

1 U-Pb dating of sub-ng g⁻¹ U garnet by LA-MC-ICP-MS

2 Aratz Beranoaguirre^{1,2}, Leo J. Millonig^{1,2}, Richard Albert^{1,2}, Horst R. Marschall^{1,2}, and Axel Gerdes^{1,2}

3 ¹Frankfurt Isotope and Element Research Center (FIERCE), Goethe-University Frankfurt, 60438 Frankfurt am Main, Germany

4 ²Goethe-University Frankfurt, Department of Geosciences, 60438 Frankfurt am Main, Germany

5 *Correspondence to:* Aratz Beranoaguirre (beranoaguirre@fierce.uni-frankfurt.de)

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

20 1 Introduction

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

32 challenging for metamorphic garnet, since its U and Pb amounts are extremely low (Deng et al., 2022). Therefore, being
33 capable of developing a robust analytical strategy for analysing metamorphic garnet would represent a major advance in
34 metamorphic petrology.

35 Unlike many geochronological systems that either record cooling and exhumation histories (e.g., apatite fission-track,
36 (U–Th)/He, and Ar-based systems) or preferentially date high-temperature metamorphic events (e.g., zircon, monazite, and
37 titanite U–Pb geochronology) (Dodson, 1973; McDougall and Harrison, 1999; Rubatto, 2002; Reiners et al., 2005; Flowers et
38 al., 2009; Kohn et al., 2017), garnet can preserve prograde metamorphic growth histories over a wide range of pressure–
39 temperature conditions (Spear and Parrish, 1996; Caddick and Kohn, 2013), in part due to its exceptionally high closure
40 temperature for the U–Pb system (potentially exceeding 1000 °C; Dahl, 1997; Shu et al., 2024). Traditionally, garnet has been
41 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
42 through these systems, they require laborious mineral separation and dissolution procedures. More recently, the use of tandem
43 mass spectrometry (ICP-MS/MS) has also enabled the in-situ Lu–Hf garnet dating (Simpson et al., 2021). However, the
44 application of in-situ Lu–Hf geochronology remains largely restricted to relatively old metamorphic systems (Caledonian or
45 older; Tamblyn et al., 2022; Kirkland et al., 2025). This limitation may arise from the low radiogenic growth of ^{176}Hf in
46 younger garnet, which hampers analytical precision and age resolution in younger orogens. In contrast, U–Pb garnet
47 geochronology has been used to resolve younger metamorphic events (Peillod et al., 2024; Manzotti et al., 2025).
48 Consequently, U–Pb garnet geochronology (eventually complemented with in-situ Lu–Hf dating) offers a unique opportunity
49 to directly constrain the timing of prograde metamorphism and deep crustal processes.

50 In this study, we investigate the lower limits of the U and Pb concentrations in garnet required to obtain meaningful
51 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,
52 low-U metamorphic garnet specimens from granulites, eclogites, and one gemstone-quality grossular-andradite (i.e.
53 demantoid). The possibility to date garnet crystals with extremely low U concentrations ($<1\text{ ng g}^{-1}$) by LA-MC-ICP-MS is
54 expected to substantially increase the field of application of garnet U–Pb dating, as most of the metamorphic garnet have <50
55 ng g^{-1} U (Millonig et al., 2020; O’Sullivan et al., 2023; Bartoli et al., 2024; Shu et al., 2024).

56 2 Methodology

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

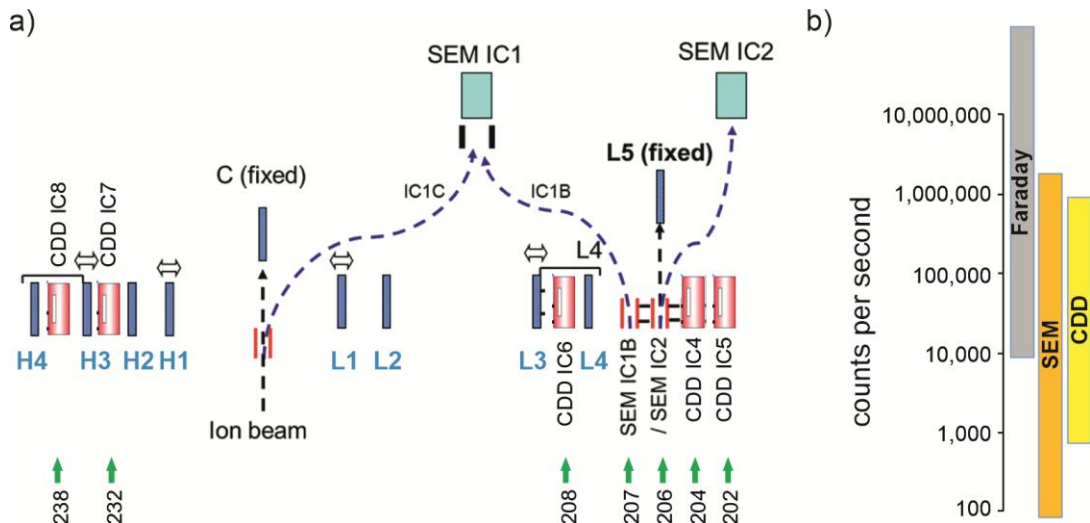


Figure 1. a) Schematic detector configuration of the Neptune Plus MC-ICP-MS used in this study, showing the positions and measured isotopes for the low-U analytical configuration (modified after Richter et al., 2016). b) Approximate signal intensity ranges covered by Faraday cups, secondary electron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

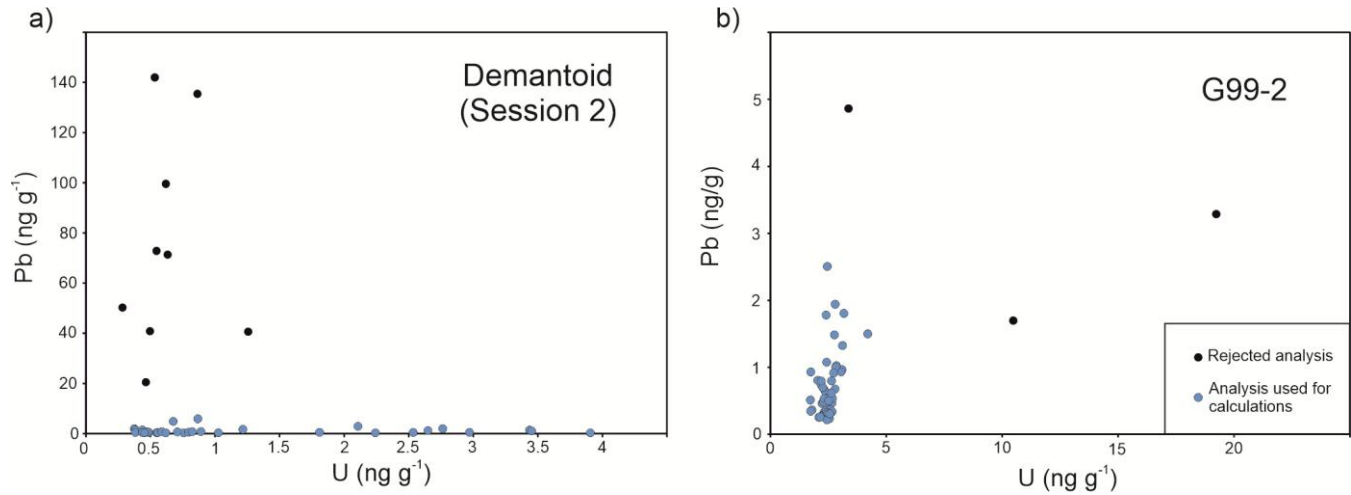
Ablation was performed in a He atmosphere (0.3 l min^{-1}) and mixed in the ablation funnel with daily tuned $0.95\text{--}1 \text{ l min}^{-1}$ Ar and $5\text{--}10 \text{ ml min}^{-1}$ N_2 . Signal strength at the MC-ICP-MS was tuned for maximum sensitivity while keeping oxide formation below 0.5 % (UO/U) and element fractionation low (e.g. Th/U ~ 0.9). This was done by line ablating the SRM NIST 614 glass (Jochum et al., 2011) using a $50 \mu\text{m}$ spot size, 6 Hz, *ca.* 3.5 J cm^{-2} fluence and a $3 \mu\text{m s}^{-1}$ line speed. The average sensitivity obtained with this setup was *ca.* 250,000 cps per $\mu\text{g g}^{-1}$ 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 $193 \mu\text{m}$ and a fluence of *ca.* 2 J cm^{-2} at 15 Hz. This yielded a depth penetration of *ca.* $0.8 \mu\text{m s}^{-1}$. 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 SRM NIST 614 was used as the primary reference material to correct for mass bias ($^{207}\text{Pb}/^{206}\text{Pb}$), inter-element fractionation and instrumental drift ($^{206}\text{Pb}/^{238}\text{U}$). 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. Stifreeva, 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 ²⁰⁷Pb/²⁰⁶Pb and ²⁰⁶Pb/²³⁸U 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 ²⁰⁷Pb/²⁰⁶Pb and ²³⁸U/²⁰⁶Pb 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.

106



107

Figure 2. Plots of U vs Pb concentration (ng g⁻¹), showing the analyses rejected and considered for the age calculations. A) Cabo Ortegual 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.

