system. It generates cratered surfaces and brecciated materials on planets, which are recorded by deformed minerals and impact melts in meteorites (e.g., Wood and Head 1976; Haack et al. 1996; Bottke et al. 2015a). Impact rates were much higher in the early stages of solar system evolution, as recorded by the well-known Moon-forming giant impact (~4.4–4.5 Ga; Jacobson et al. 2014; Bottke et al. 2015b) and the Late Heavy Bombardment (~3.8–4.2 Ga; Kring and Cohen 2002; Marchi et al. 2012) in the inner solar system. However, impact ages older than 4.2 Ga are not commonly recorded by asteroidal samples. The impact ages of chondrites are mostly concentrated in two periods: between 3.5 and 4.1 Ga and <1.0 Ga (Bogard 1995; Swindle et al. 2014). For example, Korochantseva et al. (2007) and Yin et al. (2014) obtained ages of ~470 Ma from shocked L chondrite samples, suggesting a major collision event at that time. In contrast, only a few L-melt and L-melt breccia chondrites have yielded Ar-Ar ages of ~4.4–4.5 Ga (Turner et al. 1978; Benedix et al. 2008; Wittmann et al. 2009). This lack of early impact ages for chondrites has limited our understanding of the early evolution of the solar system.

Previous studies have mainly focused on the whole rock Ar-Ar geochronology, given that this chronometer is relatively easily reset during shock heating (Bogard and Hirsch 1980; Bogard 2011). Most Ar-Ar ages for L chondrites cluster between 400 and 600 Ma with large uncertainties, due to the presence of trapped 40Ar or incomplete resetting of the K-Ar system. More recently, Korochantseva et al. (2007) and Weirich et al. (2012) obtained refined Ar-Ar ages of 470 ± 6 Ma from L chondrite samples after careful corrections. However, this dating approach cannot integrate the age results with microscale observations of the mineralogy and
petrology, which makes the significance of these ages more or less ambiguous.

On the other hand, in situ secondary ionization mass spectrometry (SIMS) U-Pb dating at the micrometer scale, integrated with secondary electron microscopy (SEM) images of U-bearing accessory minerals, is a powerful tool for reconstructing the complex metamorphic histories of samples (e.g., Wu et al. 2008; Li et al. 2014). Ca-phosphates, both apatites and merrillites, are the main U-bearing minerals and are ubiquitous in chondrites (e.g., Göpel et al. 1994; Lewis and Jones 2016). They have relatively low closure temperatures for Pb diffusion (450–500 °C; Cherniak et al. 1991) and can potentially record strong shock heating events. The development of the SIMS Ca-phosphate U-Pb dating technique (Li et al. 2012; Zhou et al. 2013) has enabled a greater number of reliable early impact ages to be determined. For example, the LL chondrite Chelyabinsk yielded a SIMS Ca-phosphate U-Pb age of 4452 ± 21 Ma (Popova et al. 2013). In addition, two impact ages (4472 ± 31 Ma and 473 ± 38 Ma) have been determined for the L chondrite Novato (Yin et al. 2014). Therefore, in situ U-Pb dating of Ca-phosphates is able to provide important insights into the early shock heating events on asteroids.

NWA 7251, a newly found dark, weakly weathered, 13 kg stone, was classified as an L-melt rock (Ruzicka et al. 2015). The occurrence of abundant melt and veins suggests that this meteorite was severely shocked, and it could be an ideal candidate to use to investigate the timing of impact events. In this study, we carried out in situ SIMS U-Pb dating of Ca-phosphates in NWA 7251, and integrated the results with petrological and mineral chemical observations. These findings, including a newly obtained early impact age, provide another piece of chronological evidence for the early impact histories in the solar system.

SAMPLES AND ANALYTICAL METHODS

Three polished thin sections, PMO-0249 (18 × 18 mm²), PMO-3049 (18 × 15 mm²), and PMO-3050 (22 × 18 mm²), were prepared from different parts of one large NWA 7251 slice (945 g). These thin sections are representative of the distinct petrological regions within this meteorite (see the Petrography section). The mineralogy and petrography of NWA 7251 were investigated using a Hitachi S-3400N scanning electron microscope equipped with an Oxford INCA 7021 energy dispersive spectroscopy (EDS), at Purple Mountain Observatory, Chinese Academy of Sciences. High-contrast, low-brightness backscattered electron (BSE) images were obtained to distinguish high-Z phases (i.e., metal, sulfide, chromite, and phosphate). Relatively low-contrast, high-brightness BSE images were obtained to distinguish low-Z phases (i.e., olivine, pyroxene, plagioclase, and glass). A combination of P:Ca:Na:Cl elemental Kα X-ray mapping was used to search for Ca-phosphate grains, including apatites and merrillites. Modal abundances were determined by using the software ImageJ on BSE images and X-ray maps, assuming that area fractions were equal to volume percentages. Modal abundances of different domains in NWA 7251 are listed in Table 1.

Major element analyses of minerals and glass were performed on a JEOL JXA-8230 electron microprobe at Purple Mountain Observatory, Chinese Academy of Sciences. Olivine and pyroxene were analyzed at a 15 kV accelerating voltage and 20 nA beam current in spot mode. The same voltage and beam current were also used for Ca-phosphates, with a beam diameter of 2–5 μm. A 15 kV accelerating voltage and 10 nA beam current with a beam diameter of 2–5 μm were used for plagioclase and glass. Fe-Ni metal and sulfide were analyzed at 20 kV, 20 nA in spot mode. Both synthetic and natural mineral standards were used, and matrix corrections were based on ZAF procedures. Chemical compositions of representative minerals in NWA 7251 are represented in Appendix S1A–F, respectively, in the supporting information.

