U-Pb dating of sub-ng g^{-1} U garnet by LA-MC-ICP-MS

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Abstract. Advances in laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) have largely focused on improving spatial resolution through progressively smaller laser spot sizes. Here, we explore the opposite end of the analytical limits by investigating the lower concentration limits of in-situ U–Pb geochronology in garnet. Using a Neptune Plus multi-collector ICP-MS equipped with seven ion counters, we developed an analytical workflow specifically designed for metamorphic garnet with ultra-low U concentrations (< 10 ng g^{-1}). The method was used to date garnet from a wide range of ages and geological settings, including granulites, eclogites and hydrothermal demantoids. Uranium concentrations were exceptionally low, even below 1 ng g^{-1} in some cases. At these concentrations, the total amount of U ablated during a single analysis is at femtogram levels, more than three orders of magnitude lower than that of a typical in-situ analysis of zircon. Despite these extremely low signal intensities, geologically meaningful ages were obtained for the analysed samples. Analytical precision depends on the U and radiogenic Pb concentrations, but we have obtained precisions of ca. 5-6 % for garnet containing less than 1 ng g^{-1} U. In garnet with higher U concentrations or ages as old as the Archean, internal precision of ca. 1 % may be achieved. These results expand the applicability of in-situ garnet U-Pb geochronology to the vast majority of metamorphic garnet, providing a powerful new tool for constraining garnet growth, prograde metamorphism, and deep crustal evolution.

1 Introduction

The combination of laser ablation (LA) systems with inductively coupled plasma mass spectrometers (ICP-MS) revolutionised in-situ chemical analysis during the 1980s (Gray, 1985; Arrowsmith, 1987). Since the pioneering works, LA-ICP-MS U–Pb geochronology of high-U accessory minerals such as zircon, monazite, or titanite has become a routine analytical tool (e.g., Fryer et al., 1993; Machado and Gauthier, 1996; Willigers et al., 2002; Kosler and Sylvester, 2003; Horstwood et al., 2016). Besides, over the last decade, these analytical capabilities have also been expanded to minerals with lower U concentrations (<10 µg g^{-1}), including carbonate (Roberts and Walker, 2016; Ring and Gerdes, 2016), sulfate (Beranoaguirre et al., 2022), fluorite (Piccione et al., 2019), and garnet (Seman et al., 2017; Millonig et al., 2020; O'Sullivan et al., 2023), among others. Continuous advances in instrumentation have also been accompanied by progressively smaller laser spot sizes (review in Sylvester and Jackson, 2016), improving the spatial resolution and enabling the distinction of multiple domains within a single crystal (e.g., Chew et al., 2017). In turn, analysing low-U minerals requires a different strategy, in which the main challenge is no longer spatial resolution, but concentration sensitivity. This issue is particularly challenging for metamorphic garnet, since its U and Pb amounts are extremely low (Deng et al., 2022). Therefore, being capable of developing a robust analytical strategy for analysing metamorphic garnet would represent a major advance in metamorphic petrology.

Unlike many geochronological systems that either record cooling and exhumation histories (e.g., apatite fission-track, (U–Th)/He, and Ar-based systems) or preferentially date high-temperature metamorphic events (e.g., zircon, monazite, and titanite U–Pb geochronology) (Dodson, 1973; McDougall and Harrison, 1999; Rubatto, 2002; Reiners et al., 2005; Flowers et al., 2009; Kohn et al., 2017), garnet can preserve prograde metamorphic growth histories over a wide range of pressure–temperature conditions (Spear and Parrish, 1996; Caddick and Kohn, 2013), in part due to its exceptionally high closure temperature for the U–Pb system (potentially exceeding 1000 °C; Dahl, 1997; Shu et al., 2024). Traditionally, garnet has been dated by Sm–Nd and Lu–Hf (e.g. Duchêne et al., 1997; Baxter et al., 2017). Although a very high precision can be achieved through these systems, they require laborious mineral separation and dissolution procedures. More recently, the use of tandem mass spectrometry (ICP-MS/MS) has also enabled the in-situ Lu-Hf garnet dating (Simpson et al., 2021). However, the application of in-situ Lu–Hf geochronology remains largely restricted to relatively old metamorphic systems (Caledonian or older; Tamblyn et al., 2022; Kirkland et al., 2025). This limitation may arise from the low radiogenic growth of ^{176}Hf in younger garnet, which hampers analytical precision and age resolution in younger orogens. In contrast, U-Pb garnet geochronology has been used to resolve younger metamorphic events (Peillod et al., 2024; Manzotti et al., 2025). Consequently, U-Pb garnet geochronology (eventually complemented with in-situ Lu-Hf dating) offers a unique opportunity to directly constrain the timing of prograde metamorphism and deep crustal processes.

In this study, we investigate the lower limits of the U and Pb concentrations in garnet required to obtain meaningful garnet U-Pb dates by LA-MC-ICP-MS. For that purpose, we have optimised the LA-MC-ICP-MS method on a series of natural, low-U metamorphic garnet specimens from granulites, eclogites, and one gemstone-quality grossular-andradite (i.e. demantoid). The possibility to date garnet crystals with extremely low U concentrations (<1 ng g^{-1}) by LA-MC-ICP-MS is expected to substantially increase the field of application of garnet U-Pb dating, as most of the metamorphic garnet have <50 ng g^{-1} U (Millonig et al., 2020; O'Sullivan et al., 2023; Bartoli et al., 2024; Shu et al., 2024).

2 Methodology

U-Pb data were acquired *in-situ* from polished garnet grain mounts and thin sections using a RESOLution 193 nm ArF excimer laser (CompexPro 102) equipped with a two-volume ablation cell (Laurin Technic S155) coupled to a multi-collector (MC)-ICP-MS (Neptune Plus, ThermoScientific) at the Frankfurt Isotope and Element Research Center (FIERCE), Goethe University Frankfurt. The Neptune Plus at FIERCE is equipped with ten Faraday cups and seven ion counters, of which two are classical discrete dynode secondary electron multipliers (SEM) and five compact discrete dynode (CDD) electron multipliers (Fig. 1). This results in two possibilities for the simultaneous detection of the U, Th, and Pb isotopes: I) for moderate U contents of ~ 0.2 to 30 µg g^{-1}, ^{238}U and ^{232}Th are detected on the Faraday cups with 10^{13} Ω amplifiers, ^{207}Pb, ^{206}Pb on the

SEM and ^{208}Pb on a CDD (method described in Beranoaguirre et al., 2022); while II) at low U of < 0.2 µg g^{-1}, ^{238}U and, if necessary ^{232}Th, can be measured on the CDD attached to the Faraday cups (H4 and H3, respectively). A summary report of the U-Pb dating procedure is presented in the supplementary material (Table S1), and the analytical results are presented in supplementary Tables S2 to S6.

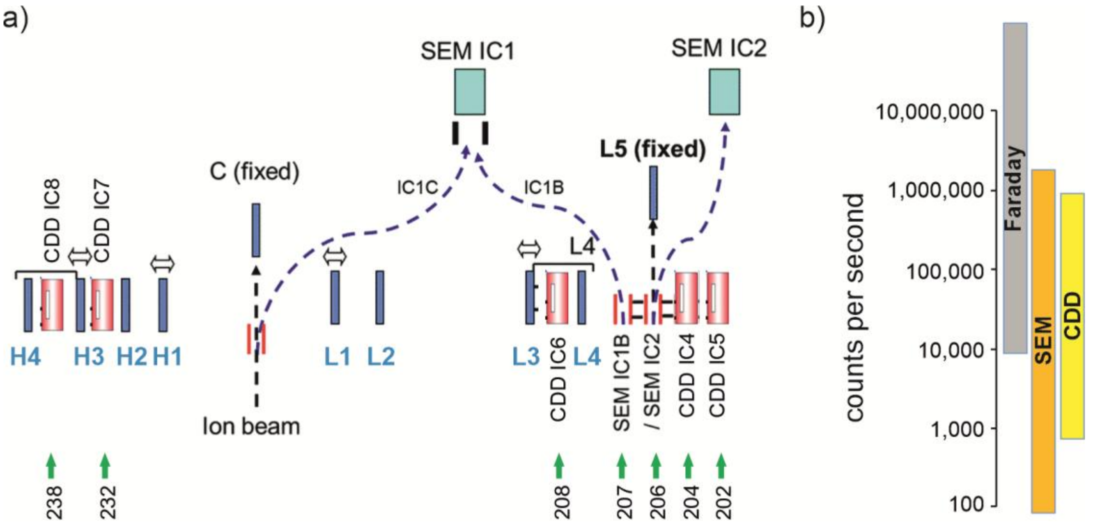

Figure 1. a) Schematic detector configuration of the Neptune Plus MC-ICP-MS used in this study, showing the positions and measured isotopes for the low-U analytical configuration (modified after Richter et al., 2016). b) Approximate signal intensity ranges covered by Faraday cups, secondary electron multipliers (SEM), and compact discrete dynode (CDD) ion counters.