110

111 Matrix-matched reference materials (RMs) are an important component of any LA-ICP-MS method (e.g. Schaltegger
112 et al., 2015). With respect to garnet, only a few well-characterised RMs are available to the LA-ICP-MS community in
113 sufficient quantities, although many research groups have developed new RMs over the last few years (e.g. Stifreeva et al.,
114 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
115 garnet RMs for U–Pb dating are still the ones published by Seman et al. (2017); the red and yellow varieties of Mali Grandite
116 (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
117 Ma; (U-Th)/He: 35 ± 5 Ma). However, U concentrations of $>2 \mu\text{g g}^{-1}$ of the aforementioned garnet RMs would saturate the
118 ion counters, and thus, they are not usable for the method applied in this study. To overcome this issue, we investigated several
119 low-U ($<0.5 \mu\text{g g}^{-1}$) garnet from the same localities investigated by Seman et al. (2017), and we identified a yellow garnet
120 from the Mali Grandite locality with an average U concentration of 15–20 ng g^{-1} , which was subsequently used as the matrix-
121 matched RM. The secondary reference materials, used for quality control, were compositionally and optically diverse grossular
122 garnet crystals from Lake Jaco, and a dark brown grandite from Balochistan. When assuming the published age of 202 Ma for
123 the yellow Mali, we obtained internally consistent results across multiple sequences for the secondary garnet RMs and different
124 samples. Although no independent age estimates (i.e. TIMS ages) are available for our matrix-match and quality control RMs
125 we consider the obtained U-Pb ages as accurate within their analytical uncertainties, based on the facts that (1) the U-Pb ages
126 for the various Lake Jaco garnet crystals are within the uncertainty of the published ages from that locality (Seman et al., 2017),
127 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
128 (Anczkiewicz et al., 2007; section 3.2). However, we will (re-)calibrate these low-U garnet crystals against well-characterised
129 low-U garnet RMs, once they become available. Furthermore, this potential age ambiguity does not affect the purpose of this
130 contribution.

131 **3 Samples and results**

132 **3.1 Cabo Ortegal demantoid (Cabo Ortegal Complex, NW Iberian Massif)**

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

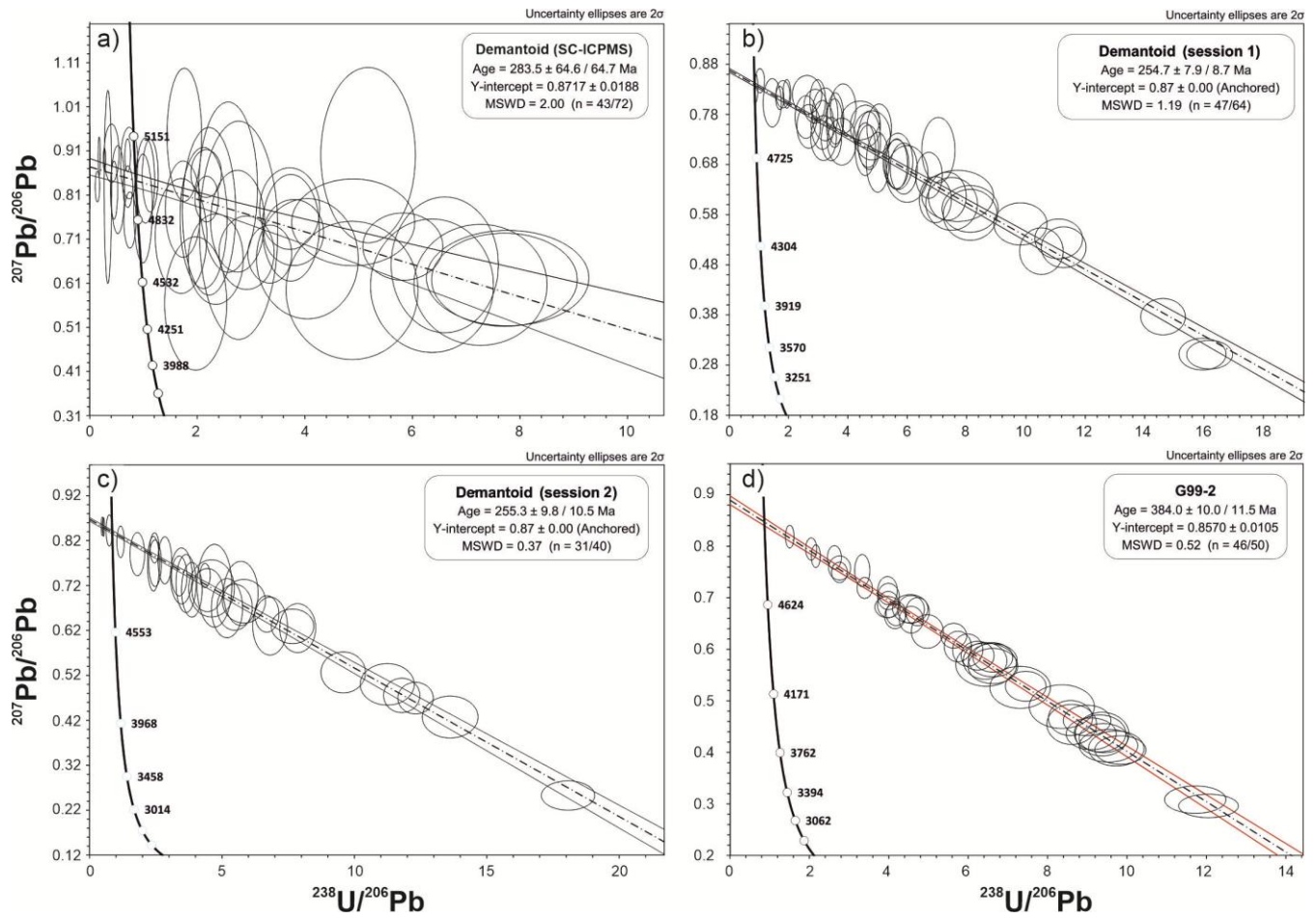
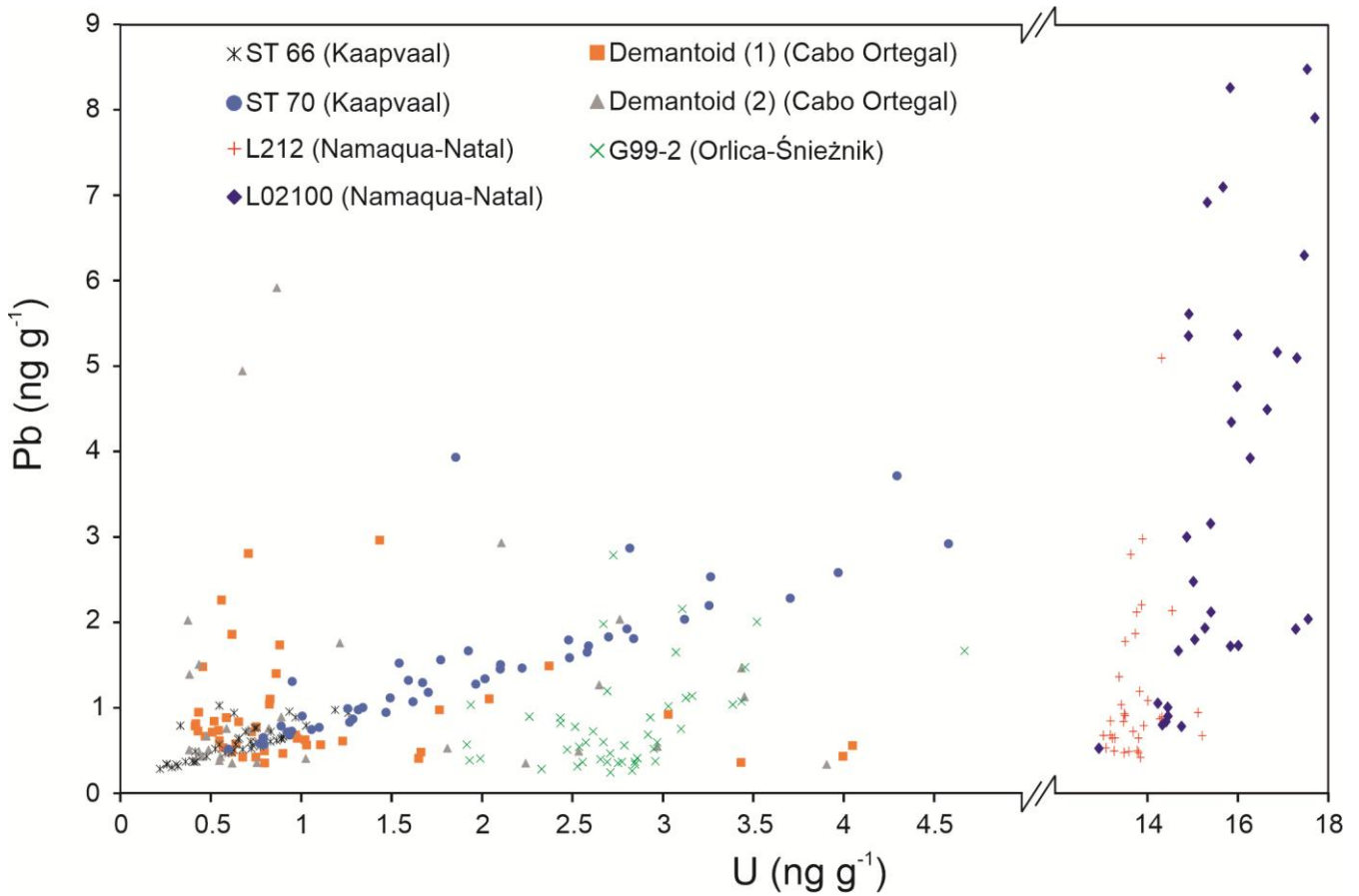


Figure 3. Tera-Wasserburg diagrams of garnet U-Pb analyses for Cabo Ortegal demantoid, analysed with the ElementXR single-collector ICP-MS (a) and Neptune MC-ICP-MS (b and c), and sample G99-2 from Orlica-Śnieżnik granulite(d).

