# Detrital garnet geochronology by in-situ U-Pb and Lu-Hf analysis: A case study from the European Alps

**Chris Mark[1]*, Gary O'Sullivan[1], Stijn Glorie[2], Alexander Simpson[2], Sergio Andò[3], Marta Barbarano[3], Laura Stutenbecker[4], and J. Stephen Daly[1,5]**

[1]UCD School of Earth Sciences and UCD Earth Institute, University College Dublin, Belfield, Dublin 4, Ireland.

[2]Department of Earth Sciences, University of Adelaide, Adelaide, Australia.

[3]Department of Earth and Environmental Sciences, Università di Milano-Bicocca, Milan, Italy.

[4]Institute of Geology and Paleontology, Westfälische Wilhelms-Universität Münster, Münster, Germany.

[5]Science Foundation Ireland Research Centre in Applied Geosciences (iCRAG), University College Dublin, Belfield, Dublin 4, Ireland.

Corresponding author: Chris Mark (chris.mark@nrm.se)

*Now at: Department of Geosciences, Swedish Museum of Natural History, Stockholm, Sweden.

**Key Points:**

- Detrital garnet U-Pb and Lu-Hf ages preferentially record the most recent metamorphic event in the source area;
- Both systems are less refractory than alternative detrital U-Pb geochronometers;
- Age recovery for Lu-Hf in garnet is considerably better than for U-Pb.

## Abstract

Detrital geochronology employing the widely-used zircon U-Pb proxy is biased towards igneous events and metamorphic anataxis; additionally, zircon is highly refractory and frequently polycyclic. Garnet, a rock-forming and thus commonly-occuring mineral, is predominantly metamorphic and much less refractory. Here, we report in-situ U-Pb and Lu-Hf ages from detrital garnet hosted in ancient and modern sediments of the European Alps. Both geochronometers are biased towards the most recent garnet-crystallising metamorphic event in the source area, with fewer inherited ages. This likely reflects efficient removal of inherited garnet during diagenesis and metamorphism, and is in contrast to detrital zircon, apatite, and rutile U-Pb data which largely record pre-Alpine ages. Neither the U-Pb nor Lu-Hf system in garnet exhibits a relationship between age recovery and composition. However, the Lu-Hf system in garnet yields significantly better age recovery than the U-Pb system. Estimated initial $^{238}U/^{206}Pb_c$ values at the time of crystallization are near unity for the garnet analysed in this study, suggesting that garnet does not significantly partition U from Pb during crystallization, at least for the generally almandine-rich garnets analysed in this study. Hence, Lu-Hf geochronology of detrital garnet offers an effective method to detect and date the most recent phase of mid-grade metamorphism in sub-anatectic source areas, in which detrital zircon U-Pb analysis may be of less utility.

## Plain Language Summary

Mountain ranges are characterized by rapid changes in their constituent rocks as these undergo metamorphism to adjust to increasing pressure and temperature during burial. These metamorphic processes drive mineral crystallization. Once cooled, each mineral acts as a geochemical reservoir isolated from the surrounding environment. Therefore, if a mineral has incorporated a radioactive isotope during crystallization, it can be dated to constrain the timings and rates of metamorphism. As erosion ultimately converts crystalline bedrock to sediment, the geological histories of these processes are preserved in the sediment shed during erosion. Consequently, these histories can be read from sedimentary rocks in adjacent sedimentary basins. Minerals traditionally used to study the sources of these sediments, such as zircons, largely grow from molten rock rather than during metamorphism, and are tough enough to be recycled through multiple tectonic events. The mineral garnet more commonly grows under metamorphic conditions and is more thus more effective at directly recording the most recent phases of significant mountain building. Here, we present uranium-lead and lutetium-hafnium ages of garnet in modern and ancient sediment from the Alps. We show that garnet preferentially records Alpine events, and is thus suitable for provenance studies targeting the most recent mountain building event.


## 1 Introduction

### 1.1 The utility of detrital garnet in sedimentary provenance analysis

Detrital geochronology is a powerful tool for interrogating the sedimentary archive of paleo-hinterland tectonic, metamorphic, and climatic processes, and can also be applied to modern river sediment as a first-pass tool to establish regional bedrock ages (e.g., von Eynatten & Dunkl, 2012; Ledent et al., 1964; Machado & Gauthier, 1996; Najman, 2006). The zircon U-Pb detrital geochronometer has seen widespread adoption in provenance analysis (3,626 of 4,471 results for the search term *detrital geochronology* also contain the term *zircon U-Pb*; Clarivate Analytics Web of Science). However, zircon fertility is strongly biased towards intermediate to felsic source rocks (Boehnke et al., 2013). Moreover, zircon neocrystallization is volumetrically limited in metamorphic terranes which do not achieve anatexis (e.g., Moecher & Samson, 2006), and is typically restricted to rim overgrowths which are vulnerable to mechanical destruction during fluvial transport, and which are also challenging to detect and analyse (e.g., Campbell et al., 2005).

Therefore, it is desirable to develop complementary provenance tools to identify metamorphic source rocks in the detrital record (Zack et al., 2011). Garnet group minerals are rock-forming in several common metamorphic lithologies and are also present as accessory minerals in a wide range of igneous and metamorphic rocks. Garnet is therefore a common constituent of clastic detritus from orogens. Here and throughout, we use the term *garnet* as a synonym for garnet group silicates in the garnet supergroup. These have the general formula $X_3Y_2Z_3O_{12}$ in which the *Z*-site is occupied by Si; the fourteen known end members of this complex solid solution include the geologically common varieties almandine $Fe_3Al_2(SiO_4)_3$, andradite $Ca_3Fe_2(SiO_4)_3$, grossular $Ca_3Al_2(SiO_4)_3$, spessartine $Mn_3Al_2(SiO_4)_3$, pyrope $Mg_3Al_2(SiO_4)_3$, and uvarovite $Ca_3Cr_2(SiO_4)_3$ (Grew et al., 2013).

The wide range of documented stoichiometry, and potential for correlation to source rock type, has resulted in extensive use of garnet composition as a detrital provenance tool (Connally, 1964; Morton, 1985; Schönig et al., 2021; Stutenbecker et al., 2017; Suggate & Hall, 2014). Importantly, the broad P-T stability range of garnet in most bulk rock compositions means that neocrystalline garnet is shed to the sediment routing network during almost every orogenic exhumational phase, beginning with epidote-garnet dominated heavy mineral assemblages from upper-greenschist-facies-grade metasedimentary cover units, through gneissose hornblende-garnet-epidote-aluminosilicate suites, culminating in debris from garnet-cordierite bearing leucogranites generated by anataxis (Andò et al., 2013; Garzanti et al., 2010a). Garnet group minerals comprise 5-42 % of the heavy mineral fraction in the bedload of rivers draining major modern orogens where sediment production is dominated by rapid exhumation of metamorphic crystalline bedrock, including the Po, Ganges-Brahmaputra, and Indus (Garzanti et al., 2005; Garzanti and Andò, 2007; Garzanti et al., 2010a; Garzanti et al., 2010b). In rivers draining tectonically quiescent continental interiors characterized by widespread ancient sedimentary cover, the garnet fraction is typically < 7 %, including the Amazon, Congo, Mississippi, Nile, and Zambezi (Garzanti et al., 2015, 2019, 2021; Mange & Otvos, 2005; do Nascimento et al., 2015).

Despite the abundance of garnet in recent surficial sediments, it is only moderately stable during burial and diagenesis. Studies of Cenozoic-Mesozoic depocenters in the North Sea, Nile Delta, Bay of Bengal and Gulf of Mexico indicate that near-complete dissolution of sand-grade garnet occurs at burial depths of 4-5 km (Andò et al., 2012; Garzanti et al., 2018; Milliken, 2007; Morton & Hallsworth, 2007). Garnet is also rapidly destroyed by prolonged residence in soils (Velbel, 1984; Andò et al., 2012). As a result, garnet is considerably less refractory than other commonly-used detrital U-Pb geochronometers including zircon, rutile, apatite, but more so than titanite, which is typically removed at 3-4 km burial depths (Andò et al., 2012; Garzanti et al., 2018; Morton & Hallsworth, 2007). Recycling of detrital garnet into younger orogens is thus expected to be rare, although it has been reported (Manzotti & Ballèvre, 2013). Garnet is also commonly eliminated from metasediment during the early stages of metamorphism (Cave et al., 2015), but preservation of inherited garnet retained in polycyclic crystalline bedrock has also been reported (Walker et al., 2021; Argles et al., 1999). Significantly, a compositional control on garnet diagenetic stability has been documented, with a decrease in the Ca content of bulk garnet separates with burial depth and an increase in Fe content (Morton & Hallsworth, 2007). As Mn and Mg contents in that example remained unchanged, this could indicate higher diagenetic vulnerability of grossular- and uvarovite-rich garnets.

