Dating phosphates of the strongly shocked Suizhou chondrite

SHAOLIN LI1,2 AND WEIBIAO HSU3,*

1Purple Mountain Observatory, Chinese Academy of Sciences, Nanjing 210034, China
2School of Astronomy and Space Sciences, Nanjing University, Nanjing 210093, China
3State Key Laboratory of Lunar and Planetary Sciences, Macau University of Science and Technology, Macau 999078, China

ABSTRACT

Impacts on undifferentiated asteroidal bodies provide invaluable information for understanding the solar system evolution. Nevertheless, dating early and small-scale impact events is technically challenging. Uranium–lead (U–Pb) systematics of U-bearing phases within shock-induced melt veins (SMVs) of chondrites may be significantly disturbed by localized heating, thus providing opportunities to date these impact events. As one of the major U hosts in chondrites, apatite in the Suizhou (L6) chondrite has been compositionally and structurally modified to varying degrees by shock metamorphism. Apatite grains in the host remained largely intact during the impact and have recorded the initial thermal cooling time (∼4550 Ma) on their parent body. Apatite grains in regions less than 100 μm bordering the SMVs or in relatively “cold” regions within the SMVs were partly decomposed to tuite, driven by the localized transient heating within the SMVs. Their U–Pb systematics were disrupted to varying extents. Apatite in regions close to the center of the SMVs has been completely transformed to tuite, which yields an age of 4481 ± 30 Ma (2σ), providing an upper limit to the impact event. This study clearly demonstrates that by integrating in situ U–Pb isotope analysis with detailed microstructural and compositional analysis of phosphates, it is possible to deduce the timing of early and small-scale celestial impact events, and hence create a more comprehensive understanding of the impact history of the solar system.

Keywords: Apatite, tuite, L chondrite, in situ U–Pb dating, early impacts in the solar system

INTRODUCTION

Impacts occur during all stages of planet formation and evolution, from the initial accretion of chondritic materials in the nebula to differentiation and secondary alteration on planetary bodies (Scott 2002). Due to impact-induced heating, isotopic chronometers of target rocks can be reset and record the timing of these impact events (Deutsch and Schärer 1994; Bogard 1995; Jourdan et al. 2009). However, impact ages are not always straightforward to interpret, largely due to the lack of knowledge about how shock metamorphism affects isotopic systematics in specific minerals and in whole rocks (e.g., Deutsch and Schärer 1994; Niihara et al. 2012; El Goresy et al. 2013; Bloch and Ganguly 2014; Darling et al. 2016).

One fundamental question is whether the isotopic chronometer is disturbed during shock compression or the prolonged post-shock annealing (Deutsch and Schärer 1994; El Goresy et al. 2013). Laboratory shock recovery experiments have been performed, followed by isotopic analysis, to decipher the relationship between the degree of shock metamorphism and isotopic disturbance since the 1960s (e.g., Fredriksson and De Carli 1964; Bogard et al. 1987; Deutsch and Schärer 1990; Gaffney et al. 2013; Niihara et al. 2012). Shock compression, up to ∼60 GPa, can hardly disturb a series of isotopic chronometers (e.g., Sm–Nd, Rb–Sr, U–Pb, and K–Ar), although the slight 40Ar loss was observed for higher shock pressures (Bogard 1995).

The general conclusion drawn from these experiments is that post-shock annealing plays the most important role in resetting isotopic chronometers, and naturally shocked and unannealed samples are unlikely to record the timing of the impact event (Deutsch and Schärer 1994). However, the duration of the high-pressure regime in laboratory recovery experiments is several orders of magnitude shorter than shock pulse in natural impact events (Sharp and DeCarli 2006). This casts doubt on whether the results obtained from recovery experiments are readily applicable to natural impact events on planetary bodies (El Goresy et al. 2013).

Natural impacts can induce localized melting by shear stress along the grain boundaries of minerals with different shock impedance, frictional heating along shear zones, and the collapse of pores during shock compression (Sharp and DeCarli 2006). Shock melt veins (SMVs) generated in these processes could reach temperatures and pressures in excess of 2500 °C and 26 GPa (Langenhorst and Poirier 2000; Sharp and DeCarli 2006; Gillet and El Goresy 2013). Various high-pressure phases can form in these SMVs under the extreme P–T–t conditions, either through solid-state transformation or crystallization from the dense silicate melt. Tuite, with the structure of trigonal γ-Ca3(PO4)2, was first identified in the SMVs of the Suizhou L6 chondrite (Xie et al. 2002) as a high-pressure polymorph of merrillite and later in other meteorites, such as martian and iron meteorites (e.g., Fritz and Greshake 2009; Litasov et al. 2011).
and Podgornykh 2017). It was also suggested that tuite could be formed by decomposition of apatite through the reaction: 2Ca₃(PO₄)₃X → 3Ca₃(PO₄)₂ + CaX₂ (Murayama et al. 1986; Xie et al. 2013), where X represents monovalent anions that are dominated by Cl in equilibrated L chondrites (Lewis and Jones 2016). Because phosphates are the major U hosts in chondrites (Göpel et al. 1994), tuite formed during impact events had great potential to date these processes. In this contribution, we present in situ U–Pb dating of tuite and apatite in the strongly shocked Suizhou chondrite. This is the first report of U–Pb dating on a high-pressure phase of phosphates. The U–Pb systematics of tuite provides insights into whether and to what extent it could be affected by the extreme P–T–t regime during natural impacts.

