Phosphate (U-Th)/He Ages from TIL07012 Acapulcoite

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45 phosphate-aggregate grains from TIL07012, an acapulcoite meteorite, were dated using the (U-Th)/He technique, reporting ages ranging from 35.39 ± 8.85 Ma to 5769.34 ± 1506.42 Ma. The larger phosphate aggregates (>180 µm), with higher U+Th+Sm contents, yielded older and less scattered ages implying that these aggregates can generate less disturbed (U-Th)/He ages. The seven oldest grains, among which six are from this group, yielded a weighted mean of 4304 ± 78 Ma. In contrast, the smaller phosphate aggregates yielded young and scattered ages. To better understand the younger ages in this meteorite, I modelled thermal diffusion of ^{4}He during compressional heating when the meteorite travels through the Earth's atmosphere. The alpha-recoil ejection from the phosphate is also considered as a secondary cause of ^{4}He loss. It is suggested that large phosphate aggregates (>180 µm) are useful to constrain the initial thermal history of a meteorite, whereas both large and small ones can be used to document later stage thermal events.

INTRODUCTION

The purpose of this research is to better understand the low-temperature thermal history of an acapulcoite by exploring the distribution of the (U-Th)/He ages from phosphate aggregates. In a smaller scope, this research can lead to improvements in the methods of (U-Th)/He analysis, and detail a more complete analogue of data on the acapulcoite meteorite thermal evolution. To a broader extent, the results can provide information needed to expedite future research projects using the meteorite's thermal evolution history to address unanswered questions about the post-condensation history of our solar system.

Background

Over the past 30 years, (U-Th)/He dating has proven to be an adequate tool for determining the low-temperature or transient thermal history of geological and planetary materials. This method, combined with other petrologic and geochemical approaches, enabled geoscientists to expand their research efforts to covering exhumation rates, landscape formation, weathering chronology, wildlife chronology, detrital thermochronology, and more recently, meteorite thermochronology. In this paper, the (U-Th)/He dating method is implemented on TIL07012, an acapulco meteorite, to study its thermal history.

For meteoritic studies, the use of (U-Th)/He system is an important tool for determining the thermal histories of meteorites. Studies using low-temperature thermochronology have been key to understanding the early evolution of our solar system, and the survivability of organic molecules via interplanetary transport. This is an important factor for an evaluation of the panspermia hypothesis (Min et al, 2003; McKay et al, 1996).

Low-Temperature Thermochronology. The practice of thermochronology relies on the natural radioactive decay of parent nuclides and the accumulation of corresponding daughter products to determine either the crystallization or the cooling ages of geological or planetary materials. In low-temperature thermochronology, the resulting age may represent the timing at which the sample was at a given temperature. The temperature at which the mineral's age attributes is known as the closure temperature defined by Dodson, (1973). When a mineral is at or above its specified closure temperature, the decay product of a given system will diffuse out of the grain and will not be retained. The concept of closure temperature varies depending on the type of thermochronometers and minerals used; however, it is not to be interpreted as a sharp and absolute temperature boundary. Realistically, closure temperature is more of a gradational window in which the decay product will partially retained as the mineral cools.

Common chronometers currently used to practice thermochronology in geosciences include ^{40}Ar/^{39}Ar method mainly for amphibole, mica, and feldspar; fission-track and (U-Th)/He primarily for apatite and zircon. In this study, the (U-Th)/He system was selected because of its unique property of having the highest sensitivity to temperature.

(U-Th)/He Dating. The current fundamental understanding of the (U-Th)/He thermochronology as it stands today is derived from Ernest Rutherford's finding of alpha particle (^{4}He atom) produced by radioactive decay (Rutherford, 1904). Immediately after this finding, it was suggested that the alpha decay can be used for age determination of rock and meteorite samples. However, it was not until more recently that the potential use of (U-Th)/He dating as a reliable thermochronometer was recognized. Zeitler et al, (1987) identified that He diffusion in apatite can be explained by Arrhenius relationship, and calculated its closure temperature. Further studies continued advancing the (U-Th)/He technique to its current capabilities, such as Wolf et al. (1998) determining the detailed diffusion parameters for a range of apatite samples.

