Single grain (U–Th)/He ages from phosphates in Acapulco meteorite and implications for thermal history

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Abstract

The cooling history of the Acapulco meteorite for \( > 400^\circ\text{C} \) is well established using various chronometers suggesting extremely fast cooling (\( > 1000^\circ\text{C}/\text{Ma} \)). In contrast, the thermal history for low temperatures (\( < 400^\circ\text{C} \)) is poorly understood because of large uncertainties in the chronometers applicable to this temperature range. To better constrain the cooling history for the low-temperature range, we applied (U–Th)/He dating techniques to individual phosphate grains. One whitlockite and 11 apatite grains yielded (U–Th)/He ages ranging from 1272 \( \pm \) 22 (1\( \sigma \), analytical error only) Ma to 4584 \( \pm \) 51 Ma, with tight clustering at \( \sim 4.55 \) Ga. The weighted mean of the five oldest ages (4538 \( \pm \) 32 Ma, 1\( \sigma \) uncertainty including systematic error) is suggested to be the minimum age representing primary cooling of the Acapulco body passing through \( \sim 120^\circ\text{C} \). Although it is impossible to precisely quantify the effects of energetic \( \alpha \) particle ejection from the outermost \( \sim 20 \) \( \mu \text{m} \) of the phosphates, petrographic evidence suggests that most dated samples are fragments likely derived from the interior of larger grains, thus greatly reducing this source of error. Indeed the five oldest samples cannot have suffered substantial ejection since the uncorrected ages are identical with the crystallization age of the Acapulco meteorite. The new (U–Th)/He data suggest rapid cooling of Acapulco down to \( \sim 120^\circ\text{C} \). This evidence suggests that the younger \(^{40}\text{Ar}/^{39}\text{Ar} \) age (4507 \( \pm \) 9 (1\( \sigma \) Ma) obtained from Acapulco plagioclase, which should reflect cooling through \( \sim 300^\circ\text{C} \), is spuriously young due to systematic errors (i.e., decay constants and/or standard data) in the \(^{40}\text{Ar}/^{39}\text{Ar} \) method, as suggested by comparison between high-precision \(^{40}\text{Ar}/^{39}\text{Ar} \) and U/Pb ages for terrestrial volcanic rocks. The scattered He age distribution \(< 4.0 \) Ga implies very heterogeneous thermal disturbances after the primary cooling of the body.

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1. Introduction

The thermal histories of meteorites are of interest for several reasons. In general, such information is key to understanding the physical evolution of planetary bodies and the dispersal of...
energy after the condensation of the solar nebula [1]. Recently, meteorites’ thermal histories (especially at lower temperatures) have become significant with regard to the survivability of organic molecules during interplanetary transport, i.e., as a factor in evaluating the ‘Panspermia’ hypothesis [2,3]. Another area of recent interest is the extent to which meteorite thermochronology can be decoupled from systematic errors between radiotrace systems [4]. In this paper, we report (U-Th)/He data for individual phosphate crystals from the Acapulco meteorite. These data are the first such determined for a meteorite, yielding the oldest (U-Th)/He ages yet reported for any object, and provide important constraints on the low-temperature thermal history of Acapulco.

The Acapulco meteorite, which fell in 1976 in Acapulco, Mexico, is well known for its unusual petrographic characteristics and chemical composition, and is the namesake of a distinctive group called ‘acapulcoites’. The bulk chemistry of acapulcoites resembles that of normal chondrites, and oxygen isotopic composition is within the range of other common stony meteorites (summarized in [5,6]). The acapulcoites are often believed to have a common parent body with lodranite meteorites, evidenced by similar mineralogy, major element chemistry, oxygen isotopes, thermal histories and exposure ages [7–9].

The cooling rate of the Acapulco meteorite has been studied using textural relationships and chemical compositions of the constituent mineral phases. After formation of the parent body, it experienced intense metamorphism/recrystallization at >950°C which can be deduced from the petrographic observations including partial melting of FeS-Fe, Ni metal phase and phosphates [5]. Very rapid cooling at 2×10⁴–7×10⁴°C/Ma for the temperature range of 650–570°C was calculated from Ca zoning patterns in olivine crystals [10]. Using the same technique combined with more chemical data and updated diffusion parameters, Zipfel et al. [11] re-estimated the cooling rate as 10³–10⁵°C/Ma in the extended temperature range of 650–450°C. Zema et al. [12] suggested extremely fast cooling for Acapulco at ~6.2×10⁷°C/Ma over the range of 490±28°C based on the Fe–Mg ordering in M1 and M2 sites in four orthopyroxene crystals. McCoy et al. [5] also suggested a high cooling rate of 10³–10⁶°C/Ma based on metallographic observation for the temperature interval of 600–400°C. They also deduced a consistent cooling rate of 10⁵°C/Ma over the range of 600–350°C from the Ni content in taenite crystals. In summary, it is widely agreed that cooling of Acapulco over the temperature range ca. 600–350°C was very fast, at least 10³°C/Ma. The rapid cooling is often attributed to a break-up of the Acapulco–lodranite parent body followed by significant heat loss from the small fragment ejected from the parent body (e.g., [12]).