## 1.2 Garnet geochronology

In crystalline bedrock, garnet is datable using the Rb-Sr, Sm-Nd, Lu-Hf, and U-Pb radioisotope systems. As with many geochronometers, the garnet host seldom completely excludes the daughter element during crystal growth: the isotopic composition of the initial daughter component must therefore be corrected during age calculation, normally by the isochron method (Nicolaysen, 1961). Garnet typically has very low Rb/Sr ratios, so the $^{87}Rb/^{86}Sr$ age is normally calculated as a model age from $^{87}Sr/^{86}Sr$, requiring assumptions regarding matrix Rb/Sr during garnet growth which cannot easily be verified in a detrital context (Christensen et al., 1989). Typical $^{147}Sm/^{144}Nd$ ratios, while higher than $^{87}Rb/^{86}Sr$, are also low (typically < 3 except in highly fractionated rocks such as pegmatites; Thöni, 2003). Coupled with the long half-life of $^{147}Sm$, analysis of a co-crystallising phase with lower initial Sm/Nd is required to anchor the Sm-Nd isochrons (e.g., Baxter & Scherer, 2013). Low Sm/Nd and slow radiogenic ingrowth probably renders impractical the use of detrital single-garnet Sm-Nd analyses coupled with initial $^{143}Nd/^{144}Nd$ estimates obtained from Nd isotope terrestrial evolution models (e.g., DePaolo & Wasserburg, 1976). This hinders application of the Sm-Nd technique to detrital studies. Although co-analysis of either bulk sediment hosting the detrital grains (Oliver et al., 2000) or garnet-hosted inclusions have been employed to allow construction of single-grain isochrons (Maneiro et al., 2019), both methods are somewhat laborious.

In contrast, the half-lives of $^{176}Lu$ and $^{238,235}U$ are shorter than for $^{87}Rb$ and $^{147}Sm$, leading to faster radiogenic ingrowth. More importantly, initial $^{176}Lu/^{176}Hf$ in garnet is typically high (Duchêne et al., 1997) and the terrestrial range of initial Hf isotopic compositions is small (e.g., Vervoort et al., 1999), such that correction for initial Hf becomes relatively trivial at the level of precision typically required for detrital studies (Simpson et al., 2021). Empirical and experimental studies show that the initial U/Pb ratio in garnet can be high (Haack & Gramse, 1972; Hauri et al., 1994); moreover, the relatively predictable isotopic evolution of crustal Pb (Stacey & Kramers, 1975) facilitates correction of single-analysis U-Pb ages for initial Pb using the same approach typically employed for detrital analysis of other common-Pb hosting phases (e.g., Chew et al., 2020). Both techniques are therefore suitable in principle for detrital single-grain analysis.

Lu-Hf dating of garnet, initially by solution and now by *in-situ* methods, is uncontroversial (Duchêne et al., 1997; Simpson et al., 2021). In contrast U-Pb dating of garnet, despite having a longer history (Burton et al., 1995; Mezger et al., 1989), has been the subject of debate centered around whether U is hosted in the garnet lattice, or as inclusions which may be inherited (DeWolf et al., 1996). However, multiple lines of evidence support incorporation of U in garnet as a trace element, although the mechanisms of incorporation and extent of possible stoichiometric controls remain unclear. Dissolution of bulk detrital garnet separates obtained from modern bedload of the Brahmaputra river indicated an average U content of 3.5 µg/g, although co-dissolution of U-hosting inclusions cannot be excluded (Garçon et al., 2014). In-situ empirical studies by etching of spontaneous fission tracks or ion microprobe analysis have demonstrated homogeneously-distributed U in garnet up to several hundred µg/g (Haack & Gramse, 1972; Smith et al., 2004), with andradite and spessartine typically containing higher U concentrations than almandine, pyrope, or grossular. Experimental synthesis of pyrope-rich and pyrope-grossular garnet from silicate melts yield U concentrations up to 60 µg/g; garnet/melt partitioning coefficients are non-zero, demonstrating that garnet does not completely reject U during formation (Hauri et al., 1994; Van Westrenen et al., 1999).

In addition to experimental studies documenting the presence of U in the lattice, mineralogical mechanisms for U-incorporation have also been articulated. Structural modelling of ferrite garnet, in which the *Z*-site Si is partially replaced by Fe, indicates that the resulting lattice distortion permits weight-percent U concentrations, in agreement with the natural occurrence of elbrusite ($Ca_3(Zr_{1.5}U^{6+}_{0.5})Fe^{3+}_3O_{12}$), a ferrite garnet in which U is a major element (Galuskina et al., 2010; Rak et al., 2011). One possible mechanism for U incorporation is the type of co-substitution found in elbrusite of $U^{6+}$ with a 2+ species at the *Y*- and *Z*-sites of schorlomite group garnet; schorlomite itself ($Ca_3Ti_2(SiO_4)(Fe^{3+}O_4)_2$) forms a solid solution with the silicate garnet group (Grew et al., 2013). This hypothesized mechanism makes the useful prediction that U should co-occur with Ti or Zr, and $Fe^{3+}$ in garnet group minerals, although these need only occur in trace quantitites as only trace quantities of U are required for U-Pb analysis. However, as Pb may directly substitute for $Fe^{2+}$, Mn, Ca, and Mg in the garnet group *X*-site (subject to ionic radius constraints), it follows that initial U/Pb ratios during crystallization may be undesirably low unless Pb has been sequestered in another phase (e.g., K-feldspar), or bulk rock U/Pb ratios are high (e.g., garnet crystallising in mantle rocks). Additionally, as with any U-host, garnet is also amenable to fission track and (U-Th-Sm)/He dating, although these lower-temperature thermochronometers have seen limited use (Aciego et al., 2003; Haack & Potts, 1972).

