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Research Paper

In situ Lu–Hf phosphate geochronology: Progress towards a new tool for space exploration

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ABSTRACT

Geochronology is fundamental to understanding planetary evolution. However, as space exploration continues to expand, traditional dating methods, involving complex laboratory processes, are generally not realistic for unmanned space applications. Campaign-style planetary exploration missions require dating methods that can (1) rapidly resolve age information on small samples, (2) be applied to minerals common in mafic rocks, and (3) be based on technologies that could be installed on future rover systems. We demonstrate the application of rapid *in situ* microanalytical Lu–Hf phosphate geochronology using samples of pallasite meteorites, which are representative examples of the deep interiors of differentiated planetoids that are generally difficult to date. Individual pallasites were dated by laser ablation tandem mass-spectrometry (LA-ICP-MS/MS), demonstrating a rapid novel method for exploring planetary evolution. Derived formation ages for individual pallasites agree with traditional methods and have <2% uncertainty, opening an avenue of opportunity for remote micro-analytical space exploration.

1. Introduction

At the dawn of a Golden Era in space exploration, developing analytical methods that allow rapid *in situ* extraction of mineral and rock formation ages, without incurring the vast expense of bringing samples to Earth, will be essential to determining the tectonic evolution of rocky planets and bodies. Phosphate minerals, which are essential nutrients for life (Schwartz, 2006; Adcock et al., 2013), have an important role in this process. Theoretical models predict phosphorus to be abundant in solid form throughout the solar system (Pasek, 2019). The phosphate concentration on Mars is five to ten times higher compared to Earth (Adcock et al., 2013), including the P-rich Wishstone class alkaline rocks containing 10%–20% rare earth element and yttrium (REY) enriched merrillite in the Gusev and Gale Craters (Usui et al., 2008). REY-rich merrillite and apatite are also common in KREEP lunar rocks (Borg et al., 2004; McLeod and Krekeler, 2017) and are present in most meteorite types. Uranium concentrations are very low (sub-ppm) in most extraterrestrial phosphates (Terada and Sano, 2003; Chernonozhkin et al., 2021), limiting their utility for U–Pb geochronology in absence of specialized ion-probe or thermal ionization mass spectrometer technology. Furthermore, the apatite U–Pb system in phosphates is readily disturbed by secondary processes (e.g. recrystallization or age resetting by diffusion) obscuring crystallization ages (Göpel et al., 1994; Zhang et al., 2016). As an alternative, Lu–Hf dating on meteorites has been instrumental to our understanding of the early evolution of the solar system (Amelin, 2005; Lapen et al., 2010; Debaille et al., 2017). Importantly, the Lu–Hf system in phosphates is thermally robust compared to U–Pb dating (Barfod et al., 2003; Chew and Spikings, 2015). However, the associated sample preparation methods, involving intensive clean-laboratory procedures, are unrealistic for rapid age determinations in remote space environments. Moreover, selective leaching can lead to preferential dissolution of small and isotopically disturbed phosphate grains (Debaille et al., 2017). The recent development of *in situ* phosphate Lu–Hf dating (Simpson et al., 2021) eliminates these problems by analyzing grains using laser-ablation technology, without the requirement for complex laboratory preparation. The *in situ* technology could allow remote age determinations as part of future rover-based space exploration programs. While that goal is in the technological future, an essential step is to show *in situ* age determinations of minerals, likely to be encountered during space exploration, is readily achievable. Additionally, the *in situ* method is minimally destructive, allowing microanalysis of the finite meteorite archive as an essential companion to physical space exploration.