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 $254.7 \pm 7.9/8.7$ Ma (MSWD = 1.19, n = 47/64, Fig. 3b) and $255.3 \pm 9.8/10.5$ Ma (MSWD = 0.37, n = 31/40, Fig. 3c). The regression lines were anchored to a $^{207}\text{Pb}/^{206}\text{Pb}$ 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).



153

154 **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**
 155 **scaling issues. Note the difference in the x-axis scale for the samples L212 and L02100. In the Kaapvaal samples, ²⁰⁸Pb was not**
 156 **measured and therefore, the Pb concentration is the sum of ²⁰⁴Pb+²⁰⁶Pb+²⁰⁷Pb. Note the discontinuity in the x-axis between 5 and 12**
 157 **ng g⁻¹. Analytical uncertainties are smaller than the plotting symbols and are therefore not visible.**

158 3.2 Orlica-Śnieżnik felsic granulite (NE Bohemian Massif)

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

163 The garnet analysed here corresponds to the felsic granulite G99-2 studied in detail by Anczkiewicz et al. (2007),
 164 who obtained garnet Lu-Hf and Sm-Nd ages of 387 ± 5 Ma and 320 ± 3 Ma, respectively. From the U-Pb analyses performed
 165 in our laboratory, an unanchored lower intercept age of $384.0 \pm 10.0/11.5$ Ma (MSDW = 0.52, n = 46, Fig. 3d) was calculated.
 166 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
 167 and 4; Table S4).

168 3.3 Granulite xenoliths from the Star kimberlite (Kaapvaal craton, South Africa)

169 Ultrahigh temperature (UHT) metamorphic crustal granulite xenoliths were found in four kimberlite diatremes from
170 along the central axis of the Witwatersrand basin in the central Kaapvaal craton (Schmitz and Bowring, 2003). The xenoliths
171 are K-free, Mg-Al-rich UHT granulites with abundant garnet, sillimanite, rutile, graphite and sulphides, and local occurrence
172 of sapphirine, orthopyroxene, plagioclase and quartz. Metamorphic conditions have been estimated at temperatures above
173 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
174 Ga (Schmitz and Bowring, 2003). The xenoliths were brought to the surface by Cretaceous kimberlite magmatism at
175 approximately 120 Ma.

176 The results of these samples have already been published and discussed in detail by Shu et al. (2024). The analyses
177 of the garnet in that publication followed the method described here, and considering that the aim of this work is purely
178 methodological, two examples of those rocks are shown: the one with the lowest U concentration (sample ST66) and the one
179 with the highest precision (ST 70). The latter was achieved by anchoring the regression line to a sillimanite crystal analysis,
180 assuming that both minerals are in equilibrium. The samples ST66 and ST70 define regression lines with lower intercepts at
181 $3096 \pm 63/70$ Ma (MSWD = 2.18, $n = 53/53$, Fig. 5a) and $3096 \pm 37/48$ Ma (MSWD = 3.05, $n = 53/58$, Fig. 5b). As stated
182 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,
183 whereas sample ST70 has a more variable U content, between 1 and 17 ng g⁻¹. Pb and U contents are positively correlated.
184 Unfortunately, it was not possible to measure the ²⁰⁸Pb isotope, so the calculated Pb content is the sum of ²⁰⁴Pb+²⁰⁶Pb+²⁰⁷Pb.
185 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
186 (Fig. 4; Table S5).

187 3.4 Eclogite xenoliths from the Namaqua-Natal Belt (South Africa)

188 Multiple Cretaceous kimberlite pipes occurring on the Proterozoic Namaqua-Natal-Fold Belt, which surrounds the
189 Archean Kaapvaal craton, have brought to the surface a significant amount of high-pressure eclogite, granulite and pyroxenite
190 xenoliths (Le Roex et al., 2020). The eclogites are mainly bimineralic (garnet-clinopyroxene) with accessory rutile and
191 coesite/quartz (and even diamond), although kyanite-bearing eclogites are also described. As for the Kaapvaal craton
192 granulites, we have analysed several samples from different kimberlites of the area, but only two of them are discussed in the
193 present manuscript. Data points from sample L02100 define a regression line with a lower intercept at $102.7 \pm 3.6/3.9$ Ma
194 (MSWD = 1.05; $n = 37/41$; Fig. 5c), whereas the analyses of sample L212 define a regression line with a lower intercept at
195 $105.5 \pm 2.5/2.9$ Ma (MSWD = 0.92; $n = 34/48$; Fig. 5d). Both samples have relatively homogeneous U contents of 14–16 ng
196 g⁻¹ on average. Sample L212 also shows a homogeneous Pb content between 0.5 and 4 ng g⁻¹, whereas sample L02100 display
197 a higher variability with up to 14 ng g⁻¹ (Fig. 4, Table S6).

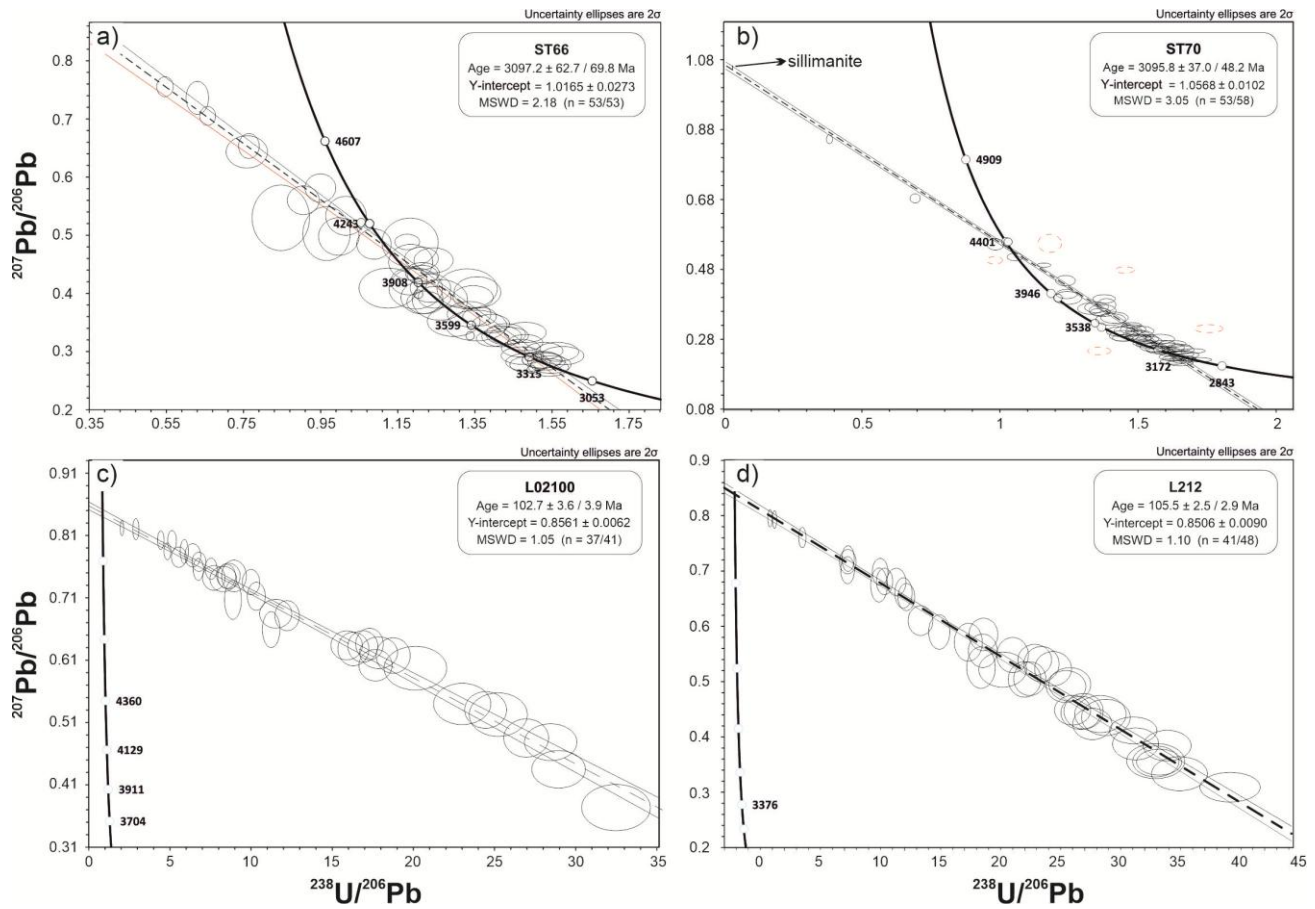


Figure 5. Tera-Wasserburg diagrams of garnet U-Pb analyses for the samples from Kaapvaal craton ST66 and ST70 (a and b; Shu et al., 2024) and Namaqua-Natal Belt, L02100 and L212 (c and d), respectively.

