Diffusional homogenization of light REE in garnet from the Day Nui Con Voi Massif in N-Vietnam: Implications for Sm–Nd geochronology and timing of metamorphism in the Red River shear zone

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A B S T R A C T

High-grade migmatitic and mylonitic gneisses from the Day Nui Con Voi massif in northern Vietnam record temperatures of 760–810 °C at pressures of 6–10 kbars. High temperature conditions have resulted in the development of major element diffusional profiles in garnet. Laser ablation ICP-MS analyses of trace elements indicate that REE and Hf closely followed Rayleigh-like fractionation trends but underwent significant post-crystallization modification. Light REE and to a lesser extent, HREE rim-to-rim zonation profiles show progressive flattening with the decreasing garnet size. Nd and Sm are completely homogenized in the crystals smaller than 1.5 mm, while Lu always preserves variable degrees of core-to-rim concentration gradient. The observed REE patterns are interpreted as resulting from the combination of protracted garnet growth of progressively smaller crystals and intracrystalline diffusion. This had profound influence on Sm–Nd geochronology and resulted in isochron ages ranging from 50 to 32 Ma. The youngest age was obtained for a sample, where all garnet crystals are smaller than 2 mm in which light REE profiles are completely or nearly completely homogenized. Thus, only the youngest age represents geologically meaningful event, and 31.7±0.9 Ma age is interpreted as the best estimate of the resetting episode due to high temperature diffusional homogenization of light REE during early Oligocene metamorphism. Older Sm–Nd ages reflect mixed analyses of variably reset individual garnet crystals. Lu–Hf isotopic analyses of bulk garnet fractions, despite yielding high parent/daughter isotopic ratios appeared very scattered and did not allow defining isochron ages. Instead, apparent ages defined by whole rock and individual garnet fractions range from c. 80 to 160 Ma. Very old apparent ages are interpreted as being the consequence of intracrystalline Lu diffusion and preservation of the original Hf distribution, which leads to lower 176Lu/177Hf ratios, and thus steeper (older) isochrons. Back diffusion of Lu during commonly observed resorption played a subordinate role in modifying isotope systematics.

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1. Introduction

The application of Sm–Nd and Lu–Hf garnet geochronology offers a quantitative link between isotopic ages and metamorphic conditions. Most commonly, the link is established on the basis of major element zonation in garnet or by means of thermodynamic calculations and textural relationships (e.g. Vance and Mahar, 1998). Such an approach is largely justified for garnets where zonation patterns developed during growth are preserved. By contrast in higher temperature ranges, where major element distributions can be partially or completely modified by diffusion, the interpretation of isotopic ages obtained by both geochronometers is subject to a large degree of uncertainty, resulting from the likely decoupling of Rare Earth Elements (REE) and High Field Strength Element (HFSE) behavior from that of the major elements. This problem is partly overcome with in situ trace element analyses in garnets in high-grade rocks (e.g. Anczkiewicz et al., 2007a; Endo et al., 2009; Kohn, 2009; Dutch and Hand, 2010). More recently trace element analyses of garnets have become fairly common. However, the interpretation of their record is often equivocal and relies on detailed knowledge of the textural relationship and crystallization history of the garnet and associated minerals. Additionally, the involvement of garnet in post-growth reactions leads to the redistribution of trace elements involved in garnet geochronology, which may lead to erroneous ages or false interpretations (e.g. Kohn, 2009; Dutch and Hand, 2010; Kelly et al., 2011). In this study we investigate the potential influence of...
diffusion and resorption on Sm–Nd and Lu–Hf garnet geochronology in polymetamorphic migmatic gneisses from the Day Nui Con Voi massif in northern Vietnam.

The Sm–Nd results for V99-8 and V99-66 were previously published in Anczkiewicz and Thirlwall (2003) in the context of presenting a new leaching technique and the reader is referred there for a detailed discussion of the isotope systematics of these two samples. Here, we include results from two more samples, and discuss our geochronological results from the perspective of the trace element analyses and their geological context.

2. Regional geology

The Red River shear zone (RRSZ) is widely regarded as a major continental discontinuity dividing SE China block from the Indochina block and was interpreted either as a deeply rooted fault penetrating through the entire lithosphere (Tapponnier et al., 1990; Leloup et al., 1995) or as a fault detached at mid-crustal level (Jolivet et al., 2001). It strikes for about 1000 km from SE Tibet towards the Tonkin Gulf in northern Vietnam (Fig. 1), and is defined by four, NW–SE trending, narrow, elongated high-grade metamorphic massifs, of which the Ailao Shan and the Day Nui Con Voi (DNCV) are the largest (Fig. 1).

The DNCV massif in northern Vietnam forms a large scale antiform, with strongly sheared limbs resembling a core complex type structure (Jolivet et al., 2001; Anczkiewicz et al., 2007b). It is composed dominantly of high-grade metapelitic and locally migmatic gneisses, the peak metamorphic conditions are estimated to have been 700–800 °C at 5–9 kbars (Nam et al., 1998; Leloup et al., 2001). Greenschist facies retrogression was estimated to be ~480 °C and ~3 kbars (Nam et al., 1998).

Isotopic systems with high closure temperature, such as U–Th–Pb in monazite and zircon, document a complex thermal history. In situ Th–Pb monazite dating revealed strong inheritance with age components ranging from 220 to 21 Ma. The oldest age was interpreted as an Indosinian event, while the younger ages were interpreted to be a result of partial resetting of monazite during Oligo-Miocene (Gilley et al., 2003). In the Ailao Shan massif in Yunnan, monazite included in garnets yielded ages between 34 and 21 Ma, interpreted as reflecting synkinematic (relatively to sinistral shear) monazite and garnet growth. The older ages have the same within error as the U–Pb zircon age constraints on deformed granitoids from within the southern Ailao Shan massif that yielded a c. 33 Ma age. This age has also been interpreted as reflecting the beginning of strike slip motion (Zhang and Schärer, 1999). Post-metamorphic cooling, established predominantly by Ar–Ar and K–Ar biotite data, reveals a wide range of ages but seems to indicate that the DNCV rocks cooled through c. 300 °C by about 23–26 Ma. (Harrison et al., 1996; Nam et al., 1998; Wang et al., 2000; Leloup et al., 2001). In contrast, the K–Ar and Ar–Ar hornblende and feldspar ages range from 34 to 27 and display quite complex age spectra (Nam et al., 1998; Wang et al., 2000). The few zircon and apatite fission track ages available for the DNCV massif span ages from 30 to 20 Ma and point to, at least locally, very fast cooling after high-grade metamorphism and sinistral shearing (Maluski et al., 2001; Viola and Anczkiewicz, 2008).