**SAMPLE AND ANALYTICAL METHODS**

**Sample**

The sample used in this study is a witnessed fall, the Suizhou chondrite (L6), which fell in Suizhou, China, in 1986. It was strongly shocked (S4–S5; Xie et al. 2001), with olivine and pyroxene exhibiting weak mosaic textures and plagioclase being partly (~30 vol%) transformed to maskelynite. The meteorite contains a few thin black SMVs (mostly 0.02–0.09 mm in width). Up to 12 high-pressure phases were identified in the SMVs, including ringwoodite, bridgmanite (vitrified), majorite, majorite-pyrope garnet, akimotoite, hemlyelite, magnesiowüstite, linguite, wadanoideasite, xieite, and a CaFe₃O₄-polymer of chromite and tuite (Xie and Chen 2016 and references therein). The assemblage of majoritic garnet + ringwoodite + magnesiowüstite in the SMVs suggests crystallization temperature of about 1800–2000 °C under pressure of 20–22 GPa (Xie et al. 2001). The presence of akimotoite, vitrified perovskite and xieite inside and directly adjacent to the SMVs suggests that the maximum pressure and temperature developed in the shocked SMVs could reach about 24 GPa and 2200 °C (Xie and Chen 2016). Under the estimated P–T–t condition, tuite in Suizhou could have been transformed from both mellirellite and apatite (Xie et al. 2013). 

**Analytical methods**

Five polished sections are carbon-coated before petrographic investigation using scanning electron microscope (SEM). Phosphates in the vicinity of the SMVs of Suizhou were identified using X-ray mapping with the Oxford X-Max energy-dispersive spectrometer equipped on the Hitachi S-3400N SEM at Purple Mountain Observatory (PMO), Chinese Academy of Sciences. Cathodoluminescence (CL) images of the phosphates were obtained using a MonoCL4 system attached to the SEM with a 15 kV accelerating voltage.

**Texture and chemistry of phosphates**

Apatite in the host of Suizhou (H-ap) contains three sets of planar fractures. But in most cases, only one or two sets are visible (Figs. 1a–1c). H-ap is homogenous and has an average Cl content of 5.61 wt%, with minor Na₂O (~0.42 wt%), and is nearly free of MgO (~0.01 wt%) (Fig. 3; Table 1; please see the Supplementary Table for complete results of EPMA analysis).

The Raman spectrum of H-ap is characterized by an intense peak at 960 cm⁻¹, three less intense peaks at 427, 589, and 1038 cm⁻¹, and two weak peaks at 612 and 1077 cm⁻¹ (Fig. 3), which are typical for unshocked chlorapatite (Xie et al. 2013).

Apatite grains adjacent to the wall of the SMVs (W-ap) exhibit two distinctive (dark and bright) parts on their BSE images with a sharp boundary roughly parallel to the edge of the SMVs (Figs. 1d, 1f, and 4a). The dark part consists of submicrometer-scale polycrystalline aggregates (herein termed “polycrystalline domains”), whereas the bright part is similar to H-ap in texture (herein termed “apatite domains”). Two domains can be more readily distinguished from their CL images, where the polycrystalline domains have a bright, cloudy texture and the apatite domains have a relatively dark and homogenous texture (Fig. 4b). The compositions and Raman spectra are correlated with textural variations observed between the two domains. Cl content in the apatite domains is similar to that of H-ap (~5.7 wt%) but drops down to 2.4 wt% in the polycrystalline domains. Meanwhile, Na₂O content decreases from ~0.42 to 0.07 wt%, and MgO content increases from less than 0.01 to 0.4 wt% (Table 1, Fig. 2). The Raman spectra for the polycrystalline domains show that the peaks for apatite have been substantially weakened and contamination during sample preparation, all sections were cleaned with ethanol and de-ionized water in an ultrasonic bath after removing previously coated carbon films and were re-coated with carbon before SIMS analysis. Because phosphates in the SMVs are mostly small in size (mostly <20 μm), O₂ was chosen over O₃ as the primary ion beam as it has higher density hence a smaller beam diameter (Liu et al. 2011). For the same reason, the Gaussian illumination mode of the primary beam was used with a 200 μm diameter aperture. A focused primary beam (10 × 15 mm) was finally obtained. The primary ion beam was accelerated at ~14 kV with an intensity of ~5–7 nA. The stimulated secondary ions were accelerated at a potential of ~10 kV. The dynamic multi-collector analysis technique was used to acquire high-precision $^{206}\text{Pb}/^{238}\text{U}$ ratios as in the static multi-collector mode without trade off in the analytical precision of the $^{204}\text{Pb}/^{238}\text{U}$ ratio of the conventional peak-hopping mono-collector mode (Liu et al. 2015). $^{207}\text{Pb}/^{206}\text{Pb}$ was used as a reference peak at a mass resolution of 8000 (defined at 50% height) for tuning of secondary ions, energy, and mass adjustments. Each spot was pre-sputtered on a square area (35 × 35 μm) for 120 s to remove the surface contamination and to enhance the secondary ion yields. Each measurement consists of 15 cycles, with the total analytical time of about 26 min.

