Supplementary Materials

Lithium in Garnet as a Tracer of Subduction Zone Metamorphic Reactions: The Record in UHP Metapelites at Lago di Cignana

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Geographic coordinates of the Lago di Cignana locality:

Longitude: 7.59447 E

Latitude: 45.87691 N

Images and Additional Geochemical Data for the Garnets in Figures 2-8

Included in this file are background images and geochemical data for each of the four garnets discussed in the text.

02-LDCS-11b-gt3 (see **Figs. 3 and 4**)

- Major element concentrations vs. distance across the garnet traverse
- REE diagram, normalized to chondrite values (values are from McDonough and Sun, 1995)
- Element map (Y) with white line indicating the traverse for the EPMA and SIMS data

CIGSED1-gt1 (see **Fig. 5**)

- Y and HREE across the garnet traverse
- REE diagram, normalized to chondrite values
- Y, HREE, and Li across the garnet traverse

CIGSED1-gt2 (see **Fig. 6**)

- Major element concentrations vs. distance across the garnet traverse
- REE diagram, normalized to chondrite values
- Lithium and Gd concentrations (ppm) and $\delta^7\text{Li}$
- Lithium, Lu, Yb, and Er concentrations

LHN18B-gt1 (see **Fig. 8**)

- Y and HREE across the traverse of the core region
- REE diagram, normalized to chondrite values

Note that element maps for Fe, Ca, and Mg in these four garnets are available upon request.

Analytical Methods

Table S1: Chemical compositions of reference garnets. $\Delta\delta^7\text{Li}^{\text{ws}}$ indicates matrix effects relative to a working standard†, and calculated as $\Delta\delta^7\text{Li}^{\text{ws}} \equiv (\delta^7\text{Li}^{\text{grt}} - \delta^7\text{Li}) - (\delta^7\text{Li}^{+\text{ws}} - \delta^7\text{Li}^{\text{ws}})$, where $\delta^7\text{Li}^{\text{grt}}$ and $\delta^7\text{Li}^{\text{ws}}$ are the f_{IMF} -corrected Li-isotope ratios of individual reference garnets and those of a working standard of the reference garnets.

Table S2: Matrix effects relative to a working standard for garnet Li-isotope analysis.

Figure S1: A representative calibration curve with a slope unity on garnet Li-isotope analysis.

Figure S2: Matrix effects on garnet Li-isotope analysis for (a) Grs and (b) Alm components.

Shaded regions indicate compositional ranges of garnets in unknown samples analyzed. Note that the matrix effects ($\Delta\delta^7\text{Li}^{\text{ws}}$) increase with Grs and Alm components, and especially Alm-rich garnets should be cautiously analyzed. The matrix effect for Grs is not significant, taking into account the analytical uncertainty of working standard grt-HK5206701d ($\pm 3\text{‰}$; 2σ).

Sample 02-LDCS-11b-gt3

Major element variation across garnet 02-LDCS-11b-gt3 (along the traverse in **Figs. 3 and 4**).

Chondrite-normalized REE data for 02-LDCS-11b-gt3, along the traverse (one-half of the traverse for clarity) in **Fig. 3**, demonstrating progressive depletion of HREE during garnet growth, and the annulus/spike.

Element map for Y for 02-LDCS-11b-gt3 showing the location of the annulus/spike (red) and the position of the line traverse for the SIMS and electron microprobe analyses in **Figs. 3 and 4** and in the figures above.

Sample CIGSED-1-gt1

Major element variation across garnet CIGSED1-gt1 (traverse location in **Fig. 5**).

Chondrite-normalized REE data for CIGSED1-gt1, along the traverse (one-half for clarity) in **Fig. 5**, demonstrating depletion of HREE during garnet growth, and the annulus/spike.

Sample CIGSED-1-gt1, continued

REE, Y, and Li concentrations across garnet CIGSED1-gt1 (along the traverse in **Fig. 5**).

Sample CIGSED-1-gt2

Major element variation across garnet CIGSED1-gt2 (along the traverse in **Fig. 6**).

Chondrite-normalized REE data for CIGSED1-gt2, along a half-traverse (see **Fig. 6A**), demonstrating depletion of HREE during garnet growth, and the annulus/spike.