The thermal history below 400°C, however, is still under debate mainly due to large uncertainties in the methods used in the estimates. Based on extinct-²⁴⁴Pu fission track densities in orthopyroxene, whitlockite and apatite, Pellás and Fiéni [13] and Pellás et al. [14] deduced a very slow cooling rate of ~1.7±0.5°C/Ma¹ for the temperature range of 280–90°C. In contrast, Marti et al. [15] estimated more rapid cooling at ~20±5°C/Ma (temperature range of 300–200°C) based on the size of island phases in the cloudy zone in the retained taenites which disagrees with the cooling rate estimated from the ²⁴⁴Pu fission track data. The timing and rate of cooling have also been estimated using radiogenic isotopes. Göpel et al. [16] measured U and Pb isotopes from whole rock samples and mineral separates of plagioclase, troilite and phosphate, and reported a ²⁰⁷Pb/²⁰⁶Pb model age of 4.557±0.002 Ga for the phosphates. Pellás et al. [14] calculated the closure temperature (Tc) of Pb diffusion in the Acapulco apatite as ~450±50°C from the data of Cherniak et al. [17]. From the same data set, Renne [4] calculated a slightly higher Tc for the U/Pb system (~553°C) based on observed grain size of Acapulco phosphates. A ¹⁴⁷Sm–¹⁴³Nd isochron age of 4.60±0.03 Ga was obtained from mineral phases and cutting lines [18]. McCoy et al. [5] used a whole rock sample for ⁴⁰Ar/³⁹Ar analyses, producing a model plateau age of 4.50 Ga. Pellás et al. [14] reported an indistinguishable ⁴⁰Ar/³⁹Ar model age of 4514±16 Ma, also from whole

¹ All uncertainties in this article are reported at 1σ level.
rock. From more detailed work on Acapulco plagioclase, Renne [4] also obtained essentially the same \(^{40}\text{Ar}/^{39}\text{Ar}\) age as the previous studies, but pointed out that large systematic errors related to standards and decay constants hinder the inference of thermochronology from radioisotopic data. For example, the more probable decay constant of Endt and Van der Leun [19] makes the \(^{40}\text{Ar}/^{39}\text{Ar}\) ages older by \(\sim 50\) Ma than those calculated from Steiger and Jäger’s [20] decay constant, making them indistinguishable from the \(^{207}\text{Pb}/^{206}\text{Pb}\) or Sm/Nd ages. Accordingly, Acapulco may have experienced rapid cooling from the closure of the Sm/Nd system (\(\sim 650^\circ\text{C}\)) to that of \(\text{Ar}\) in plagioclase (\(\sim 300^\circ\text{C}\)). This scenario, if correct, would either imply a more pronounced increase in cooling rate below 300\(^\circ\text{C}\) than inferred by Pellas et al. [14], or cast doubt on the validity of the slow cooling inferred from the \(^{244}\text{Pu}\) fission track data.

Triello et al. [21] disputed the credibility of a smaller \(^{40}\text{K}\) decay constant mainly based on the \(^{40}\text{Ar}/^{39}\text{Ar}\) ages of the meteorite Pontlyfni which was believed to be 18 \(\pm 8\) Ma older than Acapulco [22], hence its age would become presolar if the decay constants advocated by Renne [4] were used. In reply, Renne [23] cast doubt on the reliability of the old age of Pontlyfni based on: (1) small grain size of the whole rock sample used for \(^{40}\text{Ar}/^{39}\text{Ar}\) analysis which may have caused \(^{39}\text{Ar}\) recoil loss during sample irradiation yielding spuriously old ages; (2) a less model-dependent isochron age, which appears indistinguishable from that of Acapulco; and (3) questions about the accuracy of neutron fluence during sample irradiation.

Owing to the remaining uncertainty about Acapulco’s low-temperature thermal history, and its obvious relevance to the issues summarized above, we sought to apply an independent technique to the specific case of Acapulco. The \((\text{U–Th})/\text{He}\) technique applied to the mineral apatite has proven extremely useful as a thermochronometer below \(\sim 100^\circ\text{C}\) in terrestrial rocks (e.g., [23] and references therein), and is well suited to addressing these questions. Analysis of U, Th, and He whole rock concentration data from the literature was used by Wasson and Wang [25] to infer some general patterns of He retention ages for various meteorites. The availability of coarse-grained apatite in Acapulco, which has been well characterized by previous workers (i.e., [5,11,26]), provided optimism about the feasibility of a single crystal approach.

2. Sample description and major element chemistry

The Acapulco meteorite is composed of olivine, orthopyroxene, plagioclase, metallic Ni–Fe and minor amounts of diopside, troilite, chromite plus the phosphates apatite and whitlockite. The phosphate crystals are coarse and equi-granular with typical grain size of 100–300 \(\mu\text{m}\), and have 120\(^\circ\) triple junctions at the boundaries which are often used as evidence of complete recrystallization after the formation of the parent body [5].

The modal abundance of the phosphates is estimated as \(\sim 1\%\) from the backscattered electron (BSE) image of the \(\sim 0.6 \times 0.6\) cm\(^2\) surface area of the sample. Phosphate crystals larger than 200 \(\mu\text{m}\) are easily found in thin section (Fig. 1). The phosphates in Acapulco are generally anhedral, and the degree of irregularity varies grain by grain. The morphology of Acapulco phosphates varies from ‘very anhedral’ with irregular grain boundaries (Fig. 1, top row) to ‘less anhedral’ having more or less linear grain boundaries as viewed in two dimensions (Fig. 1, middle and bottom rows). The ‘very anhedral’ phosphates are commonly embayed by or contain inclusions of olivine and pyroxene crystals, but possible sources of U and Th, such as zircon, were not found in any of the apatite crystals. Fe, Ni metal and troilite veins are ubiquitous along and across the grain boundaries of the phosphates and other silicates (Fig. 1). For phosphates, the veins are more abundant in the ‘less anhedral’ grains than in the ‘very anhedral’ ones. The veins suggest that the minimum temperature of the peak metamorphism is higher than \(\sim 950^\circ\text{C}\), the cotectic temperature of Fe, Ni metal–troilite [5]. The ‘very anhedral’ phosphates are likely to be associated with partial melting and filling intergranular spaces during the metamorphism while the other silicates have recrystallized in a solid state form-
ing triple junctions at the grain boundaries. No evidence of chondrules was found, but the inferred recrystallization may have obliterated initially present chondrules.