Ablation was performed in a He atmosphere (0.3 l min^{-1}) and mixed in the ablation funnel with daily tuned 0.95–1 l min^{-1} Ar and 5–10 ml min^{-1} N_2. Signal strength at the MC-ICP-MS was tuned for maximum sensitivity while keeping oxide formation below 0.5 % (UO/U) and element fractionation low (e.g. Th/U ~ 0.9). This was done by line ablating the SRMNIST 614 glass (Jochum et al., 2011) using a 50 µm spot size, 6 Hz, *ca.* 3.5 J cm^{-2} fluence and a 3 µm s^{-1} line speed. The average sensitivity obtained with this setup was *ca.* 250,000 cps per µg g^{-1} for ^{238}U in the best of the cases. The laser parameters used for instrument tuning are independent of those employed during the analytical sessions, as the purpose of the tuning procedure is solely to optimise ICP-MS operating conditions under a stable signal rather than to reproduce the analytical ablation conditions. The garnet samples were ablated using a round spot size of 193 µm and a fluence of *ca.* 2 J cm^{-2} at 15 Hz. This yielded a depth penetration of *ca.* 0.8 µm s^{-1}. Each analysis consisted of 16 s of background acquisition followed by 18 s of sample ablation and 20 s of washout. The analyses were done in the static mode, measuring ^{206}Pb and ^{207}Pb with SEMs, and ^{202}Hg, ^{204}Pb, (^{208}Pb) and ^{238}U with the CDD and an integration time of 0.131 s (due to electronic issues with the ion counter, ^{208}Pb was not measured in all the sessions).

In each analytical session, soda-lime glass SRMNIST 614 was used as the primary reference material to correct for mass bias ($^{207}Pb/^{206}Pb$), inter-element fractionation and instrumental drift ($^{206}Pb/^{238}U$). For this purpose, a block of reference materials was analysed every 50 analyses. A low-U yellow garnet from the Mali Grandite locality (Seman et al., 2017) was used as the matrix-matched reference material to determine the difference in the Pb/U fractionation between garnet and the synthetic glass matrix. This crystal is distinct from the published Mali Grandite reference materials and was selected because its U concentration (ca. 15-20 ng g^{-1}) is sufficiently low to avoid saturation of the ion counters, which occurs at approximately 1,000,000 cps (Fig. 1b). Further details are provided below. Lake Jaco garnet (34.0 ± 1.4 Ma, Seman et al., 2017), together with an in-house quality-control garnet from Balochistan (ID-TIMS age of ca. 45.5 Ma; M. Stifeeva, unpublished data), were analysed to monitor the reproducibility of the analytical procedure. Due to the possible saturation of the ion counters, the secondary garnet crystals were pre-screened to identify domains with sufficiently low-U concentrations (< 1 µg g^{-1}). Those domains also show lower Pb content, and therefore, the $^{207}Pb/^{206}Pb$ and $^{206}Pb/^{238}U$ ratios are not affected.

Raw data were corrected offline using an in-house VBA spreadsheet program (Gerdes and Zeh, 2006, 2009). Following background and interference corrections, outliers were rejected based on the time-resolved $^{207}Pb/^{206}Pb$ and $^{238}U/^{206}Pb$ ratios, while the Pb and U signals were used to identify and reject data derived from the co-ablation of mineral inclusions or zones with clearly distinct common-Pb and U concentrations compared to the pure garnet. Likewise, outliers in U and/or Pb content were rejected for age calculations, assuming that those analyses reflect inclusions (Fig. 2). Data are displayed in Tera-Wasserburg plots (Tera and Wasserburg, 1972), and U-Pb dates were calculated as lower Concordia-curve intercepts using the same algorithms as Isoplot 4.15 (Ludwig, 2012). Age uncertainties shown in the Tera-Wasserburg plots are the within-session uncertainty, considering the within-run precision, counting statistic uncertainties of each isotope, and the excess of scatter and of variance (Horstwood et al., 2016), calculated from the SRMNIST 614 and the Mali garnet, and the expanded uncertainty, which includes the long-term variance of our in-house quality control garnet crystals (2%). All uncertainties are reported at the 2σ level.

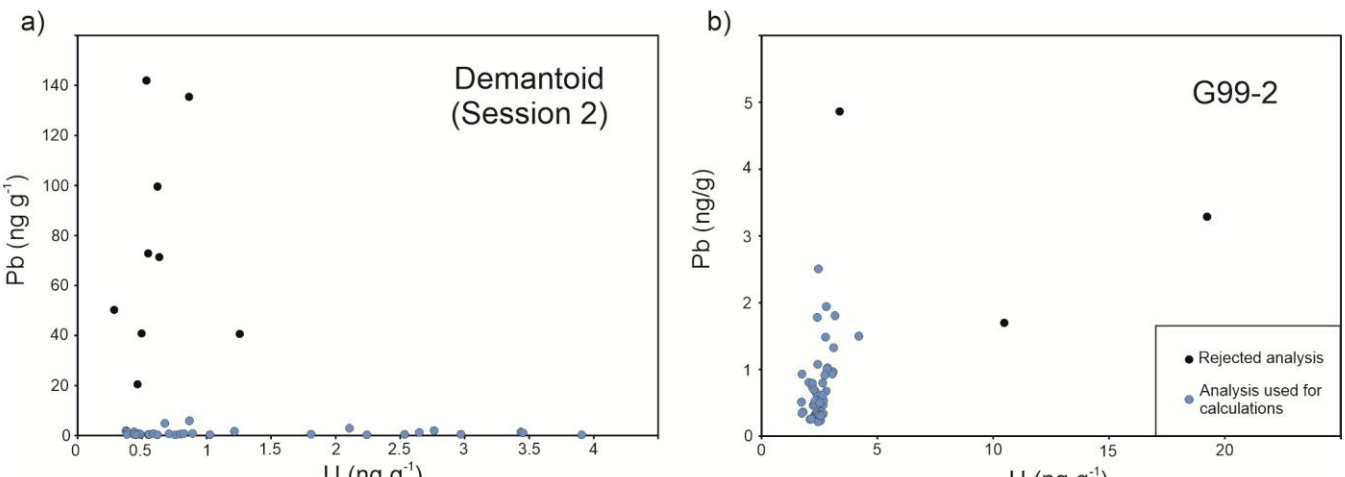

Figure 2. Plots of U vs Pb concentration (ng g^{-1}), showing the analyses rejected and considered for the age calculations. A) Cabo Ortegal demantoid (session 2) and B) garnet G99-2 from Orlica-Śnieżnik felsic granulite. Analytical uncertainties are smaller than the plotting symbols and are therefore not visible. Nevertheless, their inclusion would not alter the interpretation of the figure.