Sample CIGSED-1-gt2, continued

Lithium and Lu concentrations and $\delta^7\text{Li}$ across the traverse of garnet CIGSED1-gt2 (location of traverse on the element map in **Fig. 6A**).

Lithium, Lu, Yb, and Er concentrations across the traverse of garnet CIGSED1-gt2 (location of traverse on the element map in **Fig. 6A**).

Sample LHN18B-gt1

Lithium, Yb, Lu, and Y concentrations across the second traverse of the near-core region of garnet CIGSED1-gt1 (orange traverse in **Figs. 8A,B**).

Chondrite-normalized REE data for LHN18B-gt1, along the right side of the traverse in **Figs. 8C and D** (1000 to 2500 μm ; unaffected by the resorption and re-growth), demonstrating the depletion of HREE in the rock due to garnet growth, and the annulus/spike.

Analytical methods

Textural observations and phase identification were performed using a JEOL JSM-7001F SEM equipped with energy dispersive X-ray spectrometers (EDS) and Oxford AZtec X-Max and INCA X-act. The analyses were conducted under routine conditions (15 kV acceleration voltage, 3 or 5 nA beam current, and 100 s integration times).

Major-element abundance measurements of Si, Ti, Al, Cr, Fe, Ni, Mn, Mg, Ca, Na, K, and P, and X-ray mapping of the major elements and Y were conducted by electron probe microanalyzer (EPMA) in wavelength-dispersive mode with a JEOL JXA-8800 and a JEOL JXA-8530F. The elemental abundances were determined at conditions of a 15-kV acceleration voltage and 12-nA probe current, and the ZAF oxide method was employed for matrix correction. The X-ray mapping was performed at modified conditions using 200-nA probe currents and 10 ms dwell time per 10- μ m pixel, or 500-nA probe currents and 10 to 20 ms dwell time per 3- to 6- μ m pixels, depending on target dimension. Natural silicates and synthetic oxides on ASTIMEX MINM25-53 were used for calibration.

Trace-element abundances of Li, Sr, Y, Zr, Nb, Ba, La, Ce, Pr, Nd, Sm, Eu, Gd, Dy, Er, Yb, Lu, and Hf were obtained by secondary ion mass spectrometry (SIMS) using a Cameca ims-5f (Nakamura *et al.* 2012; Kunihiro *et al.*, 2021). Thin-sections were coated with 30 nm of Au to avoid charging. An O^- beam impacted the samples with current of 5 to 15 nA and an energy of -17 keV. Secondary ions were accelerated to $+4.5$ keV and kinetic energy filtering (-45 eV bias of the sample accelerating voltage with energy window from -20 to $+20$ eV) was employed to reduce oxide-ion interferences. The secondary ions were counted with an electron multiplier and using magnetic-peak jumping. The acquisition time for each spot was ~ 40 minutes and resultant craters were 15 to 20 μ m in diameter. For each analysis, the ion intensity of element Z, $I(^nX^+)$, relative to that of reference isotope ^{30}Si was determined. Element concentration of X was estimated using $[\text{Si}]$ on site that was determined by EPMA in advance and relative ion yield Y . The Y was obtained by analysing a series of reference materials and expressed as $Y \equiv \{I(^nX^+)/I(^{30}\text{Si}^+)\}/([X]/[\text{Si}])$. The amount of oxide-ion interference (e.g., $^nX^+$ has an interference $^{n-16}\text{ZO}^+$) was estimated using relative oxide-ion yield $\Psi(\text{ZO}^+) \equiv \{I(\text{ZO}^+)/I(\text{Si}^+)\}/([Z]/[\text{Si}])$ determined using the reference materials, including synthetic basaltic glass, clinopyroxene, orthopyroxene, and garnet (Nakamura *et al.* 2012; Kunihiro *et al.*, 2021). Trace-element concentrations of the reference materials were determined independently by wet chemistry. Total analytical uncertainties were estimated from repeated analyses of reference materials, to be 10–20%.

