

SUPPLEMENTARY FILE

Garnet trace element systematics in an amphibolite- to granulite-facies metapelitic sequence (Ivrea-Verbano Zone, Italy)

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FIGURES

Fig S1: Geological map of central IVZ with sample locations.

Fig S2: LA-ICP-MS major element (Mg, Mn, Ca, Fe) profiles of garnets within studied samples, from amphibolite-facies to ultra-high temperature conditions.

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Fig S4: LA-ICP-MS elemental maps for upper-amphibolite facies garnet IVT-21_G0 for selected elements.

Fig S5: LA-ICP-MS elemental maps for granulite facies garnet IVT-40_G0 for selected elements.

Fig S6: LA-ICP-MS elemental maps for granulite facies garnet IVT-38_G0 for selected elements.

Fig S7: LA-ICP-MS elemental maps for granulite garnet IVT-39_G0 for selected elements.

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METHODS

- a) Phase-equilibrium modelling
- b) Diffusion modelling

FIGURES

S1: GEOLOGICAL MAP OF THE IVREA VERBANO ZONE

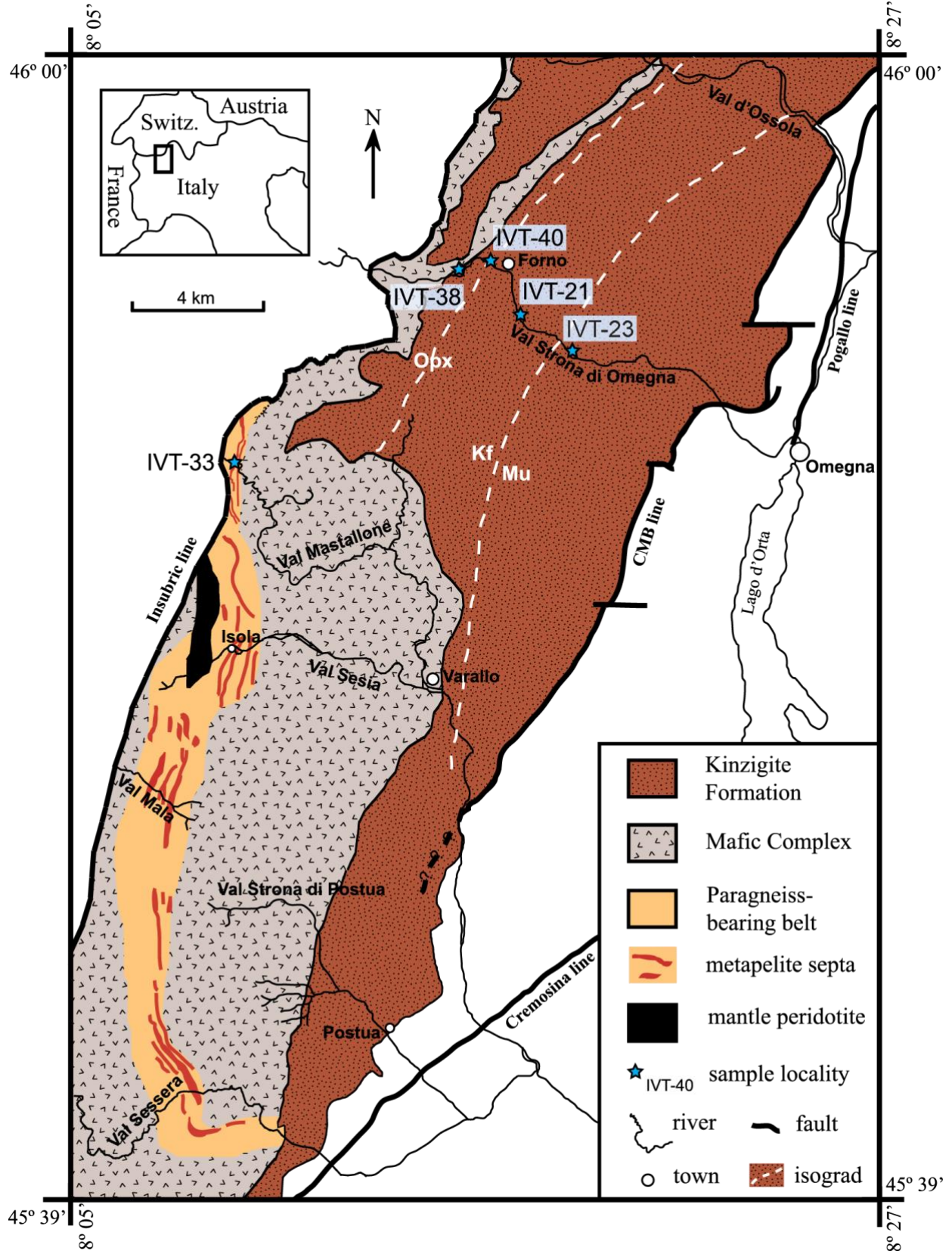


Fig. S1 – Geological map of central IVZ, taken after Ewing et al. (2013, 2014). Samples analysed in this study are marked by stars (blue). The mineral-in isograds are marked by dashed white line. The Opx-in isograd marks the first appearance of orthopyroxene in mafic rocks indicating the transition from amphibolite to granulite facies (Barboza and Bergantz, 2000). The Kf-in isograd marks the muscovite dehydration reaction and delineates the transition from mid- to upper-amphibolite facies.