Matrix-matched reference materials (RMs) are an important component of any LA-ICP-MS method (e.g. Schaltegger et al., 2015). With respect to garnet, only a few well-characterised RMs are available to the LA-ICP-MS community in sufficient quantities, although many research groups have developed new RMs over the last few years (e.g. Stifeeva et al., 2019, Salnikova et al., 2019, 2026; Li et al., 2022; Aysal et al., 2023; Beno et al., 2024, Yang et al., 2025). The most popular garnet RMs for U–Pb dating are still the ones published by Seman et al. (2017); the red and yellow varieties of Mali Grandite (LA-ICP-MS U-Pb: 202 ± 2 Ma; ID-TIMS U-Pb: 202.0 ± 1.2 Ma) and the Lake Jaco Grossular (LA-ICP-MS U-Pb: 35 ± 2 Ma; (U-Th)/He: 35 ± 5 Ma). However, U concentrations of >2 µg g^{-1} of the aforementioned garnet RMs would saturate the ion counters, and thus, they are not usable for the method applied in this study. To overcome this issue, we investigated several low-U (<0.5 µg g^{-1}) garnet from the same localities investigated by Seman et al. (2017), and we identified a yellow garnet from the Mali Grandite locality with an average U concentration of 15-20 ng g^{-1}, which was subsequently used as the matrix-matched RM. The secondary reference materials, used for quality control, were compositionally and optically diverse grossular garnet crystals from Lake Jaco, and a dark brown grandite from Balochistan. When assuming the published age of 202 Ma for the yellow Mali, we obtained internally consistent results across multiple sequences for the secondary garnet RMs and different samples. Although no independent age estimates (i.e. TIMS ages) are available for our matrix-match and quality control RMs we consider the obtained U-Pb ages as accurate within their analytical uncertainties, based on the facts that (1) the U-Pb ages for the various Lake Jaco garnet crystals are within the uncertainty of the published ages from that locality (Seman et al., 2017), and (2) the U-Pb age of 384 ± 12 Ma for garnet from sample G99-2 is similar to a Lu-Hf age of 387 ± 5 Ma from that sample (Anczkiewicz et al., 2007; section 3.2). However, we will (re-)calibrate these low-U garnet crystals against well-characterised low-U garnet RMs, once they become available. Furthermore, this potential age ambiguity does not affect the purpose of this contribution.

3 Samples and results

3.1 Cabo Ortegal demantoid (Cabo Ortegal Complex, NW Iberian Massif)

The Cabo Ortegal Complex represents an allochthonous assemblage of continental- and oceanic-derived lithologies that record subduction-related metamorphism prior to their emplacement onto the Gondwanan margin during the Variscan orogeny (e.g. Martínez Catalán et al., 2019). Previous geochronological studies of the complex suggest that the magmatic protoliths (520-460 Ma) were metamorphosed during the Variscan at *ca.* 400-390 Ma followed by a rapid decompression to shallow crustal levels (Beranoaguirre et al., 2020). The demantoid andraditic garnet analysed here was described in detail by Madon et al. (1991). It occurs associated with chlorite and serpentine in fissures cutting across the foliation of the pyroxenite. Due to these cutting relationships, it is believed that the demantoid-bearing veins postdate even the youngest regional granitoids (ca. 280 Ma; Rodríguez et al., 2007).

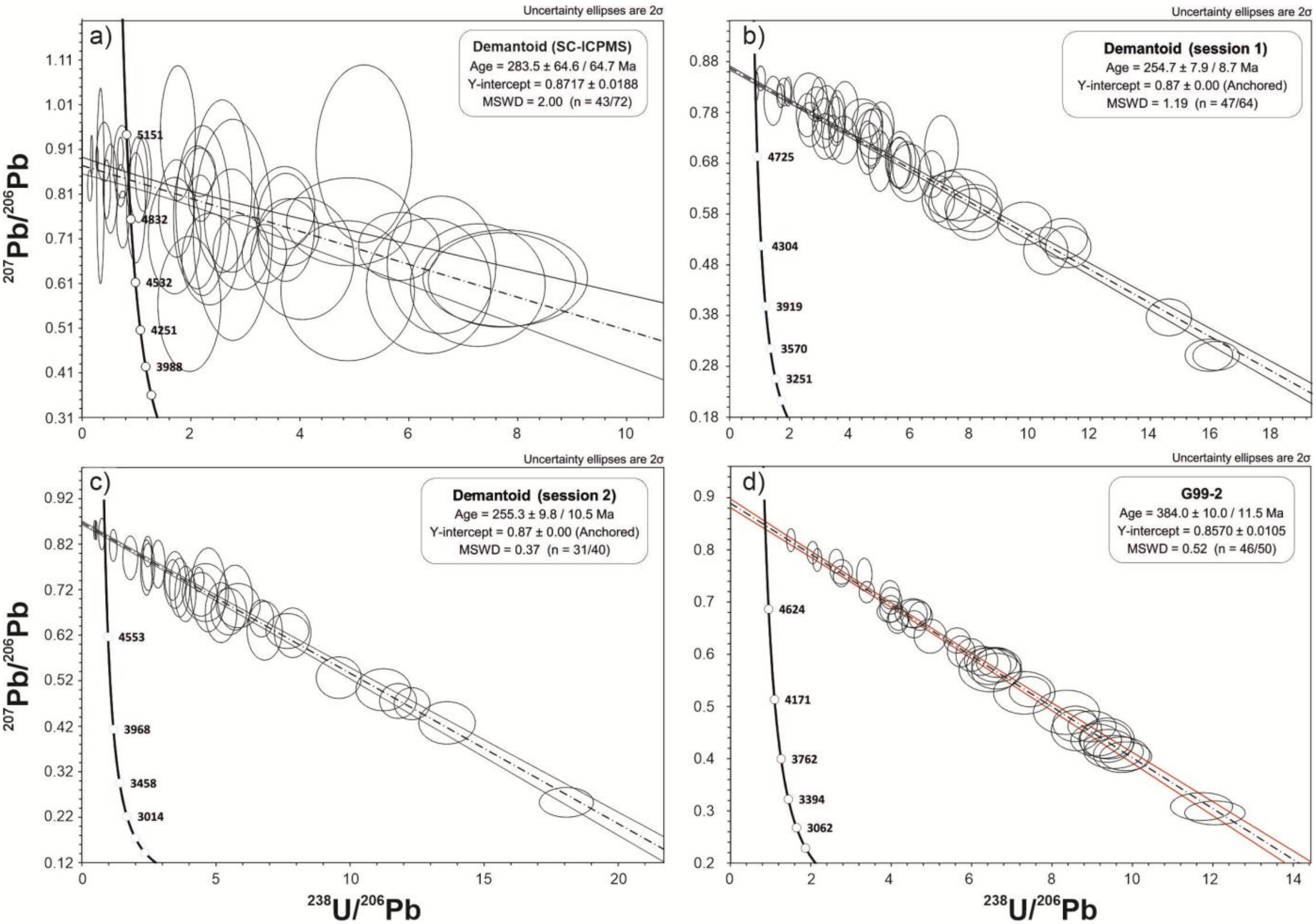

Figure 3. Tera-Wasserburg diagrams of garnet U-Pb analyses for Cabo Ortegal demantoid, analysed with the ElementXR single-collector ICP-MS (a) and Neptune MC-ICP-MS (b and c), and sample G99-2 from Orlica-Śnieżnik granulite(d).

The first attempt to date the demantoid garnet crystals was made using a single-collector ICP-MS (the method is described in Millonig et al., 2020 and Beranoaguirre et al., 2022). The resulting data defined a regression line with a lower intercept at 284 ± 65 Ma (MSWD = 2, Fig. 3a), and only 43 out of 72 analytical spots had U or Pb concentrations above the detection limits. Subsequently, two sessions were performed with the MC-ICP-MS. The resulting lower intercept dates for the sessions were 254.7 ± 7.9/8.7 Ma (MSWD = 1.19, n = 47/64, Fig. 3b) and 255.3 ± 9.8/10.5 Ma (MSWD = 0.37, n = 31/40, Fig. 3c). The regression lines were anchored to a $^{207}Pb/^{206}Pb$ ratio of 0.870 ± 0.005, derived from the mean of the unanchored upper intercept of both sessions, providing a consistent baseline for comparison. Most of the analyses have extremely low U concentrations between 0.5 and 1 ng g^{-1}, with rare exceptions up to 4 ng g^{-1} (Fig. 2a and 4; Tables S2 and S3).

