Thermoluminescence dating of sediments using mineral zircon

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5. TL RESULTS

5.1 Introduction

Natural zircon in sediments emits visible light, when it is heated to moderate temperatures (several hundred °C). This phenomenon is referred to as thermoluminescence (TL), and can in principle be applied to determine the age of the host sediment. The luminescent light originates from defect centers, which are created in the crystal lattice of zircon as a result of irradiation caused by natural radioactivity (see chapter 2).

In this chapter we investigate the thermoluminescence behavior of a suite of zircon sand from a variety of geological locales. Because in zircon, like many other minerals, the luminescence properties are governed by defects and impurities, we have determined for the most important samples the concentrations of several impurities, among which are those of the lanthanide series. After laboratory irradiation, TL-emission spectra are measured for the purpose of quantifying the effects of the individual trace elements and the extent of fading. Zircon sand samples for this study were selected from the USA, the Netherlands, and South Africa.

TL experiments on intentionally doped synthetic zircon single crystals have shown that important activators for luminescence in this material are Sm, Eu, Gd, Tb and Dy, which are all members of the Lanthanide Series (Iaconni and Caruba, 1980). Each of the luminescence activators contributes to the overall luminescence spectrum. In the TL spectra of natural zircons the contributions from the Tb and Dy activators can be distinguished clearly by the presence of the luminescence peaks located at positions, which are characteristic for these impurities. The contributions from the remaining REE-activators have not been observed. After irradiation a part of the trapped electrons recombines with holes, which leads to a decrease of the TL signal even if the sample is stored in the dark at about room temperature. This phenomenon is referred to in the scientific literature as fading. The fading properties of the individual peaks in the zircon luminescence wavelength spectrum are quite different. Some of the peaks fade rapidly, while other emission lines are stable at ambient temperatures. This observation is important, because it shows that the overall fading, which is the sum of all separate contributions, will be quite complex. It also suggests that measuring only the stable components of the luminescence spectrum offers an attractive solution to the problem of fading, which has been encountered by several scientists (see e.g. Clark and Templer, 1988).

Single grains were analyzed chemically by means of laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) to investigate the chemical heterogeneity of the population of zircon grains as a function of the color of the grains and sample locality. The overall elemental composition of the zircon samples was determined by ICP-MS analysis carried out with a totally dissolved representative fraction of the zircon concentrate.

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5.2 Characteristics of the zircon samples

A suite of seven detrital sand samples from a diversity of geographic localities (in the USA, the Netherlands and South Africa), depositional environments, age and mineral provenance terrains were selected for our investigations. The depositional age of the sediment samples used in this study varies from recent to hundreds of thousands of years, whereas the absolute ages of the zircon grains themselves range from approximately 200 million to more than 1 billion years.

For our dating efforts the age of the zircon crystal lattice (i.e., the age of crystallization) is of crucial importance, because during the full period of its existence the crystal is irradiated internally by α-particles due to the presence of the radioactive traces of the U and Th series. In addition, the crystal lattice is damaged by the recoiling heavy nuclei associated with the α-emission. Further, the 235U nucleus shows spontaneous fission, which gives rise to highly energetic fission products, leaving tracks in the minerals (fission tracks).

Both the recoiled heavy nuclei and the energetic fission products give rise to dense forms of radiation damage (track damage) in the immediate vicinity of the radioactive nuclei. This track damage appears to be highly resistant to thermal annealing. However, during our TL experiments the temperature reaches values of about 550°C, which is high enough to cause partial annealing of the above-mentioned hard damage. For more details about thermal annealing of track damage in zircon, we refer to the work in the mid 80’s by Amin et al (1983). These authors have shown clearly why “old damage” along the tracks of recoiled nuclei and fission products can have a strong and deteriorating effect on the dating quality of zircon.