(U-Th)/He thermochronometry is based on the production of alpha particles (^{4}He atoms) during every step of the natural radioactive decay series of ^{238}U, ^{235}U, ^{232}Th (and ^{147}Sm by a partly insignificant amount) to their final and stable Pb isotopes (Farley, 2002). The parent radioactive isotopes naturally occur during crystallization process in certain types of the host minerals, mainly apatite and zircon. ^{4}He atoms are produced during radioactive decays at constant rates. The radioactive production of ^{4}He can be expressed by the following equation:

$$^{4}He=8^{238}U[\exp(\lambda_{238}t)-1]+7^{235}U[\exp(\lambda_{235}t)1]+6^{232}Th[\exp(\lambda_{232}t)-1]$$

In this equation, ^{4}He, ^{238}U, ^{235}U, and ^{232}Th represent abundances of corresponding isotopes at present; λ_{238}, λ_{235}, and λ_{232} are the decay constants; t is the helium accumulation time also known as the (U-Th)/He age (Farley, 2002; Reiners, 2002).

The produced ^{4}He atoms experience diffusion, and possibly diffuse out from the host mineral at high temperatures. At lower temperatures, the ^{4}He diffusion would be slower, and some of the ^{4}He atoms accumulate in the grain. From studies by Zeitler et al, (1987) and Wolf et al, (1996), the ^{4}He diffusion kinetics was found to be most sensitive to temperature in apatite, leaving no accumulation of ^{4}He above ~80°C and complete accumulation below ~40°C.

One potential complication that arises from (U-Th)/He dating is accounting for alpha recoil ejection. The alpha particles are produced by the decay of the parent radioactive isotopes. With such kinetic energy, the alpha particles travel approximately 20 µm before coming to rest (Farley, 1996). The possibility of alpha particles ejecting or being introduced by other nearby phases in small crystals can lead to inaccurate (U-Th)/He ages.

Farley et al. (1996) established a quantitative method to correct the alpha recoil effect based on morphology of grains. However, the phosphate aggregates extracted from meteorites have very irregular shapes and with other phases around phosphates, therefore the Farley et al.'s (1996) approach provides incomplete constraints on alpha recoil correction factor. This is a potential source of the apparently young (U-Th)/He ages obtained in this study, and further discussed in the Discussion section.

Sample Description

The sample in question identifies as an acapulcoite. The meteorite sample was initially retrieved by the Korean Polar Research Institute (KOPRI) as a 30g find in the 2007 expedition of Thiel Mountains, Antarctica. Acapulcoites are a group of primitive unshocked achondritic meteorites, meaning they resemble chondrites in composition and mineralogy, belonging in the stony meteorite class. The unique oxygen isotopic composition and cosmic ray exposure ages suggest the acapulcoites originate from a common parent body with lodranites. Primitive achondrites of this type have an especially interesting formation in that the meteorites experienced partial melting with only minor melt segregation in their parent bodies before ejection (Neumann, 2018). The acapulcoites mainly consist of olivine, orthopyroxene, plagioclase, meteoric iron, and troilite, (McCoy et al, 1996) with a bulk chemical composition akin to chondrites with known specimens such as NWA 725 containing relic and distinct chondrules. While the mineral compositions of acapulcoites are intermediate between E and H chondrites, the oxygen isotopic compositions differ from that of all other known chondrite groups. Information provided from acapulcoite meteorites contribute directly to the understanding of the early differentiation stage of objects in the solar system.

Figure 1. Image taken of TIL07012 from K.O.P.R.I. collected at Thiel Mountains, Antarctica.

METHODS AND ANALYTICAL PROCEDURE

Upon receiving a small cut sample of the TIL07012 meteorite, it was carefully crushed via ceramic pestle and mortar. After crushing the sample into fine grains, the resulting grain fragments were sieved and separated into grain size intervals of 150-180 µm and 180-250 µm. The sieved samples, separated by grain size, were then carefully poured onto double-sided copper tape mounted on glass microscope slides. Because the sieved samples consist of multiple phases, a Scanning Electron Microscope (SEM) and Energy-Dispersive X-ray spectroscopy (EDS) were used for chemical mapping to identify phosphate aggregates. After chemical mapping of the designated fields were complete with (SEM) and (EDS) analysis, secondary scans were performed individually to phosphate aggregates identified from the field scans. The double-sided copper tape was beneficial for holding the grains into place as well as conducting electrons.

The selected grains were taken into the petrographic stereomicroscope lab and wrapped into Pt tube (or Pt foil for larger grains), ideal for (1) reducing the risk of the samples vaporizing and (2) conducting heat thoroughly (Pt is a good conductor) during He extraction process where temperatures reach ~900-1250°C (House et al, 2000). After wrapping the samples, the Pt tubes and foil were closed on both ends to create an envelope shape that would allow for HNO_3 (nitric acid) dissolve the samples before analysis using Inductively Coupled Plasma Mass Spectrometer (ICP-MS).