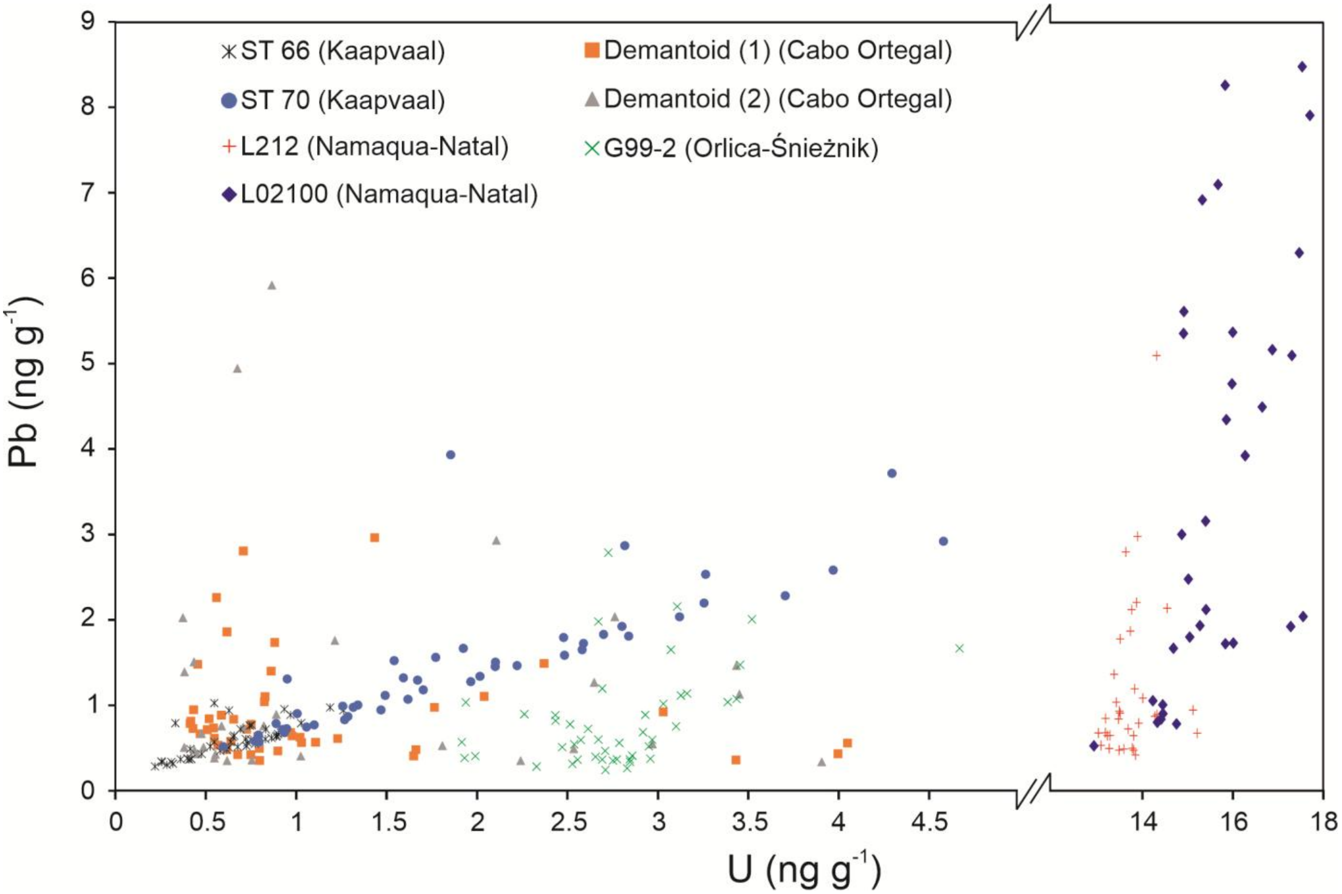

Figure 4. Plot of U vs Pb concentration (ng g^{-1}) for all the analysed garnet. The rejected analyses (Fig. 2) are not considered, to avoid scaling issues. Note the difference in the x-axis scale for the samples L212 and L02100. In the Kaapvaal samples, ^{208}Pb was not measured and therefore, the Pb concentration is the sum of ^{204}Pb+^{206}Pb+^{207}Pb. Note the discontinuity in the x-axis between 5 and 12 ng g^{-1}. Analytical uncertainties are smaller than the plotting symbols and are therefore not visible.

3.2 Orlica-Śnieżnik felsic granulite (NE Bohemian Massif)

The Orlica-Śnieżnik Dome is located on the northeastern margin of the Bohemian Massif in SW Poland. It comprises predominantly amphibolite-facies, partly migmatised, orthogneisses, hosting numerous inclusions of (ultra) high-pressure rocks (e.g. Walczak et al., 2017). Their granitic precursors intruded supracrustal sedimentary successions of Neoproterozoic to Ordovician age and were subsequently metamorphosed during the Variscan orogeny (Szczepański and Ilnicki, 2014).

The garnet analysed here corresponds to the felsic granulite G99-2 studied in detail by Anczkiewicz et al. (2007), who obtained garnet Lu-Hf and Sm-Nd ages of 387 ± 5 Ma and 320 ± 3 Ma, respectively. From the U-Pb analyses performed in our laboratory, an unanchored lower intercept age of 384.0 ± 10.0/11.5 Ma (MSDW = 0.52, n = 46, Fig. 3d) was calculated. The U and Pb contents are homogeneous, varying between 2 and 4 ng g^{-1}, and between 0.3 and 3 ng g^{-1}, respectively (Fig. 2b and 4; Table S4).

3.3 Granulite xenoliths from the Star kimberlite (Kaapvaal craton, South Africa)

Ultrahigh temperature (UHT) metamorphic crustal granulite xenoliths were found in four kimberlite diatremes from along the central axis of the Witwatersrand basin in the central Kaapvaal craton (Schmitz and Bowring, 2003). The xenoliths are K-free, Mg-Al-rich UHT granulites with abundant garnet, sillimanite, rutile, graphite and sulphides, and local occurrence of sapphirine, orthopyroxene, plagioclase and quartz. Metamorphic conditions have been estimated at temperatures above 1050°C and pressures between 0.9–1.2 GPa (Dawson et al., 1997). Zircon and monazite gave U–Pb ages of approximately 2.7 Ga (Schmitz and Bowring, 2003). The xenoliths were brought to the surface by Cretaceous kimberlite magmatism at approximately 120 Ma.

The results of these samples have already been published and discussed in detail by Shu et al. (2024). The analyses of the garnet in that publication followed the method described here, and considering that the aim of this work is purely methodological, two examples of those rocks are shown: the one with the lowest U concentration (sample ST66) and the one with the highest precision (ST 70). The latter was achieved by anchoring the regression line to a sillimanite crystal analysis, assuming that both minerals are in equilibrium. The samples ST66 and ST70 define regression lines with lower intercepts at 3096 ± 63/70 Ma (MSWD = 2.18, n = 53/53, Fig. 5a) and 3096 ± 37/48 Ma (MSWD = 3.05, n = 53/58, Fig. 5b). As stated above, sample ST66 shows the lowest U content among the samples presented in this work, varying from 0.3 to 2.2 ng g^{-1}, whereas sample ST70 has a more variable U content, between 1 and 17 ng g^{-1}. Pb and U contents are positively correlated. Unfortunately, it was not possible to measure the ^{208}Pb isotope, so the calculated Pb content is the sum of ^{204}Pb+^{206}Pb+^{207}Pb. The resulting Pb concentrations do not exceed 1 ng g^{-1} for sample ST66 and 6 ng g^{-1} for sample ST70, except in two spots (Fig. 4; Table S5).

3.4 Eclogite xenoliths from the Namaqua-Natal Belt (South Africa)

Multiple Cretaceous kimberlite pipes occurring on the Proterozoic Namaqua-Natal-Fold Belt, which surrounds the Archean Kaapvaal craton, have brought to the surface a significant amount of high-pressure eclogite, granulite and pyroxenite xenoliths (Le Roex et al., 2020). The eclogites are mainly bimineralic (garnet-clinopyroxene) with accessory rutile and coesite/quartz (and even diamond), although kyanite-bearing eclogites are also described. As for the Kaapvaal craton granulites, we have analysed several samples from different kimberlites of the area, but only two of them are discussed in the present manuscript. Data points from sample L02100 define a regression line with a lower intercept at 102.7 ± 3.6/3.9 Ma (MSWD = 1.05; n = 37/41; Fig. 5c), whereas the analyses of sample L212 define a regression line with a lower intercept at 105.5 ± 2.5/2.9 Ma (MSWD = 0.92; n = 34/48; Fig. 5d). Both samples have relatively homogeneous U contents of 14–16 ng g^{-1} on average. Sample L212 also shows a homogeneous Pb content between 0.5 and 4 ng g^{-1}, whereas sample L02100 display a higher variability with up to 14 ng g^{-1} (Fig. 4, Table S6).