3. Samples petrography and PT conditions

Four gneisses (V99-8, V99-66, V99-67 and V02-05) were selected for petrological and geochronological studies. Their locations are marked on a simplified geological map in Fig. 2 and their GPS coordinates are given in Table 1.

Sample V99-8 comes from the Yen Binh quarry located in the vicinity of Yen Bay in the central part of the DNCV massif (Fig. 2). The quarry exposes strongly deformed high-grade gneisses forming tens of meters scale antiform with an axial planar cleavage being at places intruded by leucogranites. Gneisses are composed dominantly of quartz, biotite, plagioclase, K-feldspar and garnet. Common accessories are monazite, zircon, apatite and rarely rutile. Garnet and feldspar form porphyroclasts in a finer grained matrix of quartz and biotite (Fig. 3a). Small amounts of chlorite and muscovite formed at the expense of garnet and biotite during retrogression. Garnet usually has inclusion-rich cores comprising dominantly quartz, a substantial amount of zircon, monazite and rare biotite. Monazite is distributed throughout the entire garnet, although, in the studied thin sections, it appeared

Fig. 1. Tectonic sketch of SE Asia (based on Leloup et al., 1995). RRF — Red River Fault. Main metamorphic massifs in the Red River shear zone: X.L.S — Xuelong Shan, D.C.S — Diancang Shan, D.N.C.V — Day Nui Con Voi.
to be more common in the marginal parts, where sillimanite inclusions are also sporadically present. The remaining three samples have almost identical mineralogy but display mylonitic textures (Fig. 3b–d).

Garnet in all samples is dominantly of almandine composition with a smaller amount of pyrope, and negligible grossular and spessartine. Electron microprobe traverses across garnet longer axes show constant compositions across nearly the entire crystal except for the edges, where a rise of almandine and spessartine is compensated by a decrease in pyrope and grossular. The Fe/(Fe+Mg) ratio follows the almandine content (Fig. 4). Flat zonation patterns throughout most of the grains indicate that the major elements were completely homogenized and the rims were equilibrated with the matrix minerals. Of all analyzed garnets only one crystal from sample V99-66 revealed slightly different zonation expressed by small “bulges” of grossular in the rim area (Fig. 4b).

Geothermobarometric estimates for samples V99-8 and V02-05 and V99-66 resulted in $P = 0.56 \pm 0.15 \text{ GPa}$ at $T = 810 \pm 60 \text{ °C}$ and $P = 0.70 \pm 0.16 \text{ GPa}$ at $T = 820 \pm 60 \text{ °C}$ and $T = 800 \pm 60 \text{ °C}$ at $P = 7.6 \pm 1.4 \text{ kbars}$, respectively (Anczkiewicz et al., 2007b). Similar results for the metamorphic peak were earlier obtained by Nam et al. (1998), Leloup et al. (2001) and Gilley et al., 2003 who reported slightly lower temperatures at similar pressures. Although we did not conduct $P$–$T$ estimates for sample V99-67, the consistency of the estimated temperature range for the three other samples, their identical mineralogy and proximal location to sample V99-66, imply that this rock was metamorphosed under the same metamorphic conditions as the other analyzed samples.

4. Sm–Nd and Lu–Hf garnet dating

Garnet from all four gneiss samples were dated using the Sm–Nd method and samples V99-67 and V02-05 were additionally subjected to Lu–Hf analyses. Sample dissolution, leaching procedures and column chemistry are described in Anczkiewicz and Thirlwall (2003) and Anczkiewicz et al. (2004). All measurements were carried out using a multi-collector ICP MS IsoProbe® following procedures outlined in Thirlwall and Anczkiewicz (2004). Isotopic results are summarized in Table 1 and Figs. 5 and 6. Analytical blank, standard reproducibility and reference isotopic ratios are given in the footnote to Table 1. Ages were calculated using Isoplot® by Ludwig (2001). Errors for isotopic ratios are given at the 2 se (standard error) level. Age errors, are quoted at 95% confidence level.

4.1. Sm–Nd isotopic results

A minimum of one whole rock and two garnet fractions from each sample was used for isochron constructions. Representative whole rock splits and biotite were used to determine the initial $^{143}$Nd/$^{144}$Nd ratios. Samples V99-8 and V99-66 gave the same ages within error of $39.1 \pm 0.8$ and $41.7 \pm 1.4 \text{ Ma}$, respectively (Anczkiewicz and Thirlwall, 2003). By contrast, sample V99-67 yielded a significantly younger age of $31.7 \pm 0.9 \text{ Ma}$, while V02-05 gave an age of $49.8 \pm 2.5 \text{ Ma}$. All but one of the analyzed garnet fractions yielded $^{147}$Sm/$^{144}$Nd ratios between 0.97 and 2.13, which is commonly found in metamorphic garnets (e.g. Vance and Harris, 1998; Prince et al., 2000; Thöni, 2002).
Table 1
Summary of the Sm–Nd and Lu–Hf dating results.