Lithium isotope compositions were determined by high-resolution SIMS using a modified Cameca ims-1270 (Kobayashi *et al.* 2004, Maruyama *et al.* 2009; Kunihiro *et al.*, 2019). The primary O^- beam generated by duo plasmatron was accelerated to -23 keV. The primary-beam current ranged from 0.5 to 30 nA to maintain constant secondary ion intensity. A contrast aperture of 400 μ m was used. An optical gate corresponding to 50 x 50 μm^2 on sample surface was inserted and the energy band pass was set to 0 ± 50 eV. Widths of entrance and exit slits were

set to 400 and 1200 μm , respectively, to have mass-resolution power of 1200, sufficient to eliminate interference ${}^6\text{LiH}^+$. The intensity ratio of ${}^6\text{Li}^+$ and ${}^7\text{Li}^+$ was determined in magnetic peak-jumping mode by ion counting with an electron multiplier. Integration times for ${}^6\text{Li}^+$ and ${}^7\text{Li}^+$ were 4 and 1 s in each cycle, respectively, and each run consisted of 110 cycles. Craters were less than 20 μm in diameter. Element concentrations of Li for the analyzed spots were estimated using (${}^7\text{Li}^+/\text{I}_{\text{PRI}}$), where I_{PRI} is primary ion-probe current. Instrumental mass fractionation was estimated analyzing a series of reference materials (Table S1). Their Li concentrations and isotope compositions were determined by the method described in Moriguti and Nakamura (1998), except that Li isotope measurements were carried out using a multicollector-inductively coupled plasma-mass spectrometer, Thermo-Finnigan Neptune (Tang *et al.*, 2007).

Instrumental mass fractionation involving matrix effects has been known to occur for Li isotope measurements using SIMS (e.g., Bell *et al.*, 2009; Kunihiro *et al.*, 2019; Hoover *et al.*, 2021). Therefore, we examined the matrix effects relative to a working standard garnet based on the isotope measurements of reference garnets with certain compositional characteristics. At first, we prepared and analyzed three reference garnets (grt-RVSA4, grt-m, grt-HK5206701d), which have major element compositions similar to each other (**Table S1**). The relationship between isotope ion-intensity ratio (${}^7\text{Li}^+/\text{I}_{\text{PRI}}$ or $\delta^7\text{Li}^+$) and isotope ratio (${}^7\text{Li}/{}^6\text{Li}$ or $\delta^7\text{Li}$) is shown in **Fig. S1**. We correlated the ratios by formula $\delta^7\text{Li} = \delta^7\text{Li}^+ - f_{\text{IMF}}$, where $\delta^7\text{Li}^+$ and f_{IMF} are the ion-intensity ratio and the instrumental mass fractionation including matrix effects for the major element compositions, respectively. As shown by the formula, the instrumental mass fractionations including matrix effects are calculated by simple differences. The least-square-fitted line (**Figure S1**) demonstrates that the Li-isotope composition can be determined in a range from -8 to 3‰ , which is the typical range of $\delta^7\text{Li}$ observed on garnet in unknown samples in this study, with 2.4‰ accuracy (2σ). Since we have demonstrated linearity between isotope ion-intensity and isotope ratios, we analyzed grt-HK5206701d repeatedly in each analytical session as a working standard and determined the isotope ratio of garnets in unknown samples from deviation of isotope ion-intensity ratio relative to that of the working standard. Repeated analyses of grt-HK5206701d also monitor a stability of the instrument and evaluate reproducibility of the analyses. Internal precision is estimated by standard error within an acquisition. External precision is estimated by standard deviation among acquisitions made onto a working standard. Including data for all sessions, internal and external precisions (2σ) were $0.6\text{--}3.2\text{‰}$ and $1.4\text{--}3.0\text{‰}$, respectively, thus on our figures we use $\pm 3\text{‰}$ as the uncertainty (2σ) represented by the error bars.

