Thermochronometry of metamorphic rock complexes on the SE Peloponnese, Greece, using thermoluminescence (TL): preliminary experiments

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doi: 10.12681/hnpsanp.5135

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To cite this article:

Thermochronometry of metamorphic rock complexes on the SE Peloponnese, Greece, using thermoluminescence (TL): preliminary experiments

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Abstract Here, we report preliminary results from thermoluminescence (TL) measurements on metamorphic quartz from the SE Peloponnese, Greece, and we discuss its potential for thermometric and, possibly, thermochronometric applications over longer geological periods. Extensive high pressure/low temperature (HP/LT) schists associated with a 24 Ma metamorphic age, and with cooling ages ranging between 6-14 Ma (based on fission-track and (U-Th)/He thermochronometry), encompass sizable quartzite outcrops associated with substantially low radiation (U, Th, K concentrations below the analytical detection limits), allowing TL signal to grow on longer geological timescales. Although deeper TL traps (> 360°C) appeared saturated as expected, geologically stable traps lying between around 360°C were found to be far from saturation. Once higher analytical resolution is achieved in the determination of the radioelement concentrations the recovered equivalent doses will be combined with the respective dose rates to explore the suitability of TL from quartz for longer-range thermochronometry in extremely low-radiation geological environments.

Keywords Thermoluminescence, Equivalent dose, Quartz, HP/LT metamorphic rocks

Introduction

Tectonic exhumation involves ductile thinning of the crust, mainly due to tensile faulting which lifts footwall rocks towards the earth’s surface. Erosion accounts for far more exhumation than tectonic mechanisms alone and is an important agent of crustal cooling in both tectonically active and inactive areas [1,2]. Many studies have shown that thermochronometry can reveal the thermal history of rocks in the lithosphere in relation to subsidence or denudation by measuring radioactive-decay products within mineral-thermometers. Radioactive-decay products start to accumulate as soon as the rock crosses a certain temperature [3]. This temperature is known as the closure temperature and varies with the thermometer and the cooling rate. Assuming that typical geothermal gradients in orogens range between 25-30°C/km [4] the closure temperatures of mineral thermometers can be translated into crustal depths and, hence, a cooling history can be proposed. In the field of solid-state dosimetry, the infrared-stimulated luminescence (IRSL) from feldspar has recently been exploited as an alternative thermochronometer [5,6].

Metamorphic rock complexes are exhumed from beneath overlying unmetamorphosed rock. Nevertheless, typical dose rates encountered in metamorphic rocks limit the application of IRSL to a few hundred thousand years (ka). In the current study, we explore the suitability of thermoluminescence (TL) from metamorphic quartz as an alternative thermometer to evaluate the volume of exhumation of high-pressure/low-temperature (HP/LT) metamorphic rocks on the SE Peloponnese, Greece. This approach departs from the use of TL for direct fault dating, as pioneered in

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Japan and elsewhere [7-9]. Given the low radioactivity associated with quartz [10], the implications of the TL signal for thermochronometry beyond the limits encountered by feldspar IRSL are also investigated.

**Geological setting and samples**

The Hellenic forearc ridge has been developed due to the subduction of fragments (terranes) of the African plate beneath the European plate [11]. Those terranes experienced HP/LT metamorphism soon before 24 Ma [12,13]. The resulting metamorphosed units, namely the HP/LT Arna unit (also known at the Phyllite-Quartzite series) and the Mani unit (lower-grade metamorphics, known also as Plattenkalk series) are currently evidenced as tectonic windows (Fig. 1) in the overlying unmetamorphosed nappes of the Tripolis carbonates [14,15]. Cooling ages associated with these rocks range between 6-14 Ma [16].

![Figure 1](image_url) **Figure 1** HP/LT- phyllite and marble thrust sheets (southern Mani).

For the purposes of the study, quartz samples were extracted from the schist/phyllite part of both Arna and the meta-flysch of Mani (Fig. 3), from exposures on the southern Mani and Neapolis peninsulas [16-19] (Fig. 2).

Given the relatively high dose-rates associated with the schist/phyllite portion of the metamorphic rocks, (in contrast to the remarkably low internal dose rate associated with quartz [10]) we aimed for samples from the center of sizable quartz lumps (a few decimeters in diameter) (Fig. 3) so as to ensure maximum insulation from the external dose rate.