In situ Ca-phosphate U-Pb dating was performed using a Cameca IMS-1280HR SIMS at the Institute of Geology and Geophysics, Chinese Academy of Sciences, Beijing, China. Samples were carbon-coated prior to SIMS analysis. The detailed analytical procedures for U-Pb dating of Ca-phosphate grains can be found in Li et al. (2012), and only a brief description is given here. The O⁻ primary ion beam was accelerated at ~13.9 kV, with an intensity of ~5–7 nA. Positive secondary ions were extracted with a 10 kV potential. A Gaussian beam model was used with an elliptical spot of 15 × 10 μm² on the target (Liu et al. 2011). A hybrid dynamic multicollector technique (Liu et al. 2015) with five detectors was used to determine the ion beam intensities of ²⁰⁴Pb⁺, ²⁰⁶Pb⁺, ²⁰⁷Pb⁺, ²⁰⁸Pb⁺, ²³²Th⁺, ²³⁸U⁺, ²³²-Th⁶O⁺, ²³⁸-U⁶O⁺, ²³⁸-U⁶O²⁺, and a matrix reference peak of ⁴⁰Ca₂⁺²³⁵Pb⁶O₃ at a mass resolution of 8000 (defined at 50% height). The background for all ion counting electron multipliers during the analysis was ~0.03–0.05 cps. This novel technique is able to simultaneously measure the ²⁰⁷Pb/²⁰⁶Pb ratio at a high precision using the static multicollector mode without trading off the analytical precision of the ²⁰⁶Pb/²³⁸U ratio using the peak-hopping mono-collector mode (Li et al. 2009). The ⁴⁰Ca₂⁺²³⁵Pb⁶O₃ peak was used as a reference peak for centering the secondary ion beam, energy, and mass calibration. Due to the low U and Pb concentrations of the Ca-phosphates, isotope ratios were
calculated from total counts summed over the entire analysis, which minimizes the positive bias associated with low count rates in individual cycles (Ogliore et al. 2011; Telus et al. 2012). Data were corrected for deadtime and background. The uncertainties are the standard errors of the mean of the individual ratios. Pb/U ratios were calibrated with a power law relationship between $^{206}\text{Pb}/^{238}\text{U}$ and $^{238}\text{U}/^{238}\text{O}_{2}$ relative to an apatite standard of NW-1 (1160 Ma; Wu et al. 2010) that comes from the same complex of Prairie Lake as that of the apatite standard (PRAP) applied by Sano et al. (1999). Uranium absolute abundances were determined relative to the Durango apatite standard (U $\leq$ 25 ppm; Trotter and Eggins 2006). The analytical uncertainty of the measured $^{238}\text{U}/^{206}\text{Pb}$ in the standard was propagated onto that of the unknowns. Each measurement consisted of 15 cycles with a total analytical time of about 26 min. Uncertainties on individual analyses in the data table are reported at the 1σ level. Data reduction was carried out using the Isoplot 3.0 program (Ludwig 2003), and error ellipses are plotted at the 1σ SE level. SIMS U-Pb isotopic data for the Ca-phosphates are listed in Table 2.

**RESULTS**

**Petrography**

NWA 7251 consists mainly of three petrological domains: impact melt portion (IMP), impact melt veins, and the chondrite host. All the domains contain a certain number of vesicles (black spots in Fig. 1). The IMP is the major component in the PMO-0249 section (Fig. 1a). Impact melt veins and the chondrite host are mainly represented in PMO-3050 (melt proportion ~17%, Fig. 1b) and PMO-3049 (melt proportion <2%, Fig. 1c), respectively.

The chondrite host is composed mainly of porphyritic and barred olivine and olivine–pyroxene chondrules of 0.2–1.0 mm in size (Figs. 2a and 2b). Most of the chondrule metastasis has been recrystallized with a few of chondrule glass (Figs. 2a and 2b). This chondrule glass may be primary, given the lack of nearby melt veins. The boundaries of chondrules are not sharply defined, due to the recrystallization of silicates. Pyroxene and olivine grains in the host are typically anhedral to subhedral, and some grains contain chains of metallic Fe-Ni droplets along grain margins (Figs. 2a and 2b). Some olivine grains show weak mosaic extinction. Plagioclase grains (mostly 3–5 μm) and albite glass are both found in the matrix. Ca-phosphates (merrillites and apatites) are anhedral to euhedral, with sizes up to 60 μm (Figs. 3a–f). They are typically intergrown with irregular Fe-Ni metals and troilite nodules. Vesicles are commonly found in the matrix, and have diameters up to 500 μm.