The working standard, grt-HK5206701d, is the standard garnet with the major element compositions nearest those of garnets in our samples, but still differs significantly in major element composition from the garnets investigated here. Thus, we evaluated the matrix effects on garnet Li-isotope analysis as function of almandine component ($\text{Alm} = \text{Fe}/(\text{Ca} + \text{Fe} + \text{Mn} + \text{Mg})$) and grossular component ($\text{Grs} = \text{Ca}/(\text{Ca} + \text{Fe} + \text{Mn} + \text{Mg})$) relative to the working standard, grt-HK5206701d, by analyzing five reference garnets, including grt-SAE113 and grt-mvg, in

addition to the three mentioned above (**Table S1**). We evaluated matrix effects of a series of garnet standards based on acquisitions carried out in dedicated analytical sessions, just before or after the sessions for unknown samples. As a result, we obtained correlations between the matrix effects relative to the working standard ($\Delta\delta^7\text{Li}$) and Alm or Grs component to be $\Delta\delta^7\text{Li}(\text{Alm}) = 11.23 \times (\text{Alm} - 0.43)$, and $\Delta\delta^7\text{Li}(\text{Grs}) = 5.63 \times (\text{Grs} - 0.12)$, respectively (**Table S2, Fig. S2**). The relative matrix effects increase as function of Alm and Grs components. The range of Grs component of garnets in unknown samples is shown in gray area in **Fig. S2a**. Taking the analytical uncertainty of working standard, grt-HK5206701d ($\pm 3\%$ in 2σ) into account, variation in Grs component of garnets in unknown samples does not give significant difference in the matrix effect. Therefore, we did not correct for the matrix effects of the Grs component.

However, that is not the case for Alm component. Because of a lack of reference garnets with high Alm-component that cover the range of the Alm components of garnets in the unknowns, the relative matrix effect for garnets in unknown samples must be estimated by extrapolation of the correlation obtained. Previous studies have also suggested a positive correlation of the matrix effect with iron-endmember components such as the fayalite component in olivine (Bell *et al.*, 2009; Kunihiro *et al.*, 2019) and Alm component in garnet (Hoover *et al.*, 2021). Then, we evaluated an impact of the correction in two domains with Alm from 0.45 to 0.65 and Alm from 0.65 to 0.8 that are typical compositions of core and rim of the garnets in unknown samples. In the former domain, if the extrapolation gives the correct matrix effect, it is consistent with analytical uncertainty of $\pm 3\%$. Thus we did not apply the matrix correction. In the latter domain, when the extrapolation gives the correct matrix effect, it is estimated to be 5% at most. As the Li isotope observation in this study infers the $\delta^7\text{Li}$ value of rim is smaller than that of core, the $\delta^7\text{Li}$ value of rim becomes 5% smaller at most, by applying the matrix correction to the latter domain, resulting that the matrix corrections enhances variation of $\delta^7\text{Li}$ in the garnets. Thus, even with the matrix effect estimated from the extrapolation, the correction does not impact our discussions. For those reasons and considering uncertainty on extrapolation, we opted not to apply the matrix effect collection on the latter domain as well.

We have not examined the matrix effect incorporating the spessartine component ($\text{Sps} = \text{Mn}/(\text{Ca} + \text{Fe} + \text{Mn} + \text{Mg})$) because of a lack of reference garnets that cover the range of the Sps components (0.01~0.32) of garnets in unknown samples. Hoover *et al.* (2021) have suggested that the matrix effect related to the high Sps-component ($\text{Sps} \sim 0.3$) was also significant ($\sim 4\%$) based on the Li isotope measurements using synthesized custom-made glass reference materials, but not on natural garnets. Their data indicate that the matrix effect is not clearly distinguishable from their analytical uncertainties estimated based on reproducibility precision (0.1 ~ 2.0% in 2σ) for their glass reference materials with the variation in Sps less than 0.1. In the garnets we studied, the Sps components occasionally reach up to 0.3 only at cores of the garnets but are predominantly less than 0.1 (see **Figs. 5C and 8C**). We assume an uncertainty of $\pm 3\%$ based on Li isotope measurements using the reference materials of natural garnets, so that the matrix effect related to the Sps component does not significantly alter our interpretation and discussion.

In our garnets, Alm and Sps are inversely correlated, so the dominant matrix effects could cancel each other out to some extent (Hoover *et al.*, 2021). On the other hand, if changes in $\delta^7\text{Li}$ occur in regions where matrix chemistry is less variable, the Li-isotope variation cannot be entirely attributed to matrix effects where matrix chemistry change is unidirectional. To enhance quantitative discussion without uncertainty of matrix effect, systematic preparation of reference garnets is necessary, as emphasized by Hoover *et al.* (2021).