The Pt wrapped microfurnace envelopes were placed into designated steel planchettes separated by grain sizes p111 (150-180 μm) and p112, p115 (180-250 μm). After being placed into planchettes, the Pt wrapped microfurnaces were heated via diode laser at ~7 amp. The gas extracted from the samples was mixed with a known amount of pure ^{3}He, then the mixture was analyzed by a Quadrupole Mass Spectrometer (QMS). Following the procedures established from Min et al. (2013), the samples were heated multiple times to confirm complete He extraction.

After He analysis, the degassed samples were transferred to Teflon vials, and mixed with 50 μl U-Th-Sm spike. The samples still eased in their Pt tube envelope packets were dissolved in 2.5 ml 5% HNO_3. The isotopic ratios of the sample solution were measured using Element2 ICP-MS.

To ensure accuracy during analytical procedures, calibrations, and final (U-Th)/He age calculations, Durango apatite fragments (180-250 μm) were included into the lab procedures and analysis as a standard. The Durango apatite standards are known to attain a simple thermal history being below ~60°C over the past 31 Ma (Zeiter et al., 1987). Should the ages of the Durango apatites standard yield inaccurate observed measurements, corrections in the analytical procedure would need to be resolved.

RESULTS

A total of 45 TIL07012 phosphate-aggregate grains were analyzed for (U-Th)/He analysis, with only a small fraction ~15% yielding ages older than 4.0 Ga. Of the seven grains that yielded ages >4.0 Ga, six were from p112 and p115 (180-250 μm) while one was from p111 (150-180 μm). Four distinct phosphate phases were identified, with chlorapatite being the most dominant (64%), followed by apatite (16%), merrillite (11%), and fluorapatite (9%).

The calculated ages ranged from 35.4 ± 8.9 Ma to 5769.3 ± 1506.4 Ma with the average age of all 45 grains approximating around 1600 ± 280 Ma (2σ). The seven oldest ages yielded a weighted mean of 4304 ± 78 Ma (Fig. 3), having a significant smaller analytical margin of error, notably similar, but younger than the weighted mean age 4538 ± 32 Ma reported for large phosphate grains in Acapulco meteorite (Min et al., 2003).

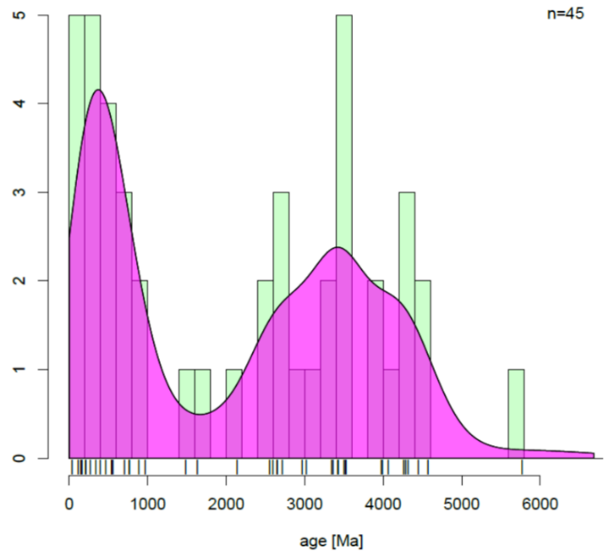

Figure 2. Sample distribution of all 45 grains. Note the bimodal distribution of the scattered lower ages constituting most of the grains analyzed.

The age distribution of all 45 total samples assembles poorly, showing few old ages while most scattered and young in such a nearly bimodal distribution (Fig. 2). Two major peaks in the age distribution cluster at ~450 Ma and ~3390 Ma.

The grains from p111 (150-180 μm) yielded generally younger ages, with a weighted mean age of 1340 ± 260 Ma, while p112 and p115 (180-250 μm) yielded an older weighted mean age of 2970 ± 320 Ma (Fig. 4). Comparatively, the ages of larger phosphate-aggregates in p112 and p115 (180-250 μm) were older and less spread than the ages from the p111 (150-180 μm). As the abundance of U+Th+Sm increased, the spread of the ages decreased (Fig. 4).