<table>
<thead>
<tr>
<th>Label</th>
<th>Sample wt [g]</th>
<th>Sm [ppm]</th>
<th>Nd [ppm]</th>
<th>147Sm/144Nd</th>
<th>143Nd/144Nd Age [Ma]</th>
<th>Initial εNd(t)</th>
<th>Lu [ppm]</th>
<th>Hf [ppm]</th>
<th>176Lu/177Hf</th>
<th>176Hf/177Hf</th>
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<tr>
<td>99-8 gneiss, Yen Bai area GPS position: N 21° 48.006′; E 104° 54.517′</td>
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<td>WR</td>
<td>0.09633</td>
<td>6.725</td>
<td>34.60</td>
<td>0.1175</td>
<td>0.511787±12</td>
<td>39.1±1.4</td>
<td>0.511757±11</td>
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<td>Biot</td>
<td>0.03246</td>
<td>0.221</td>
<td>1.177</td>
<td>0.1135</td>
<td>0.511785±24</td>
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<td>Grt.</td>
<td>1</td>
<td>0.03083</td>
<td>1.814</td>
<td>1.016</td>
<td>0.512033±14</td>
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<td>2</td>
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<td>0.388</td>
<td>1.9341</td>
<td>0.512252±13</td>
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<td>V99-66 gneiss, Bao Yen area</td>
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<td>WR</td>
<td>0.09915</td>
<td>6.871</td>
<td>35.43</td>
<td>0.1172</td>
<td>0.511776±7</td>
<td>41.4±1.3</td>
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<tr>
<td>Grt.</td>
<td>1 AL step1</td>
<td>0.0168</td>
<td>3.054</td>
<td>1.892</td>
<td>0.9759</td>
<td>0.511987±10</td>
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<tr>
<td>Grt.</td>
<td>1 AL step2</td>
<td>0.00677</td>
<td>3.222</td>
<td>1.080</td>
<td>1.0771</td>
<td>0.512041±20</td>
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<td>Grt.</td>
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<td>3.381</td>
<td>1.121</td>
<td>0.1838</td>
<td>0.511792±8</td>
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<td>Grt.</td>
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<td>0.01583</td>
<td>2.295</td>
<td>1.019</td>
<td>1.3617</td>
<td>0.512100±16</td>
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<td>0.01043</td>
<td>2.999</td>
<td>0.938</td>
<td>1.9730</td>
<td>0.512282±23</td>
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<td>0.0387</td>
<td>2.064</td>
<td>0.632</td>
<td>1.9730</td>
<td>0.512282±24</td>
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<tr>
<td>V99-67 gneiss Bao Yen area</td>
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<tr>
<td>WR 1</td>
<td>0.09525</td>
<td>4.508</td>
<td>21.84</td>
<td>0.1247</td>
<td>0.511956±11</td>
<td>31.7±0.9</td>
<td>0.511930±9</td>
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<td>WR 2</td>
<td>0.04516</td>
<td>3.555</td>
<td>1.222</td>
<td>1.7589</td>
<td>0.512296±13</td>
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<td>0.04427</td>
<td>3.705</td>
<td>1.051</td>
<td>2.1312</td>
<td>0.512367±11</td>
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<tr>
<td>Grt.</td>
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<td>3.661</td>
<td>1.202</td>
<td>1.8406</td>
<td>0.512323±22</td>
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<tr>
<td>V02-05 Trai Hut area</td>
<td>N 21° 59.927′; E 104° 34.095′</td>
<td></td>
<td></td>
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<tr>
<td>WR</td>
<td>0.11268</td>
<td>8.393</td>
<td>41.90</td>
<td>0.1211</td>
<td>0.512059±11</td>
<td>49.8±2.5</td>
<td>0.512015±9</td>
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<tr>
<td>WR</td>
<td>0.11219</td>
<td>4.705</td>
<td>18.49</td>
<td>0.1539</td>
<td>0.512061±11</td>
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<td>Grt.</td>
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<td>1.044</td>
<td>0.409</td>
<td>1.5446</td>
<td>0.512519±22</td>
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Footnote to Table 1:
Errors on isotopic ratios are 2SE and refer to the last significant digits. Errors for 147Sm/144Nd and 176Lu/177Hf ratios are 0.3 and 0.5%, respectively. Mass bias correction to 179Hf/177Hf=0.7325 and 146Nd/144Nd=0.7219. Repeated measurements of JMC475 standard 176Hf/177Hf, over the period of analyses were 176Hf/177Hf=0.282176±31 (2 s.d., error, n=20) and were normalized to value 176Hf/177Hf =0.282160. Reproducibility of Aldrich Nd standard over period of analyses was 143Nd/144Nd=0.511364±34 (2 s.d., n=23) and were normalized to preferred value of 143Nd/144Nd=0.511420. Details on long term instrument performance can be found in (Thirlwall and Anczkiewicz, 2004).

Fig. 3. Photomicrographs of the analysed samples a) V99-8, b) V99-66, c) V99-67, d) V02-05.
Garnet Grt. 1 from V02-05 is the only one with a low 147Sm/144Nd ratio and a correspondingly low 143Nd/144Nd ratio, almost the same as the whole rock values. Fraction Grt. 1 was not treated by the sulphuric acid leaching (SAL) method and hence its Nd budget was overwhelmed by monazite inclusions, which are numerous in the studied rocks. However, even leached garnets from this sample show a significant spread among measured isotopic ratios (Table 1 and Fig. 5). This is most likely due to incomplete exposure of monazite inclusions to sulphuric acid leaching (see Anczkiewicz and Thirlwall (2003) for discussion). Nevertheless, monazite influence must have been very small, since even the presence of as little as a few tens of ppm of this mineral in the “bulk” garnet separate would make dating impossible (e.g. Zhou and Hensen, 1995; Prince et al., 2000). Grinding to smaller fractions almost certainly would significantly reduce the spread among analyzed garnet separates (Anczkiewicz and Thirlwall, 2003). Some of the observed spread could also be ascribed to different proportions of garnet cores and rims in bulk separates, which have different Sm/Nd ratios (see below).

### 4.2. Lu–Hf isotopic results

The same garnet and whole rock fractions from samples V02-05 and V99-67, which were used for Sm–Nd analyses, were also dated by the Lu–Hf method. Garnets from both samples show high 176Lu/177Hf ratios ranging from 1.8 to 9.4, which normally ensure precise age estimates. Yet, garnet fractions from the same sample do not lie on a common isochron (Fig. 6). Ages for V02-05 based on two-point tie lines between garnet and the whole rock, are 86 and 91 Ma, whereas those for V99-67 are 142 and 164 Ma. Potential sources of scatter of apparent Lu–Hf ages and their relationship to Sm–Nd dates are discussed after introducing the results of trace element analyses.
5. Laser ablation ICP-MS results

Garnet trace-element concentrations were determined using the Open University Agilent 7500s quadrupole mass spectrometer coupled to frequency quintupled Nd:YAG UV (213 nm) laser system (UP213, Merchanteck-New Wave Research). Ablation was performed in pure He-atmosphere (0.65 ± 0.05 L/min) before entering the torch with a flow of Ar (≈ 1.00 ± 0.05 L/min). The ICP-MS was operated with its shield torch at 1350 W and tuned to produce maximum sensitivity for the medium and high masses, while keeping the oxide production rate low (\( {^{248}\text{Th}/^{232}\text{Th}} \leq 1 \)). NIST glass 612 (Pearce et al., 1997) was used as the calibration standard and garnet K23 (from T. Zack) was used as a reference to monitor accuracy and inter-laboratory consistency. Microprobe CaO concentrations were used as the internal standard. Analyses were achieved using a static ablation spot size of 80 \( \mu \)m and a laser fluence of 3–4 J/cm\(^2\), pulsed at a frequency of 10 Hz. Ten cycles of 10 s each were measured with gas blanks prior to each ablation spot. Each set of 8–10 unknown ablation spots was bracketed with NIST 612 glass measurements and variations in standard intensity were interpolated between successive standard measurements.