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 $\sim 2 \text{ J cm}^{-2}$ 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

212 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
 213 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
 214 with up to 75 $\mu\text{g g}^{-1}$ U. Applying the above calculations, this corresponds to *ca.* 100 pg U per ablated spot, and *ca.* 8 pg U and
 215 0.4 pg Pb for a Mali garnet analysis (6 $\mu\text{g g}^{-1}$ U and 0.3 $\mu\text{g g}^{-1}$ Pb, Seman et al., 2017). However, the metamorphic garnet rarely
 216 exceeds U concentrations of ~ 100 ng g^{-1} (Deng et al., 2022). For example, a regional metamorphic garnet with 90 ng g^{-1} U
 217 (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
 218 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
 219 (femtogram; 10^{-15} g). This is *ca.* 3,500 times less U than for a renowned GJ-1 zircon analysis (287 $\mu\text{g/g}$ U_{avg} ; 26 $\mu\text{g/g}$ Pb_{avg} ,
 220 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
 221 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

222
 223 **Table 1. Comparison of U content analysed in a single LA-ICP-MS spot analysis for different minerals. Total U per**
 224 **spot was calculated from the average U concentration of each material and the corresponding ablated mass. Garnet**
 225 **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**
 226 **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} ,**
 227 **and an ablated mass of ~ 0.012 μg . The table illustrates the extreme reduction in available parent isotope mass when**
 228 **dating low-U metamorphic garnet, with the ST66 granulite analyses containing only ~ 1 fg U per spot, approximately**
 229 **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.**

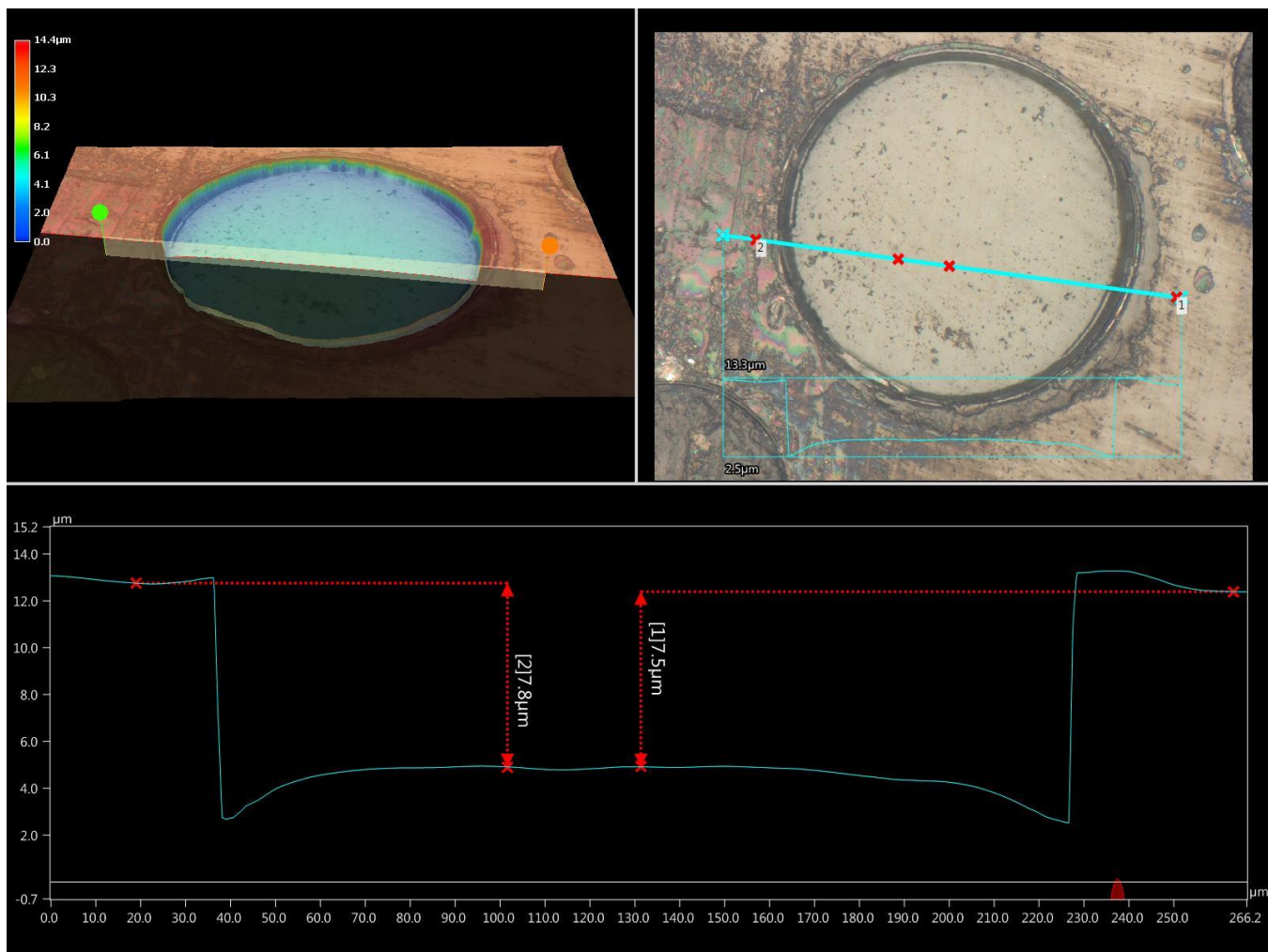
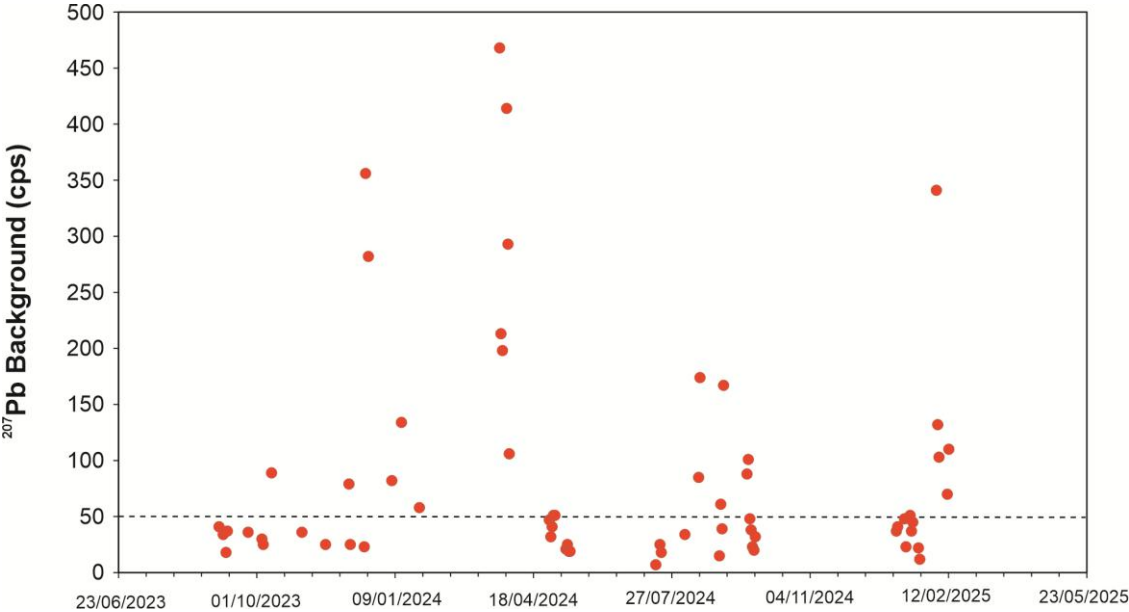


Figure 6. Illustrative example of an LA-ICP-MS ablation pit produced in garnet (sample L02100) using a 193 μm spot size, 15 Hz repetition rate, a fluence of $\sim 2 \text{ J cm}^{-2}$, and an ablation time of 18 s. The image was acquired with a Keyence digital microscope. a) Three-dimensional topographic 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 $^{206}\text{Pb} > ^{207}\text{Pb}$), 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 ($^{238}\text{U}/^{206}\text{Pb}$) and 0.25 ($^{207}\text{Pb}/^{206}\text{Pb}$), 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.

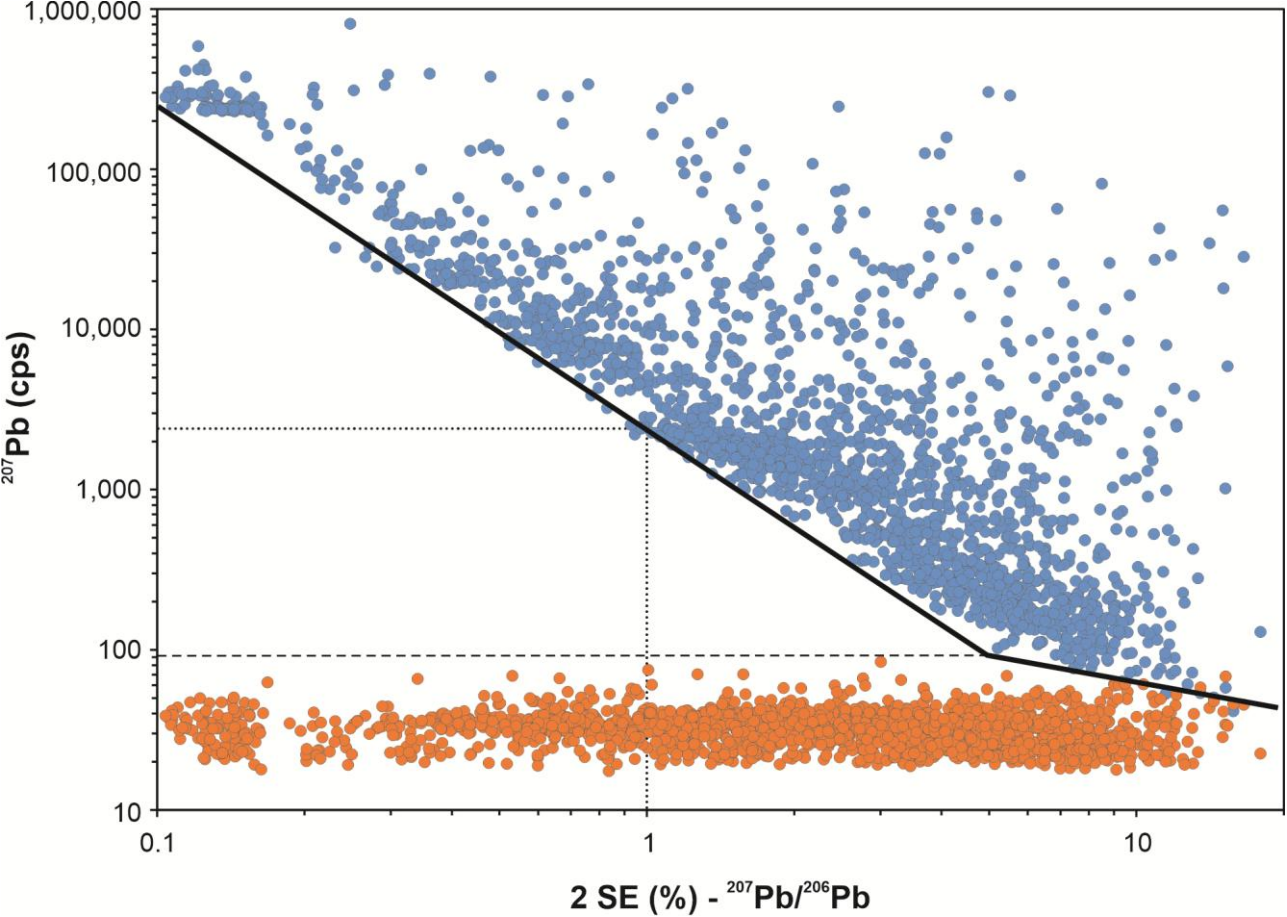
242 **4.2 Background level, limit of detection, limit of quantification and analytical precision**