The IMP has a fine-grained igneous texture (Figs. 2c and 2d), and is composed of olivine (~44.5 vol%), low-Ca pyroxene (~24.2 vol%), high-Ca pyroxene (~9.7 vol%), interstitial albite glass (~13.1 vol%), Fe-Ni metal (~3.8 vol%), troilite (~2.0 vol%), Ca-phosphates (~0.1 vol%), and vesicles (~2.5 vol%). It contains a lower percentage of opaque minerals than the

**Table 1. Modal abundances of different domains in NWA 7251 and comparison with that of L chondrites.**

<table>
<thead>
<tr>
<th></th>
<th>L chondrites</th>
<th>Chondrite host</th>
<th>Impact melt vein</th>
<th>Impact melt portion</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>wt%&lt;sup&gt;a&lt;/sup&gt;</td>
<td>wt%&lt;sup&gt;b&lt;/sup&gt;</td>
<td>vol%</td>
<td>wt%&lt;sup&gt;c&lt;/sup&gt;</td>
</tr>
<tr>
<td>Plagioclase/albitic glass</td>
<td>10.1</td>
<td>9.7</td>
<td>9.5</td>
<td>6.4</td>
</tr>
<tr>
<td>Olivine</td>
<td>47.0</td>
<td>44.8</td>
<td>47.4</td>
<td>49.2</td>
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<tr>
<td>Low-Ca pyroxene</td>
<td>22.7</td>
<td>24.2</td>
<td>25.9</td>
<td>25.2</td>
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<tr>
<td>High-Ca pyroxene</td>
<td>4.6</td>
<td>5.0</td>
<td>3.3</td>
<td>2.8</td>
</tr>
<tr>
<td>Fe-Ni metal</td>
<td>7.5</td>
<td>8.4</td>
<td>4.6</td>
<td>9.2</td>
</tr>
<tr>
<td>Troilite</td>
<td>6.1</td>
<td>5.8</td>
<td>5.5</td>
<td>6.6</td>
</tr>
<tr>
<td>Chromite</td>
<td>0.6</td>
<td>0.8</td>
<td>0.5</td>
<td>0.5</td>
</tr>
<tr>
<td>Ca-phosphate</td>
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<td>0.5</td>
<td>0.1</td>
<td>0.1</td>
</tr>
<tr>
<td>Orthoclase</td>
<td>0.6</td>
<td>0.6</td>
<td>n.d.</td>
<td>n.d.</td>
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<tr>
<td>Vesicle</td>
<td>–</td>
<td>–</td>
<td>3.3</td>
<td>–</td>
</tr>
<tr>
<td>Total</td>
<td>99.8</td>
<td>99.8</td>
<td>100.0</td>
<td>100.0</td>
</tr>
</tbody>
</table>

*Normalized to 100 vol%, n.d. = none detected.

<sup>a</sup>Data from Mason (1965).
<sup>b</sup>Data from McSween et al. (1991).
<sup>c</sup>Vol% converting to wt% followed the method of Weirich et al. (2011).
Table 2. SIMS U-Pb isotopic data of Ca-phosphates from NWA 7251.

<table>
<thead>
<tr>
<th>Sample/spot #</th>
<th>Mineral</th>
<th>U ppm</th>
<th>Th ppm</th>
<th>Th/U</th>
<th>204Pb (cps)</th>
<th>203Pb/204Pb</th>
<th>207Pb/204Pb</th>
<th>206Pb/204Pb</th>
<th>207Pb/206Pb</th>
<th>206Pb/207Pb</th>
<th>235U/206Pb</th>
<th>238U/206Pb</th>
<th>239U/206Pb</th>
<th>244U/206Pb</th>
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<tr>
<td>PMO-3050/CIMV (inherited)</td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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<td></td>
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<td></td>
<td></td>
</tr>
<tr>
<td>11@1</td>
<td>Mer</td>
<td>0.3</td>
<td>0.5</td>
<td>1.9</td>
<td>&lt;0.05</td>
<td>21</td>
<td>26.1</td>
<td>12.0</td>
<td>0.391</td>
<td>7.69</td>
<td>2.56</td>
<td>7.69</td>
<td>0.4840</td>
<td>9.2</td>
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<tr>
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<td>Mer</td>
<td>0.3</td>
<td>1.5</td>
<td>4.7</td>
<td>&lt;0.05</td>
<td>26</td>
<td>22.4</td>
<td>10.6</td>
<td>0.316</td>
<td>7.14</td>
<td>3.16</td>
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<tr>
<td>13@1</td>
<td>Mer</td>
<td>0.2</td>
<td>0.6</td>
<td>2.4</td>
<td>&lt;0.05</td>
<td>25</td>
<td>19.9</td>
<td>9.0</td>
<td>0.330</td>
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<td>3.03</td>
<td>5.22</td>
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<tr>
<td>14@1</td>
<td>Mer</td>
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<td>0.8</td>
<td>2.5</td>
<td>&lt;0.05</td>
<td>24</td>
<td>5.5</td>
<td>12.9</td>
<td>0.149</td>
<td>6.79</td>
<td>6.73</td>
<td>6.79</td>
<td>0.2703</td>
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<tr>
<td>14@2</td>
<td>Mer</td>
<td>0.4</td>
<td>1.0</td>
<td>2.7</td>
<td>&lt;0.05</td>
<td>19</td>
<td>7.7</td>
<td>12.1</td>
<td>0.162</td>
<td>7.11</td>
<td>6.19</td>
<td>7.11</td>
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<td>14@3</td>
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<td>0.8</td>
<td>2.1</td>
<td>&lt;0.05</td>
<td>12</td>
<td>12.8</td>
<td>12.6</td>
<td>0.217</td>
<td>7.19</td>
<td>4.60</td>
<td>7.19</td>
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<tr>
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<td>11.5</td>
<td>9.6</td>
<td>0.221</td>
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<td>106@1</td>
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<td>0.2</td>
<td>0.3</td>
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<td>122</td>
<td>97.1</td>
<td>6.9</td>
<td>1.136</td>
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<td>0.88</td>
<td>6.18</td>
<td>0.6202</td>
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<td>141@1</td>
<td>Mer</td>
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<td>0.8</td>
<td>1.7</td>
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<td>58</td>
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<td>9.83</td>
<td>0.4627</td>
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<td>0.7</td>
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<td>141</td>
<td>36.0</td>
<td>8.1</td>
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<td>7.01</td>
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<td>0.5</td>
<td>0.5</td>
<td>0.08</td>
<td>135</td>
<td>32.2</td>
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<td>0.4999</td>
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<tr>
<td>184@2</td>
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<td>0.7</td>
<td>0.5</td>
<td>0.05</td>
<td>828</td>
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<td>0.7</td>
<td>1.1</td>
<td>&lt;0.05</td>
<td>21</td>
<td>78.2</td>
<td>9.1</td>
<td>0.982</td>
<td>7.47</td>
<td>1.02</td>
<td>7.47</td>
<td>0.5773</td>
<td>5.2</td>
</tr>
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</table>