We analyzed 15 discrete phosphate grains using the Cameca SX50 electron probe microanalyzer at the University of Oregon, Eugene, OR, USA. All of the phosphates have chemical compositions corresponding to apatites with high fluorine and chlorine content up to $\sim 6$ wt% (table 1 in the Background Data Set$^2$). This is generally consistent with the observation of Zipfel et al. [11] that apatite is much more abundant than whitlockite in Acapulco, or Palme et al.’s [26] observation that $\sim 90\%$ by volume of the phosphate is apatite and the remaining $\sim 10\%$ is whitlockite. The average Cl content and Cl/F values are generally higher for the ‘very anhedral’ phosphates (3.4–3.6 Cl wt%; 1.4–1.9 Cl/F) than the ‘less anhedral’ grains (2.3–3.2 Cl wt%; 0.7–1.4 Cl/F), as shown in Fig. 1 and table 1 in the Background Data Set$^2$.

Fig. 1. BSE images of Acapulco apatites. All the grains are anhedral with varying degree of irregularity. Cl/F values are given with their standard errors and the number of analyses (n). The Cl/F values for ‘very anhedral’ apatites (top row) are higher than those from ‘less anhedral’ samples (middle and bottom rows).

3. Analysis

We first tried to separate phosphates from the
same piece of Acapulco studied by Renne [4], but because of the paucity of sample available and difficulty in separating phosphates, we used mineral separates from the Acapulco consortium material (University of California at San Diego, CA, USA) for U, Th and He analyses. Phosphates were separated from silicates on the basis of color and shape after treating the sample with hot 12 M NaOH for 2 min. The separated phosphate grains are also irregular, but not as much as expected from in situ examination, indicating that most of the grains were fragmented and abraded during mineral separation and chemical procedures (Fig. 2). Euhedral grains were absent both in the thin section and in the mineral separates. Approximately two thirds of the separate grains have white to clear surfaces whereas the rest of the grains have rather reddish surfaces. One of the reddish grains was mechanically broken to examine the interior, which was found to be clear to milky white, similar to the other grains. The reason for the different surface color is not clear, but it is possibly caused by contamination of interstitial materials, damage from radioactive materials or chemical treatment during the sample preparation procedure.

The separated phosphate grains were divided into three groups according to grain size: Acapulco 1 (320–250 μm), Acapulco 2 (250–200 μm) and Acapulco 3 (200–150 μm). Three to five grains were chosen from each group for single grain (U–Th)/He age determination. The phosphates, as has been previously documented, are of two kinds: apatite and whitlockite. Apatite is preferred for our purposes because of its higher concentrations of U, Th and He than those of whitlockite [11], and also because unlike apatite [24,27], whitlockite has never been studied for (U–Th)/He systematics. However, since it is difficult to distinguish apatite from whitlockite grains under the microscope without destructive analysis, we randomly chose phosphates for the analyses. All the U, Th, and He analyses were undertaken at Caltech using previously documented procedures [28]. For 4He measurement, each of the grains was wrapped in a packet made of platinum tubing and dropped into wells in a 25-well copper disk. The disk was inserted into a vacuum chamber fitted with a sapphire window, and the vacuum line was pumped overnight to ultrahigh vacuum. The sample packets were degassed sequentially using a Nd-YAG laser at \( \sim 1050^\circ C \) for approximately 7 min per sample. The extracted gas was spiked with a known amount of very pure \(^3\)He, cryopurified and the helium isotopic ratio analyzed using a quadrupole mass spectrometer. Complete He extraction was verified by a second heating, which always produced a negligible additional amount of helium. After He analyses, the samples were removed from the

![Fig. 2. Phosphate separates from Acapulco 1 (a) and Acapulco 3 (b) with (U–Th)/He ages. Note that the three oldest ages from Acapulco 1 are identical with the crystallization age of Acapulco.](image-url)
disk, dissolved in nitric acid spiked with $^{235}$U and $^{230}$Th, then analyzed using an inductively coupled plasma mass spectrometer.

The U, Th and He concentrations are calculated based on the mass of each grain, which must be estimated from linear dimensions since the grains are too small to weigh accurately. Because of the complex geometry of grain boundaries, the mass estimates (hence, concentrations) are very uncertain, probably accurate only to ±20%. In spite of the large concentration uncertainties, the ratios among the U, Th and He concentrations are highly precise and accurate since the mass terms cancel out in calculating the ratios, and hence in the (U-Th)/He ages. The analytical uncertainties are in the range of ~1% for 4He measurement and less than 1% for U and Th. Only analytical errors are reported if not specified.