After a TL experiment, which for zircon extends to temperatures as high as 550°C, the optical transmission properties improve significantly, which leads to an enhancement of the TL efficiency. Obviously, in principle this effect is very significant for zircons, which are usually extremely old, but fortunately nature provides us with reasonable amounts of transparent and colorless grains of high optical quality. We assume that during its long history from time to time the radiation-induced defects in zircon are healed as a result of e.g. re-crystallization, heating, exposure to sunlight or a combination of these conditions. From the point of view of the optical and the TL properties one could say that from time to time zircon is ‘rejuvenated’. This implies that efforts to select highly transparent grains is in fact the selection of just the younger, re-crystallized and possibly heated grains, which were -after rejuvenation- exposed in recent history to either sunlight (in case of sediments) or heat (pottery).
Table 5.1 Characteristics of the zircon sand samples

<table>
<thead>
<tr>
<th>Sample location</th>
<th>Provenance</th>
<th>Ages of zircons</th>
<th>Depositional Age</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ameland Island West Frisian Islands The Netherlands</td>
<td>Erz Mountain Region, Central Europe</td>
<td>225-275Ma(^{(1)})</td>
<td>Recent</td>
</tr>
<tr>
<td>Trail Ridge NE Florida USA</td>
<td>Piedmont province and Southern Appalachian Mountains, USA</td>
<td>300-600 Ma(^{(2)}) (Piedmont) 1.1 Ga(^{(2)}) (Appalachian)</td>
<td>Pliocene</td>
</tr>
<tr>
<td>Green Cove Spring NE Florida USA</td>
<td>Piedmont province and Southern Appalachian mountains, USA</td>
<td>300-600 Ma(^{(2)}) (Piedmont) 1.1 Ga(^{(2)}) (Appalachian)</td>
<td>Pliocene</td>
</tr>
<tr>
<td>Old Hickory deposit Virginia USA</td>
<td>Piedmont province and Appalachian (Blue Ridge) Mountains, USA.</td>
<td>300-600 Ma(^{(2)}) (Piedmont) 1.1 Ga(^{(2)}) (Appalachian)</td>
<td>Pleistocene</td>
</tr>
<tr>
<td>Namakwa Sands deposit West coast RSA</td>
<td>Namaqua Province and Gariep Belt</td>
<td>1090-1200 Ma(^{(3)}) 490-560 Ma(^{(3)})</td>
<td>Cenozoic</td>
</tr>
<tr>
<td>Iscor deposit East coast RSA</td>
<td>Namaqua-Natal Province and Karoo Supergroup</td>
<td>1090-1200 Ma(^{(3)}) 490-560 Ma(^{(3)})</td>
<td>Cenozoic</td>
</tr>
<tr>
<td>RBM deposit East coast RSA</td>
<td>Namaqua-Natal Province and Karoo Supergroup</td>
<td>1090-1200 Ma(^{(3)}) 490-560 Ma(^{(3)})</td>
<td>Cenozoic</td>
</tr>
</tbody>
</table>

(2) Donoghue, 1999.
(3) Rozendaal, 1999.
The geographic localities, mineral provenance terrains, depositional age and the age of the zircons, which were used in this investigation, are summarized in table 5.1. From table 5.1 we can see that the overall age of the zircon crystals in the Ameland samples is relatively young and therefore they are, in principle, the more suitable materials for optical dating. However, the age of crystallization of the zircon crystals in the sediments from Ameland is about 250 Ma (Andriessen, 1988; de Meijer and Donoghue, 1995), which is a factor of 2500 times the maximum age to be considered in TL dating experiments. It is probable that details of the behavior of the rock formation after the zircon crystal lattice was first created are relevant for the optical quality of the grains and the success of our dating efforts. Optically clear zircon is obtained only if during its history the relevant grains are bleached regularly and sufficiently by re-crystallization, heating or exposure to sunlight.

5.2.1 LA-ICP-MS

The concentrations of many trace elements in the zircon samples were determined by single-grain analyses using laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS). The results were based on measurements on 250 individual grains. The LA-ICP-MS analyses for single grains were carried out by the group of Prof. A. Rozendaal (University of Stellenbosch, RSA) with a Perkin-Elmer/Sciex 6000 ICP mass spectrometer in conjunction with a Cetac LSX-200 Nd-YAG laser (266 nm, frequency-quadrupled from 1064 nm) at the University of Stellenbosch, RSA. The laser beam, with a spot size of 25-40 μm, is directed onto the surface of a zircon grain. As a result a part of the surface of the zircon grain is evaporated. The atomized sample ions are then separated by their mass and analyzed.