References

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Table S1: Chemical compositions of reference garnets.

name	grt-SAE113	grt-mvg	grt-RVSA4*	grt-m*	grt-HK5206701d*†
[SiO ₂] ^{cg·g⁻¹}	41.41	41.45	39.57	39.71	40.48
[TiO ₂]	0.39	0.52	0.15	0.02	0.14
[Al ₂ O ₃]	23.36	23.71	22.43	22.69	22.52
[Cr ₂ O ₃]	0.46	—	—	—	—
[FeO]	9.94	14.44	18.28	19.47	20.75
[MnO]	0.28	0.30	0.38	0.82	0.50
[MgO]	20.06	16.62	9.61	13.09	11.64
[CaO]	4.35	5.40	9.23	4.02	4.45
[Na ₂ O]	0.04	0.08	0.05	—	—
[K ₂ O]	—	—	—	—	—
Total	100.3	102.5	99.70	99.82	100.5
[Li] ^{μg·g⁻¹}	0.39	0.52	0.93	1.21	1.56
δ ⁷ Li	0.67	4.09	-1.99	2.62	-7.27
Alm	0.193	0.282	0.384	0.399	0.435
Sps	0.005	0.006	0.008	0.017	0.011
Prp	0.694	0.578	0.360	0.478	0.435
Grs	0.108	0.135	0.248	0.106	0.120
δ ⁷ Li ^{grt}	-3.8	1.2	-2.4	3.0	-8.4
2σ	1.8	3.0	1.8	2.2	3.0
n	8	86	10	6	17
Δδ ⁷ Li ^{ws}	-3.3	-1.7	0.8	1.5	0

* used for calibration to estimate instrumental mass fractionation. † used as a working standard to estimate matrix effect. Major element compositions were determined by using EPMA. Elemental and isotope abundances of lithium were determined by wet chemistry with ICP-MS and MC-ICP-MS, respectively. Endmember components of garnet, Alm (almandine), Sps (spessartine), Pyp (pyrope), and Grs (grossular) are estimated in molar number as Fe/(Fe+Mn+Mg+Ca), Mn/(Fe+Mn+Mg+Ca), Mg/(Fe+Mn+Mg+Ca), and Ca/(Fe+Mn+Mg+Ca), respectively.

Table S2: Matrix effects relative to a working standard for garnet Li-isotope analysis.

formula	compositional range	relative matrix effect	remark
$\Delta\delta^7\text{Li}_{\text{Grs}}^{\text{ws}} = 5.63 \times (\text{Grs} - 0.12)$	$0.10 \leq \text{Grs} \leq 0.30$	$-0.1 \leq \Delta\delta^7\text{Li}_{\text{Grs}}^{\text{ws}} \leq +1.0\text{‰}$	within analytical uncertainty
$\Delta\delta^7\text{Li}_{\text{Alm}}^{\text{ws}} = 11.23 \times (\text{Alm} - 0.43)$	$0.45 \leq \text{Alm} < 0.65$	$+0.2 \leq \Delta\delta^7\text{Li}_{\text{Alm}}^{\text{ws}} < +2.5\text{‰}$	within analytical uncertainty
	$0.65 \leq \text{Alm} \leq 0.80$	$+2.5 \leq \Delta\delta^7\text{Li}_{\text{Alm}}^{\text{ws}} \leq +4.2\text{‰}$	beyond but not applied

Figure S1: A representative calibration curve with a slope unity on garnet Li-isotope analysis.

Figure S2: Matrix effects on garnet Li-isotope analysis for (a) Grs and (b) Alm components. Shaded regions indicate compositional ranges of garnets in unknown samples analyzed. Note that the matrix effects ($\Delta\delta^7\text{Li}^{\text{ws}}$) increase with Grs and Alm components, and especially Alm-rich garnets might be cautiously analyzed. The matrix effect for Grs is not significant, taking the analytical uncertainty of working standard grt-HK5206701d ($\pm 3\text{‰}$ in 2σ) into account.