**Results**

**Texture and chemistry of phosphates**

The peaks of $^{207}\text{Pb}$ and $^{206}\text{Pb}$ ages of the samples require consideration for matrix effects resulting from differences in mineral chemistry and crystal structure between samples and standards. Although the matrix effects would be less significant in our apatite analyses, the lack of a suitable tuite standard means that the tuite analyses were necessarily corrected with the apatite standard NW-1 (1160 Ma; Li et al. 2012). Due to an insufficient number of SIMS analyses on tuite, the uncertainty induced by matrix effects in tuite U–Pb age is difficult to be quantified. The uranium concentrations were calibrated relative to the Durango apatite, which contains approximately 9 ppm of U (Trotter and Eggins 2006). The U–Pb and Pb–Pb ages were calculated with the revised $^{206}\text{Pb}/^{238}\text{U}$ value of 137.88, the Pb–Pb ages of phosphates in Suizhou were reduced by ~0.95 My. The uncertainty for the U–Pb and Pb–Pb ages are given at the 95% confidence level unless otherwise specified.
replaced by tuite peaks, including an intense peak at 977 cm\(^{-1}\), three less intense peaks at 412, 578, and 1096 cm\(^{-1}\), and two weak peaks at 641 and 1002 cm\(^{-1}\) (Fig. 3; Xie et al. 2002). The Raman spectra for the apatite domains largely retain features for apatite, although they may also contain weak tuite peaks (e.g., the 977 cm\(^{-1}\) peak) at regions <100 μm bordering the SMVs (Fig. 3). The high-resolution BSE images show that patches of residual apatite are surrounded by sub-micrometer tuite crystallites in the porous polycrystalline domains (Fig. 5), whereas the apatite domains largely retain a texture similar to that of H-ap.

As indicated by the BSE and CL images, the width of the polycrystalline domains of W-ap in Suizhou is generally less than 10 μm. However, even on such a small scale, the phase transformation is heterogeneous as visualized from the Raman mapping. Raman mapping of a W-ap grain displays intensity distributions of main Raman peaks at 977 cm\(^{-1}\) for tuite (Fig. 4c) and at 960 cm\(^{-1}\) for apatite (Fig. 4d), respectively. For the polycrystalline domain, the intensity of 977 cm\(^{-1}\) peak decreases significantly...
from the middle part (convex into the SMVs center) to the two ends (depart from the SMVs center), and the reverse is true for the intensity distribution of the 960 cm$^{-1}$ peak. Corresponding to the Raman features, Cl content increases ~30% from the middle part to both ends (from 2.4 to 3.4 wt%), whereas MgO content substantially decreases (from 0.4 to 0.06 wt%).

Apatite in the SMVs (S-ap) has decomposed to polycrystal-line aggregates without planar fractures as shown on BSE images (Figs. 1g and 1h). Compared to the polycrystalline domains of W-ap, S-ap generally contains less residual Cl (Fig. 2; Table 1), and hence a smaller amount of relict apatite. This is also revealed by its Raman spectra that all the Raman peaks are characteristic for tuite except a residual weak peak at 960 cm$^{-1}$ for apatite (Fig. 3; Xie et al. 2002). The decomposition of S-ap is also heterogeneous, with the residual Cl content ranging from 2.9 to 0.2 wt%. S-ap located close to the center of the SMVs (i.e., S-ap12) has been most thoroughly transformed to tuite.

**Figure 2.** Compositions of phosphates in Suizhou. Different colors used here as well as those in Figures 3, 4, and 7 represent “grains” of H-ap (blue), W-ap (green), and S-ap (red), respectively. Decreasing scales of gray fields represent Cl, Na$_2$O, and MgO contents of apatite from other unbrecciated L chondrites from Lewis and Jones (2016), respectively. (Color online.)

**Table 1.** Representative electron microprobe analyses of phosphates in Suizhou (data in wt%).

<table>
<thead>
<tr>
<th></th>
<th>H-ap</th>
<th>W-ap</th>
<th>S-ap</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>H-ap1</td>
<td>H-ap3</td>
<td>W-ap9</td>
</tr>
<tr>
<td>CaO</td>
<td>53.3(1)</td>
<td>52.8(1)</td>
<td>53.5(1)</td>
</tr>
<tr>
<td>Na$_2$O</td>
<td>0.43(2)</td>
<td>0.40(2)</td>
<td>0.50(2)</td>
</tr>
<tr>
<td>FeO</td>
<td>0.06(1)</td>
<td>0.15(1)</td>
<td>0.28(2)</td>
</tr>
<tr>
<td>MnO</td>
<td>0.03(1)</td>
<td>b.d.</td>
<td>b.d.</td>
</tr>
<tr>
<td>MgO</td>
<td>b.d.</td>
<td>b.d.</td>
<td>b.d.</td>
</tr>
<tr>
<td>PO$_4$</td>
<td>41.0(1)</td>
<td>40.7(1)</td>
<td>41.6(1)</td>
</tr>
<tr>
<td>Cl</td>
<td>5.93(3)</td>
<td>5.59(3)</td>
<td>5.64(3)</td>
</tr>
<tr>
<td>F</td>
<td>0.43(4)</td>
<td>0.37(4)</td>
<td>0.39(4)</td>
</tr>
<tr>
<td>-O=F,Cl</td>
<td>1.52</td>
<td>1.42</td>
<td>1.43</td>
</tr>
<tr>
<td>Total</td>
<td>99.67</td>
<td>98.64</td>
<td>100.44</td>
</tr>
</tbody>
</table>

Notes: H-, W-, and S-ap represent apatite (or precursor) located in the chondrite host on the wall of SMVs and in the SMVs, respectively. b.d. = below detection limit. Numbers inside of parentheses correspond to absolute uncertainties (1σ) for the last digit.