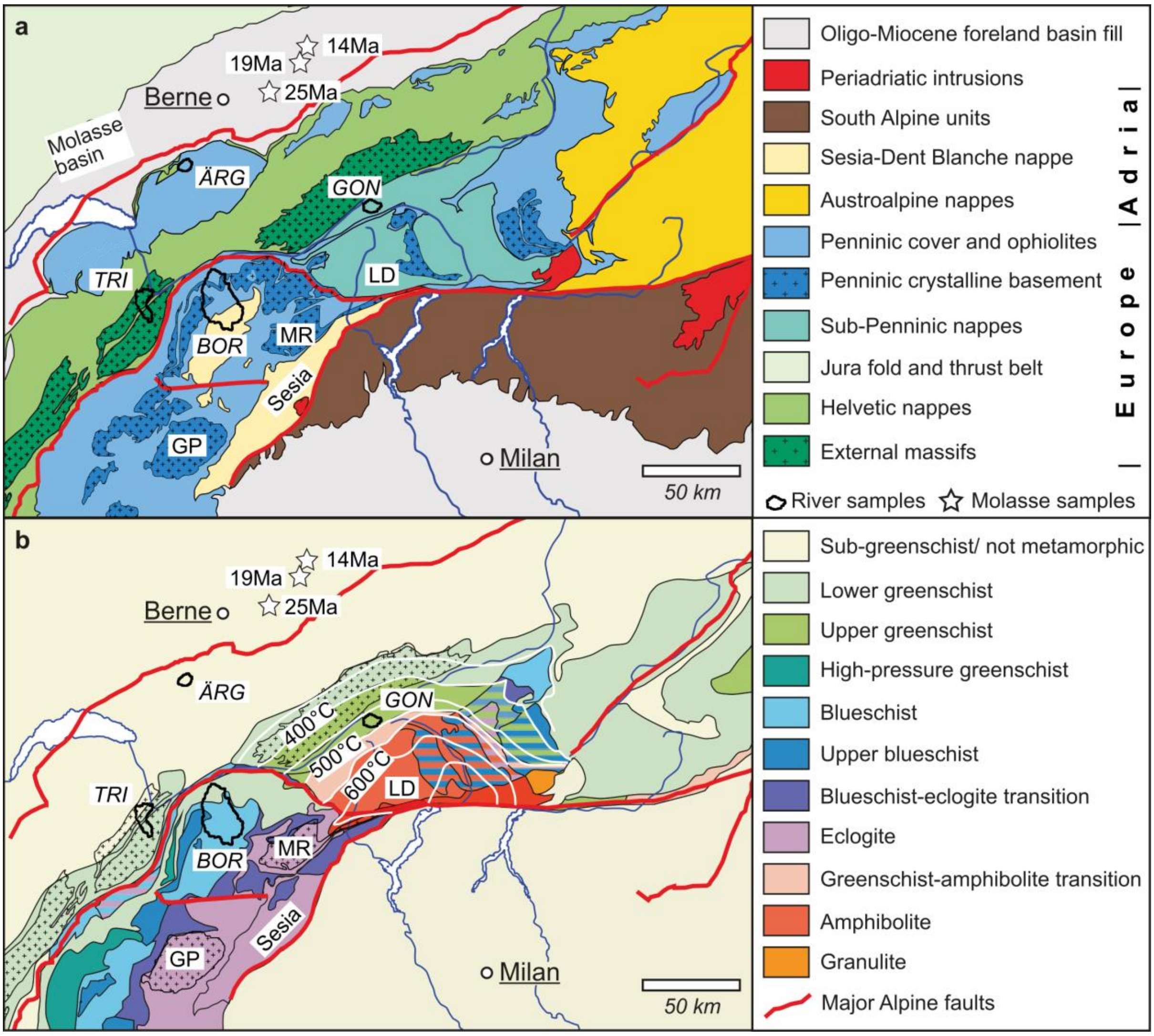
Early garnet U-Pb studies employed low-throughput bulk solution analyses, which also rendered screening for U-hosting inclusions challenging (e.g., Burton et al., 1995; Mezger et al., 1989). Recent studies employing laser ablation inductively coupled plasma mass spectrometry (LA-ICPMS) have pioneered the use of large spots to compensate for typically low U concentrations (Gevedon et al., 2018; Millonig et al., 2020; Salnikova et al., 2018, 2019; Seman et al., 2017; Yang et al., 2018). Together with identification of matrix-matched reference materials, this approach has enabled *in-situ* garnet U-Pb analysis. *In-situ* Lu-Hf analysis, previously hampered by insurmountable isobaric interference of $^{176}$Lu on $^{176}$Hf, has been enabled by use of an online mass-filtered reaction cell, (LA-ICPMS/MS) which mass-shifts $^{176}$Hf by reaction with ammonia to form an interference-free higher-mass polyatomic ion (Simpson et al., 2021; Woods, 2016). *In-situ* analysis enables the high analytical throughput necessary for routine detrital provenance analysis; if a quadrupole instrument capable of rapid peak jumps is employed, co-monitoring of relevant elemental masses (eg Zr, Ti, P, LREE) during analysis also enables efficient screening for U- or Lu-hosting inclusions.

Here, we present results from U-Pb and Lu-Hf double-dating, acquired by LA-Q-ICPMS(/MS) for detrital garnet recovered from the Oligo-Miocene pro-foreland basin of the European Alps, as well as modern Alpine river bedload. We integrate these with Raman spectroscopic data and discuss the implications for Alpine tectonics and metamorphism, as well as the future scope of detrital garnet geochronometry.

### 1.3 Geological background of the study area

A detailed review of the geological evolution of the eastern Alps is beyond the scope of this study and the following section is intended only as a brief synopsis. Readers are directed elsewhere for in-depth discussion (Handy et al., 2010, 2015; Schmid et al., 2008; Stampfli & Hochard, 2009). Following the prolonged Variscan orogenic cycle (c. 480-290 Ma; Matte, 2001), development of Neotethyan oceanic basins (including the Piedmont-Liguria and Meliata oceans) led to the separation of Africa from Europe during Late Triassic to Jurassic time, producing an intervening assemblage of continental microplates and ocean basins. Reconstructions of this complex tectonic mosaic remain subject to debate, but recent studies show consensus that the Adria microplate was the southernmost microplate, remained kinematically linked to Africa, and was separated from the adjacent microcontinent to the north, termed Alcapia, by a shear zone rather than an ocean basin (Handy et al., 2010, 2015).

**Figure 1.** Location map showing (**a**) tectonic affiliation and (**b**) metamorphic grade attained during the Alpine orogen, after Bousquet et al. (2012a,b). Internal massifs: GP – Gran Paradiso; MR – Monte Rosa; and LD – Lepontine dome and Gotthard nappe. Modern catchments (*italicised labels*): TRI – Trient; BOR – Borgne; ÄRG – Ärgera; and GON – Goneri. White stars indicate molasse sampling sites, with deposition ages.



Shortening of the Adria-Europe tectonic system led to the mid-Cretaceous Eoalpine event (c. 140-85 Ma; Handy et al., 2010), comprising partial intra-continental subduction of Alcapia beneath Adria, followed by accretion. Post-Eoalpine, shortening of the Adria-Europe system was accommodated by subduction of the Piedmont-Ligurian ocean north of Adria (Handy et al., 2010), culminating in the Alpine orogen (c. 48-15 Ma). The Eoalpine is restricted to units east of the Arosa Zone, with the exception of the autochthonous Sesia-Dent Blanche units of the western Alps. The central and western Alps are characterised by broadly orogen-parallel metamorphic zones, and include twin parallel chains (internal and external) of crystalline basement massifs (Fig.1). The External Massifs comprise polymetamorphic gneisses which attained amphibolite-granulite facies during the Eo-Variscan and Variscan orogens (c. 480-290 Ma; Matte, 2001) followed by Permo-Triassic magmatism and metamorphism (c. 290-245; (Schuster & Stüwe, 2008), but experienced only moderate (sub-greenschist to greenschist-facies) Alpine metamorphism (Bousquet et al., 2012a). The Internal Massifs experienced eclogite- to amphibolite-facies grade metamorphism during the Alpine. Alpine-age HP metamorphism up to eclogite-facies grade occurred between c. 37-30 Ma in the Internal Massifs; and at c. 48-42 Ma in the surrounding Penninic metasedimentary and meta-ophiolitic units (Liati et al., 2009; Beltrando et al., 2010). The Lepontine Dome subsequently experienced an amphibolite-facies Barrovian overprint from c. 32-27 Ma which was terminated by rapid exhumation between c. 22-15 Ma (Boston et al., 2017; Janots et al., 2009).

## 2 Materials and Methods

### 2.1 Sampling strategy

Here, we report data for samples collected both from the bedload of modern rivers draining small, quasi-monolithologic catchments, as well as from the Oligo-Miocene pro-foreland molasse basin. These samples were originally collected by Stutenbecker et al. (2017; 2019), who reported major element chemistry acquired using energy-dispersive X-ray spectrometry and electron microprobe analysis (Fig.2). Sample locations are indicated on Figure 1 and reported in Table 1. The 63-250 µm size fraction was targeted for garnet separation.