Ages are calculated based on the measured U:Th:He with natural terrestrial isotopic compositions for U and Th. Radiogenic 4He concentration was calculated by subtracting a cosmogenic component from the total measured 4He. Cosmogenic 4He was deduced from the production rate of 4He ($P_4$) and exposure age of 5 ± 1 Ma [8,26]. We calculated the $P_4$ from $P_3$ (production rate of 3He) for ordinary chondrites (1.61 × 10$^{-8}$ cm$^3$ STP/g Ma; [29]) and the assumption that $P_4$ ≈ 5 × $P_3$ (e.g., [30]). The cosmogenic component of the 4He is calculated as smaller than 0.01% for the apatites used in this study. Other possible sources of 4He production are from natural decays of 147Sm and extinct-244Pu. To incorporate the contribution of 4He from these isotopes, we assumed 17 ppm for Sm concentration [11] and 0.004 × $^{238}$U for initial concentration of $^{144}$Pu [14]. These corrections contribute less than 0.15% in the age calculation for the apatite grains older than 4.4 Ga.

To determine diffusion parameters, two phosphate grains (grains 1 and 2) with length scale of 200–250 μm were analyzed. The temperature was measured using a thermocouple pair passing through the sample package [31]. Each sample was degassed with a one cycle heating schedule: for grain 1, temperature was increased from 50°C to 300°C monotonically, then reduced down to 200°C, finally increased to > 500°C. Grain 2 was heated with more heating steps and a slightly different cycling schedule. The samples were heated for 1–4 h per step using a lamp projected through a sapphire window up to 500°C [31]. To completely extract He gas, the grains were further heated in a resistance furnace at high temperature (> 500°C). The extracted gas was mixed with

Table 1
(U-Th)/He ages from phosphates in the Acapulco meteorite

<table>
<thead>
<tr>
<th>Sample</th>
<th>U (ppm)</th>
<th>Th (ppm)</th>
<th>U/Th total (ncc/mg)</th>
<th>(U-Th)/He age (Ma)</th>
<th>$\sigma^a$ analytical (Ma)</th>
<th>$\sigma^b$ systematic (Ma)</th>
<th>MSWD</th>
<th>Color</th>
<th>$F_T^d$</th>
<th>Corr. Age (Ma)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acapulco 1-1</td>
<td>4.2</td>
<td>2.4</td>
<td>1.8</td>
<td>5450.6</td>
<td>4584</td>
<td>51</td>
<td>61</td>
<td>red</td>
<td>0.90</td>
<td>4779</td>
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<tr>
<td>Acapulco 1-2</td>
<td>10.7</td>
<td>5.2</td>
<td>2.1</td>
<td>13711.5</td>
<td>4583</td>
<td>51</td>
<td>61</td>
<td>0.00</td>
<td>red</td>
<td>0.87</td>
</tr>
<tr>
<td>Acapulco 1-5</td>
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<td>3.6</td>
<td>2.2</td>
<td>9990.6</td>
<td>4562</td>
<td>52</td>
<td>62</td>
<td>0.06</td>
<td>red</td>
<td>0.86</td>
</tr>
<tr>
<td>Acapulco 2-5</td>
<td>9.5</td>
<td>3.9</td>
<td>2.5</td>
<td>11711.9</td>
<td>4524</td>
<td>54</td>
<td>64</td>
<td>0.28</td>
<td>red</td>
<td>0.81</td>
</tr>
<tr>
<td>Acapulco 3-4</td>
<td>7.4</td>
<td>3.7</td>
<td>2.0</td>
<td>8941.4</td>
<td>4435</td>
<td>51</td>
<td>61</td>
<td>1.5</td>
<td>red</td>
<td>0.83</td>
</tr>
<tr>
<td>Acapulco 3-2</td>
<td>7.1</td>
<td>3.5</td>
<td>2.0</td>
<td>8197.5</td>
<td>4380</td>
<td>52</td>
<td>62</td>
<td>2.7</td>
<td>white</td>
<td>0.81</td>
</tr>
<tr>
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<td>1.4</td>
<td>3.3</td>
<td>4884.8</td>
<td>4304</td>
<td>51</td>
<td>61</td>
<td>4.6</td>
<td>white</td>
<td>0.84</td>
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<tr>
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<td>3.3</td>
<td>2.0</td>
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<td>39</td>
<td>red</td>
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<tr>
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<td>1.9</td>
<td>2.5</td>
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<td>94</td>
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<tr>
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<td>267</td>
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<tr>
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<td>0.0</td>
<td>189.7</td>
<td>1272</td>
<td>22</td>
<td>28</td>
<td>1094</td>
<td>white</td>
<td>0.87</td>
</tr>
</tbody>
</table>

Weighted mean of the oldest five ages: 4538

a Analytical error only.

b Systematic error from spike calibration included. Details of the spike calibration procedure are available in the Appendix.

c MSWD for ages of each sample and older ones. Analytical errors are used for the calculation.

d $F_T$ values are calculated based on a model geometry of rectangular prism.
$^3$He, purified with a cryogenic trap and analyzed with a quadrupole mass spectrometer. Diffusion coefficients were calculated from fractional gas yields and extraction time assuming a spherical diffusion geometry. Details of the analytical procedure are given by Farley [24].

4. Results

4.1. ($U$–$Th$)/He analyses

Apatite was distinguished from whitlockite by its U and Th concentrations. According to Zipfel et al. [11], Acapulco apatite has a higher U/Th ratio (1.6–2.2) than whitlockite (0.1–1.7). Out of 12 grains analyzed in this study, Acapulco 2-1 (U/Th = 0.05) has a U/Th ratio clearly consistent with whitlockite, and the remaining 11 grains are consistent with apatite (Table 1). Therefore 11 out of 12 grains analyzed are classified as apatites. For the 11apatites, the U and Th concentrations obtained from this study range from 4.2 to 10.7 ppm (mean = 6.6) and 1.4 to 5.3 ppm (mean = 3.1), respectively. These values are generally ~40–50% lower than values determined by Zipfel et al. [11] based on secondary ion mass spectrometry. The discrepancy may in part be explained by the large uncertainty (~20%) of our mass estimates, as discussed previously.