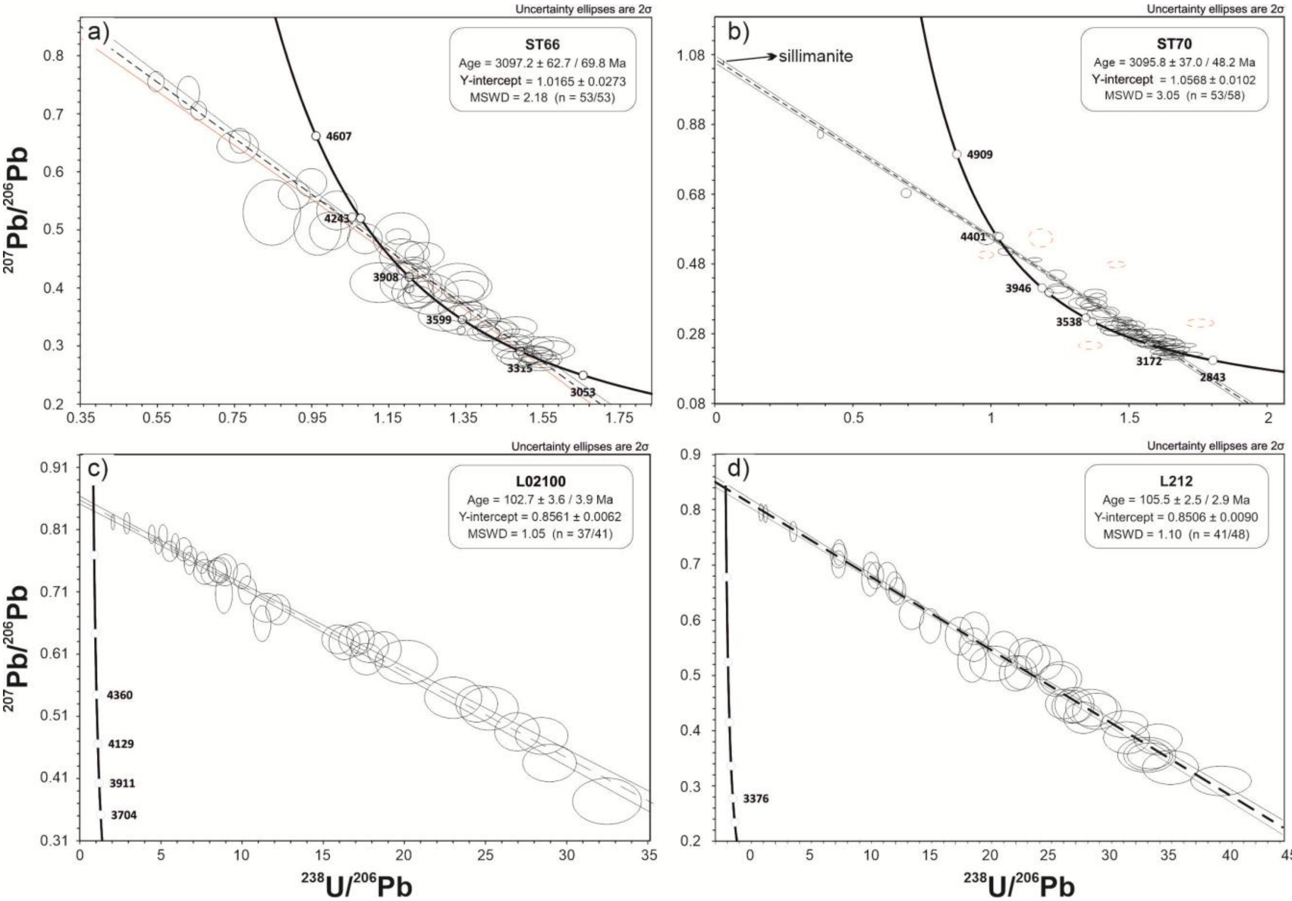

Figure 5. Tera-Wasserburg diagrams of garnet U-Pb analyses for the samples from Kaapvaal craton ST66 and ST70 (a and b; Shu et al., 2024) and Namaqua-Natal Belt, L02100 and L212 (c and d), respectively.

4 Discussion

4.1 Bulk uranium content: zircon vs. garnet

One of the main strengths of the LA-ICP-MS technique is its high spatial resolution. In contrast with the bulk dating method (TIMS), the laser ablation method only analyses a relatively small volume of the targeted mineral, and therefore, the bulk amount of U analysed is limited. Besides, not all the ablated material reaches the detector, and the useful yield for U (=ions detected/total number of atoms in sample volume for a species of interest, Schaltegger et al., 2015) is variable depending on the utilised instrument.

In the case of this study, the ablation of garnet with a 193 μm spot size, 15 Hz and ~2 J cm^{-2} for 18 seconds results in a *ca.* 15 μm deep ablation pit. The depth is variable depending on the composition of the garnet, typically between 8–22 μm. Figure 6 shows a representative ablation pit from sample L02100 together with its measured depth profile, and similar pit depth measurements were routinely performed on all analysed samples to estimate the average ablated volume as accurately as possible. Considering an average pit depth of 15 µm, each analysis corresponds to a total volume of *ca.* 600,000 μm^3 or 2.3 µg of ablated material, assuming a mean garnet density of 3.9 g cm^{-3} (Table 1). Li et al. (2022) recently reported skarn garnet with up to 75 µg g^{-1} U. Applying the above calculations, this corresponds to *ca.* 100 pg U per ablated spot, and *ca.* 8 pg U and 0.4 pg Pb for a Mali garnet analysis (6 µg g^{-1} U and 0.3 µg g^{-1} Pb, Seman et al., 2017). However, the metamorphic garnet rarely exceeds U concentrations of ~100 ng g^{-1} (Deng et al., 2022). For example, a regional metamorphic garnet with 90 ng g^{-1} U (sample SS-1 of Millonig et al., 2020) would yield *ca.* 0.1 pg U per analytical spot. In the present study, sample ST66 has the lowest U concentration, with an average concentration of 1.1 ng g^{-1}. The total U ablated during such a spot analysis is *ca.* 1 fg (femtogram; 10^{-15} g). This is *ca.* 3,500 times less U than for a renowned GJ-1 zircon analysis (287 µg/g U_{avg}; 26 µg/g Pb_{avg}, Jackson et al., 2004), which yields 3.5 pg of U and 0.30 pg of Pb per spot, calculated for a 20 µm spot size, 15 µm pit depth and *ca.* 10 ng of ablated material (considering a zircon density of 4.65 g cm^{-3}) (Table 1).

Material / Sample	U concentration (ng g^{-1})	Total U per spot (pg)
GJ-1 zircon (Jackson et al., 2004)	287,000	3.5
Mali garnet (Seman et al., 2017)	6,000	~8
Skarn garnet (Li et al., 2022)	75,000	~100
Metamorphic garnet SS-1 (Millonig et al., 2020)	90	~0.10
Namaqua–Natal eclogite L212	14	~0.032
Orlica–Śnieżnik granulite (G99-2)	2–4	~0.003–0.009
Cabo Ortegal demantoid	1.3	~0.002
Kaapvaal granulite ST66	0.7	~0.001

Table 1. Comparison of U content analysed in a single LA-ICP-MS spot analysis for different minerals. Total U per spot was calculated from the average U concentration of each material and the corresponding ablated mass. Garnet calculations assume a 193 µm spot diameter, ~15 µm pit depth, a density of 3.9 g cm^{-3}, and an ablated mass of ~2.3 µg per analysis. The GJ-1 zircon calculation assumes a 20 µm spot diameter, ~15 µm pit depth, a density of 4.65 g cm^{-3}, and an ablated mass of ~0.012 µg. The table illustrates the extreme reduction in available parent isotope mass when dating low-U metamorphic garnet, with the ST66 granulite analyses containing only ~1 fg U per spot, approximately 3,500 times less U than a typical GJ-1 zircon analysis and up to five orders of magnitude less than high-U skarn garnet.