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In this paper, we present the first *in situ* phosphate Lu-Hf ages for pallasite meteorites. We chose pallasites to demonstrate the analytical method as they represent probes from the deep interiors of differentiated planetoids (Davis and Olsen, 1991) with a primitive mineralogy (i.e. olivine, metal and accessory sulphides, chromite and phosphates) that is difficult to date. Published olivine ^{26}Al-^{26}Mg and metal phase ^{182}Hf-^{182}W pallasite model ages (1.24 $^{+0.40}_{-0.28}$ Myr and −0.30 ± 1.43 to 0.31 ± 1.74 Myr after calcium-aluminum-inclusion (CAI) formation, respectively) suggest pallasites formed early in solar system history (Baker et al., 2012; Homma et al., 2019). In the absence of sophisticated infrastructure, phosphates are the only dateable minerals in pallasites. Pallasite phosphates (merrillite and stanfieldite) generally contain lower Lu concentrations (<1 ppm) (Chernonozhkin et al., 2021) compared to those in Martian and Lunar rocks (McLeod and Krekeler, 2017). Hence, we demonstrate the applicability of the *in situ* Lu–Hf method for space exploration by extracting age information from primitive extraterrestrial rocks. Compared to the more evolved (Lu enriched) nature of the protoliths from the phosphate-rich Martian and Lunar crust, geochronology of pallasite phosphates is challenging and therefore represents an exacting test for the utility of *in situ* Lu–Hf dating.

2. Materials and methods

Merrillite and stanfieldite phosphates were identified in polished pallasite samples using an analytical workflow involving (1) a Bruker Tornado μXRF to identify phosphate-rich areas, (2) a FEI Quanta MLA-600 scanning electron microscope (SEM) to image the phosphate grains at micron-scale resolution, and (3) a Cameca SXFive electron microprobe (EMPA) to analyze the phosphate mineral chemistry. *In situ* Lu–Hf analysis was conducted on a RESOlution LR 193 nm laser system coupled to an Agilent 8900x ICP-MS/MS instrument, using 173 μm and 257 μm laser-beam diameters for merrillite and stanfieldite, respectively.

The laser-based Lu–Hf method involves mass-filtering procedures using 10% NH_3 gas in He (at a flow rate of 3 mL/min) in the reaction-cell of the mass spectrometer, which allows high order reaction products of ^{176}Hf and ^{178}Hf to be measured free from isobaric interferences at masses 258 and 260 amu, respectively (Simpson et al., 2021). In order to calculate Lu/Hf ratios, ^{176}Hf was measured as a reaction product with +82 mass shift, ^{175}Lu was measured directly as a proxy for ^{176}Lu, and ^{178}Hf (+82 mass shift) was measured as a proxy for ^{177}Hf, with present-day isotopic abundances used to convert isotopes. ^{43}Ca was measured for internal normalization of trace element abundances. Data was normalized to NIST SRM 610 glass to correct for drift and matrix independent fractionation. Subsequently, $^{176}Lu/^{177}Hf$, and $^{176}Lu/^{176}Hf$ ratios were corrected for matrix-induced fractionation using OD306 apatite (1597 ± 7 Ma; Thompson et al., 2016). In-house reference apatite Bamble-1 (corrected Lu–Hf age: 1095 ± 10 Ma) was monitored for data accuracy and is in excellent agreement with previously published data (Simpson et al., 2021). Further details on the analytical method can be found in the Supplementary Data.

3. Results

Phosphate minerals (∼0.2–0.8 mm) were identified in three pallasite samples (Seymchan, Springwater and Imilac) and dated, directly within rock blocks, using the *in situ* Lu–Hf method. The phosphate minerals occur interstitially between olivines and the Fe-Ni-metal matrix, and formed late in the petrogenesis (Fig. 1). Average Lu concentrations were ∼0.66 ppm (merrillite) and ∼0.30 ppm (stanfieldite) in Seymchan, ∼0.18 ppm in Springwater (stanfieldite), and ∼1.9 ppm in Imilac (merrillite). $^{176}Hf/^{177}Hf$ ratios range between ∼0.34 and ∼0.73 for Seymchan, between ∼3.7 and ∼8.6 for Springwater and between ∼0.41 and ∼0.49 for Imilac. Resulting *in situ* Lu–Hf ages were calculated from isochrons, anchored to the bulk solar system initial $^{176}Hf/^{177}Hf$ ratio of 0.279781 ± 0.000018 (Iizuka et al., 2015), producing phosphate ages of 4557 ± 75 Ma for Seymchan and 4552 ± 89 Ma for Springwater. A three-point isochron for Imilac gave a less precise Lu–Hf age of 4553 ± 171 Ma (Fig. 2). Uncertainties are fully-propagated 95% confidence intervals. The analytical data is presented in the Supplementary Data.