A@B stands for No.B spot analysis on the No.A phosphate grain. CIMV, crosscutting impact melt vein; Ap, apatite; Mer, merrillite. 

σ value is the standard error of isotopic ratio (i.e., 207Pb/206Pb or U/Pb ratio). The reported analytical error of 207Pb/206Pb ratio includes errors from counting statistics and propagation of external error of U/Pb fractionation calibration. 

aRefers to the radiogenic Pb compositions, common Pb correction for analyses with cps values higher than 0.05 was based on lead isotopic composition of Canyon Diablo troilite (200Pb/204Pb = 9.307, 208Pb/204Pb = 29.476); no common Pb correction was applied to the analyses with 204Pb signals less than 0.05 cps (very close to the noise background of ~0.03–0.05 cps), which assumes that all the Pb components are contributed by radiogenic background. 

bRefers to raw data that are uncorrected for background.

host or average L chondrites (Table 1). All the crystals and fragments are randomly oriented without flow alignment. The angular fragments are dominantly olivine-rich (Fig. 2c), fractured, and some are composed of fine-grained crystals (~20 μm) with interstitial albitic glass or metals. Olivine grains are equant, and typically range between ~10 and ~40 μm in size. Prismatic pyroxene grains are mostly 15–200 μm in size and poikilitically enclose olivine chadacrysts (Fig. 2d). Metallic Fe-Ni and troilite locally coexist with vesicles, and generally occur as monomineralic particles (mostly 1–10 μm) or globules (up to 600 μm). Ca-phosphate grains (merrillites and apatites) are relatively small (<20 μm), but typically form clusters. They are intergrown with interstitial albitic glass or metals (Figs. 3g–j). Locally, merrillites are rimmed by apatites (Fig. 3j).

The impact melt veins occur as pervasive type (PIMV) and crosscutting type (CIMV), although a well-preserved example of the latter is only found in PMO-3050. PIMV is pervasive in the host, and contains quenched silicates and metal/sulfides droplets, as well as interstitial albitic glass. Olivine and pyroxene grains in the veins are <10 μm in size and grew as skeletal crystal shapes. The irregular olivine/pyroxene-rich fragments in the PIMV are typically replaced by tiny silicates (<10 μm), and are filled with interstitial albitic glass and metal (Figs. 2e and 2f). Tiny crystals replacing the pyroxene fragments generally have lath-like or granular shapes with locally zoned and poikilitic textures. We suggest that these tiny crystals have inherited the fragment shapes and crystallized from a melt during an impact event, which was also observed in the L chondrite Ramsdorf by Yamaguchi et al. (1999). Ca-phosphates in the PIMV are <10–15 μm in size, and are commonly found in association with metal-sulfide grains or as interstitial grains (Figs. 3k–l). The ~600 μm wide CIMV in PMO-3050 crosscuts the host, with which it has sharp contacts. The grain sizes of silicates and metal droplets decrease toward the margins of the vein (Fig. 2g). Compared with the IMP, the CIMV has a similar texture but a much finer grain size and contains more metals (Table 1; Fig. 2h). Olivine grains are equant and small in size (<30 μm). Tiny low-Ca pyroxene laths (<20 μm) are typically rimmed by very thin pyroxene high-Ca edges (typically <1 μm). Similar to those in the IMP, the irregularly shaped olivine fragments (~30–300 μm) are usually fractured, and are composed of fine-grained crystals with interstitial albitic glass or metal in some cases (Fig. 2i). Most Ca-phosphates in the CIMV, like those in the PIMV, are anhedral to subhedral grains with sizes of <10 μm. They are associated with metal-sulfide droplets or occur interstitially (Figs. 3m and 3n). Several large Ca-
phosphate grains with sizes up to 40 μm are enclosed by or adjacent to metal veins or large irregular metal globules (up to ~300 μm) (Figs. 2j and 3o–r).

Mineral Chemistry

The chemical compositions of the Ca-phosphates (merrillites and apatites) were measured prior to U-Pb dating (Appendix S1A–S1B). The merrillite grains in the melt and host have similar Mg# values (Mg/[Mg + Fe] × 100) with a peak at 80–84 (Figs. 4a–d). The apatites in the host are Cl-rich (mostly Cl/F = 2.7–4.1), lack measurable hydroxyl components, and plot in the L chondrites field in an apatite atomic anion ternary diagram (Fig. 5). In comparison, apatite grains in the CIMV and PIMV have wider compositional ranges and are relatively F-rich (CIMV: Cl/F = 1.6–9.7; PIMV: Cl/F = 1.2–14.0). The apatite grains from the IMP show large variations in Cl/F ratios from 0.1 to 3.6, which is independent of grain size and coexisting phases (i.e., minerals and/or glass).