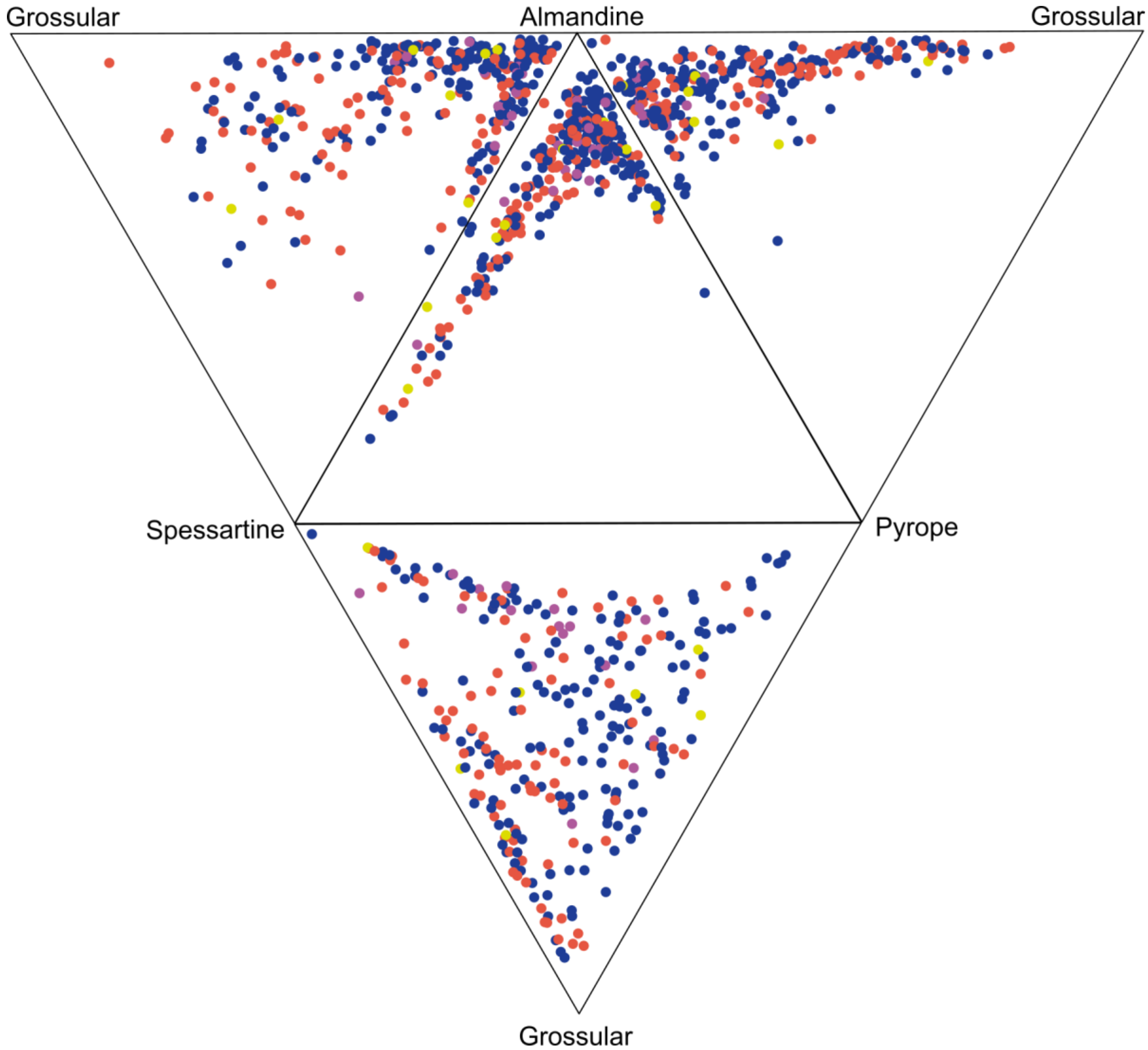
### 2.2 Garnet U-Pb and trace-element analysis by LA-Q-ICPMS

Analyses were conducted at the National Centre for Isotope Geochemistry (NCIG) at University College Dublin using a Teledyne Cetac Analyte G2 ArF 193 nm excimer nanosecond laser ablation system equipped with a HelEx II two-volume cell, coupled to a ThermoScientific iCAP Qc quadrupole ICPMS. Masses monitored comprised $^{25}$Mg, $^{27}$Al, $^{29}$Si, $^{31}$P, $^{43}$Ca, $^{49}$Ti, $^{53}$Cr, $^{55}$Mn, $^{57}$Fe, $^{60}$Ni, $^{89}$Y, $^{91}$Zr, $^{139}$La, $^{140}$Ce, $^{141}$Pr, $^{146}$Nd, $^{147}$Sm, $^{153}$Eu, $^{157}$Gd, $^{159}$Tb, $^{163}$Dy, $^{165}$Ho, $^{166}$Er, $^{169}$Tm, $^{172}$Yb, $^{175}$Lu, $^{177}$Hf, $^{202}$Hg, $^{204}$Pb, $^{206}$Pb, $^{207}$Pb, $^{208}$Pb, $^{232}$Th, and $^{238}$U. A spot size of 75 µm was employed; further analytical parameters are fully reported in supplementary table S1. Spikes of P, Ti, Y, Zr, or LREE masses in the time-resolved data were used to identify and exclude U-hosting inclusions during data reduction (supplementary Fig.S1). Conventional sample-standard bracketing was employed, with Odikhincha garnet (Salnikova et al., 2019) used as the primary reference material to correct for intra-session analytical drift, mass bias, and downhole fractionation. Data reduction employed the VisualAge_UComPbine data reduction scheme in Iolite 3 (Chew et al., 2014; Paton et al., 2011). Ages were corrected for common-Pb using the $^{207}$Pb method, implemented using the iterative approach of Mark et al. (2016) which employs the terrestrial Pb-isotope evolution model of Stacey & Kramers (1975). Age calculations were performed using Isoplot (Ludwig,

**Table 1.** Samples used in this study, taken from (Stutenbecker et al., 2017; 2019). MRS – modern river sediment; UFM – upper fluvial molasse; UMM – upper marine molasse; LFM – lower fluvial molasse. Deposition ages from magnetostratigraphy of Schlunegger et al. (1996).

| Sample | Type | Lat | Long | Description | Deposition age (Ma) | Principal units in catchment |
|---|---|---|---|---|---|---|
| LS2017-3 | Molasse bedrock | 47.0057 | 7.9713 | UFM - Napf | 14 | - |
| LS2018-5 | Molasse bedrock | 46.9391 | 7.9508 | UMM - Luzern | 19 | - |
| LS2016-18 | Molasse bedrock | 46.7746 | 7.7324 | LFM - Thun | 25 | - |
| LS2018-12 | MRS | 46.7203 | 7.2455 | Ärgera catchment | - | Gurnigel flysch |
| LS2014-19 | MRS | 46.2242 | 7.4072 | Borgne catchment | - | St Bernard-Combin-Dent Blanche nappes |
| LS2014-29 | MRS | 46.5330 | 8.3574 | Goneri catchment | - | Gotthard nappe |
| LS2014-37 | MRS | 46.1323 | 7.0463 | Trient catchment | - | Mont Blanc - Aiguilles Rouges external crystalline massif |

**Figure 2.** Compositions of garnet analysed in this study, from Stutenbecker et al. (2017; 2019). Andradite-rich garnets are excluded (n = 2). Yellow – double-dated; magenta – acceptable Lu-Hf age only; purple – acceptable U-Pb age only; blue – no acceptable age recovered.



2012). As many analyses were discordant due to the incorporation of common-Pb during crystallization, a discordance filter was not applied. However, many analyses exhibited undesirably high age uncertainty. An uncertainty filter was therefore applied following the approach of Chew et al. (2020), such that:

$$2\sigma(\%)\ limit = (5 \times age^{-0.5}) \times 100$$

Afrikanda, Dashkesan, and Chikskii garnets were used as secondary reference materials and treated as unknowns throughout the data reduction process (reference U-Pb TIMS ages 377 ± 3 Ma, 147 ± 2 Ma, and 492 ± 2 Ma respectively; Salnikova et al., 2018; Salnikova et al., 2019; Stifeeva et al., 2019). Afrikhanda yielded a lower-intercept U-Pb age of 368.1 ± 2.6 Ma (MSWD = 1.2, n = 51), and Dashkesan 146.0 ± 1.3 Ma (MSWD = 0.92, n = 50); both are slightly discordant. Chikskii analyses are over-dispersed (MSWD = 3.3) and show signs of both Pb-loss and common-Pb incorporation, so no meaningful age can be reported; this is in agreement with a previous report that the U-Pb system in Chikskii garnet is over-dispersed (O'Sullivan et al., 2023).

Trace element data were also reduced in Iolite using the Trace Elements DRS, employing $^{29}$Si as an internal standard to correct for yield variation. The primary reference material was NIST612. As no garnet trace element reference material was available, the komatiite glass GOR-132 was employed as a secondary reference material and treated as an unknown (Jochum et al., 2006). Reference values typically reproduced within 5% despite many being present at ng/g concentrations; an exception was Fe which was likely affected by a polyatomic Ca-based interference (e.g., Malinovsky et al., 2003). This was aggravated by the unnaturally high reference Ca/Fe ratio in the synthetic NIST glass. U-Pb and trace-element data are fully reported in supplementary table S2.