**Figure 3.** Representative Raman spectra of phosphates from different locations of Suizhou. The sampling sites of W-ap are marked by the red spots in Figure 4a. Vertical dashed lines represent Raman peaks for tuite. (Color online.)

**U–Pb dating of phosphates**

Six in situ SIMS analyses were performed on H-ap, seven on W-ap, and three on S-ap (Fig. 1; Table 2). Because mineral grains in the SMVs have largely been fragmented, only two relatively large tuite “grains” (30–40 μm) were found (Figs. 1g and 1h) after a careful search of five polished sections (a total exposed area of 45 cm$^2$). Two analyses of S-ap were on a tuite inclusion in a fragment of majorite (Fig. 1g) and the other was on an indi-
individual tuite grain close to the center of the SMVs (Fig. 1h). Of the seven analyses of W-ap, six are on mixing areas with variable proportions of apatite and tuite; the other (W-ap17@3) is on an area containing exclusively apatite (Figs. 1d–1f).

Apatite from large planets (e.g., Earth and Mars) could incorporate significant amounts of initial Pb (e.g., Li et al. 2012; Zhou et al. 2013), but chondritic Ca-phosphates were reported to contain a negligible level of initial Pb (Göpel et al. 1994; Yin et al. 2014). This is true for Suizhou phosphates that they usually reflect very radiogenic nature with minimal evidence of an initial Pb component (most $^{206}\text{Pb}/^{204}\text{Pb} > 1000$) (Table 2). Only five analyses yield relatively high $^{206}\text{Pb}/^{204}\text{Pb}$ ratios in the range of 170–450. Of these five analyses (except W-ap9@2), the $^{206}\text{Pb}$ signal intensity gradually decreased until it was constant after about seven scans (Fig. 6), which suggests a surface-related terrestrial Pb contamination probably was introduced during sample preparation. For those analyses with a low level of common Pb ($^{206}\text{Pb}/^{204}\text{Pb} > 1000$), the $^{204}\text{Pb}$ signal intensity is low and relatively constant from scan to scan (generally lower than 0.1 c/s; Fig. 6). The $^{204}\text{Pb}$ signal intensity in W-ap9@2 is constant (0.3 c/s) during analysis but significantly higher than other analyses on the same grain (e.g., <0.1 c/s for W-ap9@1; Fig. 6). This is probably due to contaminations from micro-cracks or non-phosphate phases. Therefore, the common Pb was corrected using the modern terrestrial Pb compositions (Stacey and Kramers 1975), as well as CDT (Tatsumoto et al. 1973) as a limiting case for comparison (Table 2). Two different common Pb corrections result in negligible difference in calculated ages (less than 1.5‰) (Table 2). We also extracted the last eight scans of the analyses with high common-Pb levels and recalculated their ages, but the refined ages are basically unchanged (differences less than 1‰).

Analyses of H-ap yield a concordia U–Pb age of 4547 ± 19 Ma (MSWD = 0.61, $P = 0.43$) on the U–Pb concordia diagram and a weighted average $^{206}\text{Pb}/^{204}\text{Pb}$ age of 4545 ± 17 Ma (MSWD = 1.5, $P = 0.2$) (Figs. 7a and 7d). If only analyses with relatively low common Pb ($^{206}\text{Pb}/^{204}\text{Pb} > 1000$) are considered, the data yield a concordia U–Pb age of 4559 ± 26 Ma and a $^{206}\text{Pb}/^{204}\text{Pb}$ age of 4558 ± 14 Ma. The U–Pb data of W-ap plot on a discordia.
Table 2. SIMS U-Pb isotopic data of phosphates in Suizhou