243 Such low U and Pb concentrations in garnet correspond to a few hundred counts per second (cps), and therefore, the
244 background level plays a vital role, especially for ^{207}Pb , the least abundant of the measured isotopes. Background Pb may come
245 from different sources, such as a memory effect in the tubing, contamination/dirt in gas-line connections, the cones or the laser
246 cell. Although careful cleaning of those parts is effective in reducing their Pb contribution, Pb derived from the Ar and He gas
247 supplies is unavoidable. This contribution varies from day to day (Fig. 7 shows the background level at the FIERCE laboratory
248 observed over one and a half years), and it is a critical factor for the analytical performance. Following the approach proposed
249 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
250 ¹ and 30 pg g⁻¹, respectively (corresponding to net signals of 2 cps and 8 cps at the detection limit, considering the
251 aforementioned sensitivity of 250,000 cps per $\mu\text{g g}^{-1}$). Although the background intensity differs by a factor of 40 in these
252 examples, the limit of detection increases by only about a factor of 4-5 because the background count rate enters the calculation
253 under the square root. On the contrary, the limit of quantification (Currie, 1995), defined as 10 times the standard deviation of
254 the measured background signal, drastically increases with increasing background intensity. For example, during low-
255 background sessions, the standard deviation of the ^{207}Pb background can be as good as 5-6 cps, corresponding to a limit of
256 quantification of approximately 50–60 cps (Fig.6). In contrast, during one of the highest-background sessions, the standard
257 deviation is ca. 200 cps, increasing the limit of quantification to 2000 cps. Thus, a high Pb background prevents reliable
258 analysis of low ^{207}Pb samples, as their signal falls below the quantification limit. In practice, samples with ultra-low-U and -
259 Pb garnet are only analysed during sessions in which the ^{207}Pb background remains below 50 cps.



260
261 **Figure 7. ^{207}Pb background (in cps) at the FIERCE laboratory during a period of ca. one and a half years. The spots**
262 **show the average ^{207}Pb background for each of the days.**

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



269 **Figure 8. Relationship between the ^{207}Pb signal intensity and the within-run precision of the $^{207}\text{Pb}/^{206}\text{Pb}$ ratio (2SE, %;**
 270 **blue symbols). Orange symbols indicate the limit of quantification, calculated as ten times the standard deviation of the**
 271 **measured ^{207}Pb background signal (Currie, 1995). The black line represents the minimum achievable within-run**
 272 **precision as a function of the ^{207}Pb signal intensity. The pronounced increase in uncertainty below approximately 100**
 273 **cps (horizontal dashed line) marks the practical analytical limit of the method. A ^{207}Pb signal of approximately 2500**
 274 **cps (dotted lines) is typically required to achieve a within-run precision of ~1 % (2SE). Analytical uncertainties are**
 275 **smaller than the plotting symbols and are therefore not visible.**
 276

277 Another potential source of uncertainty, although it is not considered in our calculations, is the variance of the U
278 decay, or in other words, the statistical uncertainty coming from the decay of a small number of radioactive atoms. In the case
279 of dating high-U minerals, as well as old samples that have been decaying for a long time, such uncertainty can be considered
280 negligible and that is likely why it is not considered in geochronology. However, physicists studying slow decay processes
281 have discussed this phenomenon (e.g. Opendak and Wildenhain, 1994). In the case of low-U and young minerals ($<1 \text{ ng g}^{-1} \text{ U}$
282 or $<10 \text{ Ma}$ old), this uncertainty may be of importance and needs to be considered. Nonetheless, young samples with such a
283 low content of U are currently not measurable with the analytical setup discussed in this study, as the amount of radiogenic
284 ^{207}Pb may be below the limit of quantification.

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

300 4.3 Applications of the technique

301 U-Pb dating of garnet is becoming a relatively common tool, above all for skarn garnet, as they typically contain
302 several $\mu\text{g g}^{-1}$ of U (e.g., Reinhardt et al., 2022). However, the applicability of the technique is rather limited in metamorphic,
303 typically almandine-pyropes, garnet due to their low U content (Millonig et al., 2020; Cerva-Alves et al., 2021; Schannor et al.,
304 2021; O'Sullivan et al., 2023; Mark et al., 2023; Peillod et al., 2024; Manzotti et al., 2025), and the common presence of high-
305 U mineral inclusions. The method described here allows for the analysis of very low-U garnet, or a reduction in laser spot sizes
306 to avoid inclusions (cf. Walters et al., 2025) and thus has enormous potential to become a routine tool for petro(chrono)logical
307 investigations.

308 Moreover, due to the high closure temperature of the U-Pb system in garnet (exceeding $1050\text{--}1100 \text{ }^{\circ}\text{C}$; Shu et al.,
309 2024), it appears to be the most reliable method for dating its formation and thus the associated mineral reactions. In many

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

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

332 The speed of data acquisition provided by laser-ablation techniques also allows for obtaining a large dataset in a short
333 time (, in contrast to the more precise acid-digestion-based garnet dating methods (Lu-Hf and Sm-Nd; e.g., Münker et al.,
334 2001; Ancykiewicz and Thirlwall, 2003). This gives the opportunity to investigate a larger number of samples, either with a
335 higher sampling density in a given area of investigation, or by extending the investigation to a much larger area. In some cases,
336 a larger dataset can reveal small-scale metamorphic processes that have been hidden due to sampling bias (including samples
337 not analysed due to the appearance of alteration). For instance, the U-Pb age of garnet from the NE Bohemian Massif obtained
338 here is within the uncertainty of the Lu-Hf age of this sample (Ancykiewicz et al., 2007). Walczak et al. (2017) dated other
339 mesocratic and mafic granulites from the same outcrop sampled by Ancykiewicz et al. (2007) using the same analytical
340 protocols. Their results pointed to a younger event of garnet formation at ca. 345–340 Ma and they attributed this inconsistency
341 to a contribution of inherited Hf in the whole-rock analysis of Ancykiewicz et al. (2007). The *in-situ* U-Pb dating in garnet
342 circumvents the inherited Hf issue as potential inclusions can be avoided by direct petrographic observations (i.e. setting spots
343 in clean domains) or rejecting analysis with distinct U and/or Pb content (Fig. 2). In any case, the fact that the sample analysed

344 by Walczak et al. (2017) is not exactly the same, may indicate that the geological evolution of the area is more complex
345 (polymetamorphic?) than previously thought.

346 **5 Conclusions**

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

351 The method yields reproducible and geologically meaningful ages across a wide range of sample ages and
352 compositions. Independent analytical sessions on the Cabo Ortegal demantoid produced indistinguishable ages within
353 uncertainty, while the age obtained for the Orlica–Śnieżnik granulite garnet agrees with previously published Lu–Hf data. The
354 precision achieved depends on the U and Pb concentrations, with internal uncertainties of ca. ±5–6 % for garnet containing <1
355 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
356 ±1 % were achieved, as older samples benefit from their higher radiogenic Pb contents.

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

363 **Data availability**

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

365 **Author contributions**

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

368 **Competing interests**

369 The authors declare that they have no conflict of interest.

370 **Acknowledgements**

371 We would like to thank Drs. Sonja Aulbach, Jose Ignacio Gil Ibarra, Qiao Shu and Robert Anczkiewicz for sharing
372 the samples analysed in this study. The help of Linda Marko and Alex Schmidt with the day-to-day operation of the instruments
373 makes everything easier. We also sincerely thank one anonymous reviewer, Dr. Ariela Mazoz and Dr. Martin Hugo Senger
374 for their constructive and insightful reviews, which significantly improved the manuscript. Finally, we thank associate editor
375 Dr. Brenhin Keller and handling editor Prof. Dr. Klaus Mezger for their careful handling of the review process.