4. Discussion

The obtained *in situ* Lu–Hf phosphate dates for individual pallasites are internally consistent and suggest phosphate crystallization occurred early in the evolution of the solar system, in agreement with previous chondrite U–Pb and Lu–Hf studies (Amelin, 2005; Debaille et al., 2017). The significant uncertainties on the *in situ* Lu–Hf dates do not allow for correlations with specific events during early solar system evolution. However, the obtained phosphate Lu–Hf dates (disregarding uncertainties) are ∼10–15 million years younger than the age of the earliest solids of the solar nebula (i.e. the ∼4567 Ma CAIs; Amelin et al., 2002) and, encouragingly, they are in agreement with models for phosphate formation from a silico-phosphate melt within ∼10 million years after solar system formation (McKibbin et al., 2016). Our results further indicate the Lu–Hf system remained undisturbed for the subsequent ∼4.5 billion years. Given we analyzed in the centre of >200 μm phosphate crystals, the possibility for isotopic disturbances due to Lu diffusion (Debaille et al., 2017) is eliminated, illustrating the power of the *in situ* method. The significantly more radiogenic $^{176}Hf/^{177}Hf$ ratios for Springwater compared to Seymchan and Imilac can be explained by prolonged interactions between silicate and metal reservoirs, such as at genuine core-mantle boundary zones (McKibbin et al., 2019). Hence, although the individual samples might have been sourced from different locations at different temperatures in one or more proto-planets, the Lu–Hf system does not record significant age differences.

We further demonstrate age precision of <2% can be achieved for phosphates with sub-ppm Lu concentrations. Precision is a function of radiogenic in-growth time, laser beam size and Lu concentration. Given that most studied Lunar and Martian phosphates commonly have an order of magnitude more Lu compared to pallasites (McLeod and Krekeler, 2017; Ward et al., 2017), the laser beam diameter can be at least halved to obtain similar or better precision for dating >1 Ga old space rocks. Hence, the *in situ* Lu–Hf method allows sufficient resolution to rapidly differentiate distinct events in planetary evolution.

More generally, we demonstrate a new rapid way of dating space-derived material using technology that requires limited human operation. Importantly, compared to traditional methods, the *in situ* Lu–Hf dating method is rapid, minimally destructive, and allows age interpretations in petrogenetic context. These are important advantages for the analysis of the finite meteorite archives as well as return mission samples. Importantly, the feasibility of *in situ* dating using the Lu–Hf system creates a driver to develop technologies that could be remotely deployed. Although the Lu–Hf dates in this study were obtained on polished samples, the polishing was mostly required for phosphate identification purposes using SEM and EMPA. Alternatively, laser-induced breakdown spectroscopy (LIBS), which is currently available on the Curiosity, Perseverance and Zhurong rovers, can be used for phosphate identification in remote applications, negating the need for