## 2.3 Garnet Lu-Hf and trace-element analysis by LA-Q-ICPMS/MS

A subset of 172 grains where sufficient material remained after U-Pb ablation were selected for Lu-Hf analysis. Analyses were conducted at Adelaide Microscopy, The University of Adelaide, using a RESOlution 193 nm laser ablation system (Applied Spectra) with a S155 sample chamber (Laurin Technic), coupled to an Agilent 8900x tandem mass spectrometer (ICPMS/MS). The method involves the addition of $NH_3$ (supplied as a 1:9 $NH_3$:He mix for safety reasons) into the reaction cell of the mass spectrometer (at a rate of 3 mL min$^{-1}$) to promote efficient formation of the $Hf((NH)(NH_2)(NH_3)_3)^+$ reaction product as a direct proxy for $^{176}$Hf. Equivalent reaction products for isobars $^{176}$Lu and $^{176}$Yb are negligible, allowing $^{176}$Hf and $^{176}$Lu to be effectively separated and measured free from isobaric interferences (Simpson et al., 2021; 2022; Glorie et al., 2023a). Following Simpson et al. (2021), $^{176+82}$Hf was measured as a proxy for 176Hf; $^{175}$Lu was measured as a proxy for $^{176}$Lu, and $^{178+82}$Hf was measured as a proxy for $^{177}$Hf. Isotope ratios were calculated in LADR (Norris and Danyushevsky, 2018) using NIST 610 as a primary standard (Nebel et al., 2009), and corrected for matrix-induced fractionation using Hogsbo garnet (1029 ± 1.7 Ma; Romer and Smeds, 1996; Simpson et al., 2021). Resulting Lu-Hf dates were calculated as 2-point (inverse) isochron ages in IsoplotR (Vermeesch, 2018), where the second point comprised an initial $^{177}$Hf/$^{176}$Hf anchor of 3.55 ± 0.05, which spans the entire range of initial $^{177}$Hf/$^{176}$Hf ratios of the terrestrial reservoir (e.g., Spencer et al., 2020; Glorie et al., 2023a). The obtained inverse isochon age for secondary reference material BP-1 garnet was 1752 ± 21 Ma (2σ uncertainty including propagated uncertainty from Hogsbo) is in good agreement with previously published Lu-Hf dates (1745 ± 14 Ma and 1744 ± 13 Ma; Simpson et al., 2023 and Glorie et al., 2023b, respectively). The same uncertainty filter applied to the U-Pb ages was employed.

Analytical parameters are fully reported in supplementary table S1. Lu-Hf and trace-element data are fully reported in supplementary table S2.

## 2.4 Garnet composition by Raman spectroscopy

A subset of garnets (n = 45), including those grains yielding acceptable U-Pb or Lu-Hf ages where sufficient material remained after ablation, was selected for Raman spectroscopic analysis. The objective was to assess whether any Raman fingerprint could be used to rapidly and non-destructively identify grains amenable to dating. This Raman signature is archived in the entire spectrum as a combination of the Si-O stretching modes represented by "peak 6" (the main high-frequency band in the 870–927 $cm^{-1}$ range of Bersani et al., 2009), OH stretching signals of the OH groups , and laser-induced luminescence bands.

Raman spectra of garnet grains were collected at the Laboratory for Provenance Studies (University of Milano-Bicocca, Italy) using a Renishaw inVia confocal Raman spectroscope, equipped with a Leica DM2500 microscope. Non-polarized micro-Raman spectra were obtained in nearly backscattered geometry, with a green 532 nm line, solid-state laser, with a spectral resolution of ±0.5 $cm^{-1}$, and power ≤ 10 mW at the sample. Before each experimental session, the system was calibrated using a silicon wafer, having its Raman peak at 520.6 ±0.3 $cm^{-1}$. A 50x LWD (long working distance) objective or, when applicable, a 20x objective were used. The acquisition of each spectrum was set at 1 second of exposure, 100% of laser power and 30 accumulations. Firstly, the analytical region was centered at 1090 $cm^{-1}$ (corresponding to a 146-1912 $cm^{-1}$ spectrum range) in order to detect the six characteristic Raman peaks of garnets, following Bersani et al. (2009). The spectra were elaborated using a Renishaw Windows®-based Raman Environment (WiRE, v. 4.4) software for determining the Raman frequencies of the peaks. Secondly, the analytical region was centered at 3700 $cm^{-1}$, to observe any Raman bands related to occurrence of OH groups. Raman luminescence fingerprint was also analyzed in the high frequency region centered at 4300 $cm^{-1}$. Raman spectroscopic data are fully reported in supplementary table S3.

# 3 Results

Age spectra for all analysed garnets are shown in Fig. 3. The Lu-Hf data yield a major modal age peak at c. 25 Ma, plus a subordinate peak at c. 330 Ma; the U-Pb data yield corresponding peaks at c. 28 Ma and c. 332 Ma, plus a peak at c. 434 Ma. 27 acceptable U-Pb and 108 acceptable Lu-Hf ages were obtained, representing success rates of 8% and 63% respectively. Raman data showed no correlation with whether an acceptable U-Pb or Lu-Hf age could be recovered, so are not discussed further.

# 4 Discussion

Garnet U-Pb age recovery is poor, likely due to low initial U/Pb during crystallisation. As shown in Fig. 4, garnet in this study is not significantly enriched in U relative to Pb during crystallization, unlike other common-Pb hosting geochronometers (e.g., rutile and apatite). Ideally the U-hosting phase effectively excludes common-Pb during crystallization (e.g., zircon), but at least some degree of U enrichment is required to permit sufficient ingrowth of radiogenic Pb over geologically relevant timescales. Lu-Hf age recovery is considerably better, but still hampered by relatively low Lu concentrations and the relative youthfulness of the Alpine orogen which reduces the time for ingrowth of $^{176}Hf$. There is no systematic relationship

**Figure 3.** Kernel density estimates for zircon, apatite, rutile, and garnet U-Pb ages, and garnet Lu-Hf ages. Zircon data are from Honegg-Napf molasse samples of Zimmermann et al. (2018), corresponding to Thun-Napf samples of this study; apatite and rutile data are from Honegg-Napf molasse samples of Mark et al. (2018); and garnet data are from this study. Density plots generated using DensityPlotter (Vermeesch, 2012). Data are filtered after approach of Chew et al. (2020), except for zircon which are filtered using a concordance probability threshold as described by Zimmerman et al. (2018); n = number of acceptable ages/total analyses. A small number of ages >800 Ma are excluded for clarity (17 zircon; 1 apatite; 0 rutile; 1 garnet U-Pb; and 1 garnet Lu-Hf).

