Dating and dosimetry using thermally- and optically- stimulated luminescence from minerals

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Luminescence-dosimetric processes in natural mineral crystals and the evaluation of dose-rates from naturally occurring radioactive materials will be briefly reviewed.

Case studies in dating and dose-monitoring of geological and cultural heritage materials will focus on spatial variability in dose rate and the luminescence behaviour of 'quartz'.

Luminescence Background

Non-thermal photon emission, *c.f*. incandescence

Ubiquitous phenomenon

Chemiluminescence observed since antiquity as bioluminescence

Minerals: phosphorescence following light exposure observed first

Thermally stimulated luminescence (thermoluminescence: TSL or TL)
Coined late C19 but probably first described scientifically by Robert Boyle in 1664

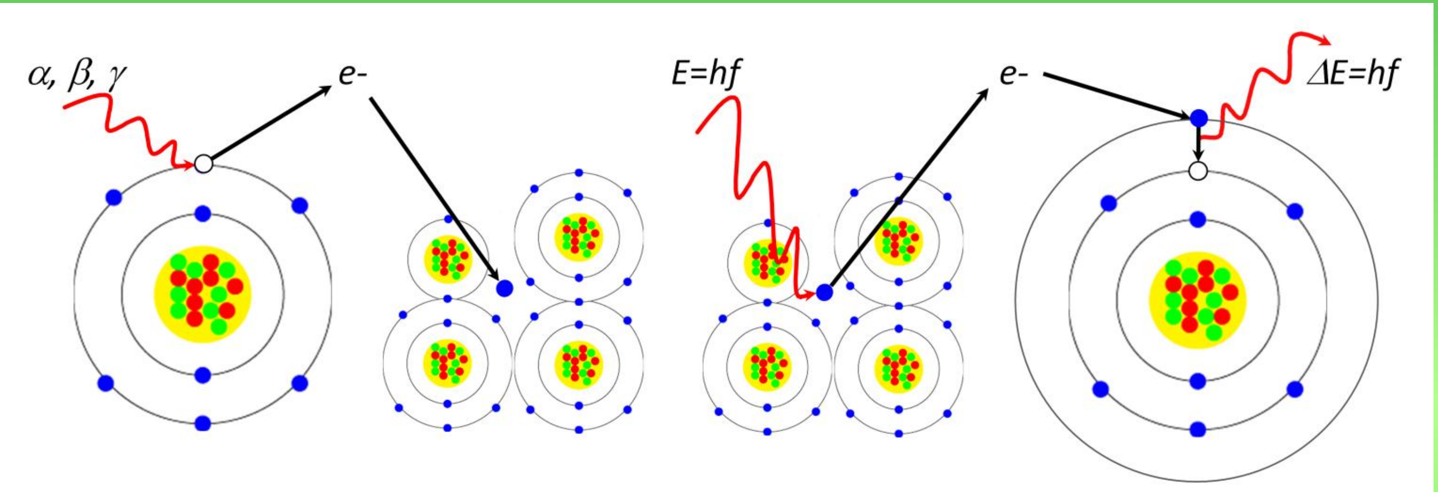
Emission of light from a diamond warmed against his skin, i.e., not incandescence

Heating is a secondary physical process in the production of the TSL signal

Ionizing radiation and its effects not understood at the time

Newton Harvey, E., 1957. Memoirs of the American Philosophical Society, V 44

Thermally- and Optically- Stimulated Luminescence Processes



Primary Irradiation: Ionisation	Migration and Trapping	Secondary Irradiation (Stimulation)	Recombination, Deexcitation, Emission:
-electron -hole	-defects -impurities -vacancies -interstitials	Heat (phonon) - thermodynamic Light (photon) - electromagnetic	- thermally stimulated luminescence - optically stimulated luminescence

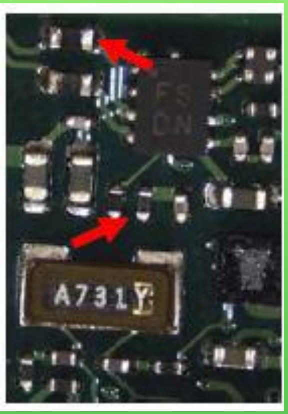
Adapted from Prudêncio et al. 2009, Pedra & Cal 42, 10-12

Materials for Luminescence Dosimetry

Anything containing inorganic crystals or micro-crystalline inclusions may be attempted *(wide bandgap)*.