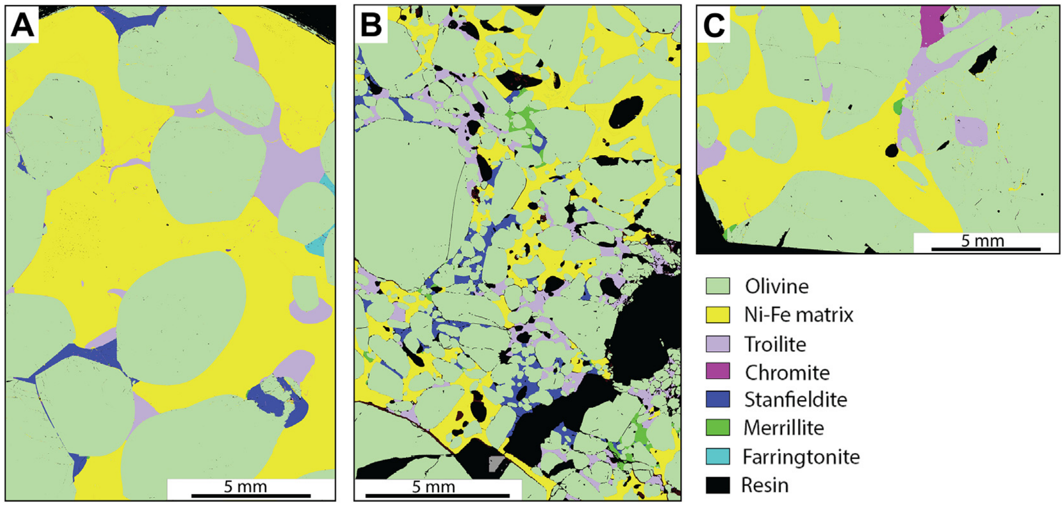

Fig. 1. False-color SEM compositional maps of pallasite polished sections showing mm-scale phosphate minerals interstitial between olivine crystals. (A) Springwater; (B) Seymchan; (C) Imilac.