The compositions of olivines, pyroxenes, albitic glass/plagioclases, and chromites from different domains in NWA 7251 are summarized in Appendices S1C–S1F and S2, respectively, in the supporting information.

Thermometry

The two-pyroxene thermometer of Kretz (1982) was applied to estimate the equilibration temperature of low-Ca and high-Ca pyroxenes in the IMP. Six coexisting low-Ca (Fs19.3–20.4Wo2.7–6.6) and high-Ca (Fs13.2–15.7Wo26.9–37.2) pyroxene pairs crystallized from the IMP were selected for calculation, and the equilibration temperature was estimated as 1180–1350 °C.

Given that pyroxenes are not completely equilibrated in type 4–5 ordinary chondrites (McSween and Patchen 1989; Wlotzka 2005), the olivine–chromite thermometer based on the method of Wlotzka (2005) was applied to calculate the equilibration temperature of the host. Six coexisting chromite (Cr/[Cr + Al] × 100 = 85–87, Fe/[Fe + Mg] × 100 = 72–77) and olivine (Fa24.2–25.6) pairs from the host yielded equilibration temperatures of 840–920 °C.

Ca-Phosphate U-Pb Dating

PMO-3049 contains the least amount of melt (<2%) and has the best-preserved chondritic texture among the three studied sections. It is likely to be the thin section that was least affected by the shock melting event. Therefore, the host Ca-phosphate grains in PMO-3049 were analyzed to constrain the thermal history of NWA 7251 before the shock melting event. The Ca-phosphate grains from the CIMV of PMO-3050 were analyzed to determine the timing of the shock melting event. All the Ca-phosphate grains analyzed were >15 μm in size and...
free of fractures. The Ca-phosphate grains from the PIMV were too small (<10–15 μm) to be analyzed, and the U concentrations of those from the IMP were too low to yield meaningful results.

Seven analyses (three of merrillites and four of apatites) were conducted on six Ca-phosphate grains from the host in PMO-3049 (Figs. 3a–f), and six analyses were conducted on four Ca-phosphate grains (only merrillites) from the CIMV of PMO-3050 (Figs. 3g–r). U-Pb isotopic data for the Ca-phosphates are listed in Table 2. Nine analyses (all in CIMV, three in the host) have low U concentrations (0.2–0.7 ppm). Aside from one analysis with a 206Pb/204Pb ratio of 122 (uncorrected for background), the other analyses have 206Pb/204Pb ratios of 12–26. These analyses have 204Pb signals less than 0.05 cps, which is very close to the background values (~0.03–0.05 cps). This implies that almost all the Pb components are radiogenic; as such, no common Pb correction was applied. The four other analyses from the host have variable U contents of 0.5–1.3 ppm, variable 206Pb/204Pb ratios of 58–828, and 204Pb signals of 0.05–0.08 cps. The common Pb-corrected 206Pb/238U ratios, based on primordial lead compositions (i.e., Canyon Diablo troilite Pb isotopic compositions; Tatsumoto et al. 1973), differ by 1–16% from the uncorrected data. Due to the relatively large analytical uncertainties, the 206Pb/238U ratios that are corrected and uncorrected for common Pb are broadly indistinguishable within errors (Appendix S3, respectively, in the supporting information). When the modern terrestrial lead compositions (Stacey and Kramers 1975) were used to correct for common Pb, the corrected 206Pb/238U ratios are ~2–33% different from the uncorrected data (Appendix S3, respectively, in the supporting information). Overall, the common Pb correction using either primordial or modern terrestrial lead compositions yields concordia intercepts that differ by less than the stated uncertainties (Fig. S1 of Appendix S3). Here, we assume that all the common Pb were introduced from the primordial lead. U-Pb concordia diagrams are shown in Fig. 6.

Seven analyses from the host form a discordia linear array on the U-Pb concordia diagram, yielding an upper intercept of 4481 ± 64 Ma and a lower intercept of 689 ± 150 Ma (MSWD = 1.6; Fig. 6a). Six grains from the CIMV that are enclosed by or adjacent to metal veins or globules were analyzed (Figs. 3o–r). These data also define a discordia line, yielding comparable results to those of the host Ca-phosphates, with an upper intercept of 4438 ± 200 Ma and a lower intercept of 528 ± 130 Ma (MSWD = 0.94; Fig. 6b). Combining all 13 analyses yields an upper intercept of 4457 ± 56 Ma and a lower intercept of 574 ± 82 Ma (MSWD = 1.3; Fig. 6c).