S2: MAJOR ELEMENT ZONING PROFILES IN STUDIED GARNET

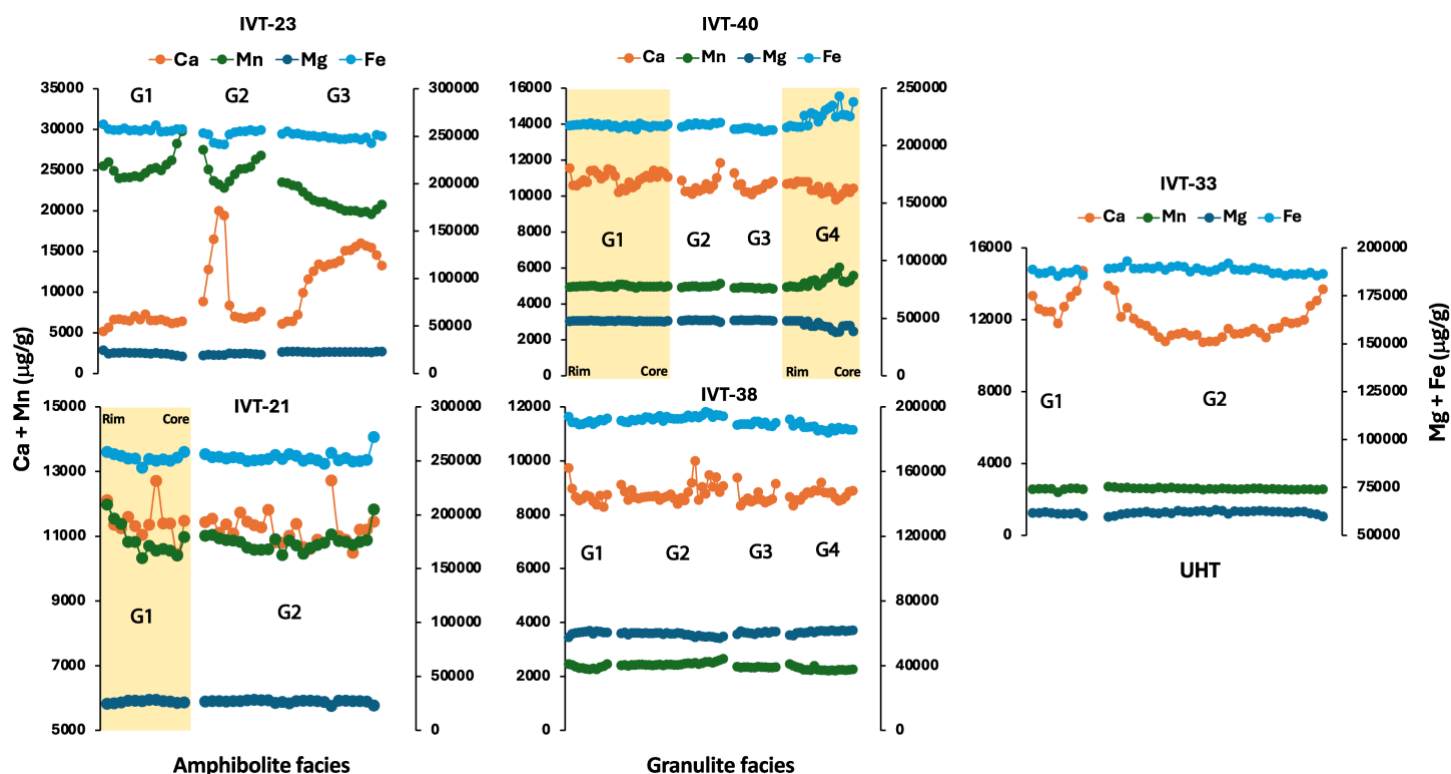


Fig. S2 – LA-ICP-MS major element profiles of garnets within studied samples. Ca and Mn contents are on the left vertical axis whereas Mg and Fe on right vertical axis. All profiles are full cross-sections (rim-rim profiles) except for three, where core-rim zoning is indicated by rectangles.

S3: TRACE ELEMENT MAPS IN IVT-23_G0

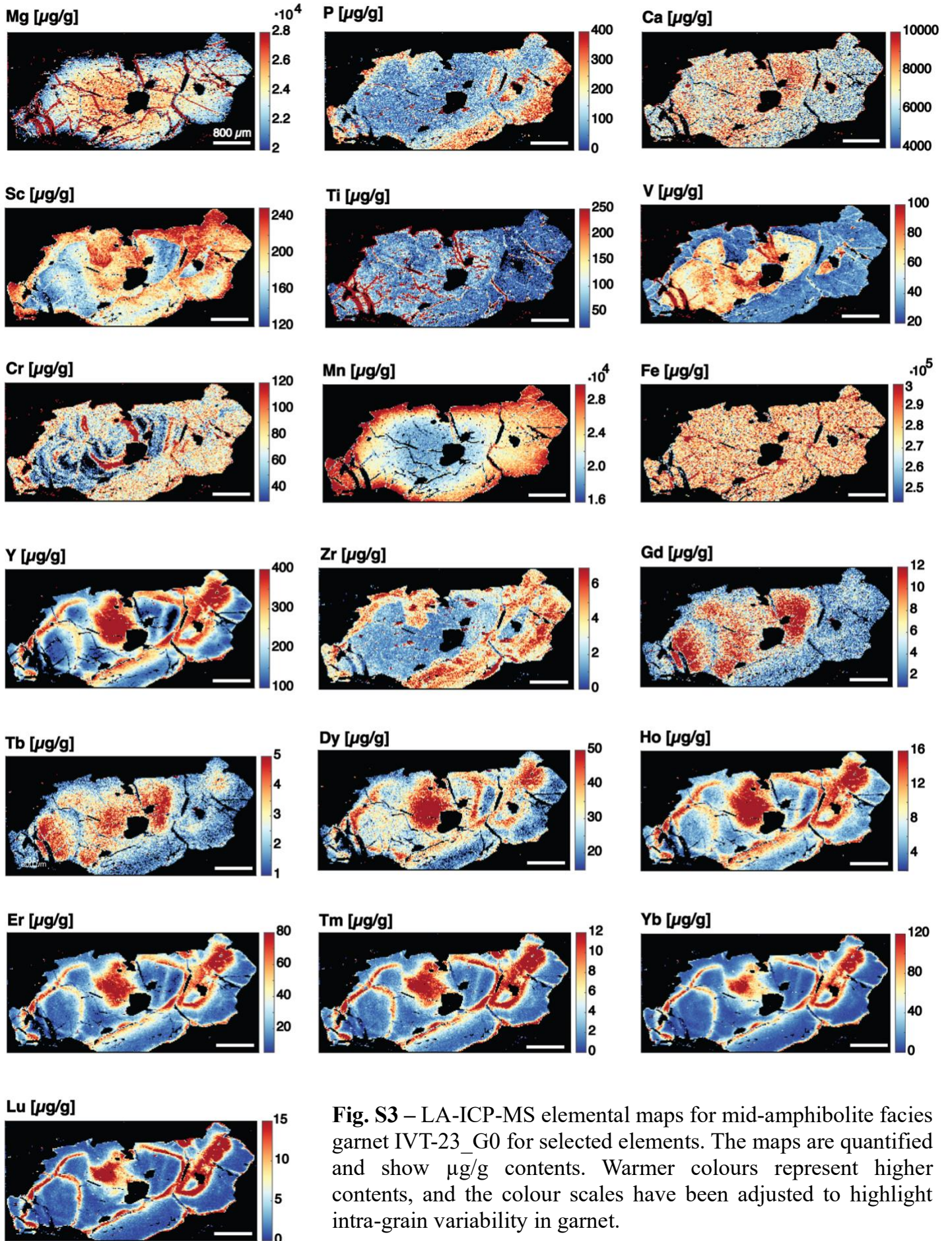


Fig. S3 – LA-ICP-MS elemental maps for mid-amphibolite facies garnet IVT-23_G0 for selected elements. The maps are quantified and show $\mu\text{g/g}$ contents. Warmer colours represent higher contents, and the colour scales have been adjusted to highlight intra-grain variability in garnet.