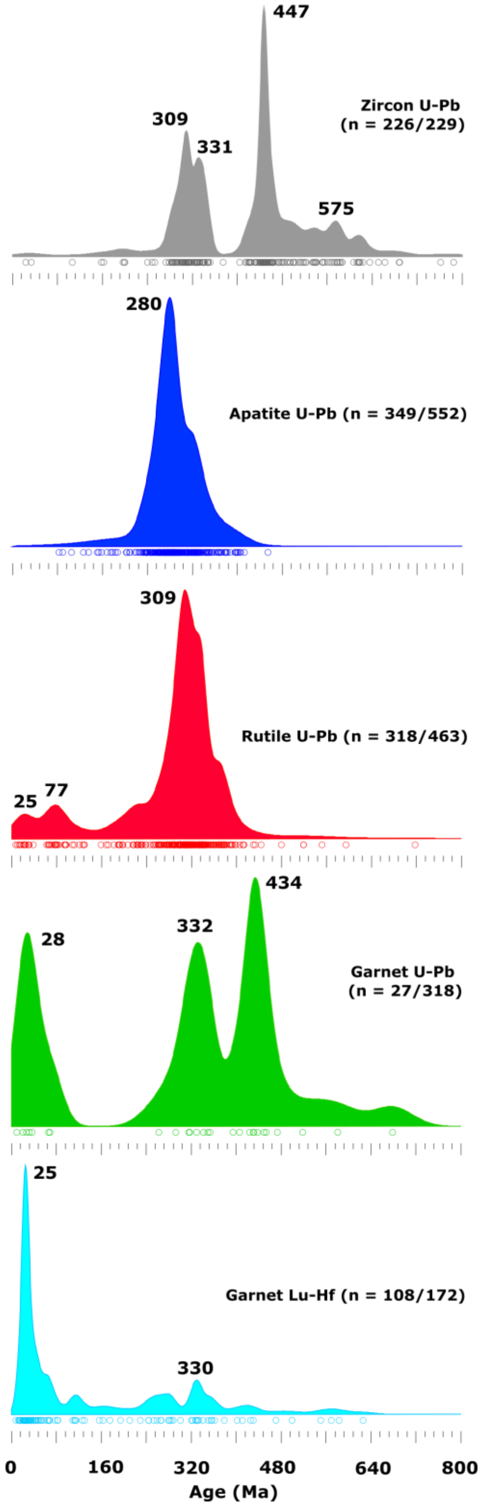
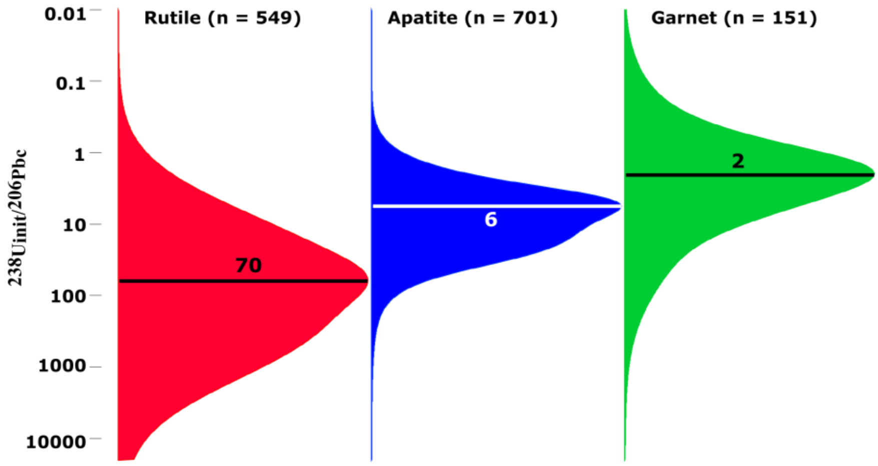


**Figure 4.** Distribution and modal values of initial $^{238}U/^{206}Pb_c$ ratios at time of crystallization, calculated for Alpine rutile, apatite, and garnet. Rutile and apatite data are from Mark et al. (2018). Garnet data are from this study, and include all analyses for which a finite age could be calculated, regardless of uncertainty.



between garnet composition and whether or not an acceptable age could be obtained, in agreement with the Raman observations (Fig. 5).

4.1 Interpretation of detrital garnet ages

The observed garnet U-Pb and Lu-Hf age peaks fit well with known hinterland tectonometamorphic events. The c. 25-28 Ma age peak records the Barrovian overprint in the Lepontine Dome (Boston et al., 2017; Janots et al., 2009; Liati et al., 2009). The c. 330-332 Ma age peak records Variscan metamorphism during the collision of Laurussia and Gondwana, which is widely preserved in polycyclic Alpine crystalline bedrock (e.g., von Raumer et al., 2009). The c. 434 Ma U-Pb peak records a Siluro-Ordovician metamorphic event documented in polycyclic units of the external massifs (Schulz & von Raumer, 2011), probably caused by docking of Armorica and Gondwana (Matte, 2001). Preservation of pre-Alpine detrital garnet in sedimentary units incorporated into the Alpine orogen and subjected to blueschist facies metamorphism has also been documented (Manzotti & Ballèvre, 2013).

However, the garnet U-Pb and Lu-Hf age spectra clearly differ, with the U-Pb system preserving more pre-Alpine ages. It is also important to consider that most garnets analysed here did not yield acceptable ages for both systems; therefore, some of the garnets yielding Carboniferous and Silurian U-Pb ages could be from sources which were not strongly affected by the Alpine orogen or which were otherwise shielded, and might have yielded compatible Lu-Hf ages had sufficient Lu been present. Nonetheless, as previously observed for other phases (e.g., the U-Pb and Lu-Hf systems in apatite; Glorie et al., 2022), garnet ages obtained from the same sample using multiple dating methods need not always agree within analytical uncertainty (e.g., Smit et al., 2013). Such disagreement is expected where radioisotope systems hosted in the same phase have differing diffusivities. Other causes of over-dispersion may include inclusions and parent zonation during geologically prolonged or polyphase mineral growth. Note that these mechanisms are not mutually exclusive. Where *in-situ* analysis is employed, as here, inclusions are readily detected and excluded by co-analysis of elements stoichiometric to the phases. Parent isotope zonation effects may be induced either by Raleigh fractionation (Kohn, 2009) or by polyphase growth. However, in detrital studies, the small age offsets caused by fractionation effects may be negligible where the objective is to distinguish between geological events well separated in time, e.g., different orogenies. Polyphase growth recording multiple orogenic events is likely to be less important in garnet than in more refractory geochronometers (e.g., the U-Pb system in zircon) because relict or detrital garnet is thought to seldom survive diagenesis and the early stages of prograde metamorphism (Garzanti et al., 2018; Cave et al., 2015; Manzotti & Ballèvre, 2013). However, inherited garnet which is retained in polycyclic crystalline bedrock without being released to the sedimentary system may record multiple metamorphic events (e.g., Walker et al., 2020; Argles et al., 1999). Thus, although anticorrelated U and Lu zoning in garnet has been documented (Raimondo et al., 2017), it is unlikely to be a widespread cause of significantly different U-Pb and Lu-Hf ages.

To assess whether the different U-Pb and Lu-Hf age spectra arise from diffusivity, we calculate the closure temperatures for both systems (Dodson, 1973) in Matlab®. The diffusivity of Lu and Hf has recently been experimentally re-evaluated in gem-quality natural spessartine garnet (Bloch et al., 2015, 2020). Unusually, both parent and daughter elements are proposed to diffuse at geologically reasonable cooling rates and grain sizes. While the closure temperature for Hf in garnet is typically > 730 °C, Lu may be mobile at temperatures as low as 600-700 °C for grain radii < 100 µm, provided cooling rates are below c. 1 °C/Ma (Fig. 6a & b). However, at the low concentrations typical in natural garnet, significant Lu diffusion was observed in experiments at atmospheric pressure but not where experimental pressures exceeded 1 GPa (Bloch et al., 2020). As experiments at intervening pressures were not

**Figure 5.** Principle component analysis plots illustrating the lack of correlation between garnet composition and age recovery (yellow – age obtained; blue – no age obtained) for **(a)** U-Pb and **(b)** Lu-Hf.