**DISCUSSION**

**Classification and Shock Metamorphism of NWA 7251**

The chemical compositions of olivine (host Fa24.9±0.7, IMP Fa25.4±1.2, CIMV Fa24.2±0.9, and PIMV Fa24.9±0.6) and low-Ca pyroxene (host Fs21.1±0.3, IMP Fs18.4±20.5, CIMV Fs18.3±25.3, and PIMV Fs15.5±20.6) from all the domains confirm that NWA 7251 is a typical L chondrite. The compositions of apatites from the host are also consistent with those of L chondrites (Lewis and Jones 2016) (Fig. 5). Type 4 chondrites are characterized by recrystallized matrix (the grain size of secondary plagioclase is ~2 μm), poorly defined chondrule boundaries, and uniform olivine (percent mean deviation [PMD = mean deviation/mean×100] Fa <5%) and low-Ca pyroxene compositions (PMD Fs <5–20%) (Schmus and Wood 1967; Huss et al. 2006; Wang et al. 2008). In the host of NWA 7251, chondrule boundaries are not sharply defined and most of the mesostasis is recrystallized. In addition, secondary plagioclase grains in the matrix are relatively small (mostly 3–5 μm) and the compositions of olivine (Fa24.9±0.7; PMD Fa = 2.4%) and low-Ca pyroxene (Fs21.1±0.3; PMD Fs = 1.1%) are relatively uniform. Accordingly, we consider that the host domain of NWA 7251 was metamorphosed to type 4. Equilibration temperatures estimated from coexisting olivine and chromite are 840–920 °C, much higher than those of most L4 chondrites (640–777 °C; Wlotzka 2005). The relatively high equilibration temperature recorded in the host could be related to a later reheating process, such as that of the type 4 chondrite Beaver Creek (818 °C;
higher than the melting point of pyroxene (i.e., indicating that NWA 7251 was heated to a temperature enough to melt pyroxene and partially melt olivine, regard, the postshock heating temperature was high enough to melt pyroxene and partially melt olivine, including the IMP, CIMV, and PIMV, are present in NWA 7251. Formation of such a whole rock impact melt texture requires a peak shock pressure of \( >30 \)–\( 35 \) GPa, which could also reach pressures as high as \( 70 \)–\( 90 \) GPa for rocks with low porosity (Stöffler et al. 1991; Hörz et al. 2005). The peak postshock heating temperature can be broadly estimated from the relic mineral types in the melt. Pyroxene-rich fragments are poorly preserved in the melt and replaced by tiny neocrystallized grains in the PIMV, suggesting that most of the original pyroxene crystals were consumed during shock-induced melting. In contrast, olivine-rich fragments are well preserved, and parts of them contain healed cracks and chains of troilite droplets along grain boundaries, which is analogous to the host olivine in texture and composition. Similar textures have been observed in other impact melt chondrites (e.g., Yamato-790964, LAP 02240, and Ramsdorf; Yamaguchi et al. 1998, 1999; Niihara et al. 2011). This suggests that parts of primary olivines survived the heating event. In this regard, the postshock heating temperature was high enough to melt pyroxene and partially melt olivine, indicating that NWA 7251 was heated to a temperature higher than the melting point of pyroxene (i.e., \( >1300 \)–\( 1500 \) °C) and probably close to that of olivine (i.e., \( \sim1600 \) °C) (Takahashi 1983; Jurewicz et al. 1995). The equilibration temperatures of 1180–1350 °C obtained from two-pyroxene thermometry also support these mineralogical estimations of the postshock heating temperature.

Formation of Ca-Phosphates

Previous studies have suggested that the formation of Ca-phosphates in equilibrated chondrites is related to the oxidation of phosphorus that was originally hosted by metals during early thermal metamorphism on parent bodies (Zanda et al. 1994; McCubbin and Jones 2015). Although there are no apparent systematic compositional variations in apatites due to their late growth during thermal metamorphism, merrillites could exhibit a compositional equilibration trend and progressive grain-size coarsening trend with increasing petrological rock type (Jones et al. 2016). For example, merrillites from L5–6 chondrites typically have a relatively narrow range of Mg\# values (L5: Mg\# = 89–95; L6: Mg\# = 84–94), whereas grains from L4 chondrites exhibit a large compositional range (Mg\# = 69–95) (Lewis and Jones 2016). In the host of NWA 7251, Ca-phosphate grains closely coexist with metals/sulfides and have a medium grain size (10–60 μm), as expected for formation during thermal metamorphism on the parent body. However, unlike L4 chondrites (Fig. 4e), most merrillite grains in the host of NWA 7251 have a very small range of Mg\# values (26 of 29 grains have Mg\# = 78–86) with a few having much lower Mg\# values (3 of 29 grains have Mg\# = 71–75) (Fig. 4d). This implies that the compositions of most merrillite grains have been modified and equilibrated at the relatively high equilibration temperature of the host (840–920 °C) during a later shock heating event.

Most Ca-phosphate grains in the melt (i.e., IMP, CIMV, and PIMV) are distinguished from those in the host by their morphology, grain size, and mineral composition. They have smaller grain sizes (single grains typically <20 μm) and typically grow interstitially with metal grains. Although the merrillite compositions in the host and melt are indistinguishable (Figs. 4a–d), Cl/F ratios of apatites in the melt (CIMV: Cl/F = 1.6–9.7; PIMV: Cl/F = 1.2–14.0; IMP: Cl/F = 0.1–3.6) have much wider ranges than those from the host (Fig. 5 and Appendix S1B, respectively, in the supporting information). Accordingly, we consider that most Ca-phosphate grains in the melt are neocrystallized grains. The growth of merrillites is attributed to the crystallization of phosphorus-saturated melt (Neal and Taylor 1991; Jolliff et al. 1993). The coexistence of two
Ca-phosphates and local overgrowth of apatites on merrillite rims suggest that the apatites crystallized from a halogen-rich melt/fluid after the formation of merrillites (Shearer et al. 2011; Gross et al. 2013). It is noted that apatites in the IMP show a large variation in Cl/F ratios (Fig. 5 and Appendix S1B, respectively, in the supporting information). This is unusual in chondrites and primitive achondrites (e.g., Keil 2014; Lewis and Jones 2016). Several processes, including igneous processes (e.g., fractionation), degassing, or the addition of metasomatic fluids, could contribute to the large apatite Cl/F ratio variations. Degassing is most likely in this case due to the occurrence of vesicles in the IMP, as is also the case for several Martian samples (McCubbin et al. 2011, 2013; McCubbin and Jones 2015).