An additional set of analyses was later performed at the Institute of Geological Sciences, Polish Academy of Sciences, Kraków Research Centre using a 193 nm excimer laser-ablation system RESOLUTION M50 by Resonetics coupled with quadrupole ICP-MS XSeries II by Thermo. Details of the RESOLUTION M50 performance are given in Müller et al. (2009). Ablation took place in pure He (flow rate of 0.9 L/min), to which Ar nebulizer gas (flow rate of 0.5–0.55 L/min) was mixed downstream of the two volume LA cell, and after passing through a signal smoothing device, the analyte was delivered to the ICP source. A small addition of nitrogen (0.006–0.008 L/min) was used to enhance the sensitivity of the ICP-MS. Oxide level (\( {^{248}\text{Th}/^{232}\text{Th}} \)) was kept below 0.5%. Analyses were performed with spot size of 80 \( \mu \)m, fluence of 3–4 J/cm\(^2\) and at repetition rate of 10 Hz. Each 40 s ablation time was preceded by 20 s blank and followed by 20 s washout. Sample runs were bracketed by measurements of NIST 612 glass (Pearce et al., 1997). Silica concentration was used as an internal standard.

Data from both laboratories were processed using Glitter software of Macquarie University, Australia (Griffith et al., 2008). Thick sections were cut parallel to the stretching lineation and perpendicular to foliation. Traverses across garnets were made along the longest axis. A summary of LA ICPMS results is presented in Figs. 7–13 and element abundances are listed in Table 2 (online supplementary material).

There are two first order features common for all analyzed garnets:

1. A very clear core-to-rim zonation among HREE and, with one exception, modest zonation among LREE, (2) well pronounced negative Eu anomaly, which most likely reflects crystallization of garnet in the presence of feldspar (Fig. 7). Although chondrite normalized plots nicely reveal primary features, many important details in the distribution of REE are masked or very difficult to decipher. Hence, below we provide rim-to-rim plots with detailed descriptions of key elements from each sample. Light REE behavior is illustrated by Nd and Sm, while heavy REE behavior is shown with Lu. Abundance of all measured trace elements is compiled in Table 2.

5.1. Sample V99-8

Nd and Sm zonation in V99-8 is illustrated in Fig. 8a. Both Nd and Sm show slight depletions at the rim relative to the grain center, the profile for Nd is relatively flat whereas that for Sm shows gentle depletion towards the core. Heavy REE (represented in Fig. 8b by Lu) show a steep decrease in concentrations from core to rim. The higher the mass of an element, the steeper the zonation gradient (Fig. 7). While light REE on the edges show decrease of concentrations, heavy REE show concentration increases in the same area (Fig. 8a and b). Hafnium content smoothly increases from core to rim, while on the edges decreases similarly to LREE (Fig. 8c). Yttrium, which is commonly used as a heavy REE proxy, indeed mimics their behavior (Fig. 8b).

5.2. Sample V99-67

Distribution of trace elements in garnets in V99-67 is similar to that described above. The main difference is confined to the LREE, which show a much smaller degree of zonation, in particular in Nd, which shows a flat rim-to-rim profile (Fig. 9a, d). As with sample V99-8, the largest Sm/Nd fractionation occurs on the edges due to the notable rise of Sm (Fig. 10a, d). Notably, abundance of both Nd and Sm in all analyzed crystals is practically the same. Heavy REE show variable abundance and zonation trends from very steep to practically flat (Fig. 9b, e). Hafnium shows flat or gently rising concentration pattern from core to rim (Fig. 9c, f).

5.3. Sample V99-66

Three types of rim-to-rim zonation profiles were observed in this sample. The first is represented by Grt. 1, in which the light REE display a steep core-to-rim gradient (Table 2 and Fig. 10), which is then, in some cases, followed by a decrease in concentration on the edges (Fig. 10a). Yttrium, (similarly Dy, Ho, and Er) displays low but uniform concentrations across the core and then a sharp, positive spike followed by a decrease in concentration towards the edges (Table 2 and Fig. 10b). Interestingly, Yb and Lu do not follow other heavy REE behavior. Instead, their concentration is fairly uniform across the core and then sharply falls towards the rim, where it remains fairly constant (Fig. 10c). The presence of the distinct spikes observed for Y, Dy, Er and Ho correlates with a minimum P content (Fig. 10b). Hafnium generally increases from core to rim with an...
inversion of this trend on the edges. There is a small but notable elevation in Hf concentration in the center (Fig. 10d).

The second type of zonation represented by Grt. 2 shows very similar light REE zonation patterns to Grt. 1 (Fig. 11a). The origin of some “dispersion” visible in the general trends is probably caused by the selection of ablation spots, which were forced to be shifted from the straight line in order to avoid cracks and inclusions, and thus neighboring spots in some cases probed the same garnet zones. Heavy REE concentration steeply decreases towards the rim, which is followed by a gentle rise on the edges (Fig. 11b). Notably, absolute concentration values for heavy REE and Y are significantly higher than those in Grt. 1. The hafnium trend is analogous with Grt. 1 described above. The only difference is that the elevation of concentration in the center is much clearer and correlates with higher U content, which points to contamination by a U-bearing inclusion. Yttrium follows the trend of HREE (Fig. 11c). The two garnet crystals described above belong to the largest and most representative for the sample. Additionally, we analyzed garnet crystals ranging from 2 to 3.5 mm. Their trace element distribution is very similar to Grt. 2, although the content of both light and heavy REE is much smaller.

Rarely, crystals are observed, which are distinctly different from the ones described above. Their light REE show very little zonation, similar to garnets from V99-8 and V99-67 (Fig. 11d). By contrast, heavy REE show very different distribution patterns, having low, but fairly uniform concentrations across the crystals but with two distinct spikes in the rims (Fig. 11e). In this respect this profile resembles Y, Dy, Ho and Er in garnet Grt. 1 described above. In Grt. 3, however, the spikes are observed for all HREE and for Y. In some crystals Lu zonation is inversely correlated with P (Fig. 12). Hafnium shows rather constant concentration throughout the crystal except for the edges, where its concentration is significantly higher (Fig. 11f).

5.4. Sample V02-05

Garnets from V02-05 have dense cracks and are particularly inclusion-rich, causing some difficulties in obtaining good quality analyses. Chondrite normalized patterns display little zonation among LREE and, in contrast to garnets from other samples, modest zonation in heavy REE (Fig. 7). More detailed plots show that elements from La to Dy have the lowest concentrations in the core, which gradually rise in the rim and then drop on the edges (e.g. Sm and Nd in Fig. 13a). Heavy REE from Ho to Lu show decreasing concentrations from core to the intermediate part of crystal and subsequently show a rise in concentrations in the rims. Yttrium broadly follows the trends of HREE. The only difference is confined to the heaviest REE, which show much clearer higher concentrations in the core (Fig. 13b). Hafnium shows a profile comparable to the LREE (Fig. 13c).