<table>
<thead>
<tr>
<th>Analytical spot</th>
<th>U (ppm)</th>
<th>Th (ppm)</th>
<th>Th/U</th>
<th>206Pb/238U</th>
<th>207Pb/235U</th>
<th>208Pb/232Th</th>
<th>206Pb/238U*</th>
<th>207Pb/235U*</th>
<th>208Pb/232Th*</th>
<th>Discordance (%</th>
<th>206Pb/238U ±1σ (Ma)</th>
<th>207Pb/235U ±1σ (Ma)</th>
<th>208Pb/232Th ±1σ (Ma)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H-ap1@1</td>
<td>7.2</td>
<td>7.2</td>
<td>1.00</td>
<td>0.022</td>
<td>1235</td>
<td>26</td>
<td>0.6284</td>
<td>1.0</td>
<td>827.4</td>
<td>-6.9</td>
<td>4567 ±15</td>
<td>4566 ±15</td>
<td>4566 ±15</td>
</tr>
<tr>
<td>H-ap1@2</td>
<td>6.0</td>
<td>6.6</td>
<td>1.11</td>
<td>0.039</td>
<td>1166</td>
<td>23</td>
<td>0.6237</td>
<td>0.8</td>
<td>903.3</td>
<td>2.8</td>
<td>4555 ±12</td>
<td>4554 ±12</td>
<td>4554 ±12</td>
</tr>
<tr>
<td>H-ap1@3</td>
<td>5.5</td>
<td>6.1</td>
<td>1.12</td>
<td>0.121</td>
<td>355</td>
<td>18</td>
<td>0.6217</td>
<td>0.9</td>
<td>886.3</td>
<td>3.3</td>
<td>4531 ±14</td>
<td>4528 ±14</td>
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<td>H-ap2@1</td>
<td>5.7</td>
<td>6.3</td>
<td>1.10</td>
<td>0.094</td>
<td>361</td>
<td>16</td>
<td>0.6208</td>
<td>0.9</td>
<td>836.3</td>
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<td>4526 ±15</td>
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<td>H-ap2@2</td>
<td>5.8</td>
<td>5.8</td>
<td>1.00</td>
<td>0.076</td>
<td>446</td>
<td>17</td>
<td>0.6173</td>
<td>0.9</td>
<td>921.3</td>
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<td>H-ap3@1</td>
<td>6.4</td>
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<td>1.09</td>
<td>0.031</td>
<td>1658</td>
<td>22</td>
<td>0.6228</td>
<td>0.8</td>
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<tr>
<td>W-ap@1</td>
<td>7.0</td>
<td>7.1</td>
<td>1.02</td>
<td>n.d.</td>
<td>&gt;10000</td>
<td>-</td>
<td>0.5983</td>
<td>0.8</td>
<td>869.3</td>
<td>4.2</td>
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<tr>
<td>W-ap@2</td>
<td>6.6</td>
<td>6.6</td>
<td>0.98</td>
<td>0.319</td>
<td>173</td>
<td>6</td>
<td>0.6336</td>
<td>0.8</td>
<td>880.3</td>
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<tr>
<td>W-ap@3</td>
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<td>6.5</td>
<td>0.92</td>
<td>n.d.</td>
<td>&gt;10000</td>
<td>-</td>
<td>0.6052</td>
<td>1.2</td>
<td>865.3</td>
<td>2.0</td>
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<tr>
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<td>6.6</td>
<td>6.3</td>
<td>0.95</td>
<td>0.014</td>
<td>3236</td>
<td>25</td>
<td>0.6126</td>
<td>0.9</td>
<td>952.3</td>
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<td>13</td>
<td>0.6359</td>
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<td>94.1</td>
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<tr>
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<td>9.3</td>
<td>1.00</td>
<td>n.d.</td>
<td>&gt;10000</td>
<td>-</td>
<td>0.6042</td>
<td>1.0</td>
<td>718.4</td>
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<td>0.94</td>
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<td>4421</td>
<td>19</td>
<td>0.6095</td>
<td>1.1</td>
<td>903.4</td>
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<td>S-ap8@1</td>
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<td>6.5</td>
<td>0.98</td>
<td>0.044</td>
<td>1007</td>
<td>15</td>
<td>0.6117</td>
<td>1.2</td>
<td>100.4</td>
<td>17.8</td>
<td>4525 ±17</td>
<td>4524 ±17</td>
<td>4524 ±17</td>
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<tr>
<td>S-ap8@2</td>
<td>6.0</td>
<td>7.2</td>
<td>1.19</td>
<td>0.014</td>
<td>1825</td>
<td>14</td>
<td>0.6108</td>
<td>0.9</td>
<td>94.1</td>
<td>-22.8</td>
<td>4527 ±16</td>
<td>4526 ±17</td>
<td>4526 ±17</td>
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<tr>
<td>S-ap12@1</td>
<td>5.8</td>
<td>6.4</td>
<td>1.10</td>
<td>0.004</td>
<td>6543</td>
<td>18</td>
<td>0.5901</td>
<td>1.0</td>
<td>80.1</td>
<td>-1.9</td>
<td>4481 ±15</td>
<td>4481 ±15</td>
<td>4481 ±15</td>
</tr>
</tbody>
</table>
| Notes: * Denotes radiogenic, i.e., common Pb corrected. The common Pb was corrected using the modern terrestrial Pb compositions (Stacey and Kramers 1975) except the apparent 206Pb/207Pb ages in the last two columns (see superscript a), which were corrected using Pb compositions of Canion Diablo Troilite (Tatsumoto et al. 1973). U concentrations are determined by corresponding variations of UO2(CaO)2/P2O5 ratios of Durango apatite with average 9 ppm U. 206Pb/206Pb >10000 means no 206Pb was detected.

Figure 6. 206Pb intensity variation during SIMS analysis.

SIMS analyses were made using a beam size of 10 × 15 µm on very small irregular shaped grains (e.g., S-ap8). Although care has been taken before each measurement, the possibility of sampling metal–sulfide veinlets and neighboring non-phosphate phases during SIMS analysis cannot be totally excluded. This may result in calibration problems leading to uncontrolled apparent normal and reverse discordance (e.g., Liu et al. 2012), and it was probably aggravated by the minor contribution of unsupported Pb from these non-phosphate phases (Fig. 1g). Second, the discordance may result from surface imperfections of the sample due to polycrystalline nature of tuite or/and from comparing samples and standards in different mounts (e.g., Liu et al. 2012). Third, the discordance may be a result of residual instrumental elemental fractionation after correction to standards (e.g., Shaulis et al. 2017). Forth, it is also possible that some normal discordance of partly decomposed apatite is due to recent Pb loss because the high surface area to volume ratios of these sub-micrometer polycrystalline aggregates would facilitate surface-related Pb loss (Kamo et al. 1996). Due to these analytical uncertainties and potential matrix effects, the 207Pb/206Pb ages are considered to be more reliable, as they are not affected by the calibration of U/Pb ratio and are not sensitive to recent Pb loss (Misawa et al. 2005).