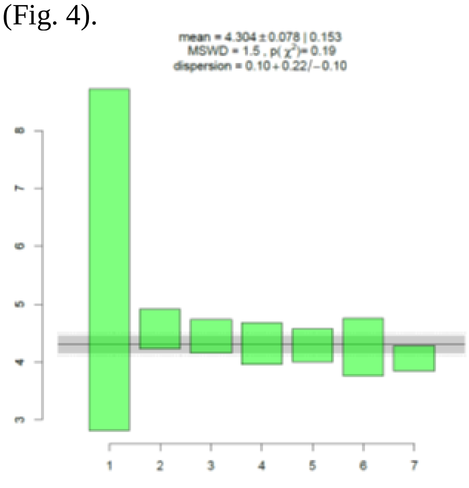

Figure 3. weighted mean of the oldest seven grains including analytical margin of error

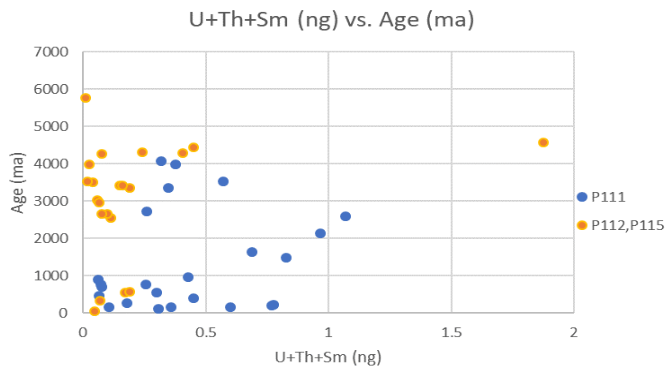

Figure 4. U+Th+Sm content (an adequate proxy for phosphate size) plotted against sample age. The series are separated by planchettes corresponding to phosphate-aggregate grain sizes sieved p112, p115 (188-250 um), p111 (150-180 um)

DISCUSSION

In this experiment, it was observed that the seven oldest grains closely resembled the initial cooling age of acapulcoites proposed by Min et al. (2003), with a weighted mean age of 4304 ± 78 Ma, representative of the minimum (U-Th)/He age for which TIL07012 cooled under ~100 ˚C. The rest of the samples contradict, exhibiting a distribution of erroneously young ages. The most probable processes to have factored in the discrepancy of young ages include such mechanisms of (1) diffusive He loss during compressional heating when the meteorite passed through the Earth's atmosphere and (2) alpha-recoil ejection.

Primary Cause of He Loss: Compressional Heating

Given that the TIL07012 meteorite sample's mass was recorded 30g (https://www.lpi.usra.edu/meteor/), and comprised of much smaller grain sizes than most acapulcoites, it would have possessed a much lower innate thermal capacity, increasing susceptibility of fractional He loss even during a transient thermal event. Because no evidence of shock is identified in acapulcoites, the most probable heating event would be compressional heating during passage through the Earth's atmosphere.

For this experiment, the potential cause of fractional He loss by compressional heating during entrance into the Earth's atmosphere is further explored by examination of the crystals morphology. It is known from previous studies by Farley (2000), He diffusive fractional loss in apatite are dependent on the size and shape of the diffusion domain, and that the diffusion domain can range from being the crystal itself to sub-grain depending on existence of potential fast pathways (e.g., cracks) for He in the crystal. This would in turn, cause the individual grains to behave differently according to their own separate diffusion domain parameters when all grains were subjected to a thermally activated event resulting in variable degrees of diffusive He loss.

To model the plausible effect morphology of phosphates grains could have on diffusive He loss instigated by heating through atmospheric passage, basic diffusion modeling was implemented.

Diffusion Modeling. For the diffusion modeling simulation to succeed, diffusion parameters determioned for acapulcoite chlorapatite (Min et al., 2003) were used with values of E_a = 44.2 kcal/mol, and D_0 = 4.2×10^6 cm^2/sec. Constraints regarding the diffusion of He in this simulation summarize the event of induced He loss as isothermal and assume the morphology of the phosphate phases as spherical.

Since the precise values of the heating duration and temperatures were reached at the passage of TIL07012 through the atmosphere, datum for maximum temperatures reached as a function of depth from fusion crust were taken from the STONE 6 experiment (Foucher et al, 2010). Possible isothermal heating temperatures to constrain the simulation range ~300-600 °C, based upon the assumption of TIL07012 possessing a maximum spherical radius 1.3 cm (calculated from converting bulk density of spherical geometry), and the bulk density equivalent to an H chondrite 3.42 g/cm^3 (Britt, Macke, 2008). The modeling was performed for two end-member heating durations of 10 and 100 seconds. The selected time intervals were shortened in comparison to actual recorded time values of heating during atmospheric passage because the selected temperature modeled for the event is experienced isothermally.