**Methodology for TL measurements**

The five samples (PK1, PK2, PK3, ELK and KK) were mechanically and chemically treated under red light. Firstly, the samples were crushed with hammer to remove the external light-exposed rind (~1cm), and then sieved in the 100–150 μm fraction. Treatment with hydrochloric acid (10%) and hydrogen peroxide (30%) aimed at eliminating possible contamination by carbonates and organic material, respectively. Finally, the samples underwent HF etching (40%) for 45 minutes to remove any felspathic content. Purified quartz grains were measured on an automated system Risø TL/OSL.
reader DA-20, equipped with a $^{90}\text{Sr}^{90}\text{Y}$ beta source (0.075 Gy/s) installed at the Archaeometry Center, University of Ioannina, Greece. TL was detected by the photomultiplier through the “filter pack” (Schott BG-39 and Corning 7-59 filters). Quartz aliquots underwent a SAR protocol adapted for TL (Table 1) [20].

![Geological map of the Peloponnese with sampling areas](image)

**Figure 2.** Geological map of the Peloponnese with sampling areas (red dots) [21].

![Sample image](image)

**Figure 3.** Samples were collected from the center of sizable quartz lumps cropping in schists and phyllites of the SE Peloponnese. The large (>30 cm) diameter of the lumps is assumed to cut off radiation contributions from the surrounding schist.

**Results**

Fig.4 illustrates a typical natural TL signal (blue line) and the subsequent test dose signal (red line). Step 5 in Table 1 was repeated several times at the end of the cycle and involved the
measurement of the background. For the given signal intensities, the background (black line) is considered negligible up to ~450°C and the pattern of increase above this temperature (black-body radiation) is practically independent of the number of repetitions.

Table 1. SAR procedure for TL [20]

<table>
<thead>
<tr>
<th>Step</th>
<th>Sequence</th>
<th>TL</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Preheat at 200°C</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>TL measurement from 0°C to 570°C</td>
<td>L_x</td>
</tr>
<tr>
<td>3</td>
<td>Test dose irradiation</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>Preheat at 200°C</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>TL measurement from 0°C to 570°C</td>
<td>T_x</td>
</tr>
</tbody>
</table>

The TL signal was then integrated at 10°C intervals. The respective growth curves and their resulting equivalent doses were calculated (Fig. 5). By plotting the D_e versus the integration temperature (Fig. 6), we discovered that the D_e increases with the integration temperature up to ~360-380°C but appears saturated at greater temperatures for the most samples (Table 2; Fig. 6). Although saturation of parts of the TL signal is indeed expected given the large metamorphic age (24 Ma), it has not, however, affected shallower but geologically stable traps such as those ranging between 360-380°C. It is a remarkable observation that traps with exceptional stability over long geological timescales (i.e., \( \tau_{320} = 1.07 \times 10^{12} \) a; [22]) yielded \( D_e \) well below the saturation levels (Fig. 6), given the Early-Miocene/Late Oligocene metamorphic age of the measured rock (24 Ma). This observation has important thermometric (and probably thermochronometric) implications as discussed in the next section. Besides, the radioelement concentrations were measured by means of ICP-MS (Table 2). For the most samples the radioelement concentrations lie below the detection limits of the method, confirming our initial prerequisite for a substantially low-radiation environment. Neutron activation analysis (NAA) has the necessary resolution (e.g. [23]) to detect radioelement concentrations below the limits of ICP-MS, eventually revealing internal dose rates of quartz at least one order of magnitude lower than those shown as maximum values in Table 2. NAA and gamma-spectrometry
analyses on these samples are currently underway to generate numerical estimates of the radioelement concentrations and, thus, dose rates and TL ages.

Table 2. Concentrations of U, Th, K, dose rates, maximum unsaturated equivalent doses and the corresponding temperature interval per sample. The increased radioelement concentrations of sample ELK are untypical of quartz. Moreover, the same sample probably suffers from signal loss across the entire range of temperatures as concluded from the lack of a pattern between De and the integration temperature interval. Therefore, sample ELK was not further considered.