Discussion

Variable response of apatite to shock metamorphism in the Suizhou chondrite

Apatite is a common phosphate phase present in terrestrial and extraterrestrial rocks. Because apatite contains a relatively high U content and has a low closure temperature for U–Pb system, it is now increasingly used for dating impact events (e.g., Grange et al. 2013; Merle et al. 2014; Norman and Nemchin 2014; Yin et al. 2014; Snape et al. 2016; Li S.-L. and Hsu 2018; Li Y. and Hsu 2018). Nevertheless, there are few studies focused on the shock metamorphic features of apatite, which would have an important implication for the interpretation of chronological data. Our study shows a remarkable variation of chemical and structural modifications of apatite in the Suizhou chondrite that
corresponds to different degrees of shock metamorphism.

H-ap in Suizhou remains essentially intact and its Raman spectra resemble those of unshocked chlorapatite (Fig. 3; Xie et al. 2013). Planar fractures observed in H-ap also exist in neighboring olivine and low-Ca pyroxene grains (Figs. 1a–1c), which are typical shock effects for weak to moderate shock metamorphism (Stöffler et al. 1991). H-ap in Suizhou is chemically similar to apatite from other weakly shocked equilibrated L chondrites, which have a Cl content of 4.43–5.68 wt%, Na$_2$O of 0.33–0.49 wt% and MgO less than 0.1 wt% (Fig. 2; Lewis and Jones 2016). The H-ap grains in Suizhou appear to have largely preserved their original structural and chemical features produced during the parent-body thermal metamorphism (Jones et al. 2014).

Both chemical composition and Raman spectra indicate that W-ap grains adjacent to the SMVs were partly transformed to tuite (Figs. 2 and 3). This can also be seen on their high-resolution BSE images, where patches of residual apatite are surrounded by tuite crystallites (Fig. 5). Tuite could be formed by decomposition of apatite at 1100–2300 °C and 10–15 GPa (Murayama et al. 1986). It can be stable up to 20 GPa or higher (Xie et al. 2013). This $P$–$T$ condition is compatible with that estimated from the high-pressure mineral inventory in the SMVs of Suizhou (Xie et al. 2001; Xie and Chen 2016). The neo-crystallized tuite is distinguished by its polycrystalline texture (Fig. 5), which can be readily identified by its cloudy appearance on the CL images (Fig. 4b). Polycrystalline (or granular) textures were also observed in zircon, baddeleyite, and monazite that have been extensively shocked in natural impact events (Krogh et al. 1993, 1996; Kamo et al. 1996; Moser 1997; Zhang et al. 2011; Darling et al. 2016). In contrast to the polycrystalline textures previously observed in these U-bearing minerals, the polycrystalline aggregates reported here consist of a high-pressure phase, probably because the rapid cooling of the SMVs prohibited its back transformation to the low-pressure polymorph. The polycrystalline domains of W-ap are located exclusively adjacent to the SMVs and parallel to the edge of the SMVs (Figs. 1d and 1f). This strongly indicates their formation is controlled by the localized transient heating within the SMVs, which was achieved by localized shear-friction stress (Xie and Chen 2016). However,
only restricted regions (generally less than 10 μm) of apatite can be extensively transformed (i.e., polycrystalline domains; Figs. 1d and 1f) and the phase transformation is highly heterogeneous even on such small regions (Fig. 4). It could be due to fact that the temperature gradient is very steep from the SMVs to the neighboring host in Suizhou, which is also indicated by the presence of three different polymorphs of chromite within a single grain adjacent to the SMVs (Chen et al. 2003). As a result, at regions >100 μm bordering the SMVs, the temperature was too low to overcome the kinetic barriers for nucleation and growth of tuite, and the apatite structure at these domains remains relatively intact.

Compared to W-ap, S-ap of Suizhou generally has a lower chlorine content and a weaker Raman peak at 960 cm\(^{-1}\). S-ap would be more thoroughly transformed to polycrystalline tuite, but the phase transition of S-ap is also heterogeneous (Figs. 2 and 3). This is probably because only a small amount of shock-induced melt was generated in the relatively thin SMVs of Suizhou, and it could not generate enough heat to increase the temperature sufficiently throughout the SMVs in a short period of time (Chen et al. 2004). Therefore, at the relatively “cold” regions, such as those included in and shielded by other entrained mineral fragments in the SMVs, the decomposition of apatite is incomplete. The remnant Cl contents in these grains are up to 2.9 wt%, which are similar to those of W-ap polycrystalline domains (2.0–3.4 wt%). Whereas for portions close to the center of SMVs, the apatite could experience a higher degree of transformation (Fig. 2), which was also observed by Xie et al. (2013).

On the basis of these observations, a sequence of increasing degrees of shock metamorphism for apatite in Suizhou can be established. (1) In regions >100 μm bordering the SMVs, including H-ap and parts of the apatite domains in W-ap, apatite was only regularly fractured and retains well-preserved chemical compositions and crystallinity. (2) In regions <100 μm bordering the SMVs (especially within the polycrystalline domains of W-ap) or in relatively “cold” regions within the SMVs, apatite could be partly decomposed to tuite with variable amounts of apatite relics. (3) In regions close to the center of SMVs, apatite was completely transformed to polycrystalline tuite. These different shock effects are closely related to the temperature conditions prevailing during the impact.

Correlated impact features with the degree of isotopic disturbance in phosphates and the age of the SMVs in Suizhou

Merrillite and apatite are the major phosphates in ordinary chondrites, with a total abundance of about 0.4–0.6 vol% (Gastineau-Lyons et al. 2002). Although merrillite is much more abundant than apatite in Suizhou, U concentrations in merrillite are too low to provide meaningful U–Pb ages in our SIMS analysis. As a result, only apatite and associated tuite were investigated in this study. By integrating in situ chemical, microstructural, and isotopic analysis of phosphates in Suizhou, it is possible to establish a correlation between the extents of isotopic disturbance with varying degrees of shock metamorphism.