6. Discussion of LA ICP-MS trace element analyses

Nearly all analyzed garnet crystals show zonation trends suggesting Rayleigh-like fractionation mechanism, as modeled for Mn by (Hollister, 1966). It is characterized by steeply decreasing abundance of an element from core to rim forming a bell-shaped trail across a crystal. Such a profile is typical of elements, which are compatible in garnet (partition coefficient > 1), while a reversed profile is expected for elements with partition coefficients < 1. Modeling of Nd, Sm and Hf zonation in garnet based on Rayleigh law conducted by Kohn (2009) suggests little
zonation for incompatible elements like Nd, Sm or Hf. Indeed, studied crystals display a very smooth rise of concentration from core to rim, which becomes steeper towards the rim area. Nevertheless, the zonation trends in larger crystals are very clear, in particular for Sm, which is more compatible than Nd, and particularly Hf (Figs. 8–13). The degree of Sm and Nd zonation clearly correlates with the crystal size (Fig. 14). Rim-to-rim profiles become progressively flatter from garnets of about 7 mm size in sample V99-66, where zonation is fairly strong, to completely flat profiles in garnets of about 1 mm size in sample V99-67 (Fig. 14). On a single hand specimen scale, such correlations are also present. Although the available range of garnet size is more limited, in sample V99–66, where the sizes of the analyzed crystals vary from about 7 to 2 mm, the light REE patterns show much stronger zonation in the larger crystals and milder among the smaller crystals. However, zonation in 2.0–3.5 mm crystals is practically the same both in terms of style as well as absolute concentrations (Fig. 15a). Smaller crystals (<2 mm) in V99-67 show very little or no LREE zonation and their Nd and Sm content is the same in all analyzed grains (Fig. 16a).

If garnet crystallization followed the Rayleigh distillation model, such rather regular changes of LREE zonation, on a hand specimen scale, could have been caused by progressively later nucleation of the smaller crystals as described for major elements by Kretz (1994). Indeed, with the exception of sample V99-67, we find higher abundances of Sm and Nd in the cores of the smaller crystals relative to the larger ones, which is expected for those elements that are less compatible in garnet (Figs. 14 and 16a). This is additionally supported by the opposite trends observed for heavy REE, although the correlation is less obvious (Fig. 15b). In sample V99-67, however, we observe the same abundance and almost completely flat Nd and Sm zonation patterns throughout all studied crystals, while Lu zonation is variable, and does not seem to show any correlation with crystal size (Fig. 16). Additionally, in the case of the prolonged garnet nucleation, we would expect to see some textural variations among studied garnet. Instead, garnets regardless of their size show the same set of inclusions and the same relationship with the surrounding matrix.

Alternatively, progressive flattening of zonation profiles with the decreasing crystal size could be a result of diffusional homogenization of Nd and Sm in garnet due to high temperature metamorphism. Such interpretation is consistent with experimental studies of Nd and Sm diffusivity, which suggest that the Sm–Nd system is, generally, open above 700 °C (Tirone et al., 2005) or 750 °C (Van Orman et al., 2002) temperature for garnet size of 1.5 mm or smaller at moderate to fast cooling rates (noteworthy, the former study shows much stronger dependence of closure temperature on cooling rate). Similar, or even slightly lower closure temperature was estimated for HREE (Van Orman et al., 2002; Tirone et al., 2005). Preservation, of steep Lu core-to-rim zonation patterns even in c. 1 mm garnets, at first glance, argues against significant diffusion of this element. However, since it is not possible to verify whether the original HREE profiles were not even steeper, we cannot entirely rule out, that some intracrystalline diffusion took place. Because of much higher HREE concentrations, partial thermal relaxation of HREE is more difficult to detect. In sample V99-66, where garnet size shows the largest variations, smaller crystals have clearly flatter profiles (Fig. 15b), which suggest that intracrystalline diffusion of Lu could have taken place.

Diffusional homogenization well explains the zonation trends particularly in V99-67, where the garnets show a narrow diameter range between 1 and 2 mm. In all investigated crystals Nd and Sm lack zonation and have practically the same abundance (Fig. 16a). Lutetium, on the other hand, shows variable content and variable degree of flatness, which could also be attributed to partial thermal relaxation (Fig. 16b).

Trace element analyses alone do not allow to unequivocally decide, whether, diffusional homogenization or progressively younger garnet crystallization during Rayleigh style crystallization is responsible for the observed trace element distribution. Combination of both cannot be ruled out either. We continue the discussion of both mechanisms in the context of the revised interpretation of the Sm–Nd and Lu–Hf dating results, below.

As already mentioned, hafnium is highly incompatible in garnet and thus, its distribution, qualitatively, is expected to be similar to light REE. Indeed, zonation of Hf in all analyzed garnets shows trends analogous to those observed for Nd and Sm in larger crystals (Figs. 8–13). However, unlike the LREE, Hf zonation is still preserved even in the smallest grains, and thus most likely, was unaffected by intracrystalline diffusion, which is in accord with its very slow diffusivity (Bloch et al., 2010; Ganguly et al., 2010).

Except for diffusional homogenization and prolonged garnet nucleation that affected REE abundance and distribution, we observed other syn- and post-crystallization modifications of simple Rayleigh-like fractionation model. The most common and the most significant post growth modification, observed in all studied samples is confined to garnet rim area. It is expressed by rise in heavy and drop of light REE abundance (e.g. Grt. 1 from sample V99-8, Fig. 8). We relate this phenomenon to resorption, evidence of which is clearly visible in thin sections (Fig. 3). Redistribution of elements by resorption can be significant. A good example is Grt. 1 from sample V02-05, where resorbed rims have heavy REE concentrations similar to those observed in the garnet center (Fig. 13). A more typical situation in the studied samples,
Fig. 9. Rim-to-rim zonation profiles of two garnet crystals from sample V99-67: Sm and Nd (a, d), Y and Lu (b, e) and Hf (c, f).

Fig. 10. Rim-to-rim zonation profiles in garnet Grt. 1 from sample V99-66.
however, is represented by Grt. 1 from sample V99-8, where resorption could have affected about 15–20% of the studied profile (Fig. 8). We tentatively link the resorption process to back diffusion from melt during anatectic metamorphism, which also caused intracrystalline diffusion of light REE described above.