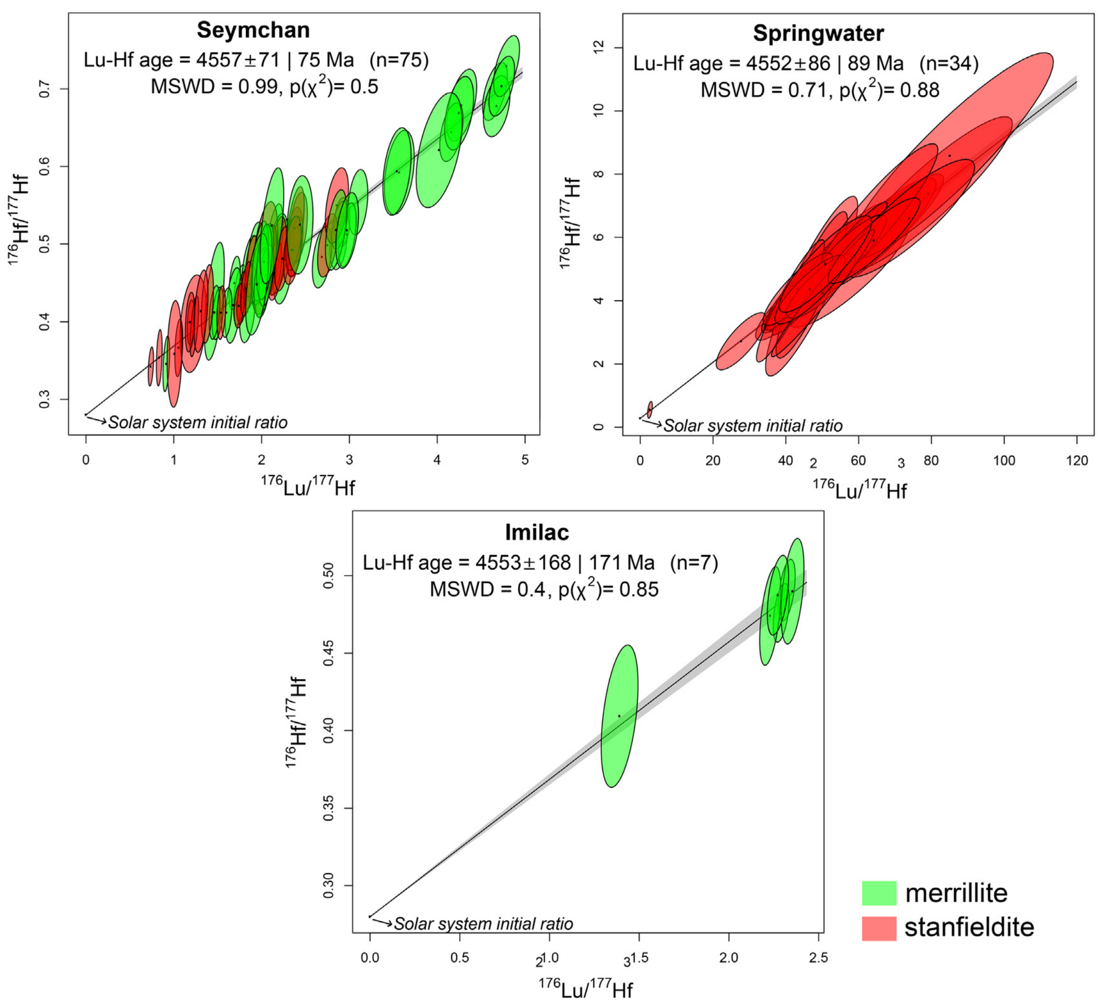

Fig. 2. *In-situ* Lu–Hf isochrons for phosphates in pallasite samples Seymchan, Springwater and Imilac. The isochrons were calculated using IsoplotR (Vermeesch, 2018) and are anchored to the bulk solar system initial ^{176}Hf/^{177}Hf ratio of 0.279781 ± 0.000018 (Iizuka et al., 2015). MSWD = mean square weighted deviation. P(χ^2) = chi-square probability to which the observed scatter in the data can be explained by the analytical uncertainties. Uncertainties are reported with and without the propagated uncertainty from the correction standard.

laboratory preparation. Developing a rover-based LA-ICP-MS/MS system will have engineering challenges. However, investments have been made into the miniaturization of plasma sources that are adapted to ambient Martian conditions (Taghioskoui and Zaghloul, 2016). Furthermore, the MOMA instrument on the ExoMars rover has an ultra-compact solid-state laser that is capable of ablating a range of mineral surfaces. Hence, technological advancements will likely allow spaceflight LA-ICP-MS capabilities for *in situ* planetary exploration missions in the next decade (Arevalo Jr et al., 2020).

Declaration of Competing Interest

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

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Author contributions

M.H. provided the samples, S.Gi. provided the reference materials. S.Gl. and M.H. conceptualized and designed the project. T.B., A. S., S.Gi. and B.W. imaged and analyzed the samples for Lu-Hf ratios. T.B., S.Gl., and A.S. interpreted the data and calculated Lu-Hf ages. S.Gl. wrote the original manuscript, while all co-authors provided assistance with editing.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.gsf.2022.101375.