H-ap grains, which have well-preserved chemical compositions and crystallinity, yield the oldest concordia U–Pb age (4547 ± 19 Ma) that agrees well with the weighted average \(^{207}\text{Pb}/^{206}\text{Pb}\) age (4545 ± 17 Ma). If only analyses with relatively low common Pb (\(^{206}\text{Pb}/^{204}\text{Pb} > 1000\)) are considered, they yield a slightly older U–Pb (4559 ± 26 Ma) and \(^{207}\text{Pb}/^{206}\text{Pb} (4558 ± 14 Ma) ages. The age of H-ap in Suizhou is consistent with the U–Pb ages of phosphates previously determined with thermal ionization mass spectrometry in other unshocked L chondrites (4511–4543 Ma; Göpel et al. 1994). Due to the large difference in condensation temperatures for Ca and P, the apatite in ordinary chondrites was thought to have formed by fluid-assistant thermal metamorphism on their parent body (Jones et al. 2014). Therefore, the U–Pb and Pb–Pb ages of H-ap most likely record the time when apatite cooled down below its closure temperature from the peak thermal metamorphic temperature on its parent body.

The apatite grain located in the center of SMVs (S-ap12) was most thoroughly decomposed to polycrystalline tuite and its chemical compositions have been altered to the greatest extent (Fig. 2). The SIMS analysis on this “grain” yields a concordia U–Pb age of 4481 ± 30 Ma (2σ) and a \(^{207}\text{Pb}/^{206}\text{Pb} age of 4481 ± 30 Ma (2σ). These ages are the youngest for all the analyzed phosphates and can be readily distinguished from the U–Pb and weighted average \(^{207}\text{Pb}/^{206}\text{Pb} ages of H-ap well beyond the 2σ level. Other analyses of W-ap and partly decomposed S-ap, which are mixtures of apatite and tuite, yield intermediate apparent \(^{207}\text{Pb}/^{206}\text{Pb} ages from 4534 to 4503 Ma (Figs. 7b–7d).

Our data clearly demonstrate that the disturbance of apatite U–Pb systematics in Suizhou strongly correlated with the compositional and structural changes induced by shock metamorphism. The most thoroughly decomposed apatite (S-ap12), which consists essentially polycrystalline tuite aggregates, yields the youngest, “concordant” age of 4481 ± 30 Ma (Fig. 7c). Nevertheless, the concordia line is nearly linear for this time interval (Fig. 7), making it difficult to identify possible slight discordance with the precision of current SIMS analysis. This is further aggravated by the potential SIMS analytical issues as mentioned earlier. As a result, the possibility of inheriting radiogenic Pb from the minor residual apatite cannot be completely ruled out, and this age is best regarded as the maximum age for the impact event.

The prevalence of ~4.48 Ga impact events in the primordial asteroid belt

Several lines of evidence indicate that major impact events occurred ~4.4 Ga on the L chondrite parent body (Keil et al. 1994; Scott 2002). For example, the cooling rates of individual metal grains from the matrices of L regolith breccias exhibit a wide range (1–1000 °C/My), which indicates their parent bodies may have been broken up and reassembled sometime between the end of slow cooling around 4.4 Ga (Taylor et al. 1987). Chronological records for very early collisional events in the solar system history are rare and sometimes ambiguous, as old impact ages could be overprinted by the contemporary or subsequent thermal metamorphism on the parent body (e.g., Weirich et al. 2010). The U–Pb systematics of phosphates in unshocked ordinary chondrites implies that the parent asteroids experienced a protracted period (~60 My) of thermal metamorphism (Göpel et al. 1994), and the phosphate U–Pb ages less than 4.5 Ga are often interpreted as impact-reset ages (Bogard 2011; Bottke et al. 2015). The U–Pb systematics of apatite grains in Novato (L6),
which define a well regressed upper intercept age of 4472 ± 31 Ma and lower intercept age of 473 ± 38 Ma, were suggested to record two impact events on the L chondrite parent body (Yin et al. 2014). A similar result was found in the phosphates of the L-impact melt breccia NWA 7251 (two impact ages at 4457 ± 56 and 574 ± 82 Ma; Li Y. and Hsu 2018). The phosphates in Sahara 98222 (L6), with a total Pb/U isochron age of 4467 ± 22 Ma, were also interpreted to record an early impact event (Ozawa et al. 2008). In addition, 39Ar–40Ar dating of the impact-melt L chondrite PAT 91501 yields a similar impact age (4461 ± 8 Ma; Benedix et al. 2008). The U–Pb ages Novata, NWA 7251 and Sahara 98222, as well as the 39Ar–40Ar age of PAT 91501, coupled with the estimated impact age of Suizhou, all point to a fact that early impact events (>4.4 Ga) occurred on the parent body of L chondrite (Fig. 8). Our study provides additional robust mineralogical evidence for such impact events. In addition to L chondrites, comparable impact ages are also observed in other types of meteorite, such as H and LL groups, enstatite chondrites and howardite–eucrite–diogenite (HED) meteorites (Bogard 2011; Popova et al. 2013; Swindle et al. 2014). These coeval impact events occurred on various parent asteroids presumably reflect a high collision rate as the accretion of planets was finishing, or speculatively they result from the peak arrival time of ejecta debris from the Moon-forming giant impact at the primordial main belt (Botcke et al. 2015).