Figure 5.1 shows the averages of the rare-earth element (REE; La, ..., Lu) concentrations in zircon from five geological locations. The values are normalized to the Chondrite standard (Evensen, 1978). Of significant interest in this figure are the consistent proportions of the heavy rare-earth elements (HREE, heavier than Eu) for all localities investigated. The absolute concentrations of the HREE vary slightly, but the interrelationships as a group are consistent. This applies to all samples, which have been investigated and is interpreted as a characteristic feature of zircon as such.

It is important to note that the principal zircon luminescence activators (Dy and Tb) are members of the HREE family, which show consistent proportions for all zircon sand samples investigated thus far. If this consistency of the HREE proportions is indeed an inherent characteristic property of all natural zircon sand samples, irrespective of their source (Hoskin and Ireland, 2000), it implies that zircons from localities around the world can potentially be used for TL dating.
Several previous investigators of the TL properties of zircon suggested that there is a strong anti-correlation between the distribution of the rare-earth elements (REE) and actinide impurities (Fremlin and Srirath, 1964; Sutton and Zimmerman, 1976; Templer and Walton, 1983; Templer and Walton, 1985; and Templer, 1985). Radioactive actinides are responsible for the internal irradiation (see chapter 3), while the rare earth impurities Dy$^{3+}$ and Tb$^{3+}$ act as luminescent centers. Anti-correlation between the distribution of the luminescent centers and the radioactive actinides would lead to the formation of radiation damage primarily in areas with reduced concentrations of rare earth elements. This reduction of luminescent ions leads to relatively low TL signals in the case of natural irradiation by actinides. Consequently, it was suggested that during antiquity most of the dose is deposited in the less TL sensitive zones (assuming the α-particles having a sufficiently small range). In contrast with this, the artificial dose, produced in the laboratory, is assumed to induce TL predominantly from regions of high luminescence sensitivity thereby producing an underestimation of the paleodose$^3$, resulting in an underestimation of the age. This would imply that the production of “natural” radiation

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$^3$ Paleodose is the dose that a sample has received during antiquity (chapter 2).
damage in zircons cannot be simulated by external sources. In those cases the only hope for reliable dating results is the application of the method of autoregeneration of TL.

![Figure 5.2](image_url)

**Figure 5.2. Relationship between heavy rare-earth element (HREE) and U+Th concentration for four sample locations.**

Figure 5.2 shows the relationship between the U+Th concentration and the heavy rare-earth element content for zircon from Ameland (NL), Namakwa sands (RSA), Trail Ridge deposit and Old Hickory deposit (USA). The diagrams show a positive and more or less linear relationship for zircons. Grains from the Namakwa Sand deposit (RSA) are particularly enriched in HREE and U+Th. Our results therefore show that there is grainwise a positive correlation between the distribution of the luminescence centers and radioactive trace elements. This means that high concentrations of HREE are found in individual zircon grains, which also contain high concentrations of U+Th. We found no evidence however that there is an anti-correlation between high luminescence regions and high radioactive content, as has been suggested. This is in agreement with our expectations based on chemistry considerations; taking into account (i) the similarity of the chemical properties of the HREE-ions and the above-mentioned actinides and (ii) the similarity of the ion sizes of these impurities, we do not expect anti-correlation effects either.

The LA-ICP-MS analyses show high concentrations of U+Th in zircon grains with high concentrations of HREE. Heavy rare-earth element ions play a central role in the processes leading to the thermally stimulated emission of light of irradiated zircon. An important feature of zircons, studied from various places around the world, is that the respective
HREE ions are always present in significant concentrations and at relatively constant ratios (see also e.g. Hoskin and Ireland, 2000).