<table>
<thead>
<tr>
<th>Sample</th>
<th>U (ppm)</th>
<th>Th (ppm)</th>
<th>K (%)</th>
<th>Dose rate (Gy/ka)</th>
<th>De (Gy)</th>
<th>Temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PK1</td>
<td>&lt;0.1</td>
<td>&lt;0.2</td>
<td>&lt;0.01</td>
<td>&lt;0.474</td>
<td>552</td>
<td>490-500</td>
</tr>
<tr>
<td>PK2</td>
<td>&lt;0.1</td>
<td>&lt;0.2</td>
<td>&lt;0.01</td>
<td>&lt;0.474</td>
<td>227</td>
<td>370-380</td>
</tr>
<tr>
<td>PK3</td>
<td>1.8</td>
<td>6.9</td>
<td>0.01</td>
<td>11.066</td>
<td>536</td>
<td>470-480</td>
</tr>
<tr>
<td>ELK</td>
<td>1.8</td>
<td>6.9</td>
<td>0.01</td>
<td>11.066</td>
<td>536</td>
<td>470-480</td>
</tr>
<tr>
<td>KK</td>
<td>&lt;0.1</td>
<td>&lt;0.2</td>
<td>&lt;0.01</td>
<td>&lt;0.474</td>
<td>218</td>
<td>330-340</td>
</tr>
</tbody>
</table>

Figure 5. Dose response curve of quartz for 350-360°C interval.

Figure 6. Equivalent dose versus the integration temperatures.

Discussion

The TL method is widely used for dating the last intense heating of crystalline minerals or the formation of mineral grains within a material [10]. It is well known that most crystal defects, responsible for the emission of luminescence in crystalline materials are created at the time of the formation of the material (e.g., solidification from melts or precipitation from hydrothermal solutions) [24]. TL can be applied to geological materials that fulfill this need and, hence, metamorphic rocks might be suitable. Despite the large geological stability of the (deeper) TL traps, metamorphic rocks cropping on the earth’s surface typically are a few million years old, whereas TL dating cannot date beyond ~0.5-1 Ma, mainly due to the saturation of the TL signal at average ambient dose rates. Nevertheless, if a low-radiation environment [25] was ensured within a metamorphic outcrop (i.e., a region of substantially low radioelement concentrations and a specific geometry cutting off radiation contributions external to the sample), would allow enhancing the TL age well beyond 1 Ma.

The quartzite samples extracted from the SE Peloponnese metamorphic rocks seem to fulfill these demands. They contain radioelements (U, Th, K) at remarkably low concentrations (even beyond the detection limits of the analytical method employed here) while they are sizable enough to cut off dose rate contributions from the surrounding schist (i.e., gamma rays penetrate up to 30 cm of rock [10]).
Very deeper traps are associated with the rock-forming processes and since their inherent TL signal closed early, it was barely affected by the lower temperatures encountered in the thermal history of these metamorphic rocks. Therefore, they reasonably appear as saturated, given the old metamorphic age (24 Ma). The presence of geologically stable but unsaturated traps around 360°C implies that the dose must have been delivered at a very low rate, substantially lower than the maximum estimates presented here (Table 2). This brings us to the next question of when the sampled metamorphic rocks crossed the depth equivalent of the ~360°C isotherm (~14 km considering an average gradient of ~25°C/km).

Obviously, higher-resolution measurements of the radioelement concentration are necessary to establish closure ages, that is the time-duration of steady accumulation of electric charge following an episode of fast cooling below 360°C where little signal loss occurs. These preliminary results make TL of quartz a promising alternative solid-state thermometer. Nevertheless, before establishing the TL of metamorphic quartz as a thermochronometer over the geological time scales considered here, the first order kinetic loss of thermoluminescence as a function of temperature (Arrhenius Law) as well as the possibility of athermal loss of signal (anomalous fading) deserve a thorough description.

Conclusions

The extremely low-radiation environment, dominating in the center of quartz lumps cropping in metamorphic rocks of the SE Peloponnesse owing to i) the substantially low radioelement concentrations and ii) the insulation effect of the dense and sizable quartz lump against the radioactivity of the surrounding schists, allows the TL signal to grow on longer geological timescales. Integration of TL signals around 360°C returned unsaturated equivalent doses as high as ~960 Gy. The associated traps can successfully make TL from quartz a versatile solid-state thermometer of metamorphic processes, alternative to the conventional ones. Using TL, the metamorphic temperatures are estimated to around 360°C, matching previous independent figures. Once greater analytical resolution is achieved, TL from quartz in extremely low-radiation geological contexts may be established as a functional thermochronometer over the entire Neotectonic period (i.e., from the Middle Miocene onwards). Moreover, future steps are planned to investigate the geological stability of the TL traps involved here such as Arrhenius plots, time consuming anomalous fading and isothermal decay tests.

Acknowledgements

This study is supported by the National Technical University of Athens Research Committee Grant. We would like to thank one anonymous reviewer for their comments.

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