S4: TRACE ELEMENT MAPS IN IVT-21_G0

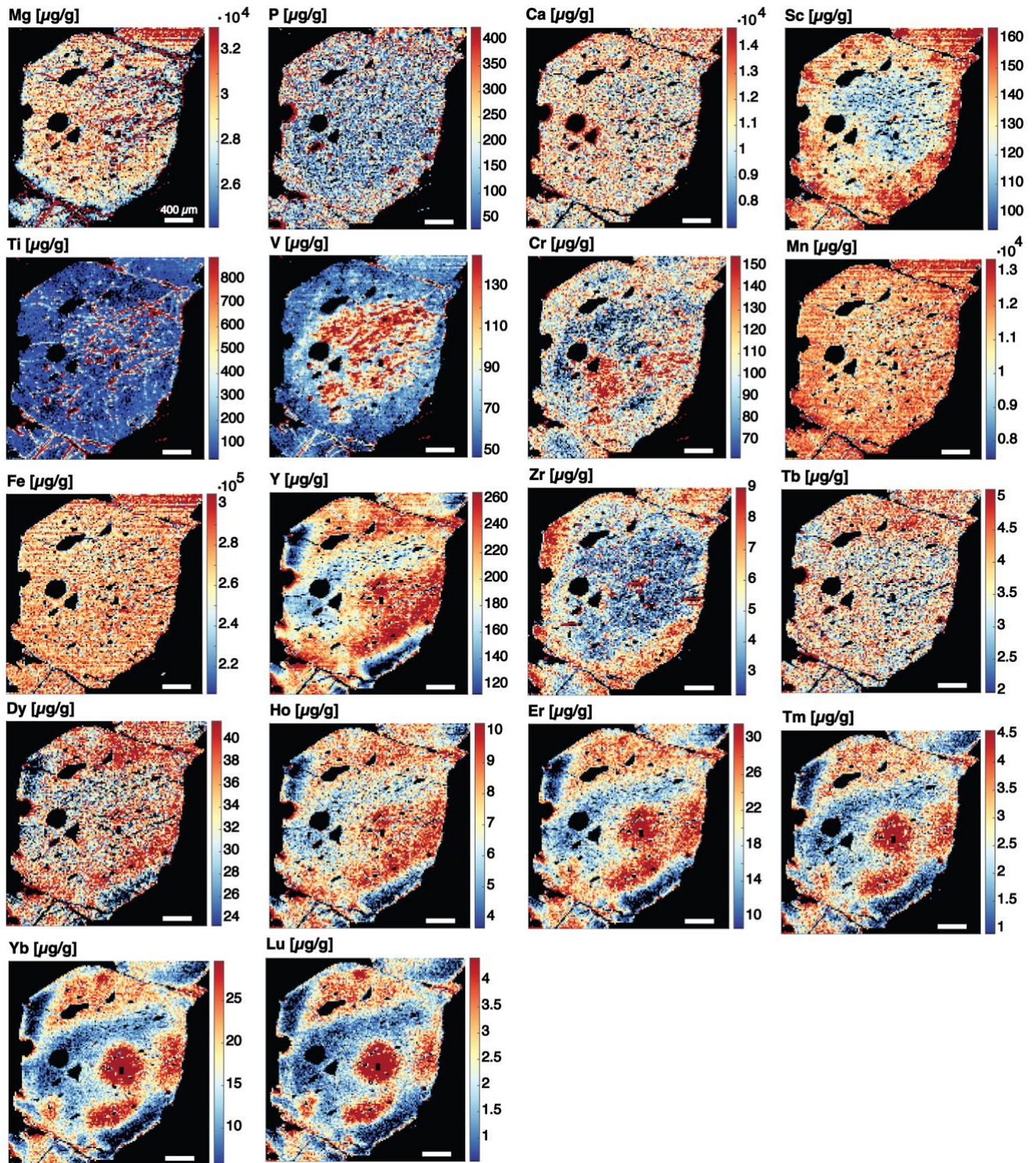


Fig. S4 – LA-ICP-MS elemental maps for upper-amphibolite facies garnet IVT-21_G0 for selected elements. The maps are quantified and show µg/g contents. Warmer colours represent higher contents, and the colour scales have been adjusted to highlight intra-grain variability in garnet. The white scale bar is 400 µm.

S5: TRACE ELEMENT MAPS IN IVT-40_G0

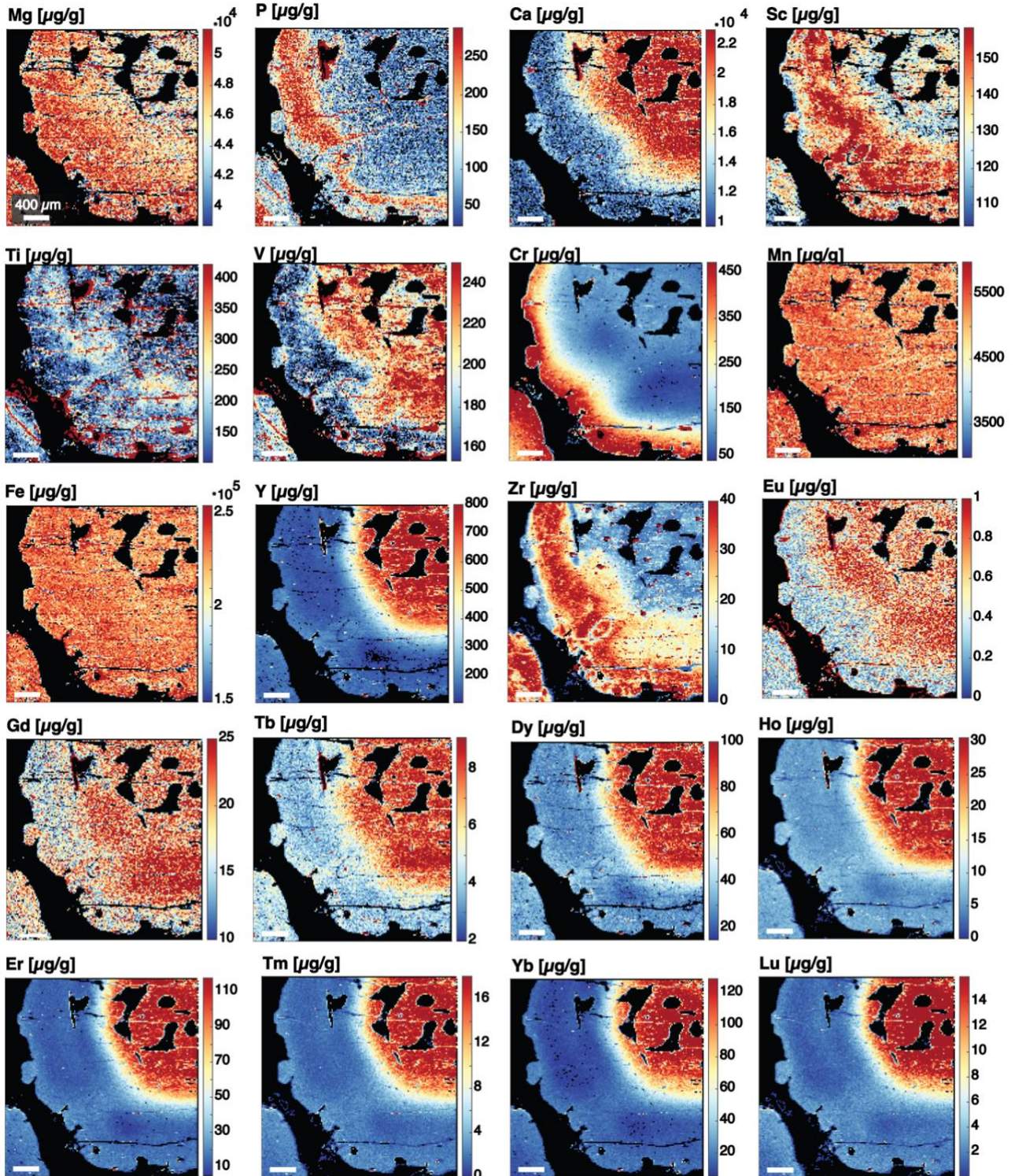


Fig. S5 – LA-ICP-MS elemental maps for granulite-facies garnet IVT-40_G0 for selected elements. The maps are quantified and show $\mu\text{g/g}$ contents. Warmer colours represent higher contents, and the colour scales have been adjusted to highlight intra-grain variability in garnet.