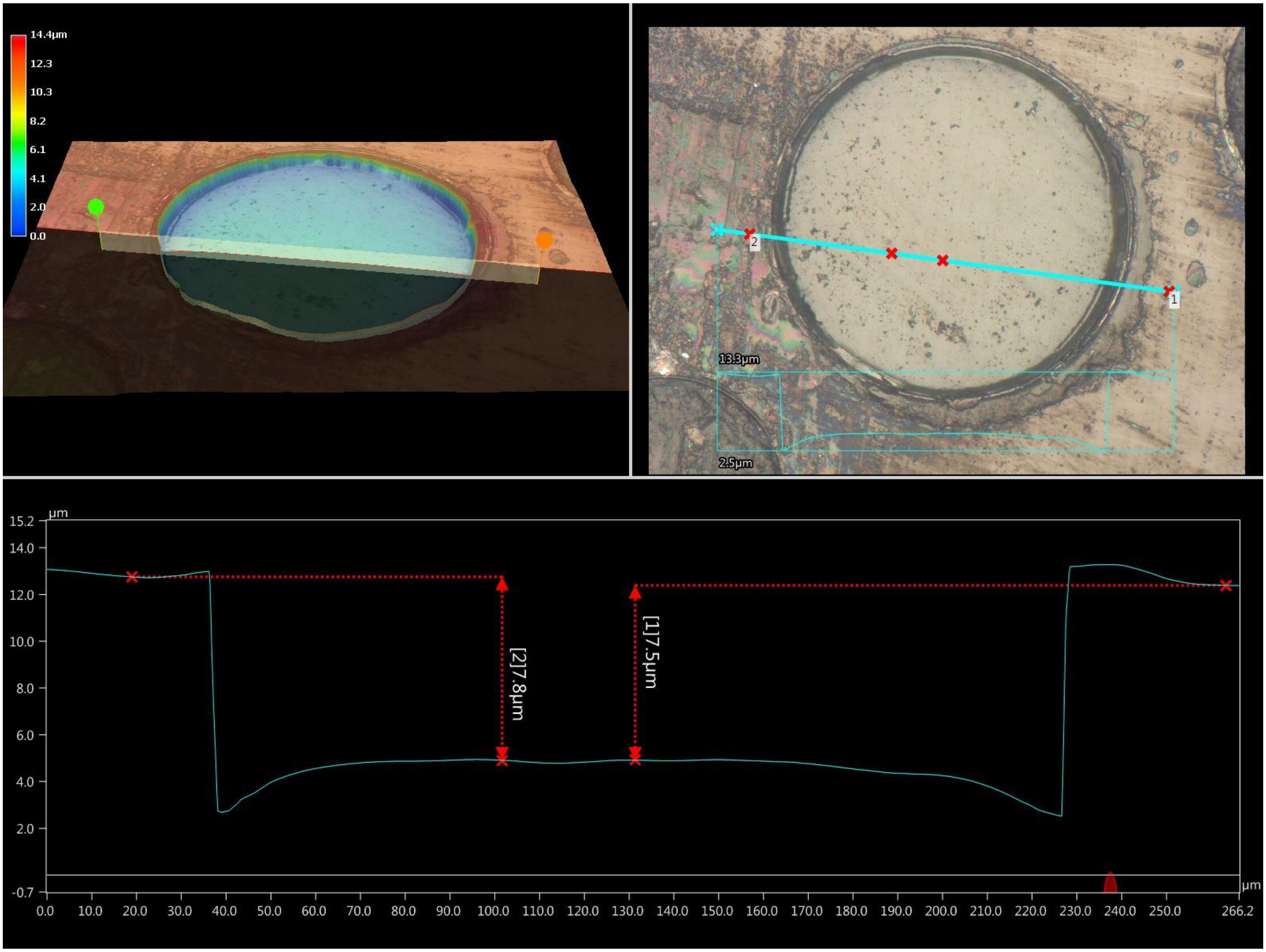

Figure 6. Illustrative example of an LA-ICP-MS ablation pit produced in garnet (sample L02100) using a 193 µm spot size, 15 Hz repetition rate, a fluence of ~2 J cm^{-2}, and an ablation time of 18 s. The image was acquired with a Keyence digital microscope. a) Three-dimensional topographic image of the ablated pit. b) Optical image showing the position of the measured depth profile. c) Corresponding depth profile across the pit. The illustrated pit is approximately 8 µm deep; pit depths measured for different garnet typically range from 8 µm to 22 µm, depending on garnet composition.

Samples with even lower amounts of U could be analysed, if they are older and have higher ^{238}U than ^{206}Pb for the majority of the spots (as well as ^{206}Pb > ^{207}Pb), with the exception of the high common-Pb analyses. As an example, a 200 Ma old concordant analysis will have *ca.* 30 times more ^{238}U than ^{206}Pb and *ca.* 20 times more ^{206}Pb than ^{207}Pb (or 600 times more ^{238}U than ^{207}Pb). In turn, a 3 Ga sample intercepts the Concordia at *ca.* 1.5 (^{238}U/^{206}Pb) and 0.25 (^{207}Pb/^{206}Pb), the ^{238}U being only *ca.* 6 times more abundant than ^{207}Pb. Hence, for such old samples, it would be possible to date a garnet with even lower U concentrations.

4.2 Background level, limit of detection, limit of quantification and analytical precision

Such low U and Pb concentrations in garnet correspond to a few hundred counts per second (cps), and therefore, the background level plays a vital role, especially for ^{207}Pb, the least abundant of the measured isotopes. Background Pb may come from different sources, such as a memory effect in the tubing, contamination/dirt in gas-line connections, the cones or the laser cell. Although careful cleaning of those parts is effective in reducing their Pb contribution, Pb derived from the Ar and He gas supplies is unavoidable. This contribution varies from day to day (Fig. 7 shows the background level at the FIERCE laboratory observed over one and a half years), and it is a critical factor for the analytical performance. Following the approach proposed by Pettke et al. (2012), the limits of detection for average background signals of 10 cps and 400 cps are approximately 6 pg g^{-1} and 30 pg g^{-1}, respectively (corresponding to net signals of 2 cps and 8 cps at the detection limit, considering the aforementioned sensitivity of 250,000 cps per µg g^{-1}). Although the background intensity differs by a factor of 40 in these examples, the limit of detection increases by only about a factor of 4-5 because the background count rate enters the calculation under the square root. On the contrary, the limit of quantification (Currie, 1995), defined as 10 times the standard deviation of the measured background signal, drastically increases with increasing background intensity. For example, during low-background sessions, the standard deviation of the ^{207}Pb background can be as good as 5-6 cps, corresponding to a limit of quantification of approximately 50–60 cps (Fig.6). In contrast, during one of the highest-background sessions, the standard deviation is ca. 200 cps, increasing the limit of quantification to 2000 cps. Thus, a high Pb background prevents reliable analysis of low ^{207}Pb samples, as their signal falls below the quantification limit. In practice, samples with ultra-low-U and -Pb garnet are only analysed during sessions in which the ^{207}Pb background remains below 50 cps.

