Invited keynote lecture:

Luminescence from high-energy irradiation of minerals – The brilliance of making and shaking defects

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The luminescence during high-energy irradiation (here X-rays or accelerated particles) is an analytical method that provides insights into the nature of defect structures in minerals. It has a number of benefits over traditional luminescence techniques. First the energy absorbed is capable of promoting electrons to energies beyond the conduction band in addition to lower energy excitation from inelastic scattering interactions that do not rely on resonant absorption, therefore probing the luminescence of the sample in a more fundamental way. It often excites (“shakes”) defects not observed in PL, providing a broader census of centre types (Friis et al. 2011). Orientation experiments can be successfully performed under such conditions to explore the anisotropy of responses (e.g. Finch et al. 2003). Second, high-energy irradiation penetrates the samples typically to microns in ways that can be modelled – these providing bulk rather than surface responses that can be atypical (Brooks et al. 2002). Third, irradiation often modifies the sample in real time in ways that can be anticipated or even numerically modelled (“making defects”). Irradiation can create new defect types it can also destroy or modify existing defects, which influences the luminescence spectrum that can be quantified as a function of dose and/or dose rate. This represents an important and insightful method to attribute confidently luminescence emissions in minerals with particular defect structures.

We review luminescence during ion implantation (Ion beam luminescence, IBL or Ionoluminescence IL) and synchrotron X-irradiation (X-ray excited optical luminescence, XEOL). Because synchrotron X-rays are pulsed with a ps pulse width and frequencies in ns analysis of the luminescence as a function of time allows time-resolved (TR–) XEOL.

Ion implantation

Ion beam luminescence can be carried out with a variety of ion and charged molecular species and here we review the results of ion implantation experiments on quartz and zircon samples. With quartz we explored the growth and destruction of luminescence as a function of dose and dose rate (King et al. 2011a). By comparing the numbers of photons emitted to the numbers of charge carriers and the dose deposited, we derive numerical models for the mechanisms by which the sample modification takes place, which we compare with hypotheses for the nature of the luminescence centres. Such experiments provide a remarkably consistent set of results showing that UV luminescence centres are depleted at effectively the same rate that red-IR ones are created. Using such criteria, we attribute the luminescence centres in quartz (see below) in a manner that explains the changes occurring during irradiation.

$$\underset{3.3\text{eV}}{[\mathrm{AlO_4/M^+}]^\circ} >> \underset{3.6\text{ eV}}{[\mathrm{AlO_4}]^\circ} + \mathrm{M^+}_{\text{(free)}} >> [\mathrm{AlO_4}]^\circ + \underset{1.9\text{ eV}}{\mathrm{NBOHC}_{\text{(free)}}}$$

Ion beam luminescence can be performed by comparing and contrasting different ion species. Analysis of irradiation of zircon develops a broad band ~600 nm in zircon when the sample is irradiated with heavy ions and we attribute this to atomic displacements caused by the momentum of the incoming ions (Finch et al. 2004). We conclude the same features in luminescence from natural zircons are formed by similar damage from natural U-series radiation.

XEOL and TR–XEOL

We present experimental results of XEOL collected on the i18 beamline of DIAMOND the UK's synchrotron facility. On the microfocus beamline, the X-ray beam used can be both focused and tuned, which allows element sensitive analysis with a high degree of spatial resolution with an excitation energy range of between 2–20 keV (Taylor et al. 2013).

As with IBL, XEOL causes sample modification and dose and dose rate can be modelled (King et al. 2011b). However, with XEOL the X-ray energy can be scanned across the core electron absorption edge of particular elements in the sample. Fine structure on such spectra, if observed, provides local coordination information of that element (X-ray Absorption Fine Structure, XAFS) (Mosselmanns et al. 2013; Sapelkin et al., submitted). In addition, since the X-rays are pulsed, we have developed TR–XEOL facilities with a time resolution capability in 10's ps – 100's ns (Mosselmanns et al. 2013). Using this system we observe that many minerals exhibit ultrafast emissions with lifetimes in ps. Natural luminescent lifetimes of allowed transitions are ns and hence these ultrafast lifetimes arise as a consequence of quenching or a competitive energy transfer mechanism. This mechanism of competitive relaxation gives unique insights into the clustering of defects centres (Taylor 2013).

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References:

Brooks RM, Finch AA, Hole D, Townsend PD, Wu Z (2002) The red to near-infrared luminescence in alkali feldspar. Contrib Mineral Petr 143:484–494

Finch AA, Hole DE, Townsend PD (2003) Orientation dependence of luminescence in plagioclase. Phys Chem Miner 30: 373–381

Finch AA, Hole D, Townsend PD, Garcia-Guinea J, Hanchar JM (2004) Ionoluminescence of zircon: Rare earth emissions and radiation damage. J Phys D Appl Phys 37:2795–2803

Friis H, Finch AA, Williams CT (2011) Multiple luminescent spectroscopic methods applied to the two related minerals, leucophanite and meliphanite. Phys Chem Miner 38:45–57

King GE, Finch AA, Robinson RAJ, Hole DE (2011a) The problem of dating quartz 1: spectroscopic ionoluminescence of dose dependence. Radiat Meas 46:1–9

King GE, Finch AA, Robinson RAJ, Taylor RP, Mosselmans JFW (2011b) The problem of dating quartz 2: Synchrotron generated X-ray excited optical luminescence (XEOL) from quartz. Radiat Meas 46:1082–1089

Mosselmans JFW, Taylor RP, Quinn PD, Finch AA, Cibin G, Gianolio D, Sapelkin AV (2013). A time resolved microfocus XEOL facility at the Diamond Light Source. J Phys Conf Ser 425:182009

Sapelkin AV, Bolmatov D, Little W, Karatutlu A, Trachenko K, Dent AFM, Cibin G, & Taylor RP (submitted) Origin of photoluminescence in Ge quantum dots. Nat Nanotechnol (in review)

Taylor RP (2013) The development of X-ray excited optical luminescence (XEOL) spectroscopic techniques for mineralogical and petrological applications. Unpublished PhD thesis, University of St Andrews, UK

Taylor RP, Finch AA, Mosselmans JFW & Quinn PD (2013) The development of a XEOL and TR XEOL detection system for the I18 microfocus beamline Diamond light source. J Luminesc 134:49–58