All other deviations from a Rayleigh-like pattern, were observed only in sample V99-66 and relate to the time of garnet crystallization. In garnet Grt. 1 broad core with nearly constant concentrations of Yb and Lu followed by a sudden drop of concentrations resembles a profile documented by Pyle and Spear (1999) for Y in garnets from staurolite zone metapelites. The authors linked the observed pattern to co-crystallization of xenotime. Adopting this type of interpretation, fairly uniform abundance of Lu in the core could suggest co-crystallization of a HREE-rich mineral. The third type of “anomalous” profile was observed in the same crystal and is expressed by very high spikes of Y, Dy, Ho and Er, which correlate with minimum P content (Fig. 10b, c). Possible interpretations of such patterns were discussed by Lanzirotti (1995). Correlation of Y peaks with change in P zonation suggests that this type of modification could be related to a change in a phosphate mineral being in equilibrium with garnet and breakdown of a Y-rich mineral (Yang and Rivers, 2002). Another important feature of this particular garnet is that the Y distribution trend is not coupled with the trends of two the heaviest REE. Yttrium does not display any resemblance neither with Yb nor Lu. Moreover, in the same thin section neighboring crystals show “normal” behavior, where Y zonation is compatible with zonation of all HREE. We interpret differences in zonation trends in proximate garnets as resulting from small scale matrix heterogeneities and variations in reactions with accessory phases.

The only analyzed garnet that does not fit into any of the categories described above is garnet Grt. 3 from sample V99-66. The profile is rarely found and only in the crystals smaller than about 3 mm. It is practically flat with two distinct spikes near the margins, similar to Y and HREE (with exception of Yb and Lu) observed in Grt. 1 from the same sample. Again, similarly to Grt. 1 the spikes correlate with P zonation, which points to the importance of reactions involving phosphates in REE partitioning and the resulting profile probably reflects small scale matrix heterogeneities.

Fig. 11. Rim-to-rim trace element zonation profiles of Grt. 2 (a–c) and Grt. 3 (d–f) from sample V99-66.

Fig. 12. Rim-to-rim trace element zonation profiles of Grt. 3 from sample V99-66. Note inverse correlation of Lu and P.
Comparison of ID and LA ICPMS results

Comparison of Sm/Nd and Lu/Hf ratios obtained by isotope dilution (ID) method with “true ratios” obtained by in situ laser ablation ICPMS allows us to estimate the extent of contribution from REE- and Hf-rich inclusions to our isotopic analyses. If our mineral separates were pure and sulfuric acid leaching effectively removed monazite and apatite inclusions, the Sm/Nd ratios recovered by ID should be close to those measured by laser ablation ICP-MS. In Fig. 17 we presented Sm/Nd and Lu/Hf ratios for individual ablation spots and marked the highest ID values obtained for bulk garnet separate from the same samples. The plots show excellent agreement of Sm/Nd ratios measured by ID and LA ICPMS for all samples but V02-05. In the latter case, in situ measurements show ratios twice as high as those obtained by isotope dilution (Fig. 17c), which indicates that Sm–Nd dating of this sample could be unreliable. Remarkable agreement in Sm/Nd ratios obtained by both techniques for the remaining samples, indicates that monazite inclusions were efficiently eliminated by sulfuric acid leaching during sample preparation. Some variations among 147Sm/144Nd ratios in different garnet fractions are interpreted as resulting primarily from different proportions of core and rim in bulk separate, but also from certain, rather minor, contribution from inclusions (e.g. feldspar or biotite), which is unavoidable.

At first glance it may seem that Lu/Hf ratios obtained by ID analyses, do not reproduce “true” Lu/Hf ratios determined by LA ICP-MS (Fig. 17). However, the departure from “true value” is subjected to large uncertainty due to very strong Lu zonation. Except for comparing Lu/Hf ratios, the influence of Hf-rich inclusions can additionally be controlled by comparison of HF concentrations derived by LA ICP-MS and ID methods. In the case of sample V99-67, the ID method recorded 200 and 300 ppb Hf concentrations in comparison to about 100 ppb obtained by laser ablation (Table 1 and Fig. 9). Thus, some influence of inherited HF could explain lower Lu/Hf ratios recorded by isotope dilution in garnets and additionally contributed to strong scatter observed in the isochron diagram (Fig. 6). In the case of sample V02-05, however, both techniques point to about 100 ppb Hf concentration, which indicates, that Lu/Hf ratios in this sample measured by ID reflect rather clean garnet separates (Table 1 and Fig. 13) and points to some other source of scatter among the Lu–Hf analyses. We develop this topic in the next section.

8. Interpretation of garnet dating results in the context of trace element analyses

Combining Lu–Hf and Sm–Nd isotopic analyses with in situ laser ablation ICPMS measurements of trace element abundance, puts a new perspective on the interpretation of Lu–Hf and Sm–Nd garnet dating from the DNCV gneisses. Geochronology, on the other hand, helps to understand some of the REE zonation features in garnet (see below). In the case of Sm–Nd dating LA ICP-MS documents two key features. Firstly, remarkable agreement of Sm/Nd ratios measured by LA ICPMS and isotope dilution shows that garnet separates were very well purified prior to analyses and mixing with any inherited Nd cannot be a reason for the observed large age variations. Secondly, progressive flattening of the Nd and Sm zonation profiles with decreasing garnet size indicates that diffusional homogenization, and thus variable (size dependent) degree of resetting in garnets, is the most likely cause of the observed age differences (Fig. 14). Some contribution to the observed pattern could be caused by prolonged growth of progressively smaller garnets (Kretz, 1994). In samples V99-8 and V99-66 garnet size varies from about 2 mm to more than couple of cm (with a median size of about 3 and 5 mm, respectively). Hence, despite the fact that isochrons defining both ages are of very good quality, they are unlikely to date any specific geological episode.
(regardless of the reason for the variation in Nd and Sm distribution). In both cases they represent a mixture of variably reset individual garnet crystals (or a mixture of grains nucleating over a prolonged time period) and provide a minimum age for early garnet growth and a maximum age for a resetting episode (or the youngest growth).

The time of the resetting episode is best approximated by the youngest 31.7 ± 0.9 Ma age recorded by V99-67. In the latter sample the largest crystals are about 2 mm, while the majority are smaller than 1.5 mm. All analyzed garnets practically lack zonation and show the same Nd and Sm abundance, which we interpret as a result of diffusional homogenization (Fig. 16a).