References

Adcock, C.T., Hausrath, E.M., Forster, P.M., 2013. Readily available phosphate from minerals in early aqueous environments on Mars. Nat. Geosci. 6 (10), 824–827.
Amelin, Y., 2005. Meteorite phosphates show constant ^{176}Lu decay rate since 4557 million years ago. Science 310 (5749), 839–841.
Amelin, Y., Krot, A.N., Hutcheon, I.D., Ulyanov, A.A., 2002. Lead isotopic ages of chondrules and calcium-aluminum-rich inclusions. Science 297 (5587), 1678–1683.
Arevalo, R., Ni, Z., Danell, R.M., 2020. Mass spectrometry and planetary exploration: A brief review and future projection. J. Mass Spectrom. 55 (1), e4454.
Baker, J.A., Schiller, M., Bizzarro, M., 2012. ^{26}Al-^{26}Mg deficit dating ultramafic meteorites and silicate planetesimal differentiation in the early Solar System? Geochim. Cosmochim. Acta 77, 415–431.
Barfod, G.H., Otero, O., Albarède, F., 2003. Phosphate Lu–Hf geochronology. Chem. Geol. 200 (3-4), 241–253.
Borg, L.E., Shearer, C.K., Asmerom, Y., Papike, J.J., 2004. Prolonged KREEP magmatism on the Moon indicated by the youngest dated lunar igneous rock. Nature 432 (7014), 209–211.
Chernonozhkin, S.M., McKibbin, S.J., Goderis, S., Van Malderen, S.J.M., Claeys, P., Vanhaecke, F., 2021. New constraints on the formation of main group pallasites derived from in situ trace element analysis and 2D mapping of olivine and phosphate. Chem. Geol. 562, 119996.
Chew, D.M., Spikings, R.A., 2015. Geochronology and thermochronology using apatite: Time and temperature, lower crust to surface. Elements 11 (3), 189–194.
Davis, A.M., Olsen, E.J., 1991. Phosphates in pallasite meteorites as probes of mantle processes in small planetary bodies. Nature 353 (6345), 637–640.
Debaille, V., Van Orman, J., Yin, Q.-Z., Amelin, Y., 2017. The role of phosphates for the Lu–Hf chronology of meteorites. Earth Planet. Sci. Lett. 473, 52–61.
Göpel, C., Manhès, G., Allègre, C.J., 1994. U-Pb systematics of phosphates from equilibrated ordinary chondrites. Earth Planet. Sci. Lett. 121 (1-2), 153–171.
Homma, Y., Iizuka, T., Ishikawa, A., 2019. Hf-W dating of main-group pallasites. Proceedings of the 50th Lunar and Planetary Science Conference, p. LPI Contrib. No. 2132.
Iizuka, T., Yamaguchi, T., Hibiya, Y., Amelin, Y., 2015. Meteorite zircon constraints on the bulk Lu-Hf isotope composition and early differentiation of the Earth. Proc. Natl. Acad. Sci. USA 112 (17), 5331–5336.
Lapen, T.J., Righter, M., Brandon, A.D., Debaille, V., Beard, B.L., Shafer, J.T., Peslier, A. H., 2010. A younger age for ALH84001 and its geochemical link to shergottite sources in Mars. Science 328 (5976), 347–351.
McKibbin, S.J., Ireland, T.R., Holden, P., O'Neill, H.S.C., Mallmann, G., 2016. Rapid cooling of planetesimal core-mantle reaction zones from Mn-Cr isotopes in pallasites. Geochem. Perspect. Lett. 2, 68–77.
McKibbin, S.J., Pittarello, L., Makarona, C., Hamann, C., Hecht, L., Chernonozhkin, S. M., Goderis, S., Claeys, P., 2019. Petrogenesis of main group pallasite meteorites based on relationships among texture, mineralogy, and geochemistry. Meteorit. Planet. Sci. 54 (11), 2814–2844.
McLeod, C.L., Krekeler, M.P.S., 2017. Sources of extraterrestrial rare earth elements: To the Moon and beyond. Resources 6 (3), 40. https://doi.org/10.3390/resources6030040.
Pasek, M.A., 2019. Phosphorus volatility in the early solar nebula. Icarus 317, 59–65.
Schwartz, A.W., 2006. Phosphorus in prebiotic chemistry. Philos. Trans. R. Soc. B: Biol. Sci. 361 (1474), 1743–1749.
Simpson, A., Gilbert, S., Tamblyn, R., Hand, M., Spandler, C., Gillespie, J., Nixon, A., Glorie, S., 2021. In-situ Lu-Hf geochronology of garnet, apatite and xenotime by LA ICP MS/MS. Chem. Geol. 577, 120299.
Taghioskoui, M., Zaghloul, M., 2016. Plasma ionization under simulated ambient Mars conditions for quantification of methane by mass spectrometry. Analyst 141 (7), 2270–2277.
Terada, K., Sano, Y., 2003. In situ U-Pb dating and REE analyses of phosphates in extraterrestrial materials. Appl. Surf. Sci. 203-204, 810–813.
Thompson, J., Meffre, S., Maas, R., Kamenetsky, V., Kamenetsky, M., Goemann, K., Ehrig, K., Danyushevsky, L., 2016. Matrix effects in Pb/U measurements during LA-ICP-MS analysis of the mineral apatite. J. Anal. At. Spectrom. 31 (6), 1206–1215.
Usui, T., McSween, H.Y., Clark, B.C., 2008. Petrogenesis of high-phosphorous Wishstone Class rocks in Gusev Crater, Mars. J. Geophys. Res.-Planets 113 (E12). https://doi.org/10.1029/2008JE003225.
Vermeesch, P., 2018. IsoplotR: A free and open toolbox for geochronology. Geosci. Front. 9 (5), 1479–1493.
Ward, D., Bischoff, A., Roszjar, J., Berndt, J., Whitehouse, M.J., 2017. Trace element inventory of meteoritic Ca-phosphates. Am. Miner. 102 (9), 1856–1880.
Zhang, A.-C., Li, Q.-L., Yurimoto, H., Sakamoto, N., Li, X.-H., Hu, S., Lin, Y.-T., Wang, R.-C., 2016. Young asteroidal fluid activity revealed by absolute age from apatite in carbonaceous chondrite. Nat. Commun. 7, 12844.