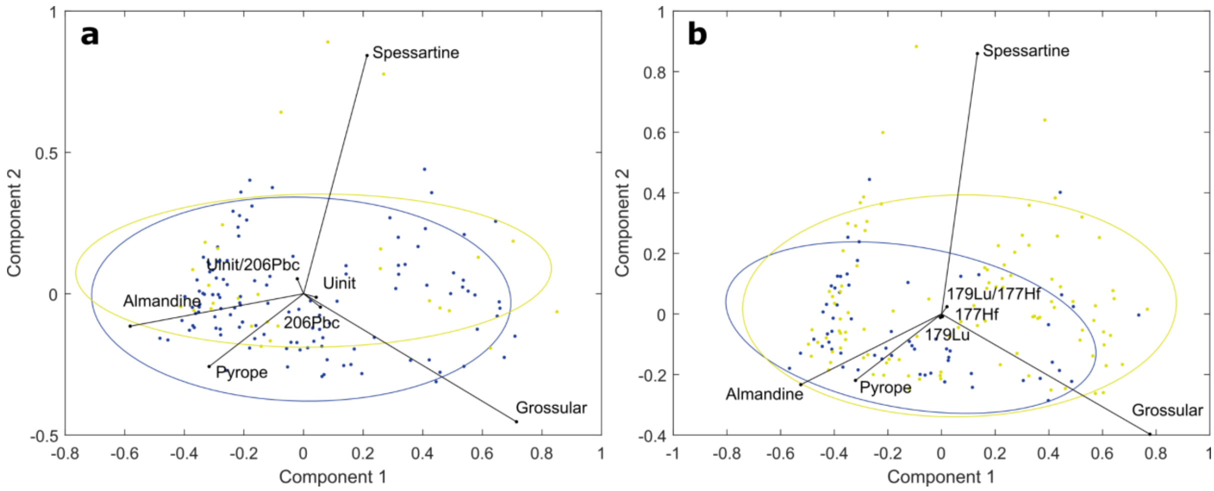
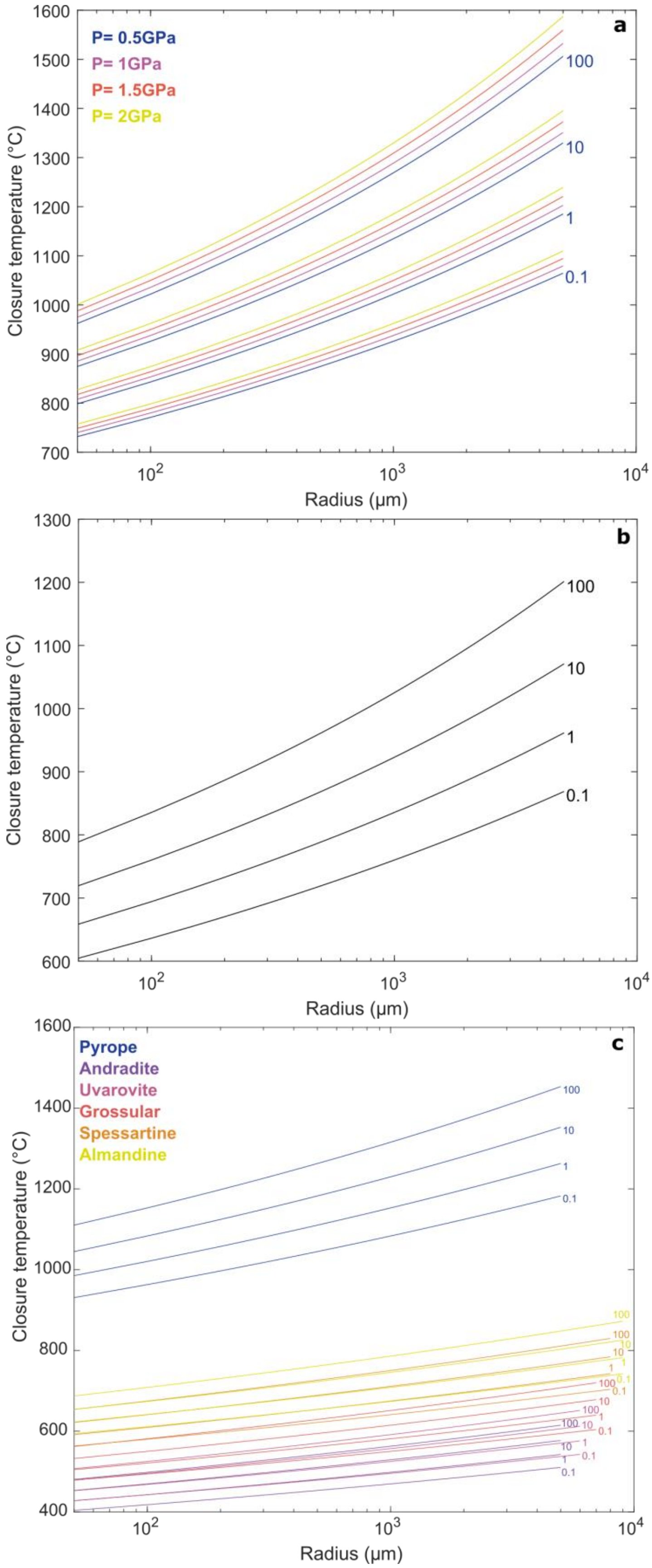


**Figure 6.** Closure temperature estimates for Hf **(a)**, Lu **(b)**, and Pb **(c)** in garnet, for cooling rates of 0.1 to 100 °C $Ma^{-1}$.



performed it is unclear whether significant Lu diffusion may be expected at geologically plausible PT conditions. The documented preservation of oscillatory Lu zoning in garnet growing during prograde conditions > 600 °C and < 1 GPa suggests Lu diffusion in geologically relevant PT conditions may be less significant than experimental data suggest (Guilmette et al., 2018). A pressure control was more definitively documented for Hf diffusivity, but the effect is relatively minor: a 1.5 GPa increase in pressure increases closure temperature by < 8% (Bloch et al., 2020). A dependence on Si activity is even more minor and is not considered here.

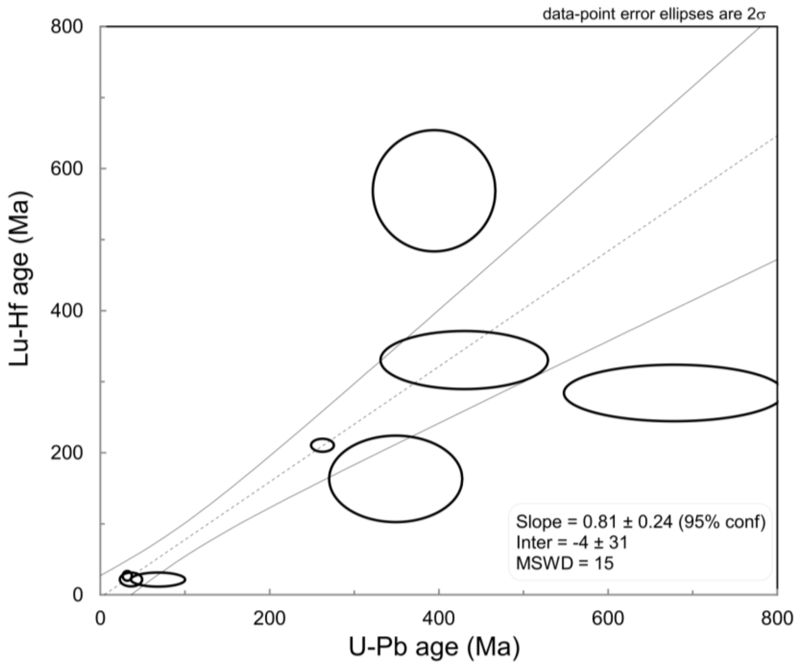
For the U-Pb system in garnet, experimental diffusivity data are unfortunately not available and empirical data are limited. Therefore, we use Pb diffusivity documented in other phases and the empirical relationship between ionic porosity and diffusivity to estimate closure temperatures (Dahl, 1997; Zhao & Zheng, 2007). The resulting estimates show a strong compositional control, with the U-Pb system in pyrope having very high closure temperatures (Fig. 6c). As the closure estimates presented here are for pure end-members, it is not clear how to quantify closure temperature for more commonly observed intermediate garnet compositions. However, the majority of garnets analysed in the study are almandine-dominated, which is the second most retentive end-member for Pb after pyrope. Thus, garnets dominated by almandine-pyrope conceivably have higher closure temperatures for U-Pb than for Lu-Hf, especially at low pressures where Lu may be mobile. Unfortunately, it is not possible to calculate Lu-Hf closure temperatures in other garnet end-members for direct comparison using the ionic porosity model, as Hf diffusivity has been determined only in a small number of phases, some of which exhibit very similar diffusivity (almandine, forsterite, rutile, spessartine, and zircon; Bloch et al., 2015, 2020; Cherniak, 2003; Cherniak et al., 2007; Jollands et al., 2014). However, measured diffusivities for these minerals do not display the linear relationship to ionic porosity identified by Zhao & Zheng (2007), and REE and Hf diffusivity was not observed to vary significantly between almandine and spessartine garnet (Bloch et al., 2015).

However, for the small subset ($n = 9$) of garnets analysed here which yielded both acceptable Lu-Hf and U-Pb ages, the ages from both systems define a line with a slope and intercept within uncertainty of one and zero respectively, when plotted together (Fig. 7). The small sample size means that the relationship should be treated with some caution, and some ages are clearly in disagreement. Nonetheless, these double-dated grains suggest that ages obtained from both systems are likely to be in agreement, and do not indicate a systematic tendency for either radioisotope system to yield older ages, which would be expected if one system had significant diffusivity at Alpine metamorphic temperatures.