S6: TRACE ELEMENT MAPS IN IVT-38_G0

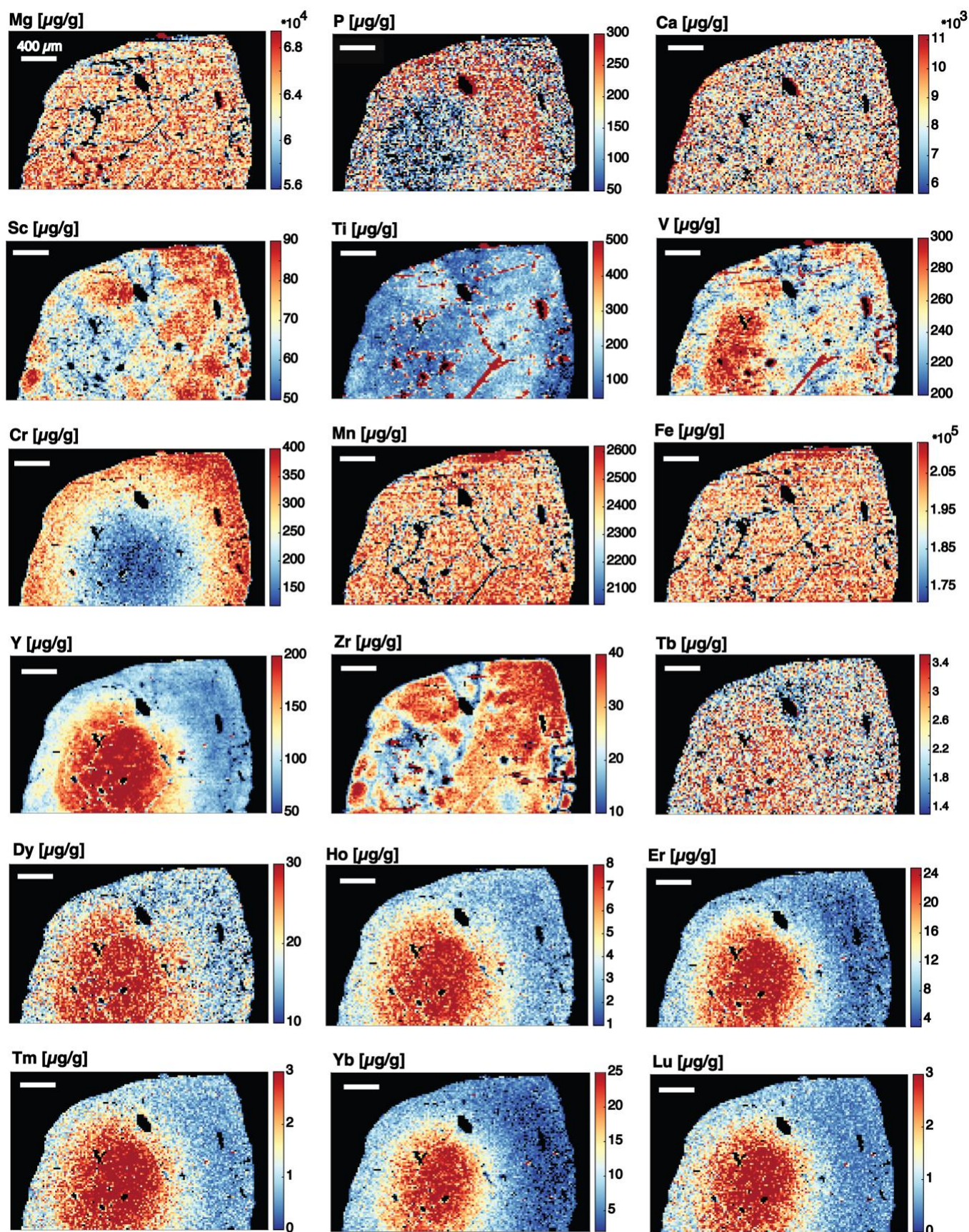


Fig. S6 – LA-ICP-MS elemental maps for granulite-facies garnet IVT-38_G0 for selected elements. The maps are quantified and show μg/g contents. Warmer colours represent higher contents, and the colour scales have been adjusted to highlight intra-grain variability in garnet.

S7: TRACE ELEMENT MAPS IN IVT-39_G0

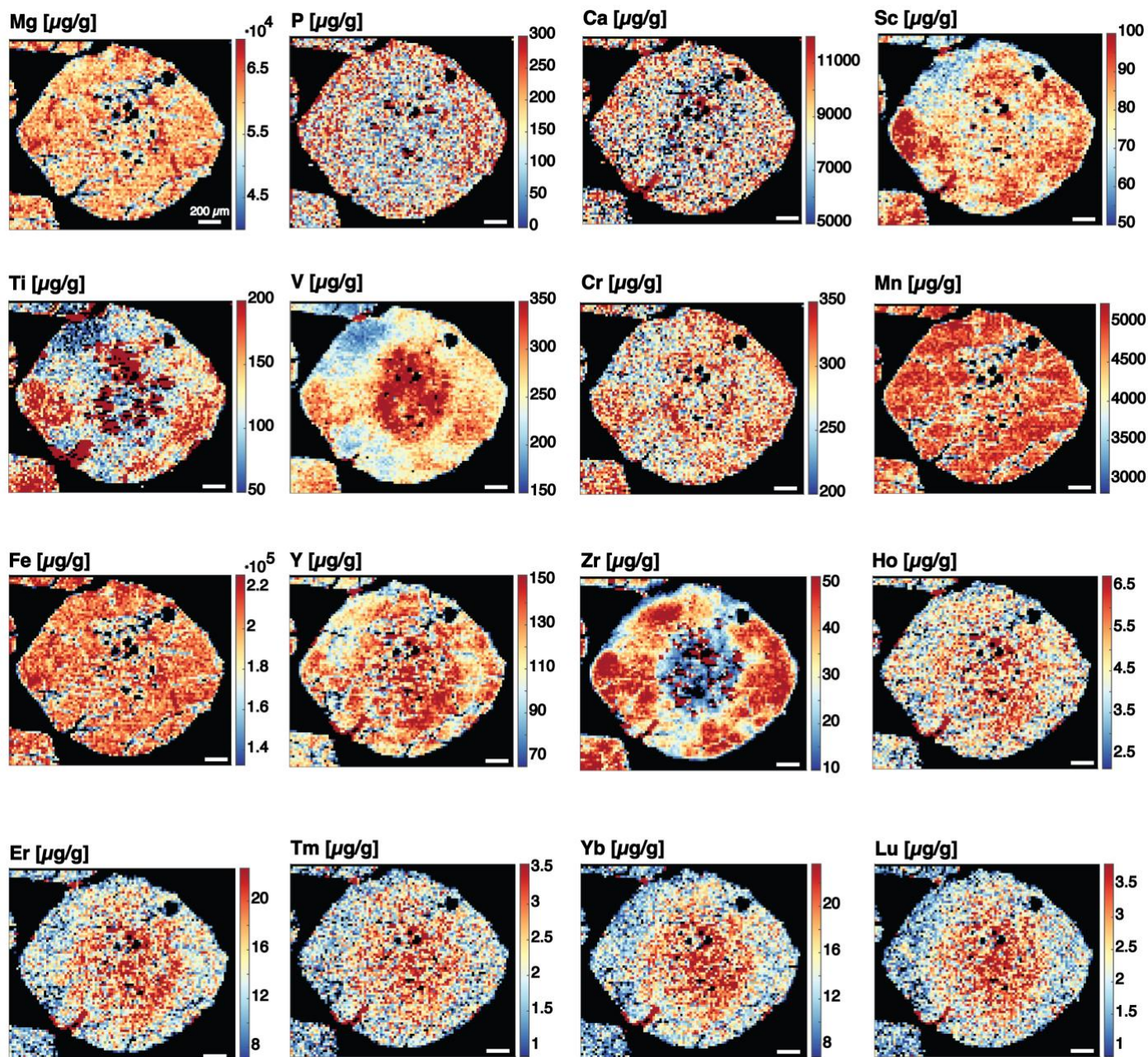


Fig. S7 – LA-ICP-MS elemental maps for granulite-facies garnet IVT-39 for selected elements. The maps are quantified and show $\mu\text{g/g}$ contents. Warmer colours represent higher contents, and the colour scales have been adjusted to highlight intra-grain variability in garnet.