5.2.2 ICP-MS

The overall elemental composition of the zircon samples was determined by ICP-MS analysis carried out with a dissolved representative fraction of the zircon concentrate. I.e. unlike the LA-ICP-MS experiments, which have been performed as described in section 5.2.1 on single grains, the ICP-MS experiments presented in this section have been carried out with zircon concentrates consisting of many grains. The ionized sample ions were separated according to the mass/charge ratio and then analyzed by their mass.

Figure 5.3. Chondrite-normalized average rare-earth elements distribution in zircons from seven sample locations. (The ICP-MS measurement was carried out by the group of A. Rozendaal from the Department of Geology, University of Stellenbosch, RSA)

Figure 5.3 shows the averages of the rare-earth element concentrations in zircon from Ameland, the Trail Ridge deposit, Green Cove Spring, the Old Hickory deposit, Namakwa Sands, RBM, and the Iscor deposit. The values are normalized to the Chondrite standard (Evenson, 1978). Figure 5.3 shows like figure 5.1 a consistent concentration profile of the HREE for all localities investigated. Unfortunately, due to technical problems the results for Tb have not been obtained, but it is clear from the results that both the LA-ICP-MS and the ICP-MS data show a consistent behavior for all HREE-ions investigated.

The ICP-MS analyses show a high concentration of total HREE in natural zircon for all sand samples investigated. The normalized concentration profiles of HREE are similar for zircons from various locations and their values exceed the Chondrite concentrations by two
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or three orders of magnitude. With regard to optical dating, our results appear to show that it is very likely that optical dating of zircons by means of the Tb\textsuperscript{3+}-emission is possible for the vast majority of the zircon-bearing sediments from around the world.

5.3 TL experiments

Initially, seven zircon samples from detrital sand deposits and fifteen zircon samples from crushed rock were selected for our detailed TL experiments and in addition the sand samples were studied for their fading behavior. The rock samples were separated and crushed to sand size. An overview of the characteristics of the sand samples, used for our experiments, has been given in table 5.1. The TL results of the crushed-rock samples are not discussed in this chapter because the TL properties of some of these zircon samples were mainly used almost exclusively for the EPR experiments, discussed in chapter 6. In figure 6.2 we show the TL output of two crushed-rock zircon samples.

The zircons were separated from the sediments as described in chapter 4 and have the following grain-sizes: Florida and Virginia (USA): grain-sizes < 250 μm; Ameland P18/19 (Netherlands): grain sizes < 125 μm; Namakwa sands deposit, Iscor deposit, and RBM deposit (Republic of South Africa): grain sizes 75–150 μm.

Prior to the TL experiment, the samples were irradiated using a \textsuperscript{137}Cs γ-ray-source, with a dose rate of approximately 2.5 Gy/min and a total dose of 10 kGy. Because we have used a high-energy γ-ray source to irradiate a sufficiently thin layer of zircon grains we can be sure that the production of radiation damage in the samples is homogeneous. (See chapter 3). Immediately after irradiation, and, in case of the sand samples, periodically thereafter, portions of the samples were measured for their TL response, using the OMA detection system at Solid State Physics laboratory, University of Groningen. To prevent (partial) resetting of the TL signal, all preparations in the laboratory were carried out in darkness or under subdued red-light conditions.

5.3.1 Experimental set up

5.3.1.1 The OMA set up

An Optical Multichannel Analyzer (OMA) is capable of providing information about the wavelength composition of the TL light as a function of the temperature (this type of experiment is referred to as 3D-TL). In case of zircon this is a useful feature, because it allows one to recognize easily whether or not we are dealing with the right type of grains. Zircons show a characteristic TL response, which can be readily distinguished from the TL signal of for example quartz. A further advantage of this method is that the TL signal originates from a large number of grains, implying that the result is an average over the variations arising from individual grains. The disadvantage of this method is that the sensitivity of the detector is relatively poor compared to the sensitivity of photo-multiplier systems. For this reason the OMA system is not the most useful instrument to detect the weak signals generated in real dating experiments. On the other hand one obtains valuable
information about the TL process if samples with sufficient amounts of radiation damage are studied.