- Quartz and feldspars most common natural minerals
- Fluorides, sulphates, alumina, etc. as manufactured TLDs

- Zircon, glasses, quartzite, calcite, electronic components etc, etc … but their characteristics are often more complex
- Other oxides, iodides, etc. as scintillators



In all cases it is their defects that permit luminescence dosimetry

Types of Luminescence Induced by Radiation

Prefix	**Irradiation**		**Detection**
-Luminescence	Type	Energy	Energy[a]
Primary Irradiation			
Photo-	Photon beam/radiation	Theory: any including ionising. Practice: generally MidIR-UV: 10^{-2} - 10^{2} eV	Mainly Stokes
Cathodo-	Low energy accelerated electron	10^{0} - 10^{3} eV	Any
Radio-	Ionising radiation: X; γ; β/high energy accelerated electron; α	10^{3} - 10^{7} eV	Any
Iono-	Ion beam: accelerated ion ranging in mass from proton to heavy charged particle	10^{3} - 10^{7} eV	Any
Secondary Irradiation			
Thermo- / Thermally Stimulated-	Thermodynamic eviction of charge from traps filled during primary irradiation	Limits defined by coolant and incandescence: 77-1000 K = 10^{-3} - 10^{-1} eV	Any
Photon / Optically Stimulated-	Electromagnetic eviction of charge from traps filled during primary irradiation	Theory: any including ionising. Practice: generally NIR-UV: 10^{-1} - 10^{2} eV	Use Anti-Stokes
a. Generally MidIR-UV: 10^{-2} - 10^{2} eV			

Burbidge, 2012. Spectroscopy Letters 45, 118–126

Luminescence Signals and Timing

Signal		Photon Emission				
	Process	Precursor Process	Time-scale	Energy Distribution	Energy Region	Temperature Dependence
Fluorescence	Absorption of energy and promotion of electrons in atoms/molecules to excited states	De-exitation	$\sim10^{-12} - 10^{-8}$ s	Permitted electronic transitions for de-excitation of centre	Less than precursor energy (Stokes), unless molecule / atom already excited	- Energy distribution (line broadening) - Intensity (quenching)
		Delayed de-exitation (quantum state change)	$\sim10^{-12} - 10^{-3}$ s			
Phosphorescence	Absorption of energy and excitation of electrons of atoms/molecules to a dissociated state (ionization)	De-exitation following trapping and / or recombination	$\sim10^{-12}$ s $- \infty$		As above, or unrelated to precursor energy if recombination occurs in a centre other than the donor	- Decay rate (detrapping) - Energy distribution (line broadening) - Intensity (decay rate/ quenching/ assistance)

Thermally- and optically- stimulated luminescence are forms of recombination phosphorescence where the signals emerge so slowly that they require secondary irradiation (stimulation) to be produced at detectable rates

Adapted from Burbidge, 2012. Spectroscopy Letters 45, 118–126

Representations of Charge Trapping and Transfer

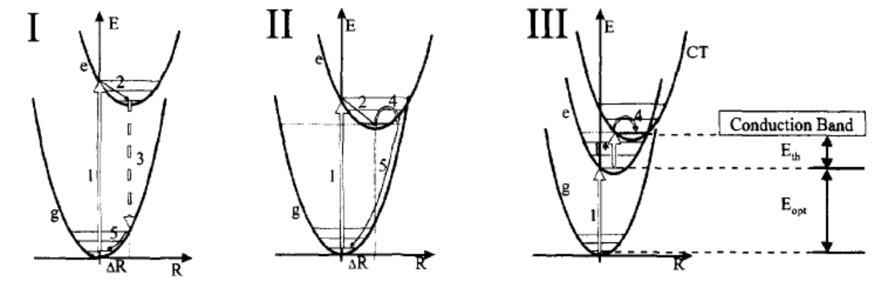
Configurational coordinate diagram
- Energy and Spatial
- Trap/Centre
- Excitation and recombination
- ... Emission energies ...

Spatial probability distribution
- Migration and Trapping
- Lattice
- Mobility of charges/ions/defects

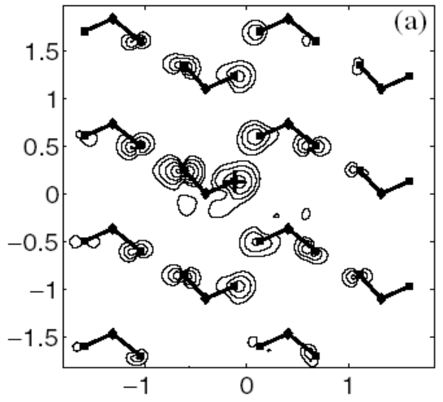
Energy level diagram
- System of Traps/Centres
- All steps but just E