S8: TRACE ELEMENT MAPS IN IVT-33_G0

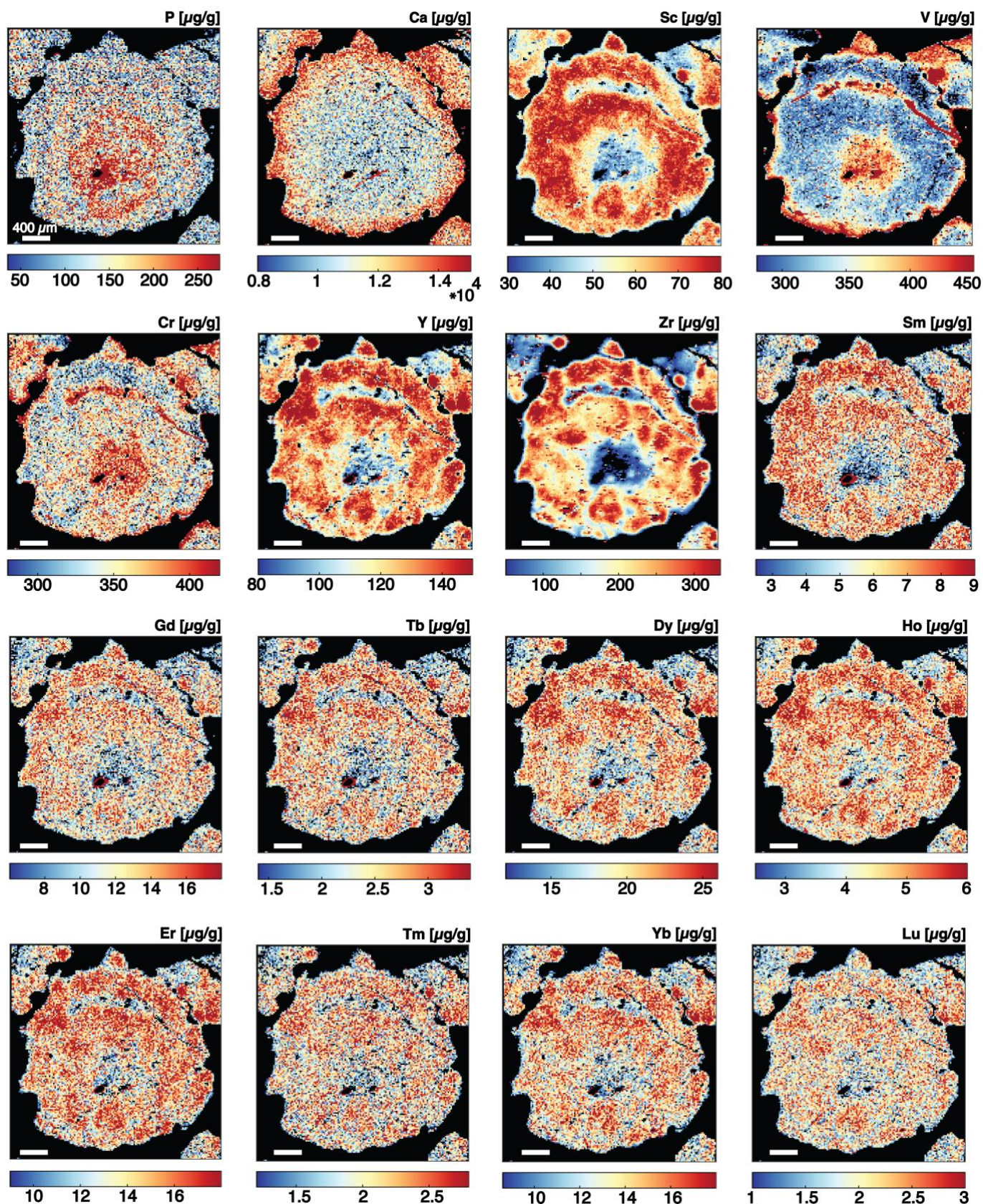


Fig. S8 – LA-ICP-MS elemental maps for ultra-high temperature metamorphic garnet IVT-33_G0 for selected elements. The maps are quantified and show μg/g contents. Warmer colours represent higher contents, and the colour scales have been adjusted to highlight intra-grain variability in garnet.

S9: TRACE ELEMENT PROFILES IN ALL STUDIED GARNET

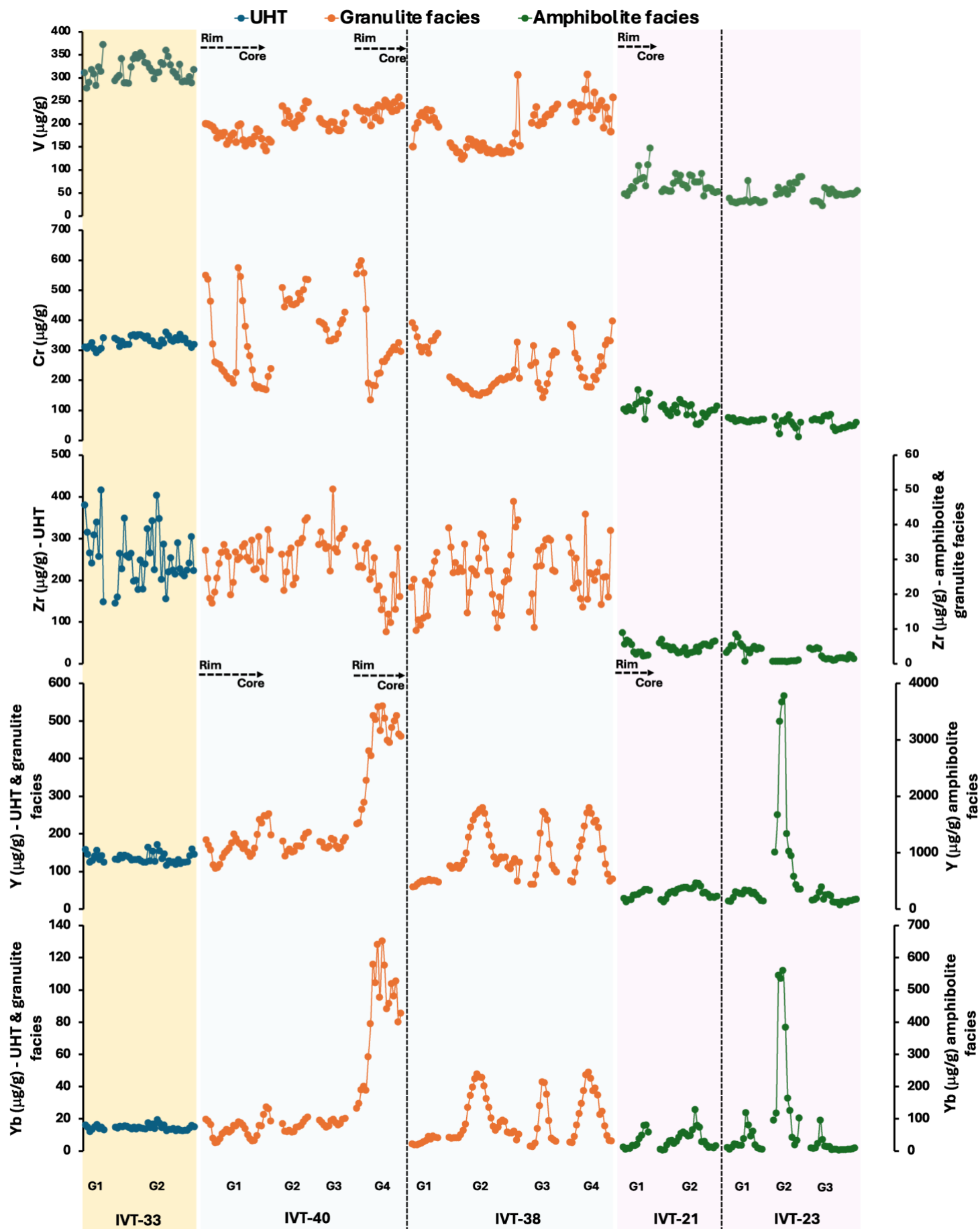


Fig. S9 – LA-ICP-MS elemental profiles of garnet grains from the five studied samples. All profiles are full cross-sections except for three, where core-rim zoning is indicated by an arrow. From left to right: IVT-33 (G1-3) - the profiles display relatively flat patterns across the grains for most elements with Zr showing patchy, heterogeneous contents (with average of ~250 mg/g). IVT-40 and 38 (G1-4) - profile patterns generally align with zoning observed in the maps, though Zr display more heterogeneity and the V-profiles in IVT-40 is opposite to the map. IVT-21 (G1-2) - the G2 profile shows the highest Y, Yb content with lowest Zr and an oscillatory Cr zoning pattern indicative of early sub-solidus garnet growth. IVT-23 (G1-3) - the G2 profile shows a decrease in contents of Y and Yb from core to rim with few elevated peaks which could correspond to the enriched zones in the map. The other profiles align with the maps.