The OMA TL set up consists of a Differential Scanning Calorimeter (DSC) oven, an optical spectrograph and a photodiode detector array connected to a personal computer (see figure 5.4). During 3D-TL experiments the samples were heated linearly with time in a computer controlled DSC oven. The DSC set-up provides a computer-controlled heating facility for a constant heating rate. With the DSC set-up it is also possible to anneal samples at a constant temperature. During the heating process, the TL light emitted by the sample in the DSC oven is focused by a quartz lens on the entrance slit of an optical spectrograph. Inside the spectrograph the light is reflected by a grating of 1200 grooves/mm and the light is diffracted into its wavelength components. The exit slit of the spectrograph is mounted directly onto a silicon photodiode array detector. The detector consists of 512 elements and it is connected with an optical multichannel analyzer (OMA).

Figure 5.4. Schematic representation of the OMA TL set-up.

The photodiode detector is controlled by the OMA system, which is also connected with the DSC set-up. During heating of the sample the photodiode array is scanned regularly by the OMA. A 3D-TL spectrum consists of 40 scans. Each scan represents a spectral distribution (between 237 nm and 786 nm) of the emitted light during a short time in a narrow and well-defined temperature interval, between 100°C and 550°C. With the OMA TL set up described above, wavelength dependent thermoluminescence (3D-TL) measurements have been carried out for all zircon samples used for this investigation.

5.3.1.2 Improvements: DCC camera

For samples showing a relatively low TL intensity, e.g. very young samples, the TL signal cannot be distinguished from the background signal because of the poor sensitivity of the OMA detector. To improve the detection limit of the TL system the OMA detector has been replaced in the second stage of this investigation by a cooled DCC camera (300/1340 pixels) with higher sensitivity. However, for TL dating measurements, the superior and highly sensitive Risø TL reader with a photo-multiplier detection system is used, because usually the TL signals are very weak.
5.3.1.3 Risø TL set-up

Glow curves (TL intensity vs. the temperature) have been measured with a computer-controlled Risø TL set-up consisting of a 24-sample glow oven/sample changer, contained in a vacuum chamber, a Sr-Y (90) β-source, and a photo-multiplier detector (see figure 5.5). With the TL reader it is, in principle, possible to measure sequences, which include irradiation of samples, preheat and TL measurements (For more information about the Risø TL Reader see: http://www.risoe.dk/).

The Risø set-up is far more sensitive than the OMA set-up and the DCC camera, because of the high sensitivity of the photo-multiplier. The disadvantage of this TL set-up is that no wavelength information of the TL signal can be obtained. To overcome this disadvantage, but still utilizing the high efficiency of the photomultiplier tube we have inserted narrow-band optical interference filters to select the stable (545 nm Tb\(^{3+}\)) line for detection by the TL reader. With this procedure we are sure that in real dating experiments the light from all other sources, which disturbs the dating results, is removed before it reaches the detection system.

5.3.2 TL spectra of selected zircon sand samples

The OMA detection system was used in all TL experiments described in this chapter. The TL output was measured over a temperature range, from 100 to 550°C, at a heating rate of 150°C/min. The mass of the samples was 20 mg or more. In this mass range, the TL output was found to be independent of the mass (Hantke, 1991). The 3D-TL spectra, for all sand samples analyzed in this chapter, exhibit similar features (figure 5.6). At temperatures higher than 150°C the spectrum exhibits a number of peaks, forming ridges at particular wavelengths. At temperatures lower than 150°C a broad swell and two narrow peaks are observed.