A similar phenomenon has been recently reported by Dutch and Hand (2010) who observed younging of garnet ages with decreasing crystal size in an early Proterozoic granite due to a high temperature overprint. The authors explained the observed pattern by higher closure temperatures in larger crystals. At the same time, they note that REE were not mobilized, which may indicate that some mechanism other than diffusion could be responsible for larger degrees of resetting in smaller crystals.

The question arises, how accurately the youngest sample dates the resetting episode. The cooling rates for early evolution of DNV based on available thermochronology vary from about 100 °C/Ma (Nam et al., 1998) to about 50 °C/Ma (Leloup et al., 2001). Using computer program of Ganguly et al. (1998) and thermodynamic data of Tirone et al. (2005), we estimated closure temperature Tc for Nd in 1 mm diameter garnet undergoing cooling from peak temperature Tp = 800 °C at rates between 50 and 100 °C/Ma as 713–724 °C (Fig. 18). Analogous estimates for garnets of 7 mm diameter results in Tc just 10–15 °C below the temperature peak.

Thus, because closure temperature in V99-67 garnets is significantly below the temperature peak, the estimated age should reflect early cooling phase. Accepting cooling rates mentioned above, about 2.1 to 4.6 Ma of age resetting during cooling could have taken place (calculated using computer program of Ganguly and Tirone, 1999, and thermodynamic data of Tirone et al., 2005). As mentioned above, cooling rate is a subject of some speculation but it is likely to be on the higher side of the proposed range. This is suggested by the oldest zircon and apatite fission track ages, which range from 30 to 25 Ma (Viola and Anczkiewicz, 2008) and are only slightly younger than Sm–Nd garnet age presented here. Thus, the temperature peak, occurred, probably, some 2 Ma earlier than Sm–Nd closure in V99-67 garnets.

Lu–Hf dating did not provide isochron ages. High scatter of the analyses in both samples does not permit defining an age for any of them. An obvious possibility of data scatter that has to be considered is contamination by inherited Hf from zircon inclusions, which are numerous in garnets and in the matrix. Mixing of inherited Hf from zircons with Hf from garnets tends to lower the measured 176Hf/177Hf and 176Lu/177Hf ratios, reducing the slope of an isochron and resulting in artificially younger ages (e.g. Prince et al., 2000; Scherer et al., 2000). This view is correct providing the initial 176Hf/177Hf was determined accurately. However, whole rock splits used for estimating initial 176Hf/177Hf ratio are affected by inherited zircons too. Hence, “too low” 176Hf/177Hf ratios in the whole rocks, could make isochrons steeper and thus, artificially, “too old” (providing garnet ratios were accurate). A hint of which of the two scenarios prevailed is provided by εHf(t) for tie lines defined separately by each garnet fraction with the whole rock. They give values of −8 and −10 for sample V99-67, and −11 and −12 for sample V02-05 (calculated using reference ratios of Bouvier et al., 2008). Such values are expected for metasedimentary rocks and correlate well with the corresponding εNd(t) of −13.0 and −10.9 for the same samples (calculated using reference values of Jacobsen et al., 1980). Hence, we can assume that the initial ratios, although certainly, to some extent, were influenced by Hf scavenged from zircons (digestion took place on a hotplate, which limits zircon dissolution), are reasonably well constrained and thus, the major source of potential age inaccuracy we ascribe to Lu–Hf analyses of garnet fractions. It is also noteworthy, that in the case of high parent/daughter ratios in garnet, accuracy of initial ratio determination for the Lu–Hf decay system is a lot less critical than for Sm–Nd because of significantly higher ratios of the former system. Isotopic ratios in garnet

Fig. 15. Sm and Lu rim-to-rim zonation profiles of garnets in dependence on their size from V99-66.

Fig. 16. Rim-to-rim Sm/Nd and Lu/Hf ratios zonation in garnets measured by LA ICPMS.
fractions show spread large enough, to provide age estimates based on garnets alone. They define \(84.1 \pm 2.3\) Ma age for sample V99-67 and \(77.0 \pm 1.9\) Ma for sample V02-05 (Fig. 6). Although dates are somewhat similar, their hugely positive \(\varepsilon_{\text{CHUR}}\) of about 105 and 50 are unrealistic, and thus both two garnet tie line ages are undoubtedly false.

Although, at least in the case of sample V02-05 we cannot rule out some inherited Hf mixing, we do not consider this as a main reason for the observed complexities of our Lu–Hf dating efforts. Applying the same way of reasoning as with Sm–Nd system, extended in time garnet nucleation should be taken into account as a mechanism responsible for the observed systematics. Individual apparent garnet ages, would represent a mixture of crystals defining the minimum age for the beginning of crystallization. However, if protracted garnet crystallization was the only operative mechanism, we would expect to observe good degree of similarity of the Lu–Hf and the Sm–Nd ages obtained for the same fractions. These, however, show dates up to about 100 Ma younger. Thus, prolonged garnet crystallization of progressively smaller crystals alone does not explain the observed REE zonation patterns and the obtained ages.

Under high temperature conditions much faster diffusion of Lu relative to Hf combined with garnet dissolution could lead to lower \(^{176}\text{Lu}/^{177}\text{Hf}\) ratios, while keeping the same \(^{176}\text{Hf}/^{177}\text{Hf}\) ratios, causing “counter clockwise rotation” of isochrons, thus increasing the apparent Lu–Hf ages (Kohn, 2009; Ganguly et al., 2010). Because this process also depends on crystal size, variable degrees of resetting could potentially lead to the observed scatter and shift Lu–Hf ages towards older ranges. Such an interpretation is particularly appealing, especially, when taking into account the high temperature of metamorphism, much younger Sm–Nd ages and almost the same diffusivity of light and heavy REE postulated by the experimental data (Van Orman et al., 2002; Tirone et al., 2005). Our LA ICP-MS data seem to support such scenario. Although Lu still shows very clear zonation in most of the small crystals, this could be due to the fact that their original pattern was considerably stronger than that of LREE and complete homogenization did not take place. Hafnium on the other hand, rather consistently shows one type of profile and likely preserved disequilibrium growth conditions (with some minor modifications particularly in the rim area, see above). Thus, thermally driven intracrystalline diffusion of Lu combined with very “stationary” Hf behavior, could lead to the counterclockwise rotation of the isochron and to the observed much older apparent Lu–Hf ages (Kohn, 2009; Ganguly et al., 2010). Additional factor that has to be taken into account is resorption. Back diffusion of Lu into garnet and loss of Hf during high temperature dissolution, makes Lu/ Hf ratios higher and leads to “younger” of original crystallization ages (Kelly et al., 2011). Bearing in mind that we conducted Lu–Hf analyses of only two samples, we note that garnet separates from sample V02-05, which underwent a significant larger degree of resorption (see trace element zonation in Figs. 9 and 13), show much younger ages, as expected in the sample with larger degree of resetting. Thus, we observe two counteracting processes (intracrystalline diffusion and resorption), which did not allow to obtain meaningful Lu–Hf isochron dates.