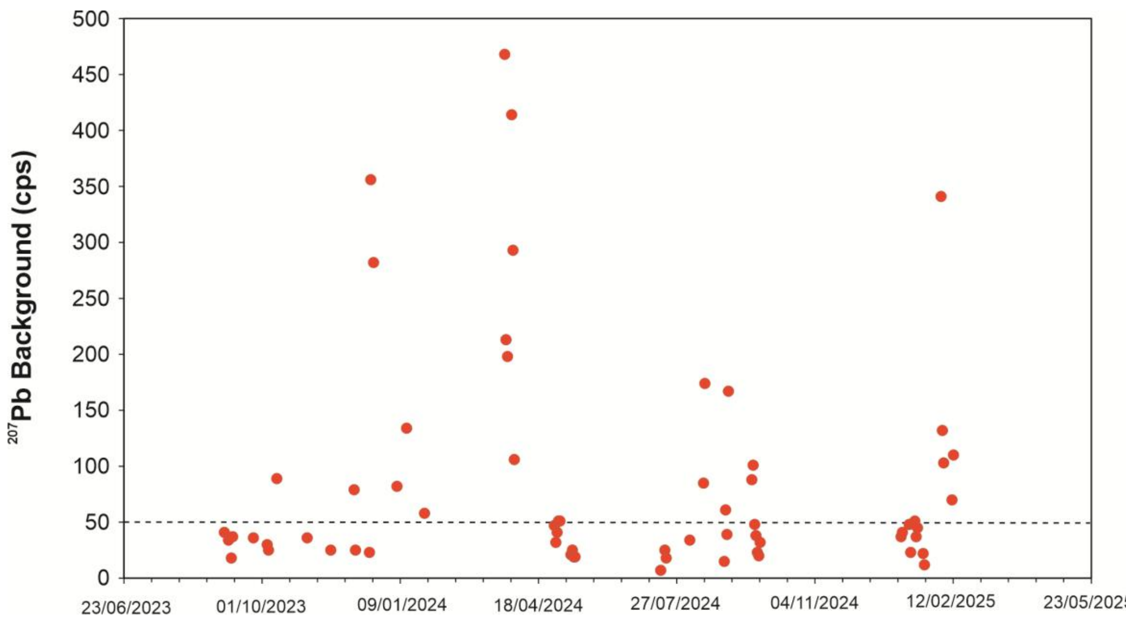

Figure 7. ^{207}Pb background (in cps) at the FIERCE laboratory during a period of ca. one and a half years. The spots show the average ^{207}Pb background for each of the days.

However, even though the Pb can be reliably detected, the precision of each analysis is also crucial. Figure 8 shows the relationship between the ^{207}Pb signal intensity and the within-run precision of the $^{207}Pb/^{206}Pb$ ratio, over several sequences covering a large range of ^{207}Pb concentrations. As could be expected from counting statistics, a lower ^{207}Pb signal results in a lower precision. Analyses yielding ^{207}Pb signals above 2,500 cps commonly achieve uncertainties of less than 1% (2 SE), whereas signals below 2,500 cps typically result in uncertainties above 1% (2 SE). Furthermore, as the signal gets closer to the limit of quantification (≤ 100 cps), there is a strong increase in the uncertainty, which highlights the limit of the technique.

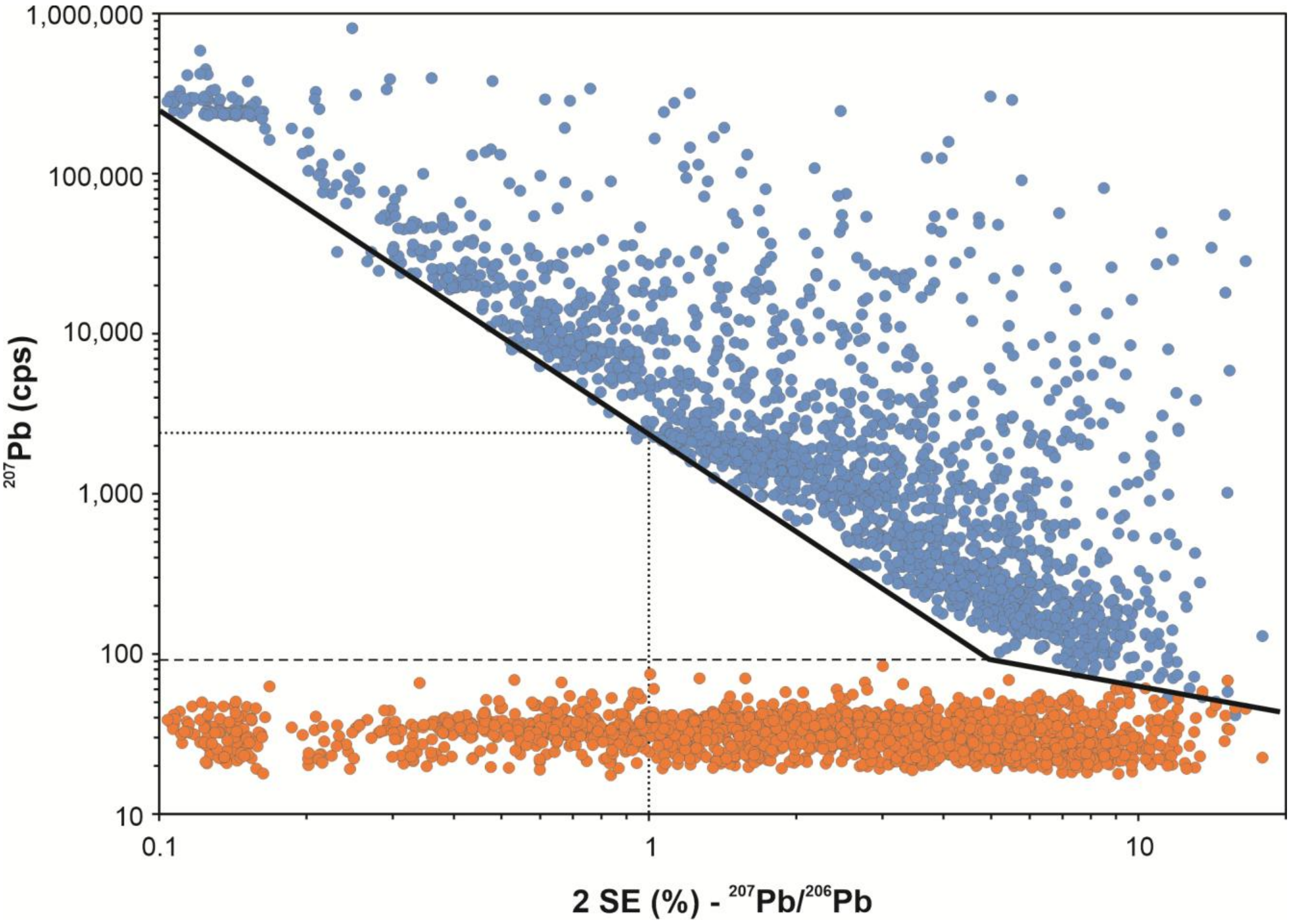

Figure 8. Relationship between the ^{207}Pb signal intensity and the within-run precision of the $^{207}Pb/^{206}Pb$ ratio (2SE, %; blue symbols). Orange symbols indicate the limit of quantification, calculated as ten times the standard deviation of the measured ^{207}Pb background signal (Currie, 1995). The black line represents the minimum achievable within-run precision as a function of the ^{207}Pb signal intensity. The pronounced increase in uncertainty below approximately 100 cps (horizontal dashed line) marks the practical analytical limit of the method. A ^{207}Pb signal of approximately 2500 cps (dotted lines) is typically required to achieve a within-run precision of ~1 % (2SE). Analytical uncertainties are smaller than the plotting symbols and are therefore not visible.

Another potential source of uncertainty, although it is not considered in our calculations, is the variance of the U decay, or in other words, the statistical uncertainty coming from the decay of a small number of radioactive atoms. In the case of dating high-U minerals, as well as old samples that have been decaying for a long time, such uncertainty can be considered negligible and that is likely why it is not considered in geochronology. However, physicists studying slow decay processes have discussed this phenomenon (e.g. Opendak and Wildenhain, 1994). In the case of low-U and young minerals (<1 ng g^{-1} U or <10 Ma old), this incertitude may be of importance and needs to be considered. Nonetheless, young samples with such a low content of U are currently not measurable with the analytical setup discussed in this study, as the amount of radiogenic ^{207}Pb may be below the limit of quantification.