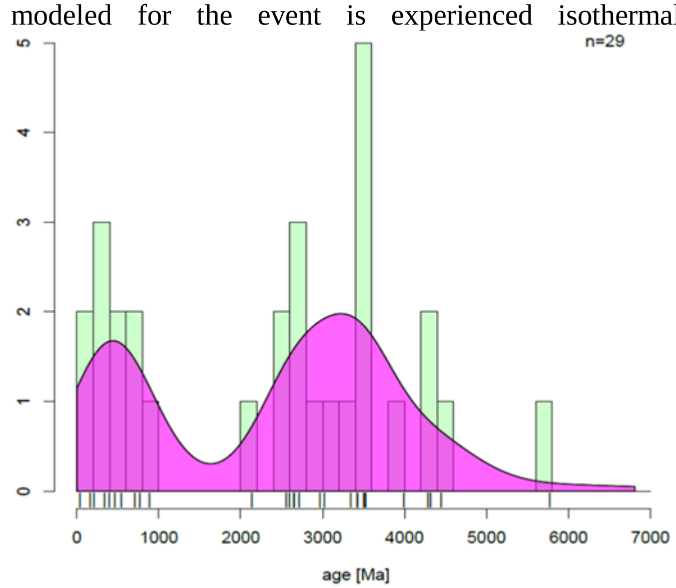

Figure 5. Sample age distribution of chlorapatite samples.

Chlorapatite aggregates made a majority of the sample size (64%), and they exhibited an age distribution identical and representative of the bulk age distribution for all phosphates (Fig. 5). The average peak ages from the bulk of all samples was used to represent the peak ages for the chlorapatites. The perceived fractional He loss percentages was then determined by calculating the percentage of the two average age peaks in the bimodal distribution diverged from the accepted average weighted mean age of the oldest seven grains 4304 ± 78 Ma (younger peak average age ~ 450 Ma = ~ 90% fractional He loss, older peak average age ~3390 Ma = ~ 26% fractional He loss).

The modeled results of the crystals morphology effect on fractional He loss during atmospheric passage is summarized in the scenario exhibited with Fig. 6. The plot shows how the diffusion domain radius changes as a function of heating temperature to yield the measured fractional He loss (26%) corresponding to the older age peak (average age for peak ~3390 Ma).

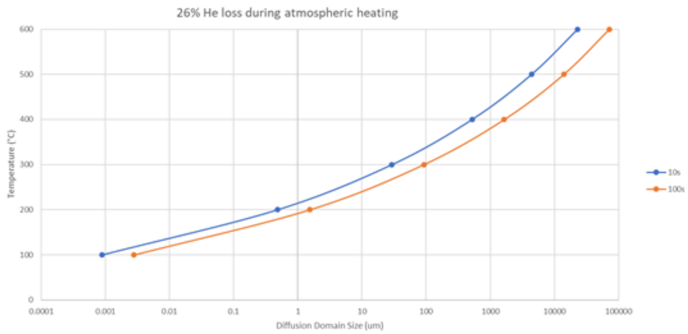

Figure 6. Relationship displayed diffusion domain size (radius) of the crystal (um) needed to obtain a constant percentage of fractional He loss at various temperatures. Different series represent proposed minimum and maximum time length used for the modeled isothermal heating duration.

The diffusion modeling results imply that for a crystal to have a specific amount of fractional He loss, the grain must have a specific diffusion domain size at a given temperature during the time which heating through atmospheric passage took place. To better constrain the temperature-time conditions, it is required to constrain the diffusion domain size(s) and depth of each sample from the fusion crust. The size of the phosphate portion in each sample was approximated using 2-D surface area calculations via SEM chemical maps processed with image-j, an image processing program. The resulting surface area, however, do not show strong linear trend with U+Th+Sm content, suggesting this approach within each grain was not compelling enough to carry on further calculations.

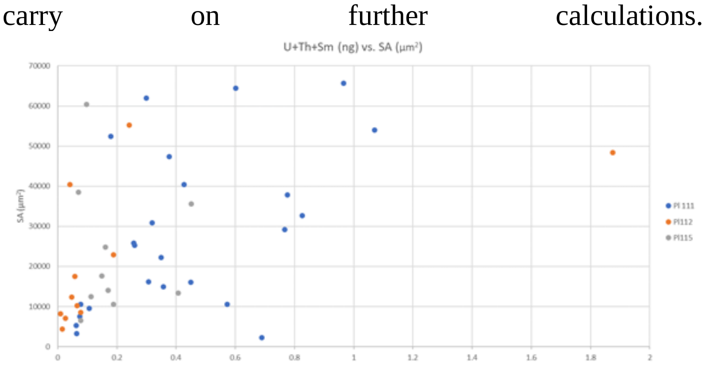

Figure 7. Scatter plot displaying the phosphate surface area measurements and U+Th+Sm content of the grains selected for analysis.