Calculated ages range from 1272 ± 22 Ma to 4584 ± 51 Ma. There is a general trend of tight clustering for old ages and wide scattering for young ages (Fig. 3). For example, the three oldest ages are very closely distributed within their uncertainties whereas five young ages are scattered in the range of ca. 1.3–3.7 Ga. The three oldest ages (from Acapulco 1, the group with the largest grain size) are tightly grouped and yield a weighted mean age of 4576 ± 30 Ma (MSWD = 0.06). At 95% confidence, the five oldest grains are mutually indistinguishable, and yield a weighted mean age of 4538 ± 23 Ma with a more desirable MSWD of 1.5. Including one or two more ages from the next oldest samples increases the MSWD to 2.7 and 4.6, respectively. Since the MSWD from the five samples (1.5) is closer to 1 than the others, hence the dispersion is more consistent with that expected from analytical errors, we conclude that the five samples should be included to constrain the timing of cooling from peak metamorphism without any significant later stage disturbance. Another probable age can be estimated by summing up all possibility functions, which are assumed Gaussian in this case, deduced from each age and its uncertainty. The peak of the resulting ideogram is near 4561 Ma which is within the mean age of the five oldest ages (Fig. 3). Within each group (Acapulco 1, 2, and 3), the grains with reddish surfaces yielded older ages than those from white or clear grains.

Systematic error must be considered for absolute age determination. One of the major sources of systematic error in ($U$–$Th$)/He age is from the He spiking procedure which is essential for quantitative $^4$He measurement. To estimate the uncertainty of the amount of standard gas delivered, we tried to estimate the uncertainty produced during gas propagation in the line. According to our measurement and calculation, the spike calibration error is about 0.53% and this error was added in the final ($U$–$Th$)/He age determination. Because of the non-linearity of the age equation, this uncertainty contributes only about 0.22% to the age error at the age of interest. Details of the error propagation procedure are given in the Appendix.
Energetic emission of $\alpha$ particles from the outermost $\sim 20$ $\mu$m of a crystal can produce spuriously young He ages, particularly in materials with a high surface to volume ratio [32]. Unlike most work on terrestrial apatite, in the case of Acapulco, we could not simply correct for this effect because we did not have whole euhedral apatite crystals for analysis. Petrographic examination indicates that most of the roughly equant crystals in the separate are fragments of originally more complex and larger grains in the meteorite. To the extent that these fragments are from $> 20$ $\mu$m from an original grain boundary, the ejection effect is reduced. Since we cannot correct for the ejection effect we are left with two choices: (a) abrade the grains to eliminate the outermost 20 $\mu$m to ensure elimination of all primary surfaces, or (b) accept that the ages are minimum values. Abrasion of such a small number of small grains is challenging, and to avoid loss of material we chose the second alternative.

To assess the maximum possible correction for this effect, we estimated the $\alpha$ ejection correction factor ($F_T$) for each grain based on a model geometry of rectangular prism which resembles the morphology of the mineral separates. The length and width of each grain were measured under the microscope and the height is assumed to be the average of the two dimensions. The $F_T$ values are approximated using the calculated surface to volume ratios ($\beta$) and the equation $F_T = 1 - \left(\text{stopping distance}/4\right) \times \beta$ [32]. The corrected $^4$He is estimated based on:

$$\text{corrected } ^4\text{He} = \frac{\text{measured } ^4\text{He}}{F_T}$$

then, ages are recalculated with the corrected $^4$He. Note that this procedure is slightly different from that proposed earlier [32] because the correction is made to the He content rather than to the final age. This modification is necessary because at the extremely high ages of these phosphates the He age is no longer linear with He concentration.

When corrected in this way, some of the He ages are unreasonably old, exceeding the age of the solar system, confirming our expectation that the ejection correction calculated in this way overestimates the amount of primary surface on the analyzed grains. Based on the natural shapes observed from BSE images (Fig. 1) and the morphology of the final separates (Fig. 2), it is more probable that edges of crystals were removed during the mineral separation and chemical etching procedures. Although precise estimation of the correction factor is difficult due to the nature of occurrence of the Acapulco phosphates, we believe that correction factors, at least for the five oldest samples, are very close to 1 because the uncorrected ages are already identical with the age of the solar system within their uncertainties. Since we ignore the possible preservation of original ejection-effected surfaces, our He ages should be considered minima.

### 4.2. Diffusion experiment

Despite different heating schedules for grains 1 and 2, results from the two grains are very consistent showing close overlap in the Arrhenius plot (table 3 in the Background Data Set and Fig. 4). A linear pattern is clear for data points corresponding to the temperature range 100–300°C. Those steps produced $\sim 15\%$ of the total He extracted. Data from high-temperature (300°C–500°C) steps deviate from the linear trend.

Fig. 4. Linear array of the data marked with filled circles (from grain 1) and filled diamonds (from grain 2) was used for the calculation of the diffusion parameters. Inset shows grain 1 used for the diffusion experiment.
toward lower activation energy, suggesting the onset of a distinct transport mechanism less likely to reproduce nature. This pattern is also commonly observed in terrestrial apatites [24,27,33].