376 **Financial support**

377 This work has been supported by the Deutsche Forschungsgemeinschaft (DFG) project number 521366037, granted
378 to AB. FIERCE is financially supported by the Deutsche Forschungsgemeinschaft (DFG: INST 161/921-1 FUGG, INST
379 161/923-1 FUGG and INST 161/1073-1 FUGG), and received financial support from the Wilhelm and Else Heraeus
380 Foundation, which is gratefully acknowledged. This is FIERCE contribution No. 253.

381 **References**

382 Anczkiewicz, R. and Thirlwall, M. F.: Improving precision of Sm–Nd garnet dating by H₂SO₄ leaching: A simple solution to
383 the phosphate inclusion problem, Spec. Publ. - Geol. Soc. Lond., 220, 83–91, <https://doi.org/10.1144/GSL.SP.2003.220.01.05>,
384 2003.

385 Anczkiewicz, R., Szczepański, J., Mazur, S., Storey, C., Crowley, Q., Villa, I. M., Thirlwall, M. F., and Jeffries, T. E.: Lu–Hf
386 geochronology and trace element distribution in garnet: implications for uplift and exhumation of ultra-high pressure granulites
387 in the Sudetes, SW Poland, Lithos, 95, 363–380, <https://doi.org/10.1016/j.lithos.2006.09.001>, 2007.

388 Arrowsmith, P.: Laser ablation of solids for elemental analysis by inductively coupled plasma mass spectrometry, Anal. Chem.,
389 59, 1437–1444, <https://doi.org/10.1021/ac00137a014>, 1987.

390 Aysal, N., Guillong, M., Bayanova, T., Fukuyama, M., Leonard, N., Yılmaz, İ., Varol, E., Tükel, F. Ş., Kadioğlu, Y. K.,
391 Haniç, N., Uzun, F., and Kaygısız, E.: A New Natural Secondary Reference Material for Garnet U–Pb Dating by TIMS and
392 LA–ICP–MS, Geostand. Geoanal. Res., 47, 297–310, <https://doi.org/10.1111/ggr.12493>, 2023.

393 Bartoli, O., Millonig, L. J., Carvalho, B. B., Marschall, H. R., and Gerdes, A.: The age of granulite-facies metamorphism in
394 the Ivrea–Verbano Zone (NW Italy) determined through in situ U–Pb dating of garnet, J. Petrol., 65, egae083,
395 <https://doi.org/10.1093/petrology/egae083>, 2024.

396 Baxter, E. F., Caddick, M. J., and Dragovic, B.: Garnet: A rock-forming mineral petrochronometer, Rev. Mineral. Geochem.,
397 83, 469–533, <https://doi.org/10.2138/rmg.2017.83.15>, 2017.

398 Beno, C. J., Lackey, J. S., Schmitz, M. D., Bowman, J. R., Stearns, M. A., Bartley, J. M., and Fernandez, D. P.: Assessment
399 of Natural Reference Materials for U–Pb Geochronology of Grossular–Andradite Garnet, Geostand. Geoanal. Res., 48, 909–
400 925, <https://doi.org/10.1111/ggr.12561>, 2024.

401 Beranoaguirre, A., García de Madinabeitia, S., Sanchez-Lorda, M. E., Puellas, P., Ábalos, B., and Gil Ibarguchi, J. I.: U-Pb,
 402 Hf isotope and REE constraints on high-pressure acid migmatites from the Cabo Ortegal Complex (NW Spain): New evidence
 403 of short-duration metamorphism in a Variscan subduction channel, *Lithos*, 372–373, 105660,
 404 <https://doi.org/10.1016/j.lithos.2020.105660>, 2020.

405 Beranoaguirre, A., Vasiliev, I., and Gerdes, A.: In-situ LA-ICPMS U-Pb dating of Sulfates: Applicability of carbonate
 406 reference materials as matrix-matched standards, *Geochronology*, 4, 601–616, <https://doi.org/10.5194/gchron-4-601-2022>,
 407 2022.

408 Caddick, M. J. and Kohn, M. J.: Garnet: Witness to the Evolution of Destructive Plate Boundaries Elements, 9, 427–432,
 409 <https://doi.org/10.2113/gselements.9.6.427>, 2013.

410 Cerva-Alves, T., Hartmann, L. A., Queiroga, G. N., Lana, C., Castro, M. P., Maciel, L. A. C., and Remus, M. V. D.:
 411 Metamorphic evolution of the juvenile Serrinha forearc basin in the southern Brasiliano Orogen, *Precambrian Res.*, 365,
 412 106394, <https://doi.org/10.1016/j.precamres.2021.106394>, 2021.

413 Cherniak, D. J.: Pb diffusion in rutile, *Contrib. Mineral. Petrol.*, 139, 198–207, <https://doi.org/10.1007/PL00007671>, 2000.

414 Chew, D. M., Petrus, J. A., Kenny, G. G., and McEvoy, N.: Rapid high-resolution U–Pb LA-Q-ICPMS age mapping of zircon,
 415 *J. Anal. At. Spectrom.*, 32, 262–276, <https://doi.org/10.1039/C6JA00404K>, 2017.

416 Currie, L. A.: Nomenclature in evaluation of analytical methods including detection and quantification capabilities (IUPAC
 417 Recommendations 1995), *Pure Appl. Chem.*, 67, 1699–1723, <https://doi.org/10.1351/pac199567101699>, 1995.

418 Dahl, P. S.: A crystal-chemical basis for Pb retention and fission-track annealing systematics in U-bearing minerals, with
 419 implications for geochronology, *Earth Planet. Sci. Lett.*, 150, 277–290, [https://doi.org/10.1016/S0012-821X\(97\)00108-8](https://doi.org/10.1016/S0012-821X(97)00108-8),
 420 1997.

421 Dawson, J. B., Harley, S. L., Rudnick, R. L., and Ireland, T. R.: Equilibration and reaction in Archaean quartz-sapphirine
 422 granulite xenoliths from the Lace kimberlite pipe, South Africa, *J. Metamorph. Geol.*, 15, 253–266,
 423 <https://doi.org/10.1111/j.1525-1314.1997.00017.x>, 1997.

424 Denèle, Y., Paquette, J. L., Olivier, P., and Barbey, P.: Permian granites in the Pyrenees: the Aya pluton (Basque Country),
 425 *Terra Nova*, 24, 105–113, <https://doi.org/10.1111/j.1365-3121.2011.01043.x>, 2012.

426 Deng, Y., Zhong, R., Li, D., Li, Y., and Cui, H.: Hunting the Datable Garnet using the LA-ICP-MS U-Pb Method: Predicting
 427 Garnet U Concentration, based on Major and Minor Elements, *Acta Geol. Sin.*, 96, 2148–2157, [https://doi.org/10.1111/1755-
 428 6724.14921](https://doi.org/10.1111/1755-6724.14921), 2022.

429 Dodson, M. H.: Closure temperature in cooling geochronological and petrological systems, *Contrib. Mineral. Petrol.*, 40, 259–
 430 274, <https://doi.org/10.1007/BF00373790>, 1973.

431 Duchêne, S., Blichert-Toft, J., Luais, B., Télouk, P., Lardeaux, J. M., and Albarède, F.: The Lu–Hf dating of garnets and the
 432 ages of the Alpine high-pressure metamorphism, *Nature*, 387, 586–589, <https://doi.org/10.1038/42446>, 1997.

433 Flowers, R. M., Ketcham, R. A., Shuster, D. L., and Farley, K. A.: Apatite (U–Th)/He thermochronometry using a radiation
 434 damage accumulation and annealing model, *Geochim. Cosmochim. Acta*, 73, 2347–2365,
 435 <https://doi.org/10.1016/j.gca.2009.01.015>, 2009.

436 Fryer, B. J., Jackson, S. E., and Longerich, H. P.: The application of laser ablation microprobe-inductively coupled plasma-
 437 mass spectrometry (LAM-ICP-MS) to in situ U–Pb geochronology, *Chem. Geol.*, 109, 1–8, [https://doi.org/10.1016/0009-2541\(93\)90058-Q](https://doi.org/10.1016/0009-2541(93)90058-Q), 1993.

439 Gerdes, A. and Zeh, A.: Combined U–Pb and Hf isotope LA-(MC-)ICP-MS analyses of detrital zircons: comparison with
 440 SHRIMP and new constraints for the provenance and age of an Armorican metasediment in Central Germany, *Earth Planet.*
 441 *Sci. Lett.*, 249, 47–61, <https://doi.org/10.1016/j.epsl.2006.06.039>, 2006.

442 Gerdes, A. and Zeh, A.: Zircon formation versus zircon alteration – new insights from combined U–Pb and Lu–Hf in-situ LA-
 443 ICPMS analyses, and consequences for the interpretation of Archean zircon from the Central Zone of the Limpopo Belt, *Chem.*
 444 *Geol.*, 261, 230–243, <https://doi.org/10.1016/j.chemgeo.2008.03.005>, 2009.

445 Gray, A. L.: Solid sample introduction by laser ablation for inductively coupled plasma source mass spectrometry, *Analyst*,
 446 110, 551–556, <https://doi.org/10.1039/AN9851000551>, 1985.

447 Harlov, D. E., Andersson, U. B., Förster, H.-J., Nyström, J. O., Dulski, P., and Broman, C.: Apatite–monazite relations in the
 448 Kiirunavaara magnetite–apatite ore, northern Sweden, *Chem. Geol.*, 191, 47–72, [https://doi.org/10.1016/S0009-2541\(02\)00148-1](https://doi.org/10.1016/S0009-2541(02)00148-1), 2002.

