# On the way to a quantification of radiation damage in accessory minerals using $REE^{3+}$ photoluminescence spectroscopy

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The long-term impact of natural radioactivity may cause severe structural damage in minerals. Self-irradiation-induced structural damage is created mainly in alpha-decay events in the $^{232}$Th, $^{235}$U, and $^{238}$U decay chains, by the nuclear interaction (atomic "knock-ons") of recoiled heavy daughter nuclei (e.g., Weber et al. 1990). Many accessory minerals incorporate variable amounts of actinides, whose radioactive decay creates structural disorder, in their crystal structure. The generally increased susceptibility of radiation-damaged minerals to chemical alteration or aqueous leaching is of enormous importance, as these processes may for instance bias results of chemical and isotopic age determinations (e.g., Kuiper 2005; Zamyatin et al. 2017).

The investigation of gradually radiation damaged and metamict minerals, and their synthetic analogues, has increased appreciably over the past two decades, stimulated by the potential use of mineral-like ceramics as waste forms for the immobilisation of reprocessed spent nuclear fuel and other radioactive waste (e.g., Lumpkin 2016). Information obtained from studies on radiation-damage-assisted alteration in accessory minerals has important implications for the validation of the long-term performance of analogue nuclear waste forms for the disposal in geological repositories, as radiation damage affects negatively the ability of solids to immobilise radionuclides. In both research fields, however, a fast and inexpensive technique that operates on the micrometre-scale and provides direct quantitative information on the structural disorder, may open up new opportunities in the characterisation of radiation damage.

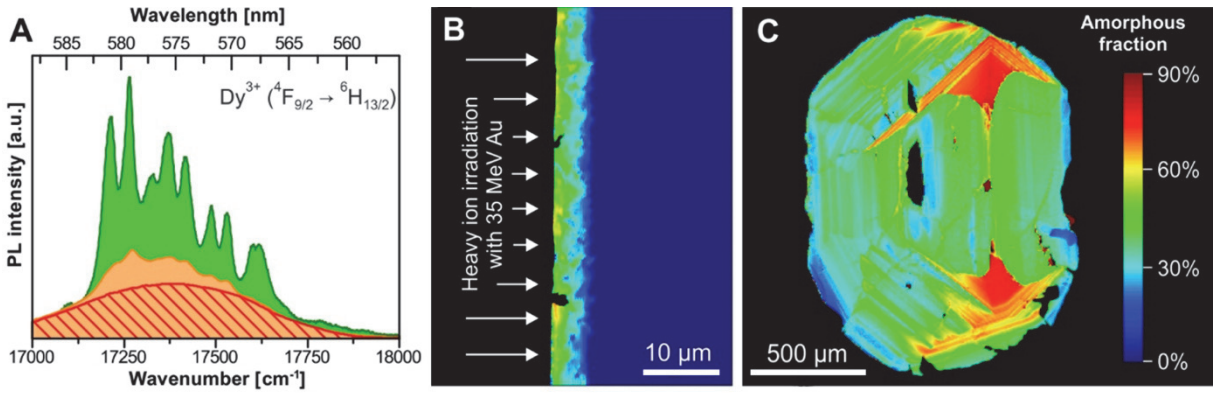


***Fig. 1.*** *Use of PL spectra of $Dy^{3+}$ to quantify radiation damage in zircon. (**A**) PL spectra of mildly (green) and strongly (ochre) radiation damaged zircon, normalized to an "amorphous" model spectrum (red). The integrated area of the amorphous model in relation to that of the observed spectrum may be used as an estimate for the amorphous fraction (e.g., 75% for the ochre and 40% for the green spectrum). (**B**) Colour-coded, hyperspectral PL map of a cross-section of an Au-irradiated $ZrSiO_4$ ceramic pellet. (**C**) Colour-coded, hyperspectral PL map of a zircon single-crystal from Plešovice, Czech Republic (Sláma et al. 2008). High concentrations of U and Th result in high damage accumulation over geological periods of time*

Recently, confocal photoluminescence (PL) spectroscopy of rare-earth elements ($REE^{3+}$) incorporated in natural zircon crystals, has been used as structural probe for the characterisation of radiation damage due to the self-irradiation by decay of trace U and Th (Lenz and Nasdala 2015). Similar to results from Raman spectroscopy (Nasdala et al. 1995), the width of PL emission lines has been used as a measure of radiation damage accumulated. One major challenge for using linewidths of PL signals for a quantitative measure of radiation effects, is its calibration using reference samples of known amorphous fraction or α-dose. Attempted calibrations based on the study of naturally radiation-damaged minerals, however, are often biased. This is because of insufficient knowledge of their thermal and, hence, annealing history (Nasdala et al. 2001).

Here, we present a new concept based on the luminescence emission of $REE^{3+}$, which aims at the direct determination of the amorphous fraction from a single PL measurement using state-of-the-art confocal spectrometers with spatial resolution in the µm-range. Careful investigation of PL spectra from self-irradiated zircon samples from Sri Lanka as well as artificially irradiated single crystals and analogous polycrystalline ceramics (heavy-ion Au irradiation with energies up to 35 MeV) revealed that the detected luminescence emission of e.g., $Dy^{3+}$ in zircon is basically a superposition of emissions from Dy ions in various, structurally different sites. The latter comprise ions in fully ordered crystallographic environment and/or sites from stressed, but still crystalline remnants and from completely altered sites within the amorphous fraction. We found that the relative integrated area of a fitted model spectra from an amorphous reference sample in relation to the full integrated area of the luminescence emission obtained gives a good estimate of the amorphous fraction present in the probed sample volume (Fig. 1a). The application of the latter approach for the interpretation of point-by-point hyperspectral maps opens up the possibility to investigate the accumulation of radiation damage in natural zircon single crystals (Fig. 1b) in very detail and give rise to direct comparison with damage accumulation in heavy ion irradiation experiments (Fig. 1c). In addition to the emission of $Dy^{3+}$ in zircon, we succesfully tested this concept for further accessory mineral-type phases, such as for $Nd^{3+}$ in xenotime ($YPO_4$) and zirconolite ($CaZrTi_2O_7$).

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