In addition to the analytical precision of each individual spot measurement, the precision of U-Pb dating for non-concordant minerals like garnet when using a Tera-Wasserburg diagram is also controlled by how accurately the regression line can be defined. This strongly depends on the variability of the $^{238}U/^{206}Pb$ and $^{207}Pb/^{206}Pb$ ratios; while samples with high common-Pb contributions tend to cluster near the upper intercept, a larger spread in these ratios yields a smaller uncertainty on the lower intercept with the Concordia curve and, consequently, a more precise age. The internal precision for the analyses of the Cabo Ortegal demantoid are ± 4.7 % and ± 6.3 % for the absolute garnet ages, even with only 40 analytical spots and an extremely low U concentration (mainly below 1 ng g^{-1}, Fig. 4). In turn, U concentrations of 2–4 ng g^{-1}, as for the G99-2 garnet (Orlica-Śnieżnik granulite), significantly improve the precision to ca. ± 3 % absolute age uncertainty. Furthermore, the analyses of sample ST70 resulted in an internal age precision of ca. ± 1 %. In this case, two factors concurred to result in such precise data: I) higher U and Pb contents and II) the Archean age of the sample, as older samples benefit the most from the technique due to their more abundant daughter isotopes ^{206}Pb and ^{207}Pb. However, in samples as young as the Cretaceous Namaqua-Natal belt eclogites, we have obtained precisions of ca. ±3 % at U concentrations of ca. 14–16 ng g^{-1}. The results obtained for the demantoid in two independent sessions are reproducible within uncertainty. Likewise, the U-Pb age of the garnet from G99-2, 384 ± 12 Ma, is in agreement with the Lu-Hf age reported by Anczkiewicz et al. (2007, 387 ± 5 Ma). Thus, the procedure described in this study produces accurate results within the internal precision of the technique.

4.3 Applications of the technique

U-Pb dating of garnet is becoming a relatively common tool, above all for skarn garnet, as they typically contain several µg g^{-1} of U (e.g., Reinhardt et al., 2022). However, the applicability of the technique is rather limited in metamorphic, typically almandine-pyrope, garnet due to their low U content (Millonig et al., 2020; Cerva-Alves et al., 2021; Schannor et al., 2021; O'Sullivan et al., 2023; Mark et al., 2023; Peillod et al., 2024; Manzotti et al., 2025), and the common presence of high-U mineral inclusions. The method described here allows for the analysis of very low-U garnet, or a reduction in laser spot sizes to avoid inclusions (cf. Walters et al., 2025) and thus has enormous potential to become a routine tool for petro(chrono)logical investigations.

Moreover, due to the high closure temperature of the U-Pb system in garnet (exceeding 1050-1100 ºC; Shu et al., 2024), it appears to be the most reliable method for dating its formation and thus the associated mineral reactions. In many cases, these events cannot be accurately constrained by traditional geochronometers like zircon, apatite, rutile, or monazite due to inherent limitations in such settings. For instance, rutile exhibits relatively low U-Pb closure temperatures (<600 °C, depending on grain size; Cherniak, 2000; Zack and Kooijman, 2017). Similarly, minerals like apatite and monazite are prone to fluid-assisted coupled dissolution–reprecipitation or recrystallisation during subsequent hydrothermal events (e.g., Harlov et al., 2002; 2011; Putnis, 2009). Conversely, highly resilient minerals like zircon frequently retain inherited domains that complicate both their geochronological analysis and geological interpretation (e.g., Rubatto, 2017). Furthermore, if such minerals occur as inclusions within garnet, they may remain shielded from fluid interaction, thereby recording pre-metamorphic ages. Finally, many of these accessory phases are scarce or absent in mafic and ultramafic rocks. The granulite and eclogite xenoliths from the Kaapvaal craton and Namaqua-Natal belt analysed here are good examples, similar to the peridotitic garnet dated by O'Sullivan et al. (2023). Even though scarce rutile has been found in a few samples, the most common mineral assemblage is formed only by garnet and clinopyroxene. In addition, the low U content and their small grain sizes do not necessarily make metamorphic rutile a better geochronometer. In this work, we have successfully dated garnet from those geological contexts, despite their very low U contents. Larger sample sets of both the Kaapvaal craton granulites and the Namaqua-Natal belt eclogites have been analysed, and the results are reported and discussed in Shu et al. (2024).

Likewise, at present, the only possible way to date the hydrothermal garnet-chlorite-serpentine veins crosscutting the pyroxenites at Cabo Ortegal is by U-Pb dating of the Cabo Ortegal demantoid. The rock is near-monomineralic garnet, and because the associated chlorite lacks K and Rb, traditional K–Ar or Rb–Sr geochronological techniques cannot be applied. As the garnet occurs in fissures cutting across the foliation of the pyroxenite, and likely the whole complex in depth, ages younger than the plutons of the area were expected (youngest plutons are ca. 280 Ma, Rodriguez et al., 2007). The results of ca. 255 Ma obtained here are similar to the Aia Pluton age in the westernmost Pyrenees (dated to 267 Ma, Denèle et al., 2012). Those authors interpreted the age as reflecting the earliest evidence of an extensive regime that led later to the formation of the Bay of Biscay rift. Thus, the garnet-bearing veins at the Cabo Ortegal Complex may have formed during the same event.

The speed of data acquisition provided by laser-ablation techniques also allows for obtaining a large dataset in a short time (, in contrast to the more precise acid-digestion-based garnet dating methods (Lu-Hf and Sm-Nd; e.g., Münker et al., 2001; Anczkiewicz and Thirlwall, 2003). This gives the opportunity to investigate a larger number of samples, either with a higher sampling density in a given area of investigation, or by extending the investigation to a much larger area. In some cases, a larger dataset can reveal small-scale metamorphic processes that have been hidden due to sampling bias (including samples not analysed due to the appearance of alteration). For instance, the U-Pb age of garnet from the NE Bohemian Massif obtained here is within the uncertainty of the Lu-Hf age of this sample (Anczkiewicz et al., 2007). Walczak et al. (2017) dated other mesocratic and mafic granulites from the same outcrop sampled by Anczkiewicz et al. (2007) using the same analytical protocols. Their results pointed to a younger event of garnet formation at *ca.* 345–340 Ma and they attributed this inconsistency to a contribution of inherited Hf in the whole-rock analysis of Anczkiewicz et al. (2007). The *in-situ* U-Pb dating in garnet circumvents the inherited Hf issue as potential inclusions can be avoided by direct petrographic observations (i.e. setting spots in clean domains) or rejecting analysis with distinct U and/or Pb content (Fig. 2). In any case, the fact that the sample analysed by Walczak et al. (2017) is not exactly the same, may indicate that the geological evolution of the area is more complex (polymetamorphic?) than previously thought.

5 Conclusions

This study demonstrates that meaningful U–Pb ages can be obtained by LA-MC-ICP-MS from garnet containing U concentrations lower than 1 ng g^{-1}. The analysis of all Pb and U isotopes using ion counters, combined with high-sensitivity analytical conditions, permits reliable regression lines to be defined in Tera–Wasserburg space, even for minerals that contain up to 300,000 times less U than commonly analysed accessory minerals such as the GJ1 reference zircon.

The method yields reproducible and geologically meaningful ages across a wide range of sample ages and compositions. Independent analytical sessions on the Cabo Ortegal demantoid produced indistinguishable ages within uncertainty, while the age obtained for the Orlica–Śnieżnik granulite garnet agrees with previously published Lu–Hf data. The precision achieved depends on the U and Pb concentrations, with internal uncertainties of ca. ±5–6 % for garnet containing <1 ng g^{-1} U and ca. ±3 % for samples with higher U contents (2–4 ng g^{-1}). Moreover, in Archean samples, uncertainties as low as ±1 % were achieved, as older samples benefit from their higher radiogenic Pb contents.

These results significantly expand the applicability of in-situ garnet U–Pb geochronology. As most of the metamorphic garnet contain only a few ng g^{-1} U or less, this analytical approach opens the possibility of dating a much broader range of metamorphic rocks. The methodology described here provides a valuable new tool for petrochronology and for directly constraining the timing of garnet growth, prograde metamorphism, and deep crustal processes. Garnet U-Pb geochronology can be used together with other conventional accessory mineral geochronometers but may be particularly powerful in geological settings where such chronometers are absent, scarce, or unsuitable.

Data availability

The data presented in this manuscript are available in the supplementary material.

Author contributions

AB conceptualised the study, obtained funding and carried out the formal analyses. Data curation, validation, and writing were done by all the authors through a continuous discussion process.

Competing interests

The authors declare that they have no conflict of interest.

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