The 3D-TL spectra in figure 5.6 show the TL output shortly after laboratory irradiation with 10 kGy of γ-radiation from a \(^{137}\)Cs source. The Trail Ridge, Green Cove Spring and Old Hickory samples (figures 5.6a, b, c, respectively) exhibit good TL response immediately after irradiation. The 3D-TL spectra feature two narrow, high intensity peaks at
temperatures $<150^\circ$C and 6 narrow lines extending over a temperature range from 200$^\circ$C to 400$^\circ$C. In addition, the samples exhibit a broad band at about 400 nm (for $T < 150^\circ$C).
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The TL intensity of the Ameland P18/19 sample (figure 5.6d) is much lower than that of the three USA samples described above, although it is comparable with the TL signal of the Namakwa Sands, Iscor and RBM deposits (figures 5.6e, f, g, respectively). Nevertheless, see table 5.1 for a more detailed description of the samples than the ones from the Trail Ridge deposit.

Figure 5.6. 3D-TL spectra of various zircon sand samples from seven locations: a) Trail Ridge deposit (USA) b) Green Cove Spring (USA) c) Old Hickory deposit (USA) d) Ameland P18/19 Island (NL) e) Namakwa Sands deposit, (RSA) f) Iscor deposit (RSA) g) RBM deposit (RSA), after artificial γ-irradiation (dose 10 kGy for all samples investigated). Note that the intensity scale is in relative units and varies among samples. See table 5.1 for a more detailed description of the samples than the ones from the Trail Ridge deposit.
the two narrow peaks for T<150°C and the 6 narrow lines at higher temperatures can be distinguished clearly in all cases. The difference in intensity for the various samples might be related to the degree of coloring of the grains or possibly the optical quality of the surface of the grains. Furthermore, it has been observed that the intensity of the TL response of the samples decreases with increasing opacity of the zircon grains.

The enhanced TL properties of the Trail Ridge (USA) sample are attributed to the high purity of the sample. Electrostatic separation has been used as a final stage, to produce a highly transparent zircon concentrate with few colored grains. This is in contrast with many of the other samples, such as the Ameland P18/19 (NL) sample, which has a much darker appearance. The Ameland P18/19 sample, used in the investigations presented in this chapter, has not been separated electrostatically. As a consequence it contains significant numbers of colored and dark grains, which might affect the TL properties of the sample.

5.3.2.1 Analysis of the spectra

To analyze the nature of the peaks, we have divided the results in three temperature ranges: the low (100-175°C), intermediate (200-300°C) and high temperature range (300-400°C). The low temperature results show two dominant narrow peaks and a broad band. For all samples the results in the high temperature range show six narrow peaks.

The TL spectra for the three temperature intervals (low, intermediate and high) were averaged and plotted as a function of the wavelength. Figure 5.7 shows as an example the averaged TL intensities for a sample from the Trail Ridge (Florida, USA) deposit. Together with the two inserts from Iacconi and Caruba (1980), we can see that our spectra compare well with those for synthetic zircon doped intentionally with Dy$^{3+}$ and Tb$^{3+}$.

From the comparison with the inserts in figure 5.7 the two narrow luminescence peaks at 480 nm and 580 nm observed at low temperatures can be assigned to Dy$^{3+}$ ions. The broad and weak emission peak at 365 nm in the insert of figure 5.7, for synthetic zircon doped with Dy$^{3+}$, is not observed in the natural sand samples. In our samples, the doublet associated with Dy$^{3+}$ (at 480 and 580 nm) and the broad band at about 400 nm are the main emission bands at low temperatures. At high temperatures the Tb$^{3+}$ lines (377, 419, 485, 545, 585, and 621 nm) dominate the emission spectrum.

With increasing temperature, the Dy$^{3+}$ peaks disappear as a result of annealing and the spectrum shows overwhelmingly the six-lines Tb$^{3+}$ signal (see also Iacconi and Caruba, 1980). It is important to emphasize that, for all sand samples used in this investigation, the 3D-TL spectra show the same Dy$^{3+}$ peaks at low temperatures and Tb$^{3+}$ peaks at high temperatures (Jain, 1978, Huntley et al, 1988). We therefore conclude that TL of terbium and dysprosium impurities in zircon is common for zircon sand deposits around the world and when a useful TL dating technique can be developed for either of these two groups of TL peaks, it is likely that the technique can be generally applied to zircons.
5.3.2.2 Fading