450 Harlov, D. E., Wirth, R., and Hetherington, C. J.: Fluid-mediated partial alteration of monazite: the role of dissolution–
 451 reprecipitation reactions, *Contrib. Mineral. Petrol.*, 162, 329–348, <https://doi.org/10.1007/s00410-010-0599-7>, 2011.

452 Horstwood, M. S. A., Košler, J., Gehrels, G., Jackson, S. E., McLean, N. M., Paton, C., Pearson, N. J., Sircombe, K., Sylvester,
 453 P., Vermeesch, P., and Bowring, J. F.: Community-derived standards for LA-ICP-MS U-(Th-)Pb geochronology–Uncertainty
 454 propagation, age interpretation and data reporting, *Geostand. Geoanal. Res.*, 40, 311–332, <https://doi.org/10.1111/j.1751-908X.2016.00379.x>, 2016.

456 Jackson, S. E., Pearson, N. J., Griffin, W. L., and Belousova, E. A.: The application of laser ablation-inductively coupled
 457 plasma-mass spectrometry to in situ U–Pb zircon geochronology, *Chem. Geol.*, 211, 47–69,
 458 <https://doi.org/10.1016/j.chemgeo.2004.06.017>, 2004.

459 Jochum, K. P., Weis, U., Stoll, B., Kuzmin, D., Yang, Q., Raczek, I., Jacob, D. E., Stracke, A., Birbaum, K., Frick, D. A.,
 460 Günther, D., and Enzweiler, J.: Determination of reference values for NIST SRM 610–617 glasses following ISO guidelines,
 461 *Geostand. Geoanal. Res.*, 35, 97–429, <https://doi.org/10.1111/j.1751-908X.2011.00120.x>, 2011.

462 Kirkland, C. L., Ribeiro, B. V., and Slagstad, T.: In situ garnet Lu–Hf geochronology and constraints on metamorphism in the
 463 northernmost Norwegian Caledonides, *J. Geol. Soc. Lond.*, <https://doi.org/10.1144/jgs2024-193>, 2025.

464 Kohn, M. J., Engi, M., and Lanari, P.: Petrochronology: Methods and applications, *Rev. Mineral. Geochem.*, 83,
 465 <https://doi.org/10.2138/rmg.2017.83.0>, 2017.

466 Košler, J. and Sylvester, P. J.: Present trends and the future of zircon in geochronology: laser ablation ICP-MS, *Rev. Mineral.*
 467 *Geochem.*, 53, 243–275, <https://doi.org/10.2113/0530243>, 2003.

468 Le Roex, A., Tinguely, C., and Gregoire, M.: Eclogite and Garnet Pyroxenite Xenoliths from Kimberlites Emplaced Along the
 469 Southern Margin of the Kaapvaal Craton, Southern Africa: Mantle or Lower Crustal Fragments?, *J. Petrol.*, 61, egaa040,
 470 <https://doi.org/10.1093/petrology/egaa040>, 2020.

471 Li, D., Fu, Y., Hollings, P., Mitchell, R. H., Zurevinski, S., Kamo, S., Zhang, R., Zhang, Y., Liu, Q., Liao, J., Liang, Y., and
 472 Sun, X.: PL57 garnet as a new natural reference material for in situ U–Pb isotope analysis and its perspective for geological
 473 applications, *Contrib. Mineral. Petrol.*, 177, 19, <https://doi.org/10.1007/s00410-021-01884-4>, 2022.

474 Ludwig, K. R.: User’s Manual for Isoplot Version 3.75–4.15: a Geochronological Toolkit for Microsoft Excel, Berkeley
 475 Geochronological Center Special Publication, 5, 2012.

476 Machado, N. and Gauthier, G.: Determination of 207Pb/206Pb ages on zircon and monazite by laser-ablation ICP-MS and
 477 application to a study of sedimentary provenance and metamorphism in southeastern Brazil, *Geochim. Cosmochim. Acta*, 60,
 478 5063–5073, [https://doi.org/10.1016/S0016-7037\(96\)00287-6](https://doi.org/10.1016/S0016-7037(96)00287-6), 1996.

479 Madon, M., Gil-Ibarguchi, J. I., Via, J., and Girardeau, J.: Characterization and thermodynamic properties of andradite,
 480 $\text{Ca}_3\text{Fe}_2\text{Si}_3\text{O}_{12}$, *Am. Mineral.*, 76, 1249–1260, 1991.

481 Manzotti, P., Millonig, L. J., Gerdes, A., Whitehouse, M. J., Jeon, H., Poujol, M., and Ballèvre, M.: Protolith age, and timing
 482 of burial and exhumation of the UHP Chasteiran Unit (Dora-Maira Massif, Western Alps), constrained by zircon, garnet and
 483 rutile petrochronology, *Lithos*, 496–497, 107951, <https://doi.org/10.1016/j.lithos.2025.107951>, 2025.

484 Mark, C., O’Sullivan, G., Glorie, A., Simpson, A., Andò, S., Barbarano, M., Stutenbecker, L., Daly, J. S., and Gilbert, S.:
 485 Detrital Garnet Geochronology by In Situ U-Pb and Lu-Hf Analysis: A Case Study From the European Alps, *J. Geophys. Res.*
 486 *Earth Surf.*, 128, e2023JF007244, <https://doi.org/10.1029/2023JF007244>, 2023.

487 Martínez Catalán, J. R., Gómez Barreiro, J., Dias da Silva, I., Chichorro, M., López-Carmona, A., Castiñeiras, P., Abati, J.,
 488 Andonaegui, P., Fernández-Suárez, J., González Cuadra, P., and Benítez-Pérez, J. M.: Variscan Suture Zone and Suspect
 489 Terranes in the NW Iberian Massif: allochthonous Complexes of the Galicia-Trás os Montes Zone (NW Iberia), in: *The*
 490 *Geology of Iberia: A Geodynamic Approach, Volume 2: The Variscan Cycle*, Springer, 99–130, [https://doi.org/10.1007/978-](https://doi.org/10.1007/978-3-030-10519-8_4)
 491 [3-030-10519-8_4](https://doi.org/10.1007/978-3-030-10519-8_4), 2019.

492 McDougall, I. and Harrison, T. M.: *Geochronology and Thermochronology by the $^{40}\text{Ar}/^{39}\text{Ar}$ Method*, 2nd Edn., Oxford
 493 University Press, New York, 269 pp., ISBN 978-0195109207, 1999.

494 Millonig, L. J., Albert, R., Gerdes, A., Avigad, D., and Dietsch, C.: Exploring laser ablation U-Pb dating of regional
 495 metamorphic garnet - The Straits Schist, Connecticut, USA, *Earth Planet. Sci. Lett.*, 552, 116589,
 496 <https://doi.org/10.1016/j.epsl.2020.116589>, 2020.

497 Munker, C., Weyer, S., Scherer, E. E., and Mezger, K.: Separation of high field strength elements (Nb, Ta, Zr, Hf) and Lu
 498 from rock samples for MC-ICPMS measurements, *Geochem. Geophys. Geosyst.*, 2, 1088,
 499 <https://doi.org/10.1029/2001GC000183>, 2001.

500 Opendak, M. and Wildenhain, P.: On the analysis of the decay of a small number of radioactive atoms in radiochemical solar
 501 neutrino experiments, *Nucl. Instrum. Methods Phys. Res. A*, 345, 570–575, [https://doi.org/10.1016/0168-9002\(94\)90517-7](https://doi.org/10.1016/0168-9002(94)90517-7),
 502 1994.

503 O’Sullivan, G. J., Hoare, B. C., Mark, C., Drakou, F., and Tomlinson, E. L.: Uranium–lead geochronology applied to pyrope
 504 garnet with very low concentrations of uranium, *Geol. Mag.*, 160, 1010–1019, <https://doi.org/10.1017/S0016756823000122>,
 505 2023.

506 Peillod, A., Patten, C. G. C., Drüppel, K., Beranoaguirre, A., Zeh, A., Gudelius, D., Hector, S., Majka, J., Kleine, B. I., Karlson,
 507 A., Gerdes, A., and Kolb, J.: Disruption of a high-pressure unit during exhumation: example of the Cycladic Blueschist Unit
 508 (Thera, Ios and Naxos islands, Greece), *J. Metamorph. Geol.*, 42, 225–255, <https://doi.org/10.1111/jmg.12753>, 2024.

509 Pettke, T., Oberli, F., Audétat, A., Guillong, M., Simon, A. C., Hanley, J. J., and Klemm, L. M.: Recent developments in
 510 element concentration and isotope ratio analysis of individual fluid inclusions by laser ablation single and multiple collector
 511 ICP-MS, *Ore Geol. Rev.*, 44, 10–38, <https://doi.org/10.1016/j.oregeorev.2011.11.001>, 2012.

512 Piccione, G., Rasbury, E. T., Elliott, B. A., Kyle, J. R., Jaret, S. J., Acerbo, A. S., Lanzirotti, A., Northrup, P., Wooton, K., and
 513 Parrish, R. R.: Vein fluorite U–Pb dating demonstrates post-6.2 Ma rare-earth element mobilization associated with Rio Grande
 514 rifting, *Geosphere*, 15, 1958–1972, <https://doi.org/10.1130/GES02139.1>, 2019.

515 Putnis, A.: Mineral replacement reactions, *Rev. Mineral. Geochem.*, 70, 87–124, <https://doi.org/10.2138/rmg.2009.70.3>, 2009.