Some merrillite grains enclosed by or adjacent to metal veins or globules of the CIMV may have a different origin. Compared with those that crystallized from the melt, these grains usually have larger grain sizes (20–40 μm), which are in sharp contrast with the surrounding skeletal silicates that crystallized during impact melting. In fact, their grain sizes, morphologies, and limited range of Mg# values (78–83) are very similar to merrillites in the host. Considering the presence of inherited radiogenic lead (see below), we suggest that some merrillite grains enclosed by or adjacent to the metal veins or globules in the CIMV are inherited grains from the host. The presence of inherited Ca-phosphates was also reported in melt from Apollo 14 breccias (Merle et al. 2014).

Multiple Shock Heating Events

Calcium-aluminum-rich inclusions, formed at 4.567 Ga, and chondrules, formed no more than a few Myr later, are the oldest solids in the early solar nebula (Amelin et al. 2010; Connelly et al. 2012). Thereafter, ordinary chondrite parent bodies were accreted and may

Fig. 4. Histograms of Mg# (Mg/(Mg + Fe) × 100) values of merrillites in the CIMV (a), PIMV (b), IMP (c), and host (d). The Mg# values of merrillites from the Santa Barbara L4 chondrite (e) are plotted for comparison (Lewis and Jones 2016). The abbreviations are as in Fig. 2.

Fig. 5. Apatite atomic Cl-F-Other anion ternary diagram for NWA 7251. Apatite grains in the host fall into the L chondrite group region. The gray fields of apatite data from L, H, and LL chondrites are from Lewis and Jones (2016). The abbreviations are as in Fig. 2. (Color figure can be viewed at wileyonlinelibrary.com.)
have experienced thermal metamorphism induced by radioactive decay of short-lived radionuclides ($^{26}$Al and $^{60}$Fe) (Huss et al. 2006). Several Ca-phosphates from unshocked ordinary chondrites have yielded Pb-Pb ages clustering between 4.50 and 4.56 Ga, recording the timing of cooling below the Ca-phosphate closure temperature (i.e., ~500 °C) (Göpel et al. 1994; Amelin 2000; Bouvier et al. 2007). Blackburn et al. (2017) further suggested that the ages of Ca-phosphates show a younging trend from ~4560 Ma (type 4) to 4500 Ma (type 6) with increasing petrologic type, which supports the onion-skin model (e.g., Trieloff et al. 2003). Thus, ordinary chondrite parent bodies experienced a short period of heating exceeding Ca-phosphate closure temperature for <60 Myr after their formation (Göpel et al. 1994; Bennett and McSween 1996; Trieloff et al. 2003). The merrillites in the host domain of NWA 7251 have distinct compositional ranges compared with those in less shocked L4 samples, implying that the initial Ca-phosphate grains were severely modified by a later event. Furthermore, SIMS U-Pb dating of Ca-phosphates in NWA 7251 yielded an upper intercept age of 4457 ± 56 Ma. This age is younger than those of Ca-phosphate ages (~4.50–4.56 Ga), particularly for type 4 rocks (~4.56 Ga), which were formed during the early thermal metamorphism of the parent body. So we consider that the age of 4457 ± 56 Ma records an early impact event rather than early thermal metamorphism process on the parent body. Previous studies have reported $^{39}$Ar-$^{40}$Ar ages older than 4.4 Ga for a few L chondritic impact melt samples. Aside from MIL 05029 (L-melt rock) that yielded a relatively old impact age (~4.53 Ga; Weirich et al. 2011), PAT91501 (L7) and Shaw (L7) both have impact ages clustering between 4.43 and 4.46 Ga (Turner et al. 1978; Benedix et al. 2008). Recently, Yin et al. (2014) obtained an upper intercept age of 4472 ± 31 Ma for Novato (L6) based on SIMS Ca-phosphate U-Pb dating; Li and Hsu (2016) also reported a SIMS Ca-phosphate $^{207}$Pb/$^{206}$Pb age of 4482 ± 30 Ma for Suizhou, which is a heavily shocked L6 chondrite with the presence of tuite (a high pressure polymorph of Ca-phosphate). Our age results are broadly consistent with these previous whole rock Ar-Ar ages and in situ U-Pb dating of Ca-phosphates. Furthermore, several chondrite classes (e.g., EL, EH, E-melt/aubrites, L, LL, and H chondrites) also record a 4.4–4.5 Ga shock heating event in both U-Pb and whole rock Ar-Ar dating (e.g., Kring et al. 2000; Terada and Bischoff 2009; Bogard 2011; Popova et al. 2013; Swindle et al. 2014; Bottke et al. 2015b). This may imply that this event influenced a wide range of objects in the asteroid belt (e.g., Kring et al. 2000; Terada and Bischoff 2009; Bogard 2011; Popova et al. 2013; Bottke et al. 2015b). Based on the results of numerical simulations, Bottke et al. (2015b) suggested that some high-speed projectiles from the giant impact
may strike the asteroid belt at ~4.47 Ga, which may lead to the degassing of a number of chondritic samples.