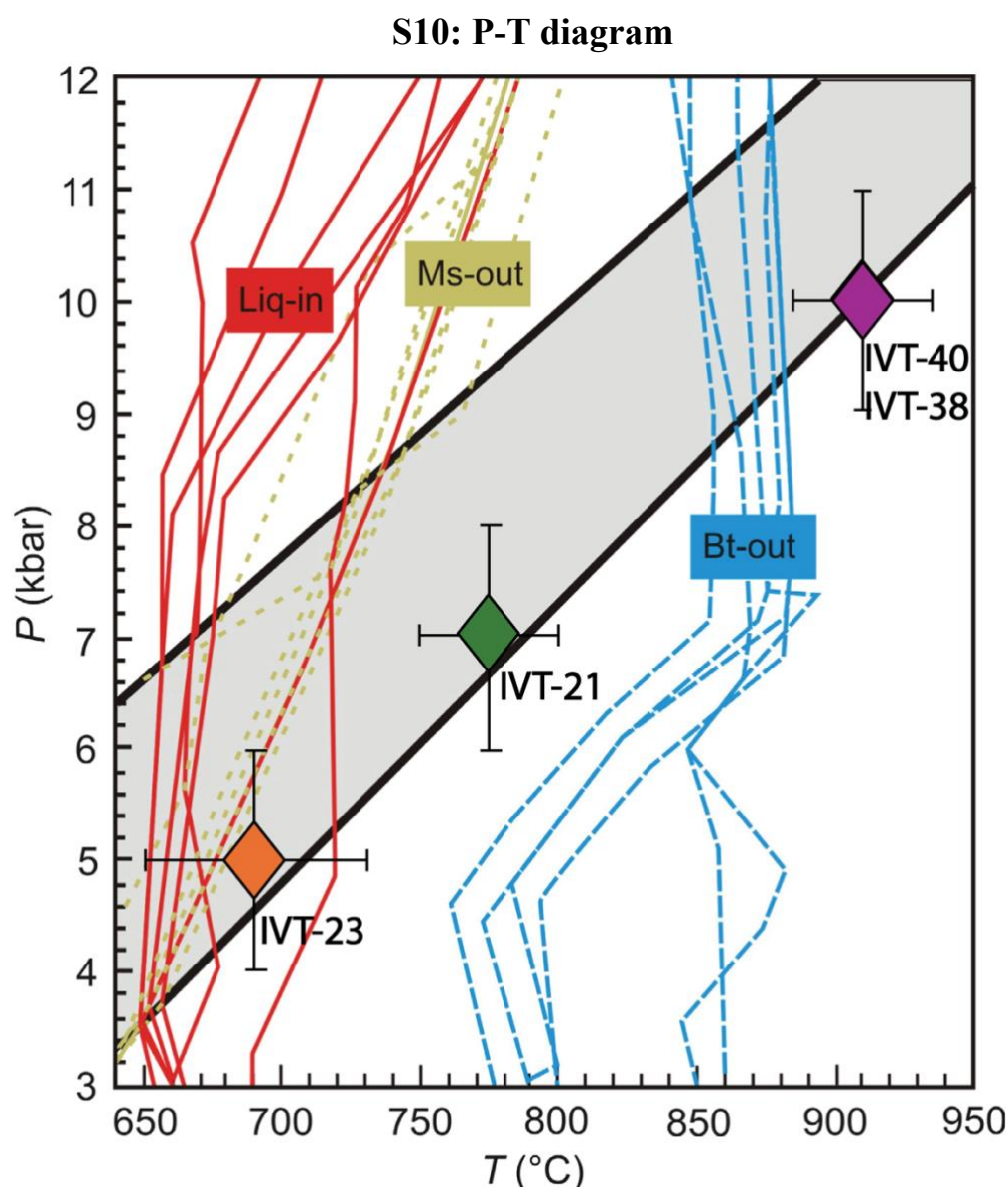


Fig. S10 – P-T estimates of the studied metapelite samples from amphibolite facies (IVT-23, 21) to granulite-facies (IVT-40, 38) plotted on a summary diagram by Carvalho et al. (2019) showing the P-T estimates of the liquid-in, muscovite-out and biotite-out curves reported in the literature.

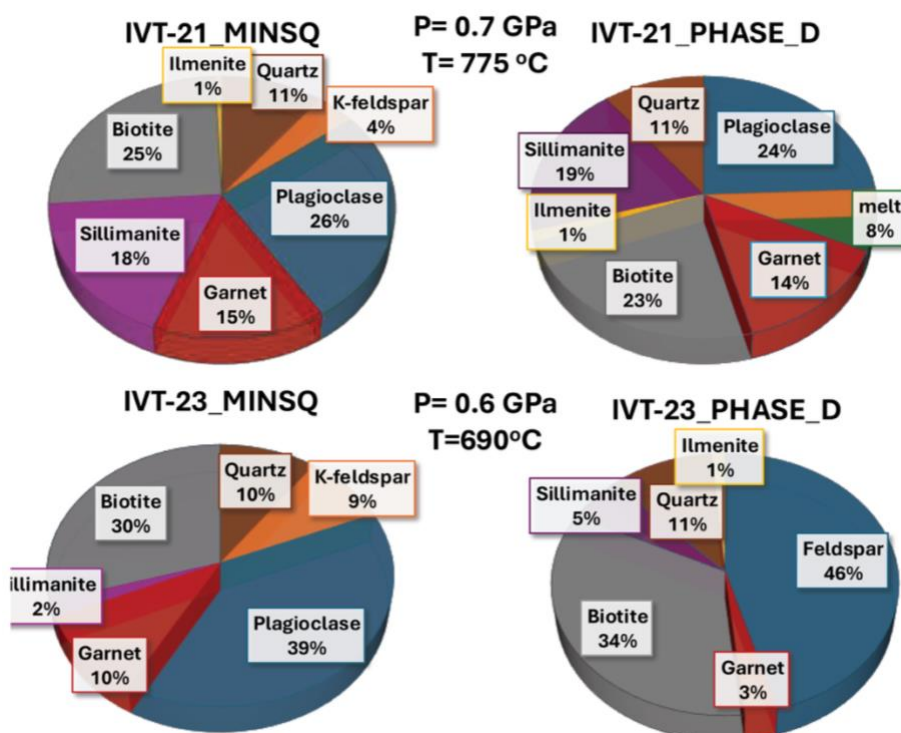
METHODS

a) Phase-equilibrium modelling

Phase equilibria modelling was performed for all the studied samples (IVT-21, 23, 40, 33) based on the available bulk compositions (see supplementary sheet 1) using *werami* function in *Perple_X* (Connolly 2005). The primary aim of applying equilibrium thermodynamic modelling was to compare the calculated and predicted mineral assemblages and their modal amount at relevant P-T conditions.