The effects of natural shock on U–Pb isotopic systematics of apatite

Shock recovery experiments suggest that post-shock annealing plays the most important role in resetting isotopic clocks, and naturally shocked and unannealed samples are unlikely to record the timing of impact events (e.g., Fredriksson and De Carli 1964; Bogard et al. 1987; Deutsch and Schärer 1990; Gaffney et al. 2011; Niihara et al. 2012). However, our results clearly point to the other direction. The preservation of various metastable high-pressure phases in Suizhou indicates it could not have experienced extensive post-impact annealing after pressure release; otherwise, these high-pressure phases would revert readily to their more stable low-pressure polymorphs. For example, ringwoodite in Suizhou would have totally back transformed to olivine within 1.5 h at post-shock temperature of 760 °C (Ming et al. 1991); while akimotoite would have completely decomposed at 700 °C within 1 h at most (Ito and Navrotsky 1985). Our observations strongly indicate a localized high-temperature pulse during shock compression is essential for disturbance of the U–Pb isotopic systematics of phosphates in Suizhou. This was also observed in the Sixiangkou L6 chondrite (Li S.-L. and Hsu 2018).

We suggest the disparity could be mainly attributed to the different shock durations and temperature conditions between natural impact events and laboratory shock experiments. The shock-pulse duration in shock-recovery experiments is usually less than 10 μs, which is 4–6 orders of magnitudes shorter than those of natural shock events (Sharp and De Carli 2006; El Goresy et al. 2013). Furthermore, most shock experiments were performed on dense non-porous target, and the peak temperature was mostly along the principal Hugoniot of those minerals, which is significantly lower than the temperature experienced by the SMVs in meteorites that were naturally shocked to S4–S6 levels (Sharp and De Carli 2006). Under these extreme P–T–t conditions, Pb loss in apatite (and tuite) appears to be more efficiently achieved. The porous texture of the decomposed apatite (Fig. 5) in Suizhou implies Pb volatilization as a possible mechanism. Porous textures have been observed on the shocked terrestrial zircon from K/T boundary ejecta (Bohor et al. 1993) and the fallback breccia of Sudbury impact structure (Krogh et al. 1996), as well as shocked lunar zircon (Zhang et al. 2011). All these shocked zircons have experienced substantial Pb loss, although zircons in the first two examples have only experienced flash heating like S-ap and W-ap in Suizhou. Similar textures were also reported on zircon grains experimentally heated to 1400–1650 °C under vacuum (Ansdell and Kyser 1993). During the heating, Pb loss was detected with concomitant breakdown of zircon to porous baddeleyite (Ansdell and Kyser 1993). Considering the temperature in the SMVs of Suizhou could have readily exceeded 2000 °C, which is much higher than the temperature required for Pb evaporation in the experiment of Ansdell and Kyser (1993), we suggest volatilization could account for the rapid Pb loss occurred in the phosphates of Suizhou. Alternatively, Pb loss may be achieved by substantial partitioning into the newly formed chloride through the possible decomposition reaction \(2\text{Ca}_4(\text{PO}_{4})_3\text{Cl} \rightarrow 3\text{Ca}_3(\text{PO}_4)_2 + \text{CaCl}_2\) (Murayama et al. 1986; Xie et al. 2013). Under the P–T conditions experienced by the SMVs of Suizhou during the impact, CaCl could have a PbCl₂-type structure (Léger et al. 1998). However, despite an intensive search for chloride phases, they were neither detected in natural samples nor in the products of high-pressure experiments (Murayama et al. 1986; Xie et al. 2013). A counterpart (i.e., CaF₂) was also not identified in the experimental decomposition of fluorapatite by X-ray diffraction (Murayama et al. 1986). It may be possible that the fractions of these components are too small (<10 wt%) and too widely dispersed in the polycrystalline tuite (Murayama et al. 1986), or they have been leached during the preparation of polished thin sections (Xie et al. 2013). Nevertheless, this mechanism is feasible, and it could provide an additional pathway for Pb loss from the system.

**Implications**

Dating the high-pressure phosphates in the shock melt veins (SMVs) of Suizhou opens a new window for a comprehensive

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**Figure 8.** Comparison of the nearly coeval impact ages of Suizhou and other meteorites. Data for other meteorites are from Bogard (2011), Popova et al. (2013), Swindle et al. (2014), and references therein.
study of impact history of the solar system. Impact dating using isotope systems is generally applied to lithologies that were almost completely molten or minerals newly crystallized from such melt because their radioactive clocks tend to have been reset (Jourdan et al. 2009). Only relatively large parent bodies, like the Moon and Vesta, could sustain such a large impact (Bogard 2011). Undifferentiated meteorites are most likely derived from small asteroidal bodies on which large impacts would completely destroy their parent bodies; small impacts, on the other hand, would not be able to generate sufficient heat to reset their isotopic chronometer on a whole-rock scale (Bogard 2011). However, small impacts could induce localized melting during shock compression. From this study, it is apparent that phosphates in the SMVs or shock melt pockets of undifferentiated meteorites could be able to record the timing of these small-scale impact events.

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LI AND HSU: DATING PHOSPHATES OF THE STRONGLY SHOCKED SUIZHOU CHONDRITE

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Endnote:

1Deposit item AM-18-116582, Supplemental Table. Deposit items are free to all readers and found on the MSA web site, via the specific issue’s Table of Contents (go to http://www.minsocam.org/MSA/AmMin/TOC/2018/Nov2018_data.html).