Twelve (grain 1) and 36 (grain 2) data points (filled symbols in Fig. 4) composing the linear regime were combined for linear regression yielding an activation energy ($E_a$) of 44.2 kcal/mol and a frequency factor ($\ln(D_0/a^2)$) of 24.1 s$^{-1}$. These estimates are higher than Wolf et al.’s [34] values ($E_a$ of 29–39 kcal/mol; frequency factor of 9–22 s$^{-1}$) for chlorine- or fluorine-rich apatites. Warnock et al. [33] reported exceptionally high values of $E_a$ (47.3 kcal/mol) and the frequency factor (26 s$^{-1}$) for fluoroapatite from a borehole suite in Germany. Our results suggest high $E_a$ and frequency factor are also possible from meteoritic phosphate. A closure temperature of 116°C was calculated using Dodson’s [35] equation assuming a model geometry of a sphere and a rapid cooling rate of 100°C/Ma. The closure temperature is not very sensitive to cooling rate or model geometry. For example, changing the cooling rate to 10°C/Ma decreases $T_c$ by ~15°C, and applying slab geometry decreases $T_c$ by only ~4°C. The closure temperature is also insensitive to effective diffusion radius at grain sizes as large as those analyzed in our study, assuming that diffusion radius ($\alpha'$) is comparable to physical grain dimensions.

5. Discussion

5.1. Cooling history of Acapulco

The minimum (U–Th)/He age of 4538 ± 32 Ma (including systematic error), obtained from the five oldest ages, agrees within uncertainties with the Pb/Pb age of 4557 ± 9 Ma ([16] with minimum uncertainty calculated in [4]), suggesting very rapid cooling of Acapulco for the temperature range of ca. 550°C–120°C. In Fig. 5, path 1 represents the most realistic cooling history deduced from all available chronologic data except $^{244}$Pu fission track ages which will be discussed in Section 5.3.

Path 2, inferred from the $^{40}$Ar/$^{39}$Ar age with the decay constant of Steiger and Jäger [20] plus $^{244}$Pu fission track data [14], is inconsistent with the cooling rates estimated from the Ni content in taenite [5] and Ca zoning in orthopyroxene [11]. To be consistent with McCoy et al.’s [5] data, cooling would have been very rapid (~10$^5$°C/Ma) down to ~350°C, then suddenly slowed greatly (~1°C/Ma = (350–300°C)/50 Ma) down to 300°C, the closure temperature of Ar in plagioclase. No simple explanation of this dramatic change of cooling rate at around ~350°C has yet been offered.

According to the cooling history suggested by the new (U–Th)/He data, the $^{40}$Ar/$^{39}$Ar age of plagioclase, corresponding to closure at ~300°C, should be within the range of the two isotopic ages from Pb/Pb and (U–Th)/He systems. Simple linear interpolation of the Pb/Pb and (U–Th)/He ages yields an age of 4546 Ma (at ~300°C). This age is ~40 Ma (~1%) older than the $^{40}$Ar/$^{39}$Ar ages calculated based on the decay constant of Steiger and Jäger [20]. The age discrepancy generally agrees with the bias observed between $^{40}$Ar/$^{39}$Ar and U/Pb systems in terrestrial volcanic rocks confirming the growing evidence of overes-
timated decay constant and/or underestimated ages of monitoring standards. The comparison between ⁴⁰Ar/³⁹Ar and U/Pb systems from five samples, including Acapulco, was undertaken by Kwon et al. [36] yielding a ⁴⁰K decay constant of 5.476 ± 0.017 x 10⁻¹⁰/yr and age of Fish Canyon sanidine of 28.27 ± 0.07 Ma. In the calculation, they assumed that all the ⁴⁰Ar/³⁹Ar ages used are identical with corresponding reference ages which are plausible for very rapidly cooled materials. The new (U-Th)/He data validate the assumption of rapid cooling for Acapulco in the temperature range of calculated closure temperatures for the U/Pb and ⁴⁰Ar/³⁹Ar systems.

In view of our results, the ⁴⁰Ar/³⁹Ar ages of other meteorites calculated from the decay constant of Steiger and Jäger [20] should be reconsidered. From 14 unshocked chondrites, Turner et al. [37] obtained a mean ⁴⁰Ar/³⁹Ar age of 4.48 ± 0.03 Ga. McCoy et al. [5] noted that the mean age is younger than Pb/Pb ages by about 30–50 Ma, and suggested later stage impact or internal metamorphism to explain the age gaps. Our results indicate that the age differences are, at least to some extent, from the decay constant and age of standards used for the ⁴⁰Ar/³⁹Ar age calculations. As shown in the case of Acapulco, the ⁴⁰Ar/³⁹Ar ages of other meteorites should also be shifted by ca. 30–50 Ma when updated decay constants are applied. This results in significant increases of cooling rates for several other meteorite bodies over the closure temperature range of Ar in each system.

5.2. Thermal history after early cooling

The scattering of young apatite He ages can be explained either by emission of α particles (ejection effect) which would be significant for crystal fragments derived from near the margins of the original grain, or alternatively by disturbance of the samples after their peak metamorphism. The ejection effect alone cannot explain all of the bias because even if we corrected for α ejection effects based on the morphology of the separates, the distribution of the corrected ages still has a similar pattern as the original ages (Fig. 6). To maximize the ejection effect, it is necessary to assume complete conservation of the original crystal shape for young samples (F ≈ 0.8–0.9) and no α emission for old samples (F ≈ 1). Even in such an extreme case, the corrected ages for the younger samples are still far younger than the mean of the older ages, therefore this effect cannot explain the entire age distribution.