All the samples were modelled in the system $\text{MnO-Na}_2\text{O-CaO-K}_2\text{O-FeO-Al}_2\text{O}_3\text{-MgO-SiO}_2\text{-H}_2\text{O-TiO}_2$ with the thermodynamic dataset of Holland and Powell (2011). The phases considered in the modelling and corresponding solution models used (except for quartz and/ rutile (for granulite-facies) which are considered as pure phases) are: garnet, orthopyroxene, biotite (White et al. 2014); ternary feldspar in IVT-23 (Holland and Powell 2003) whereas separate plagioclase (Newton et al. 1981) and K-feldspar (Waldbaum and Thompson 1968) for the other samples; melt (White et al. 2014); ilmenite (White et al. 2014) and magnetite (White et al. 2000) The H_2O content in the model was taken as per the measured LOI from the bulk.

The absolute difference in the modal mineralogy between the least-squares method (MINSQ) and phase equilibrium modelling (Phase_D) is within <1-5% for all samples as shown in the figures (Figs. S11a and b) below. All the data are provided in supplementary file



1.

Fig. S11a– Comparison of modal abundance estimates between calculated (least squares method) and phase-equilibrium modelling for amphibolite-facies samples. MINSQ – least squares method; Phase_D: Phase diagram

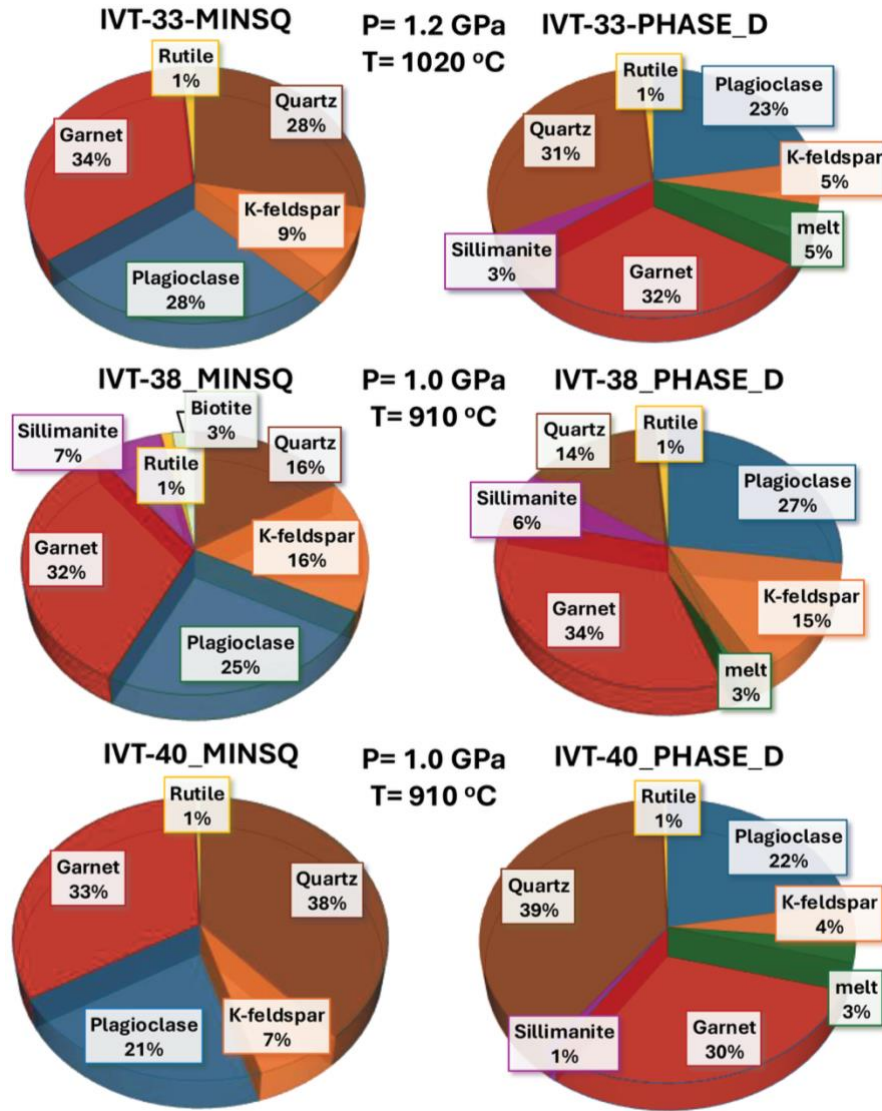


Fig. S11b– Comparison of modal abundance estimates between calculated (least squares method) and phase-equilibrium modelling for granulite-facies and UHT samples. MINSQ – least squares method; Phase_D: Phase diagram

b) Diffusion modelling of Y + REE in IVT-38 garnet

The diffusion of Y + REE was treated as single-component diffusion of trace elements within a homogeneous medium along a one-dimensional semi-infinite profile, without accounting for the spherical geometry of the crystal. This simplified approach was adopted to obtain first-order, order of magnitude estimates of diffusivities. The measured element contents were fitted by solving the Fick's 2nd law of diffusion using an analytical solution:

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} \dots (1)$$

Here, the composition C is expressed in mg/g. The diffusion coefficient D (in m²/s) is mostly T dependent and follows Arrhenius relationship via:

$$D = D_0 e^{(-E_a/RT)} \dots\dots (2)$$

where D_0 is the pre-exponential factor (in m²/s), E_a the activation energy for diffusion (in J/mol), R is the universal gas constant (8.31 J/mol) and T the temperature (in Kelvin).

The generalized analytical solution for solving diffusion equation is given by:

$$C_{(x,t)} = C_{x=0} + (C_{inf} - C_{x=0}) \operatorname{erfc}(x/2\sqrt{Dt}) \dots\dots (3)$$

Representative compositional profiles for diffusion modelling in IVT-38 garnet were extracted using the tool “integrated lines (strip)” function in XMapTools (Lanari et al. 2014, 2019). This method involves the integration of multiple parallel compositional transects within a defined rectangular region of interest. The rectangle was positioned from core to rim, and oriented as perpendicular as possible to the core-rim boundary. The resulting average profile was considered for modelling as it provides smoother profiles compared to the individual ones and reduces the effective LOD for each element compared to single pixel LOD. Multi-elemental compositional profiles (HREE, Y, MREE) were extracted from the same area.

The initial profile is a step function, assuming that the compositions in the core and rim were flat on both side of the interface. The interface was centred on 1074.80 μm using the Matano interface method (equal area under the curve on both side of the interface) for Yb and this value was kept constant for every element. All measured distance values were shifted relative to this interface so that $x=0$ corresponds to the original boundary. The input parameters for the modelling were temperature-time (T - t) conditions and a pre-exponential factor (D_0). The compositional profile after diffusion for a total duration of 2 My at 910 °C and duration of 25 My at 800 °C were obtained by solving equation 1. The initial element contents at each end of the profile were defined and were kept constant.

The activation energy E_a and diffusivity D were treated as the fitting parameters. An initial guess of 220 kJ/mol was used based on experimental studies (Bloch et al. 2020) with a lower bound of 0 and no upper bound. The best-fit value of E_a , which was then used to calculate D using equation (2), were obtained using a least-square curve fitting between measured element content profile and modelled diffusion profile defined by

$$\text{minimize } \sum_{i=1}^n [C_{\text{measured},i} - C_{\text{model},i}]^2 \dots\dots (4)$$

This procedure was repeated to fit compositional profiles for Y, Yb and Dy to obtain diffusivity for these elements at two T - t conditions and then compared with the literature data.