Secondary Causes of He Loss: Alpha-Recoil Ejection

While diffusive He loss induced from compressional heating is likely a primary contributor to most of the fractional ^{4}He loss, it is probable that alpha-recoil ejection may have also contributed to the anomalous young ages.

As mentioned above, precise alpha recoil correction is impossible due to irregular grain morphology and other phases attached to phosphate. The effect of alpha-recoil persists with the retentivity of ^{4}He alpha particles being subject to the surface/volume ratio of the crystal regardless of shape (Farley et al., 1996). One possible solution that could simplify and quantify the retentivity of alpha particles (^{4}He) contributing to the lowering of ages is to apply a basic alpha-recoil retentivity model, developed by Farley et al. (1996). The alpha-recoil model depicted in Fig. 8 calculated for a spherical geometry.

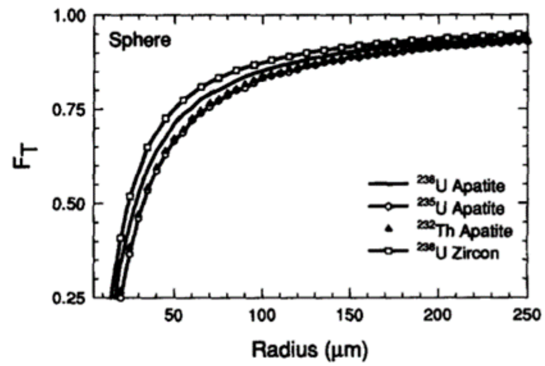

Figure 8. Model derived from Farley et al (1996), relating the variables r and F_T, indicating the relationship between the diffusion domain size radius and the alpha retentivity in sphere domain apatite shapes.

The model could conceivably give a rough estimate for the alpha recoil correction factor (F_T = retentivity). Given the nature of the phosphate aggregate size ranging from 180-250 µm having crystals with smaller diffusion domains (mean diffusion domain radius measured from image-j ~90 um), it is intuitive to believe alpha recoil as another probable cause of the unrepresentative young ages.

Equivalent to the limitations preventing actual quantification of fractional He loss from compressional heating, the lack of relationship between the phosphate phase surface area and U+Th+Sm content suggests that that the calculated surface areas are uncharacteristic of the phosphate crystals, and diffusion domain size. More important, however, the approximation of retentivity using the basic alpha-recoil model is dependent upon the factor of the crystals being isolated and excluded from surrounding phases. The addition of partially surrounding phases potentially retaining ^{4}He outside of the phosphate crystal further complicates and restricts calculations. In spite of the curtailments of modeling and surrounding phases, Alpha-recoil persists as being another possible constituent of the young age distribution.

CONCLUSION

Thermal histories of meteorites aid in cataloguing a more complete understanding of the timing and evolution of thermal processes early in the formation of our solar system. In this experiment, 45 acapulcoite meteorite phosphate aggregates were analyzed with an observed relationship of tight clustering in ages of the correspondence of U+Th+Sm and age in the seven oldest and largest grains, suggesting a (U-Th)/He age of 4304 ± 78 Ma. For the rest of the analyzed grains with lower U-Th-Sm concentrations, a bimodal distribution of unrepresentative young ages was present. While it is not within reason to fully explain and quantify the mechanisms of the uncharacteristicly young ages due to natural limitations and feasibility restrictions, the most likely attribute to the skew is believed to be the probable interplay between the mechanisms of He loss from compressional heating during entrance into the Earth's atmosphere, and alpha-recoil ejection. To improve future (U-Th)/He analysis with meteorites, more constrained datasets consisting of larger and more uniform grains could benefit in limiting the effect of scatter of distributions in the ages.

ACKNOWLEDGMENTS

I would like to show my gratitude for Kyoungwon (Kyle) Min at UF Depertment of Geological Sciences, for sponsoring me during the course of this research. As my mentor, he has taught me more than I could ever possibly give credit, showing by example how a successful scientist should approach research. Without him, it would not have been possible.

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