Our Ca-phosphates U-Pb dating results show that all data scatter along a discordia line on the U-Pb concordia diagram, with inherited grains in the CIMV being close to the lower intercept of ~574 Ma and those from the host being close to the upper intercept. This implies that Ca-phosphate grains in the CIMV have been affected by a later event to higher degrees. Two possibilities may account for this observation. First, Ca-phosphate grains in the melt might have ever undergone more severe devolatilization, including Pb loss, in the shock event. If this were the case, tuite, transformed from apatite at pressures of >12 GPa (Xie et al. 2016), is expected, because the peak shock pressure for the formation of the impact melt was ~30–35 GPa. However, no tuite is observed in NWA 7251. Xie et al. (2002) suggested that rapid quenching was essential for the preservation of high-pressure polymorphs in the L6 chondrite Suizhou. It is very likely that back transformation of tuite to merrillite took place during relatively slow cooling, which is evident from the well-recrystallized euhedral silicates in the melt. Alternatively, different shock heating temperatures in the melt and host might account for the different degrees of Pb loss in the Ca-phosphates. The diffusion coefficient is positively related to temperature, and the effective diffusion radius is a function of the diffusion coefficient and time (Crank 1975; Cherniak 2010). Ca-phosphate grains in the CIMV experienced more severe thermal heating (~1300–1500 °C) than those in the host (840–920 °C), which may have resulted in nearly complete Pb loss. Overall, we suggest that NWA7251 was heavily shocked at 574 ± 82 Ma, and that the impact melt was formed during this event.

Compared with H (~9% from the Meteoritical Bulletin Database [MBD]) and LL chondrites (~21% from the MBD), more L chondrites reached the shock stages of S4–S6 or contain impact melt (~32% from the MBD). Ar-Ar impact ages for L chondrites cluster at ~400–500 Ma (20 of 42 impact ages; table 1 of Swindle et al. 2014), related to the breakup of the L chondrite parent body (Stöffler et al. 1991; Bogard et al. 1995; Swindle et al. 2014). Korochantseva et al. (2007) and Weirich et al. (2012) obtained precise Ar-Ar ages of 470 ± 6 Ma for this event after careful corrections to their data. To avoid the problem of incomplete Ar degassing, Yin et al. (2014) further used the in situ SIMS Ca-phosphate dating method and obtained a comparable age of 473 ± 38 Ma. Evidence for the breakup of the L chondrite parent body has also been found in terrestrial rocks on Earth: abundant extraterrestrial materials of L chondritic components have been found in mid-Ordovician strata in Sweden, China, and Russia, indicating an increase of two orders of magnitude in the flux of L chondritic materials at that time (Schmitz et al. 1997, 2003; Lindskeg et al. 2012); there was a factor of 3–4 enhancement in crater number on Earth during 450–480 Ma (Schmitz et al. 2001; Schmitz 2013). These extraterrestrial materials found in mid-Ordovician strata have very short cosmic-ray exposure ages of 10^5 to 10^6 yr, and are locked in the limestone with an age of 467.3 ± 1.6 Ma, which accurately dates the breakup of the L chondrite parent body (Heck et al. 2004, 2008). Our impact age of 574 ± 82 Ma for NWA 7251 is broadly consistent with these previous ages, and is another piece of evidence for the disruption of L chondrite parent body.

**SUMMARY**

1. Petrological and mineralogical studies have shown that NWA 7251 is composed of three domains: the chondrite host, impact melt portion, and two types of melt veins (CIMV and PIMV). The host is an L4 chondrite with a shock stage of S4. The impact melt was generated at pressures of >30–35 GPa and temperatures of >1300–1500 °C. NWA 7251 may be better classified as an L-impact breccia rather than an L-melt rock.

2. The compositions of Ca-phosphate grains in the chondrite host were affected by impact events. Most of the Ca-phosphate grains in the impact melt were neocrystallized during the impact heating event, and the large variation in CI/F ratios in apatites of the IMP were most likely due to degassing. The Ca-phosphate grains enclosed by or adjacent to metal veins or globules of the CIMV were inherited from the host.

3. SIMS Ca-phosphate U-Pb dating yielded an upper intercept of 4457 ± 56 Ma and a lower intercept of 574 ± 82 Ma on a normal U-Pb concordia diagram. We suggest that the age of 4457 ± 56 Ma records an early impact event rather than thermal metamorphism. The impact melt in NWA 7251 generated at 574 ± 82 Ma is another piece of evidence for the disruption of the L chondrite parent body.

**Acknowledgments**—We thank X. H. Li, Q. L. Li, G. Q. Tang, Y. Liu, J. Li, and X. X. Ling for their help with SIMS phosphate U-Pb dating. The authors also thank A. Zhang, Y. Wu, S. Liao, Y. Wang, and S. Li for their constructive suggestions at the different stages of manuscript preparation. We are grateful to A. Ruzicka, T. D. Swindle, M. E. Zolensky (AE), and two anonymous reviewers for their suggestions that greatly improved the manuscript. This work was supported by the National Natural Science Foundation of China (Grant No. 41773059, 41573059), FDCT (039/2013/A2, 005/2017/A1), the Minor Planet Foundation of China, and the Natural Science Foundation of Jiangsu Province (Grant:
U-Pb dating of Ca-phosphates in the NWA 7251


and other debris from an H-chondrite parent body (abstract #1688). 31st Lunar and Planetary Science Conference. CD-ROM.