Anomalous fading has been one of the most serious obstacles of the development of zircon luminescence dating (Wintle, 1973; Sutton and Zimmerman, 1976; Templer, 1985; Durrani and Amin, 1985). Even at room temperature, the trapped electrons have a small but non-zero probability to escape from the meta-stable traps and to recombine with holes, which leads to quenching of the TL-output. Electrons in shallow traps have a short lifetime. The lifetime of the trapped electron increases exponentially with the trap-depth (see chapter 7). For deep traps the life-time can be as long as millions of years. In some cases after exposure to laboratory irradiation the number of electrons escaping from deep traps seems to be significantly larger than expected from thermal excitation. This phenomenon is called anomalous fading. The aim of this investigation was to develop a protocol to eliminate the contributions of the defects producing short-term fading, which has previously been

Figure 5.7. Averaged low (100-175°C, left) and high (300-400°C, right) temperature emission spectra of zircons from Trail Ridge (Florida, USA) after 1 week of storage following 10 kGy irradiation. The inserts represent the emission spectra (in arbitrary units) due to Dy$^{3+}$ (left) and Tb$^{3+}$ (right) in doped synthetic zircon published by Iacconi and Caruba (1980).
observed for laboratory-irradiated materials (and are absent in long-term naturally irradiated samples). This allows us to establish what the stable component of the TL signal is. This component should be the same as the TL signal acquired by “natural” irradiation.

To study the long-term fading behavior of zircon, we have measured the TL signal of subsamples of a large irradiated batch of zircon from the Trail Ridge deposit, Green Cove Spring, and the Old Hickory deposit. The samples were stored as long as two years in the dark at room temperature after irradiation. Samples were taken periodically from storage in darkness and measured for TL, starting at one week after laboratory irradiation. Inter-sample comparison and reproducibility of the measurements was checked for all samples. At best there is a delay of 1-2 hours between the end of the exposure to laboratory

Figure 5.8. 3D-TL spectra of a sample from the Old Hickory deposit (Virginia, USA) after 1 week, 20 weeks, and 2 years storage following 10kGy of γ-irradiation.
irradiation source and the TL measurement. Immediately after irradiation the TL intensity decays rather rapidly and the accuracy of the TL measurements carried out a few hours after irradiation is rather poor and insufficient for our purpose.

During storage in darkness at room temperature the Dy signal (see figure 5.7) is found to decrease rapidly in intensity due to fading. After 16 weeks storage, the Dy peaks almost disappeared. This indicates that shallow and unstable traps produce the Dy-dominated signal during recombination. Another part of the spectrum, observed at high temperatures, which is dominated by the Tb luminescence however, does not show this extensive fading behavior. After 16 weeks storage at room temperature, the TL emission primarily exhibits the Tb-dominated spectrum. As an example we show figure 5.8, which displays the fading results for a sample from the Old Hickory Deposit after 1 week, 20 weeks, and 2 years storage.

![Figure 5.9](image)

**Figure 5.9.** Averaged high-temperature emission spectrum of zircon from the Trail Ridge deposit (Florida, USA) after 1 week (a) and 2 years (b) storage following 10 kGy γ irradiation.

Prolonged and extensive fading experiments have been carried out for zircon sand samples from the Trail Ridge deposit (Florida), Green Cove Spring (Florida) and the Old Hickory deposit (Virginia). In figure 5.9 the averaged high-temperature TL spectra of zircon from Trail Ridge after 1 week and after 2 years fading are presented. The spectra show almost exclusively the luminescence peaks associated with Tb$^{3+}$. To study the long-term fading behavior of the Tb-signal in more detail, the 545 nm Tb line was analyzed and the integrated peak area of this line was plotted as a function of the storage time. The results for zircon sand samples from Trail Ridge have been plotted in figure 5.10. After approximately 16 weeks of storage the signal is stable and shows no further fading. Similar results have been obtained for the samples from the Green Cove Spring and Old Hickory Deposits.
In dating experiments we want to use the 545 nm Tb$^{3+}$ line because of its favorable fading properties (see figure 5.10). One should avoid simultaneous detection of Tb and Dy-light. One of the Dy-lines (i.e. the 480 nm) almost coincides with a reasonably strong Tb line (i.e. the 488 line). Fortunately, the dominant Tb-line at 545 nm (548 nm at high temperatures) shows a negligible overlap with the 580 nm peak of Dy. Therefore this most intense and stable segment of the Tb-dominated region of the TL spectrum, the 545 nm Tb line, was selected by peakfitting to study the zircon fading behavior. The averaged TL spectra in the high temperature range after 1 week and 2 years fading have been plotted in figure 5.9. It is clear that after 2 years storage in the dark, there has been a moderate decrease due to fading in TL intensity as compared to 1 week storage.