516 Reinhardt, N., Gerdes, A., Beranoaguirre, A., Frenzel, M., Meinert, L. D., Gutzmer, J., and Burisch, M.: Timing of magmatic-
 517 hydrothermal activity in the Variscan belt - LA-ICP-MS U–Pb geochronology of skarn-related garnet from the Schwarzenberg
 518 district, *Erzgebirge, Mineral. Deposita*, 57, 1071–1087, <https://doi.org/10.1007/s00126-021-01084-x>, 2022.

519 Reiners, P. W., Ehlers, T. A., and Zeitler, P. K.: Past, present, and future of thermochronology, *Rev. Mineral. Geochem.*, 58,
 520 1–18, <https://doi.org/10.2138/rmg.2005.58.1>, 2005.

521 Richter, S., Konegger-Kappel, S., Boulyga, S. F., Stadelmann, G., Koepf, A., and Siegmund, H.: Linearity testing and dead-
 522 time determination for MC-ICP-MS ion counters using the IRMM-072 series of uranium isotope reference materials, *J. Anal.*
 523 *At. Spectrom.*, 31, 1647–1657, <https://doi.org/10.1039/C6JA00203J>, 2016.

524 Ring, U. and Gerdes, A.: Kinematics of the Alpenrhein-Bodensee graben system in the Central Alps: Oligocene/Miocene
 525 transtension due to formation of the Western Alps arc, *Tectonics*, 35, 1367–1391, <https://doi.org/10.1002/2015TC004085>,
 526 2016.

527 Roberts, N. M. W. and Walker, R. J.: U–Pb geochronology of calcite-mineralized faults: absolute timing of rift-related fault
 528 events on the northeast Atlantic margin, *Geology*, 44, 531–534, <https://doi.org/10.1130/G37868.1>, 2016.

529 Rodriguez, J., Gil Ibarguchi, J. I., and Paquette, J. L.: Variscan synchronous magmatism across the Iberian Massif: new U–Pb
 530 ages in granitoids from the Fisteria area (A Coruña, Spain), *XV Semana – VI Congreso Ibérico de Geoquímica*, 2007.

531 Rubatto, D.: Zircon trace element geochemistry: Partitioning with garnet and the link between U–Pb ages and metamorphism,
 532 *Chem. Geol.*, 184, 123–138, [https://doi.org/10.1016/S0009-2541\(01\)00355-2](https://doi.org/10.1016/S0009-2541(01)00355-2), 2002.

533 Rubatto, D.: Zircon: the metamorphic mineral, *Rev. Mineral. Geochem.*, 83, 261–295, <https://doi.org/10.2138/rmg.2017.83.9>,
534 2017.

535 Salnikova, E. B., Chakhmouradian, A. R., Stifeeva, M. V., Reguir, E. P., Kotov, A. B., Gritsenko, Y. D., and Nikiforov, A.
536 V.: Calcic garnets as a geochronological and petrogenetic tool applicable to a wide variety of rocks, *Lithos*, 338–339, 141–
537 154, <https://doi.org/10.1016/j.lithos.2019.03.032>, 2019.

538 Schaltegger, U., Schmitt, A. K., and Horstwood, M. S. A.: U-Th-Pb zircon geochronology by ID-TIMS, SIMS, and laser
539 ablation ICP-MS: Recipes, interpretations, and opportunities, *Chem. Geol.*, 402, 89–110,
540 <https://doi.org/10.1016/j.chemgeo.2015.02.028>, 2015.

541 Schannor, M., Lana, C., Nicoli, G., Cutts, K., Buick, I., Gerdes, A., and Hecht, L.: Reconstructing the metamorphic evolution
542 of the Araçuaí orogeny (SE Brazil) using in situ U–Pb garnet dating and P–T modelling, *J. Metamorph. Geol.*, 39, 1145–1171,
543 <https://doi.org/10.1111/jmg.12605>, 2021.

544 Schmitz, M. D. and Bowring, S. A.: Constraints on the thermal evolution of continental lithosphere from U–Pb accessory
545 mineral thermochronology of lower crustal xenoliths, southern Africa, *Contrib. Mineral. Petrol.*, 144, 592–618,
546 <https://doi.org/10.1007/s00410-002-0419-9>, 2003.

547 Seman, S., Stockli, D. F., and McLean, N. M.: U-Pb geochronology of grossular-andradite garnet, *Chem. Geol.*, 460, 106–
548 116, <https://doi.org/10.1016/j.chemgeo.2017.04.020>, 2017.

549 Shu, Q., Beranoaguirre, A., Albert, R., Millonig, L. J., Walters, J. B., Marschall, H. R., Gerdes, A., Hoefer, H. E., Hezel, D.,
550 and Brey, G. P.: Multi-stage ultrahigh temperature metamorphism in the lower crust of the Kaapvaal craton recorded by U–Pb
551 ages of garnet, *Contrib. Mineral. Petrol.*, 179, 49, <https://doi.org/10.1007/s00410-024-02121-4>, 2024.

552 Simpson, A., Gilbert, S., Tamblyn, R., Hand, M., Spandler, C., Gillespie, J., Nixon, A., and Glorie, S.: In situ Lu–Hf
553 geochronology of garnet, apatite and xenotime by LA-ICP-MS/MS, *Chem. Geol.*, 577, 120299,
554 <https://doi.org/10.1016/j.chemgeo.2021.120299>, 2021.

555 Spear, F. S. and Parrish, R. R.: Petrology and cooling rates of the Valhalla Complex, British Columbia, Canada, *J. Petrol.*, 37,
556 733–765, <https://doi.org/10.1093/petrology/37.4.733>, 1996.

557 Stifeeva, M. V., Salnikova, E. B., Samsonov, A. V., Kotov, A. B., and Gritsenko, Y. D.: U-Pb geochronology of garnet from
558 Daschkasan skarn deposit (Lesser Caucasus), *Dokl. Earth Sci.*, 487, 953–956, <https://doi.org/10.1134/S1028334X19080178>,
559 2019.

560 Stifeeva, M., Salnikova, E., Adamskaya, E., Millonig, L. J., Ivanov, A., Mottram, C., Kovach, V., Kotov, A., Bryanskiy, N.,
561 Karimov, A., Gladkochub, E., Peytcheva, I., Gerdes, A., Bowie, S., and Gritsenko, J.: Kovdor-GRT – A New Natural Reference
562 Material for Garnet U-Pb Dating, *Geostand. Geoanal. Res.*, <https://doi.org/10.1111/ggr.70040>, 2026.

563 Sylvester, P. J. and Jackson, S. E.: A Brief History of Laser Ablation Inductively Coupled Plasma Mass Spectrometry (LA–
564 ICP-MS), *Elements*, 12, 307–310, <https://doi.org/10.2113/gselements.12.5.307>, 2016.

565 Szczepański, J. and Ilnicki, S.: From Cadomian arc to Ordovician passive margin: geochemical records preserved in
 566 metasedimentary successions of the Orlica-Snieznik Dome in SW Poland, *Int. J. Earth Sci.*, 103, 627–647,
 567 <https://doi.org/10.1007/s00531-013-0993-2>, 2014.

568 Tamblyn, R., Hand, M., Simpson, A., Gilbert, S., Wade, B., and Glorie, S.: In situ laser ablation Lu–Hf geochronology of
 569 garnet across the Western Gneiss Region: campaign-style dating of metamorphism, *J. Geol. Soc. Lond.*, 179, jgs2021-094,
 570 <https://doi.org/10.1144/jgs2021-094>, 2022.

571 Tera, F. and Wasserburg, G. J.: U-Th-Pb systematics in three Apollo 14 basalts and the problem of initial Pb in lunar rocks,
 572 *Earth Planet. Sci. Lett.*, 14, 281–304, [https://doi.org/10.1016/0012-821X\(72\)90128-8](https://doi.org/10.1016/0012-821X(72)90128-8), 1972.

573 Walczak, K., Anczkiewicz, R., Szczepański, J., Rubatto, D., and Košler, J.: Combined garnet and zircon geochronology of the
 574 ultra-high temperature metamorphism: Constraints on the rise of the Orlica-Śnieżnik Dome, NE Bohemian Massif, SW Poland,
 575 *Lithos*, 292–293, 388–400, <https://doi.org/10.1016/j.lithos.2017.09.013>, 2017.

576 Walters, J. B., Garber, J. M., Beranoaguirre, A., Millonig, L. J., Gerdes, A., Grützner, T., and Marschall, H. R.: Zircon micro-
 577 inclusions as an obstacle for in situ garnet U-Pb geochronology: An example from the As Sifah eclogite locality, Oman,
 578 *Geochronology*, 7, 309–333, <https://doi.org/10.5194/gchron-7-309-2025>, 2025.

579 Willigers, B. J. A., Baker, J. A., Krogstad, E. J., and Peate, D. W.: Precise and accurate in situ Pb-Pb dating of apatite, monazite,
 580 and sphene by laser ablation multiple-collector ICP-MS, *Geochim. Cosmochim. Acta*, 6, 1051–1066,
 581 [https://doi.org/10.1016/S0016-7037\(01\)00838-9](https://doi.org/10.1016/S0016-7037(01)00838-9), 2002.

582 Yang, Y., Wu, S., Wang, H., Kamo, S. L., Ma, Q., Liang, T., Xu, L., Xie, L., Huang, C., Wan, B., Yang, J., and Wu, F.: Three
 583 new natural secondary reference materials for in situ andradite U–Pb geochronology, *J. Anal. At. Spectrom.*, 40, 326–337,
 584 <https://doi.org/10.1039/D4JA00290C>, 2025.

585 Zack, T. and Kooijman, E.: Petrology and geochronology of rutile, *Rev. Mineral. Geochem.*, 83, 443–467,
 586 <https://doi.org/10.2138/rmg.2017.83.14>, 2017.

587

588