## 4.2 Relationship of detrital garnet ages to other detrital geochronometers

The detrital garnet Lu-Hf and U-Pb ages can also usefully be compared with the age spectra of other detrital geochronometers recovered from the same molasse units (Fig. 3). The Alpine orogen is essentially unrecorded by the U-Pb system in zircon, due to the very limited degree of anataxis which is restricted to the Periadriatic line plutons (e.g., the Bergell and Adamello). Outwith these volumetrically small intrusions, Alpine zircon neocrystallisation is limited to epitaxial overgrowth (Rubatto & Hermann, 2003). The U-Pb system in apatite also yields only a small number of Alpine ages, and is dominated by Variscan metamorphism and post-Variscan magmatism (c. 290 Ma; Cassinis et al., 2011). While Alpine rocks yield abundant apatite, the widespread greenschist to amphibolite facies grade metamorphism of the central Alps is associated with low-U apatite, likely rendering many Alpine-age apatite grains undatable by U-Pb (Henrichs et al., 2019; Malusà et al., 2017). The U-Pb system in rutile does

**Figure 7.** $Age_{U\text{-}Pb}$ *vs* $Age_{Lu\text{-}Hf}$ for double-dated garnets (n = 9) yielding acceptable ages for both systems. These define a line with a slope and intercept within uncertainty of one and zero, respectively; however, some ages are not in agreement as indicated by the high MSWD. Consistent agreement between the two age systems is not necessarily expected given the differences in closure temperature.



yield subordinate Alpine age peaks, but at c. 77 Ma and c. 25 Ma; the former likely records Eoalpine metamorphism in the Sesia unit, and the latter likely records cooling through the Pb partial retention zone towards the end of the Lepontine Barrovian overprint. However, the dominant rutile U-Pb age peaks are Variscan.

Thus, detrital garnet ages appear strongly biased towards the most recent garnet-crystallising metamorphic event, with fewer pre-Alpine ages than other detrital geochronometers. This is probably due to garnet being much less refractory than rutile or zircon, although polycyclic garnet has been documented (e.g., Argles et al., 1999; Manzotti & Ballèvre, 2013). The U-Pb system in detrital rutile also provides a proxy for metamorphism as rutile rarely forms as a primary igneous mineral (Force, 1980), but the much more refractory nature of rutile means that a larger number of polycyclic grains yielding inherited ages are likely to be analysed as well. Garnet is readily removed from heavy mineral assemblages during diagenesis; in contrast, rutile, together with zircon and tourmaline, is typically among the most persistant heavy minerals (Hubert, 1962). Both garnet and rutile are also likely to break down during the sub-greenschist-facies-grade stages of prograde metamorphism (Cave et al., 2015). Detrital garnet geochronology may thus hold potential as a proxy for the most recent mid-grade metamorphism in the source area, especially for less deeply eroded orogens preserving widespread metapelitic rocks which are likely to be rich in garnet. In this context, mid-grade metamorphic source rocks attain sufficiently high pressures and temperatures to crystallise garnet, but fall short of anataxis and therefore do not crystallise zircon. The PT conditions for the garnet-in isograd will evidently vary considerably depending on rock composition, but temperature estimates between c. 450 – 550 °C for metapelitic rocks are commonly reported, i.e., within the upper-greenschist-facies- and upper-blueschist-facies-grades (e.g., Florence & Spear, 1993). However, spessartine-rich garnet is stabilised in Mn-rich metapelites at temperatures at least as low as 400 °C (White et al., 2014) and potentially as low as 300-350 °C (Kennan & Murphy, 1993), showing the importance of integrating garnet composition with age interpretion. These temperatures are lower than typical rutile formation temperatures of > c. 450 °C (Chambers & Kohn, 2012), illustrating that detrital garnet geochronology may be usefully applied to lower-grade orogens which did not extensively crystallise rutile. While such orogens may also be appropriate targets for $^{40}Ar/^{39}Ar$ or $^{87}Rb/^{87}Sr$ analysis of detrital mica, garnet is less prone to alteration or hydrodynamic fractionation during transport (Garzanti et al., 2008).

The similarity of the garnet and rutile Alpine age peaks (c. 28-25 Ma *vs* c. 25 Ma, respectively) is in reasonable agreement with documented Alpine PT conditions. Pseudosection modelling using average bulk compositions of passive margin pelite and greywacke can be used to approximate global PT stability fields for these phases (Yakymchuk et al., 2018). Such modelling is evidently rather idealized and it is unclear if similar PT stability fields may be expected from metagranitoids, which are widespread in the western and central Alps, or in metasedimentary rocks which significantly deviate from average global compositions. Nonetheless, these models do provide at least some indication of likely mineral PT stability fields. For these bulk compositions, rutile is completely removed between c. 460-670 °C at pressures < 1 GPa, with rutile stability increasing with pressure. In contrast, garnet is present throughout this temperature range. At pressures > 1 GPa, both rutile and garnet are stable (Yakymchuk et al., 2018). Assuming these metasedimentary rock types are reasonable approximations for Alpine source rocks, neocrystalline Alpine rutile and garnet can only yield similar ages if source rocks have equilibrated at peak PT conditions within the rutile stability field, i.e. at < c. 460-670 °C if pressure is < 1 GPa. These values agree reasonably well with documented PT conditions for Alpine Barrovian metamorphism of c. 350-700 C and ≤ 0.8 GPa (Todd and Engi, 1997).

Additionally, the overlap between Alpine garnet and rutile ages suggests that post-peak cooling to temperatures below the thermal sensitivity of the U-Pb system in rutile must have been geologically rapid. Diffusivity of Pb in rutile is well established, with experimental and empirical studies indicating a partial retention zone of c. 490 – 640 °C for geologically typical grain sizes and cooling rates (Cherniak, 2000; Kooijman et al., 2010). Thermal sensitivity of both the U-Pb and Lu-Hf systems in garnet is less well constrained, but considered to be c. 600 - 1050 °C for the almandine-dominated garnets analysed here, of typical detrital grain size (50-100 µm radius) subjected to geologically common cooling rates (e.g., Bloch et al., 2020; O'Sullivan et al., 2023; Smit et al., 2013). Therefore, prolonged residence at temperatures > 490 °C would be expected to yield rutile U-Pb ages younger than garnet ages. Similar rutile and garnet Alpine ages agree with documented rapid cooling of the Lepontine Dome and southern Aar-Gotthard massif between c. 22-15 Ma (Boston et al., 2017; Janots et al., 2009).

## 5 Conclusions

Both the U-Pb and Lu-Hf isotope systems in garnet are biased towards the youngest garnet-crystallising metamorphic event in the source area, in agreement with the less refractory nature of garnet compared to rutile or zircon. Detrital garnet geochronology therefore shows utility where the objective is to identify sediment sourced from the youngest and, hence, likely most rapidly exhumed component of an orogen without co-analysis of large numbers of inherited ages. Age recovery for both systems is not compositionally biased, at least for the generally almandine-rich garnets analysed here. However, the Lu-Hf system shows considerably better age recovery than the U-Pb system (8% *vs* 63%), due to the failure of garnet to concentrate U relative to Pb during crystallisation. While possible compositional and pressure controls on both the U-Pb and Lu-Hf system in garnet may complicate age interpretation, the ability of this study to reproduce the age of Alpine Barrovian metamorphism indicates that these complexities are generally unimportant. Detrital garnet Lu-Hf dating, coupled in future with compositional analysis and crystallisation pressure estimates using thermoba-Raman-try (Kohn, 2014) and Zr-in-rutile or –titanite detrital thermometry, may offer scope for rapid first-order reconstruction of source area pressure-time evolution, especially in areas difficult to access directly.

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## Open Research Statement

The data reported in this study are fully tabulated in the supplementary materials accessible at [www.doi.org/10.5281/zenodo.7900189](www.doi.org/10.5281/zenodo.7900189). The most recent version of the Iolite software used for U-Pb and trace-element data reduction is available from www.iolite.xyz (a division of Elemental Scientific, Inc.). The LADR software used for Lu-Hf data reduction is available from www.norsci.com. Both data reduction packages are available under proprietary license.

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