Diffusion modelling of IVT-38

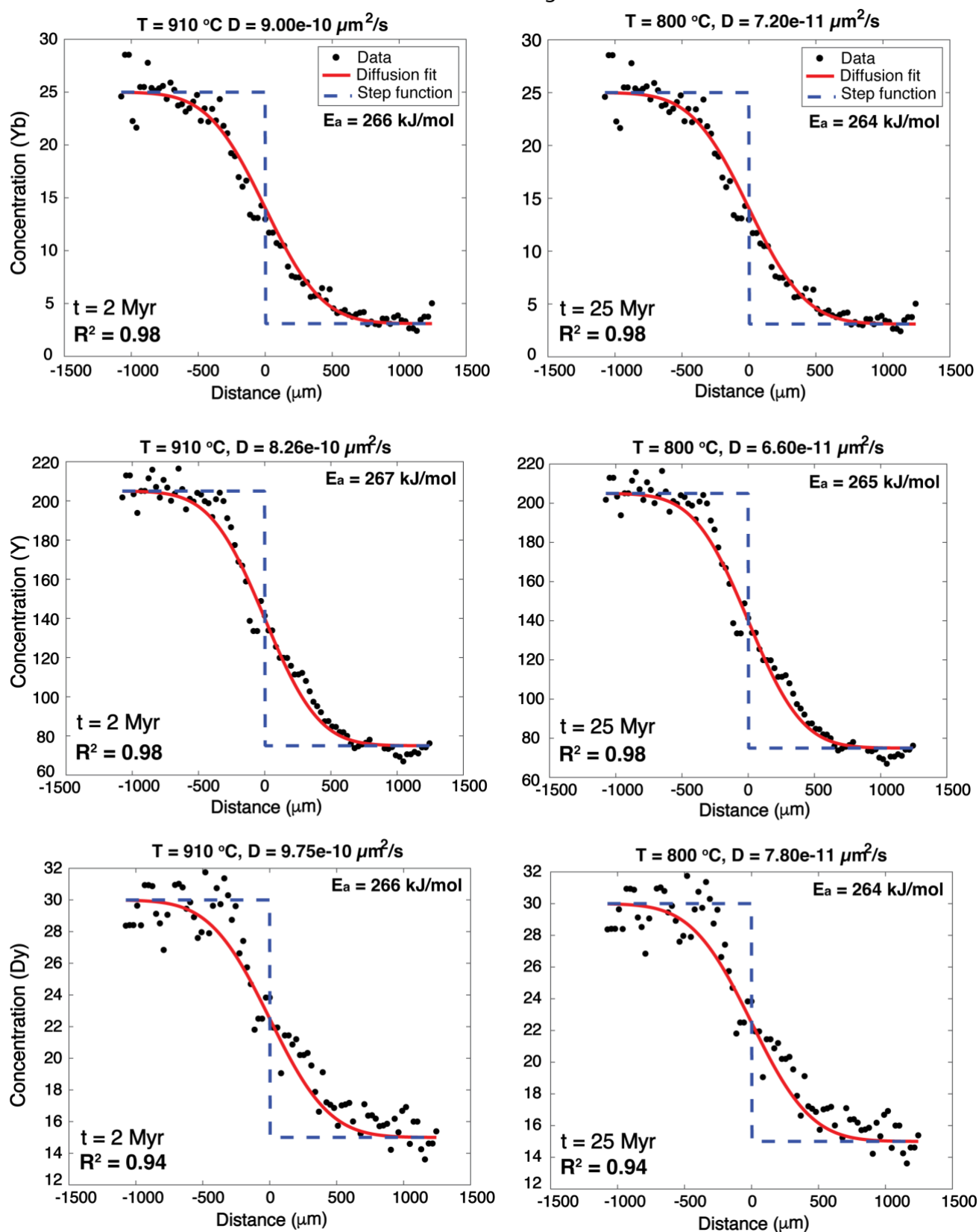


Fig. S12– Diffusion modelling (IVT-38 garnet) over a period of 2 My at 910 °C (left) and 25 My at 800 °C (right) for Yb (top), Y (middle) and Dy (bottom).

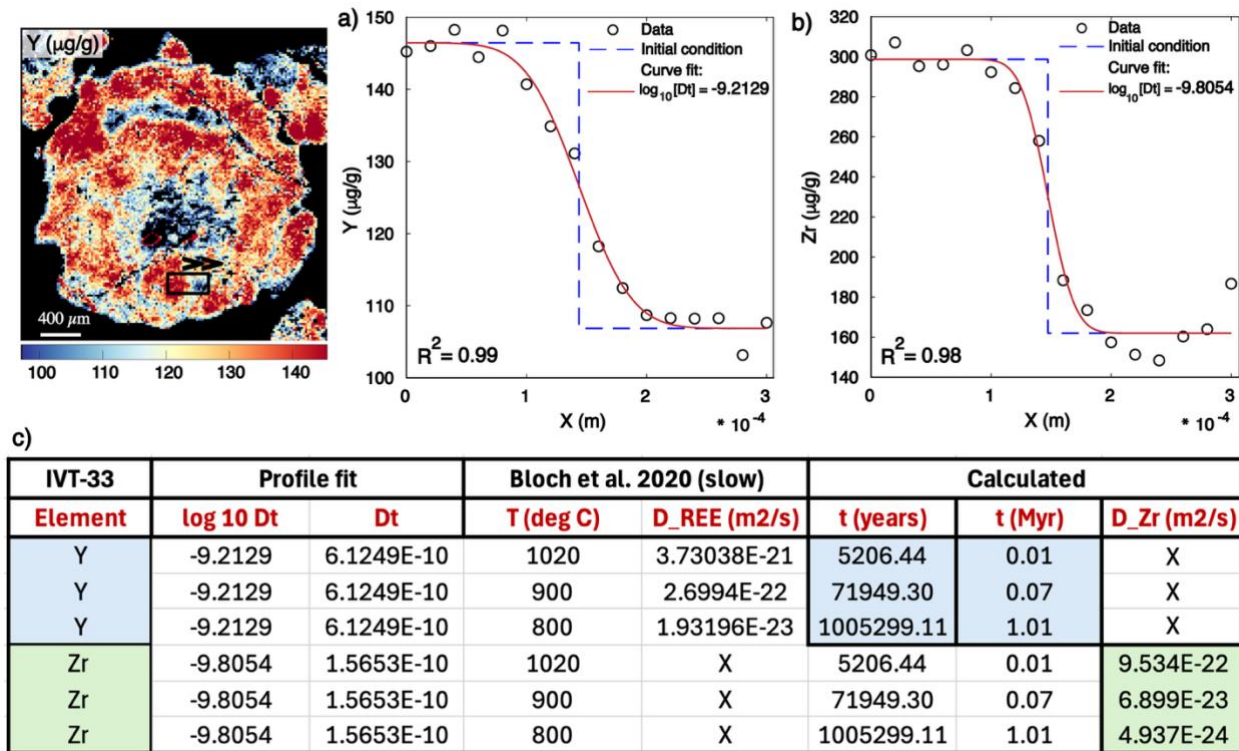


Fig. S13– Diffusion modelling of IVT-33 UHT-garnet for Y and Zr. Representative Y and Zr concentration profile across “Island-Moat” textures (black rectangle) showing smooth Zr + Y gradients (black circles in a and b). The measured profiles are fitted using the Diffuser web application (Wu et al., 2022) to get time-integrated diffusivities $\log_{10}Dt$ (a and b). The obtained $\log_{10}D_{Yt}$ was used to constrain the timescales (t marked in blue in c) since garnet-melt interaction using the slow REE-diffusivity in garnet (Bloch et al. 2020) at temperatures of 1020 °C, 900 °C and 800 °C (considering isothermal diffusion). The resulting timescales were then used in $\log_{10}D_{Zr}t$ obtained by fitting the Zr profile (b) to estimate the diffusivity of Zr in garnet (D_{Zr} in m²/s, marked in green in c) The diffusivity obtained for Zr in garnet is one order of magnitude slower compared to the slow REE diffusivity in garnet of Bloch et al. (2020) (D_{REE} in m²/s in c).

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