An explanation that seems more probable involves heterogeneous heating caused by collision event(s). Shock heating to temperatures greater than 2000°C, on highly localized scales as small as a few micrometers, has been documented in some meteorites even in the absence of mesoscale shock features (e.g., [38], and references therein). Such a mechanism would be consistent with our results, which seem to require heat deposition and subsequent dissipation to be heterogeneous on the scale of a few centimeters.

Heterogeneous alteration, or admixture of a significantly younger secondary phase, in Acapulco was detected from one of the ⁴⁰Ar/³⁹Ar age spectra for plagioclase [4]. The ⁴⁰Ar/³⁹Ar data from two ~0.1-mg plagioclase aliquots, randomly collected from a ~2-cm piece of Acapulco, yield consistent plateau and isochron ages, but one aliquot produced significantly younger ages for the low-temperature steps with high K/Ca ratio. Based on the age vs. K/Ca correlation, the presence of K-rich disturbed material at or near a grain boundary is suggested, although the identity and paragenesis of the secondary phase is not

Fig. 6. Age distribution with and without α ejection correction as discussed in the text. The correction is based on the morphology of the mineral separates. Note that seven out of 12 corrected ages are older than the age of the solar system.
known. From the (U–Th)/He and $^{40}\text{Ar}/^{39}\text{Ar}$ data, it appears that the Acapulco meteorite has experienced heterogeneous thermal disturbance/alteration after its early cooling.

5.3. Comparison with $^{244}\text{Pu}$ fission track data

The fast cooling scenario deduced from the present (U–Th)/He data conflicts with the slow cooling history suggested by Pellas et al. [14], who deduced a rate of $\sim 1.7^\circ\text{C}/\text{Ma}$ in the temperature range of 280–90°C from the $^{244}\text{Pu}$ fission track dating technique (path 2 in Fig. 4). From annealing experiments and fission track counting, they estimated closure temperatures for orthopyroxene ($T_c = 280^\circ\text{C}$), whitlockite ($120^\circ\text{C}$), and apatite ($90^\circ\text{C}$), and assigned age differences among those three mineral phases. The $^{244}\text{Pu}$ fission track method provides relative ages due to its reliance on low-accuracy estimates of the extinct $^{244}\text{Pu}$ content and complex correction procedures, and Pellas et al. [14] used $^{40}\text{Ar}/^{39}\text{Ar}$ age as an anchor point for relative ages. However, as discussed above, the $^{40}\text{Ar}/^{39}\text{Ar}$ ages have uncertainties in the decay constant and the age of the monitoring standard, although they are more precise and accurate than the Pu fission track technique. Therefore, more attention should be paid to improving the accuracy of $^{40}\text{Ar}/^{39}\text{Ar}$ ages before using those ages as a reference for absolute fission track age calculation.

The cooling rate ($\sim 1.7^\circ\text{C}/\text{Ma}$) deduced from track densities in orthopyroxene and phosphate minerals should be valid provided that closure temperatures are known and no subsequent track annealing has occurred. However, it is possible that the track densities of apatite and whitlockite may have been reduced by later thermal disturbance(s), which is clearly shown by the (U–Th)/He age distribution. The new (U–Th)/He ages show a large scatter with an average of $\sim 3.8$ Ga, which is younger than the inferred $^{244}\text{Pu}$ fission track ages, but the most probable pristine age was inferred from the distribution of individual ages. Meaningful $^{40}\text{Ar}/^{39}\text{Ar}$ plateau or isochron ages of Acapulco are also distinguished from the altered younger ages by interpreting the age distribution and corresponding chemical compositions [4]. Pooled ages, such as total fusion ages in a $^{40}\text{Ar}/^{39}\text{Ar}$ system, suggest meaningless and spuriously young ages. Therefore, it is essential to identify and exclude the later stage disturbance component, if any, to determine meaningful ages. Since the closure temperatures of $^{244}\text{Pu}$ fission tracks for whitlockite ($\sim 110^\circ\text{C}$) or apatite ($\sim 90^\circ\text{C}$) are comparable with that of He in apatite ($\sim 120^\circ\text{C}$), and lower than the Ar closure temperature in plagioclase ($\sim 300^\circ\text{C}$), the fission tracks are very likely to have been affected by later stage thermal event(s). Turner et al. [37] raised questions about the slow cooling rate estimated from $^{244}\text{Pu}$ fission track dating measured for several other chondrites because the cooling rates deduced from $^{40}\text{Ar}/^{39}\text{Ar}$ techniques are higher than that from the fission tracks, also suggesting the possibility of track annealing by reheating at relatively low temperature.

If this interpretation is correct, the ratio of track densities between orthopyroxene and apatite or whitlockite on adjacent crystal planes should show a skewed distribution, as is commonly seen in $^{40}\text{Ar}/^{39}\text{Ar}$ systems for partially altered samples. To check this, it would be desirable to estimate individual track density ratios for each plane, rather than obtain average density data from each phase. By analyzing the distribution of track ratios, and possibly the distribution of track lengths as is commonly done in $^{238}\text{U}$ fission track analysis, it may be possible to recognize such secondary effects and to reconcile the Pu track data with constraints from the (U–Th)/He and other data.

6. Conclusions

1. This study provides the oldest single grain (U–Th)/He ages for apatite crystals yet obtained, suggesting practical application of this technique to very old samples. The weighted mean of the five oldest grains ($4538 \pm 32\text{ Ma}$) provides a minimum apatite closure time for He at $\sim 120^\circ\text{C}$ soon after the Acapulco parent body had passed a peak metamorphic temperature.
2. The new results confirm that Acapulco cooled rapidly down to \( \sim 120^\circ \text{C} \). This is consistent with Renne’s [4] postulation, but the constraint of rapid cooling is now extended to a considerably lower temperature than that recorded by plagioclase (\( \sim 300^\circ \text{C} \)).