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**Fig. 17.** Nd closure temperature \(T_c\), profiles for 1 mm diameter garnet for 50 and 100 °C/Ma cooling rates. Dashed lines indicate mean closure temperatures. See text for details.
Habler et al. (2007) and Bestmann et al. (2008) showed that development of micro-scale deformation zones in garnet may be a significant factor affecting garnet dating results. Our study of deformation fabrics was limited to optical microscopy and BSE imaging, and does not allow us to decide, whether deformation could have significantly contribute to the observed microgeochemistry and isotope systematics. Application of more advanced techniques would certainly help, but this was beyond the scope of this study.

9. Implications for timing of metamorphism in the Red River shear zone

Timing of metamorphism and shearing in the Red River shear zone was previously constrained mainly by indirect estimates using U–Pb zircon dating of granitic melts from the Ailao Shan massif in China (Schärer et al., 1990, 1994; Zhang and Schärer, 1999). Schärer et al. (1990) and Schärer et al. (1994) reported ages between 26 and 22 Ma for vast majority of dated granitic dykes. One of these dykes, outside the main shear zone but following its trend, was dated at 35 Ma and interpreted as a minimum age for the onset of left lateral shearing, which continued until 20 Ma. Similar time constraints were estimated by Zhang and Schärer, 1999 who reported ages between 33 and 22 Ma applying the same technique and similarly interpreted this time interval as the duration of left lateral shearing along the RRF. In situ Th-Pb dating of monazite included in garnets from northern segments of RRZSZ in Yunnan province in China gave very similar result to the U–Pb dating ranging from 34 to 21 Ma (Gilley et al., 2003). On the basis of microstructural and petrological observations, the latter authors linked dated monazites to synkinematic garnet growth, which led them to the conclusion that left lateral shearing started at 34 and continued until 21 Ma. The same approach applied to DNCV massif defining the southern segment of the fault, appeared inconclusive. Th–Pb monazite ages showed scatter from >200 to 20 Ma, which revealed severe inheritance problems. Large variations among monazite ages included in garnets, were interpreted by Gilley et al. (2003) as suggesting multiple garnet growth episodes. Anczkiewicz et al. (2007b) obtained 40 Ma Sm–Nd garnet ages and interpreted them as a record of an early extensional event contemporaneous with emplacement of highly potassic intrusions in SE Asia also dated at 40–30 Ma (Chung et al., 1997 and references therein). Additional garnet dating along with trace element analyses presented in this contribution places a different perspective on the interpretation of garnet ages. Thanks to trace element analyses, we could demonstrate that age variations result from thermal relaxation and possibly also from prolonged garnet nucleation under high temperature conditions. In the case of Lu only partial diffusional homogenization took place, while Nd and Sm in sample V99-67 underwent complete or nearly complete relaxation as indicated by the same abundance and homogenous distribution of both elements in all garnet crystals. Consequently, only garnets of the smallest size provide best time information on the resetting event. The obtained 31.7 ± 0.9 Ma age is about 2 Ma younger than the postulated age of Oligocene metamorphism in the Ailao Shan massif (Gilley et al., 2003). However, when taking into account about 2 to 5 Ma age resetting during cooling (see above), we can postulate, that metamorphic peak and left lateral shearing in both DNCV and the Ailao Shan occurred approximately at the same time.

10. Conclusions

Migmatitic gneisses in the Day Nui Con Voi massif bear a record of polynemorphic history of Indochina. Geothermobarometric calculations determined conditions of the last high-grade metamorphism as 760–810 °C at 6–10 kbars pressure. High temperature conditions lead to complex Lu–Hf and Sm–Nd isotope systematics, which are better understood in the context of in situ trace element distribution analyses in garnet. While major elements record diffusive profiles, REE and Hf display a Rayleigh-like fractionation style with significant impact of post-garnet crystallization modifications. Rim-to-rim zonation profiles of Nd and Sm show progressive flattening with the decreasing crystal size, being completely homogenized in garnets smaller than about 1.5 mm. Similar correlation, although not so well pronounced, was documented for HREE. The observed correlation is interpreted as a combination of relatively long lasting crystallization of progressively smaller garnets and intracrystalline diffusion. Complete diffusional homogenization of Lu did not occur due to much higher initial abundance and concentration gradient of this element, because of its high compatibility in garnet. Both Nd and Sm show identical behavior, which is in accord with the experimental data postulating the same diffusivity of these elements. Thus, 31.7 ± 0.9 Ma Sm–Nd garnet age obtained for the sample with the smallest crystal size, where light REE show flat profiles, is interpreted as providing best time estimate for high temperature resetting episode related to the Early Oligocene metamorphism in the Red River shear zone. The obtained date is in excellent agreement with the proposed timing of metamorphism and the beginning of left lateral shearing in the Ailao Shan massif, northern continuation of the Red River shear zone. Older Sm–Nd ages are interpreted as mixed analyses of variably reset individual garnet crystals.

Lu–Hf isotopic analyses, despite yielding high parent/daughter isotopic ratios appeared very scattered and did not define isochrons. Ages derived for individual garnet fractions range from about 80 to 160 Ma and are interpreted as being a consequence of very different diffusive properties of Lu and Hf (Ganguly et al., 2010). Intracrystalline diffusion of Lu combined with practically immobile Hf, leads to counterclockwise rotation and older apparent ages (Kohn, 2009). A commonly observed resorption, on the other hand, tends to make ages younger (Kelly et al., 2011). However, back diffusion of Lu during resorption, generally, shows relatively small enrichment and is limited to a very narrow rim area, which makes its influence on isotope systematics relatively small. These two counteracting processes did not permit to obtain meaningful Lu–Hf dates.

Thus, only the youngest Sm–Nd age obtained for the smallest crystals, where Nd and Sm show practically complete thermal relaxation, is interpreted as geologically meaningful. Taking into account that closure temperature for the Sm–Nd system in 1 mm garnet was estimated to be some 80 °C below the temperature peak, the 31.7 ± 0.9 Ma age is interpreted as cooling from Oligocene high-grade metamorphism in the DNCV massif. Taking into account some 2 to 5 Ma of cooling related age resetting, metamorphism in the DNCV and the Ailao Shan massifs, that delineate most of the Red River shear zone, occurred approximately at the same time.

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