![Figure 5.10. Fading behavior of the Tb$^{3+}$ 545 nm line for the Trail Ridge (USA) zircons, following 10 kGy of $\gamma$-irradiation.](image)

In the literature it is suggested that it is not possible to exclude the fading part of the TL spectra by means of filters (Templer, 1985). Our results show clearly that the long-term fading problem is solved by selecting the stable part of the luminescence spectrum (the 545 nm Tb$^{3+}$ line) by confining the TL detection to a very narrow wavelength interval around 545 nm.

The effects of short-term fading can be diminished by a pre-heat between 100 and 150°C. (See chapter 8). During this treatment the contribution from unstable defects is removed, while the radiation-induced electrons and holes redistribute over the most stable traps (see
The resulting TL signal, which consists predominantly of contributions from the most stable defects, is suitable for dating.

### 5.4 Summary and conclusions

An extensive study has been carried out for zircon sand samples from various locations around the world. Our bulk sample analysis (with ICP-MS) of zircon concentrates reveals that the concentration profile of the heavy rare earth elements (HREE) is similar for all sand samples, which have been studied in this investigation. In addition, we have found that the concentrations of the HREE exceed the chondrite concentrations by two to three orders of magnitude.

The LA-ICP-MS analyses of single grains from several geological locations around the world confirm the results of the ICP-MS experiments of bulk zircon samples. An important result for the development of a zircon TL dating method is that we have shown by means of single grain LA-ICP-MS experiments that a positive correlation exists between the concentrations of U and Th and the concentrations of the HREE. This contradicts earlier speculations (Fremlin and Srirath 1964, Sutton and Zimmerman 1976, Templer and Walton 1983, Templer and Walton 1985 and Templer 1985) that due to inhomogeneous distribution of the irradiation sources (U and Th) and the luminescence activators α-induced radiation damage is not created in the close vicinity of luminescence centers. This type of anti-correlation of the concentrations of radiation sources and luminescence centers would suppress TL. We have found no evidence for such suppression.

An important property of natural zircon is that heavy rare-earth ions are always present in zircon sand samples as trace impurities. Our analyses of the wavelength spectra of natural zircons as a function of the temperature and a comparison with the TL spectra observed for intentionally doped synthetic zircons have revealed that Tb and Dy ions are the most relevant members of this group of impurities, because they are responsible for the dominant part of the TL output after exposure of zircon to ionizing radiation.

A comparison of the TL spectra of natural zircon sand samples immediately after exposure to ionizing radiation in the laboratory and samples, which were stored for a very long period of time in darkness, revealed that the TL signal associated with Dy is unstable and fades within a few weeks. On the other hand, the TL due to Tb shows limited fading even after storage up to two years. This implies that the signal associated with Tb is suitable for TL dating.

The TL signal of Tb consists of narrow lines, and this turns out to be an important feature for dating experiments, because it allows us to reduce eventual unwanted and disturbing contributions to the TL glow curve from defects different from Tb, e.g. shallow hole traps such as Dy. To achieve this, we have to use the highly sensitive photomultiplier detection system of our Risø reader combined with a narrow band interference filter to detect only the 545 nm band of the TL spectrum of Tb (see chapter 8).
In summary it can be stated that the results presented in this chapter show that natural zircon sand, in which we have always found sufficient amounts of Tb, has the ideal properties to serve as a medium for TL-dating.

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