3. One or more later stage thermal pulses are detected from the distribution of \((\text{U}-\text{Th})/\text{He}\) ages. The timing, duration and intensity of the disturbance(s) are not clear yet, but it is evident that the disturbance was very heterogeneous within a centimeter scale.

4. The new results contradict the slow cooling rate inferred from the extinct\(^{244}\text{Pu}\) fission track data. The most probable interpretation is that the \(^{244}\text{Pu}\) fission track ages for the low-retentivity minerals (phosphates) can be easily disturbed by thermal pulse(s) producing anomalously younger ages analogous to what we observe with the \((\text{U}-\text{Th})/\text{He}\) ages.

5. The rapid cooling inferred for Acapulco over the temperature range of ca. 600 to \( \sim 100^\circ \text{C} \) provides further justification for the use of Acapulco in constraining the decay constant of \(^{40}\text{K}\) and the age of a standard [36].

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Appendix

To estimate the contribution of spike calibration to the systematic uncertainty of \(^{4}\text{He}\) measurement, we expressed the amount of \(^{3}\text{He}\) spike introduced to the vacuum line in terms of known volume and pressure estimates, then applied the Monte-Carlo method. The configuration of the line is given in figure A-1 in the Background Data Set.

\[
P_{\text{Reservoir}}: \text{pressure of reservoir (valve 1 closed)}
\]

\[
P_{I}: \text{pressure of I when gas propagated into I (valves 1 open, 2 closed)}
\]

\[
P_{\text{Pipette}}: \text{pressure of pipette when gas propagated into pipette (valves 1 closed, 2 open, 3 closed)}
\]

\[
P_{\text{Tank}}: \text{pressure of tank when gas propagated into tank (valves 1, 2 closed, 3 open)}
\]

A1. Expressing the amount of gas from a single pipetting

\[
P_{\text{Reservoir}}V_{\text{Reservoir}} = P_{I}(V_{\text{Reservoir}} + V_{I})
\]

\[
P_{I} = P_{\text{Reservoir}} \frac{V_{\text{Reservoir}}}{V_{\text{Reservoir}} + V_{I}}
\]  \( \text{(1)} \)

\[
P_{I}V_{I} = P_{\text{Pipette}}(V_{\text{Pipette}} + V_{I})
\]

\[
P_{\text{Pipette}} = P_{I} \frac{V_{I}}{V_{I} + V_{\text{Pipette}}}
\]  \( \text{(2)} \)

\[\text{(1)} \rightarrow \text{(2)}\]

\[
P_{\text{Pipette}} = \frac{P_{\text{Reservoir}}V_{\text{Reservoir}}}{V_{\text{Reservoir}} + V_{I}} =
\]

\[
P_{\text{Reservoir}} \frac{V_{\text{Reservoir}}V_{I}}{(V_{\text{Reservoir}} + V_{I})(V_{I} + V_{\text{Pipette}})}
\]  \( \text{(3)} \)

\[
P_{\text{Pipette}}V_{\text{Pipette}} = P_{\text{Tank}}(V_{\text{Pipette}} + V_{\text{Tank}})
\]

\[
P_{\text{Tank}} = P_{\text{Pipette}} \frac{V_{\text{Pipette}}}{V_{\text{Pipette}} + V_{\text{Tank}}}
\]  \( \text{(4)} \)

\[\text{(3)} \rightarrow \text{(4)}\]
\[ P_{\text{Tank}} = P_{\text{Reservoir}} \frac{V_{\text{Reservoir}} V_I}{V_{\text{Pipette}}} (V_{\text{Pipette}} + V_{\text{Tank}}) \]

The amount of gas delivered by a pipetting can be expressed as \( N = P_{\text{Tank}} V_{\text{Tank}} \) after opening the pipette valve. Therefore, from Eq. 5:

\[ N = P_{\text{Reservoir}} \frac{V_{\text{Reservoir}} V_I V_{\text{Pipette}}}{(V_{\text{Reservoir}} + V_I)(V_I + V_{\text{Pipette}})(V_{\text{Pipette}} + V_{\text{Tank}})} \times V_{\text{Tank}} \]

### A2. Estimates and uncertainties of each term

\[ V_{\text{Reservoir}} = 6.889 \times 10^{-2} \text{ l} \quad \sigma(V_{\text{Reservoir}}) = 0.01\% \]
\[ P_{\text{Reservoir}} = 1.3237 \times 10^{-4} \text{ atm} \quad \sigma(P_{\text{Reservoir}}) = 0.3\% \]
\[ V_I = 5 \times 10^{-3} \text{ l} \quad \sigma(V_I) = 0.2\% \]
\[ V_{\text{Pipette}} = 6.271 \times 10^{-4} \text{ l} \quad \sigma(V_{\text{Pipette}}) = 0.2\% \]
\[ V_{\text{Tank}} = 5.815 \text{ l} \quad \sigma(V_{\text{Tank}}) = 0.2\% \]

### A3. Monte-Carlo method

By applying the Monte-Carlo method, we have obtained

\[ N = 6.91 \times 10^{-8} \quad \sigma(N) = 0.53\% \]

### References


[21] M. Trieloff, E.K. Jessberger, C. Fiéni, Comment on \(^{40}\text{Ar}/^{39}\text{Ar}\) age of plagioclase from Acapulco meteorite and the problem of systematic errors in cosmochronol-