- Response to dose
- Response to activated predose

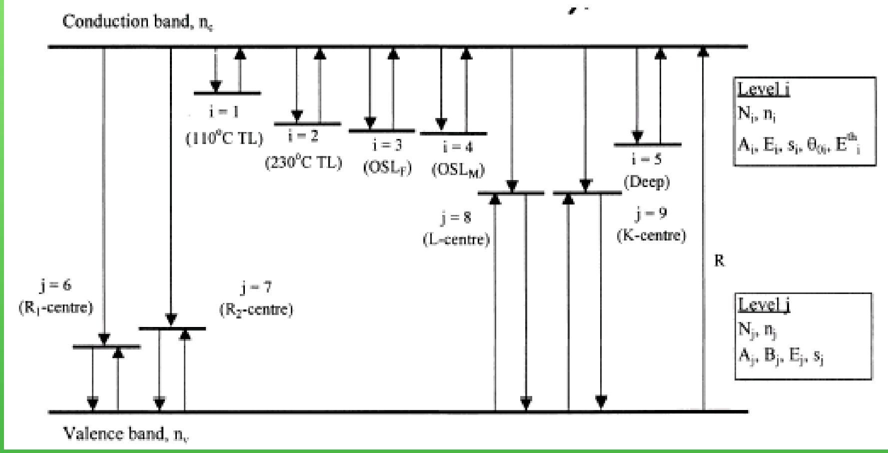
Trapping energetically unstable
- "Metastable", "Thermal lifetime"
- **fundamental limit on dating**



Krbetschek et al., 1997. Radiat. Meas. 27, 695-748.

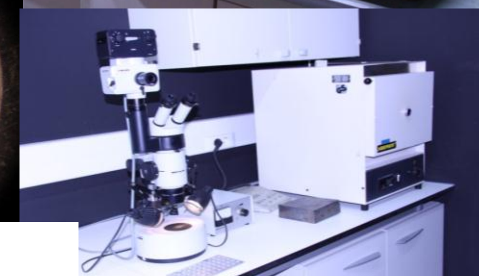


Bailey, 2001. Radiat. Meas. 33, 17-45.



Luminescence Dosimetry – Experimental Setup



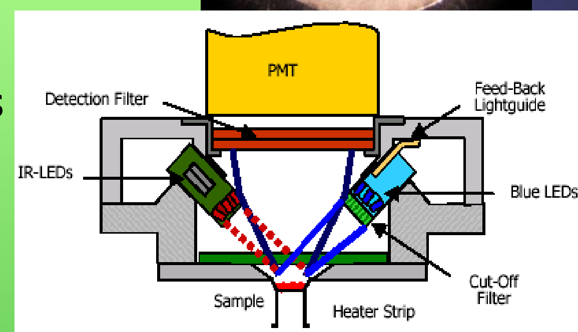


Sample

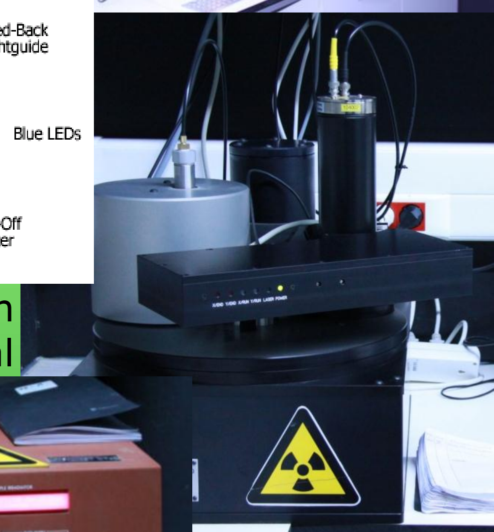
- Defined mineral and grain -size fraction prepared
- Light sensitive signals, so dark-room conditions
- Presented on 1 cm steel disk in monolayer

Measurement Chamber

- Heater plate
- PMT directly above
- Incident LED/Laser sources
- Detection (and stimulation) filters



Detector Configuration
Risø Manual




Calibration Source(s)

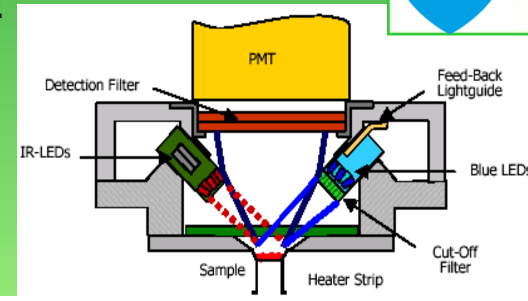
- Sealed radioactive source
- Beta ^{90}Sr/^{90}Y plaque
- Alpha ^{241}Am foil
- (or X-ray tube)
- (or external gamma)
- Simplest if energy response of mineral grains is equivalent to the exposure to be evaluated

Thermally- and Optically- Stimulated Emissions

Wavelength

Various bands identified: most by TL
Similar for OSL (conduction band)

Detector
Configuration
Risø Manual

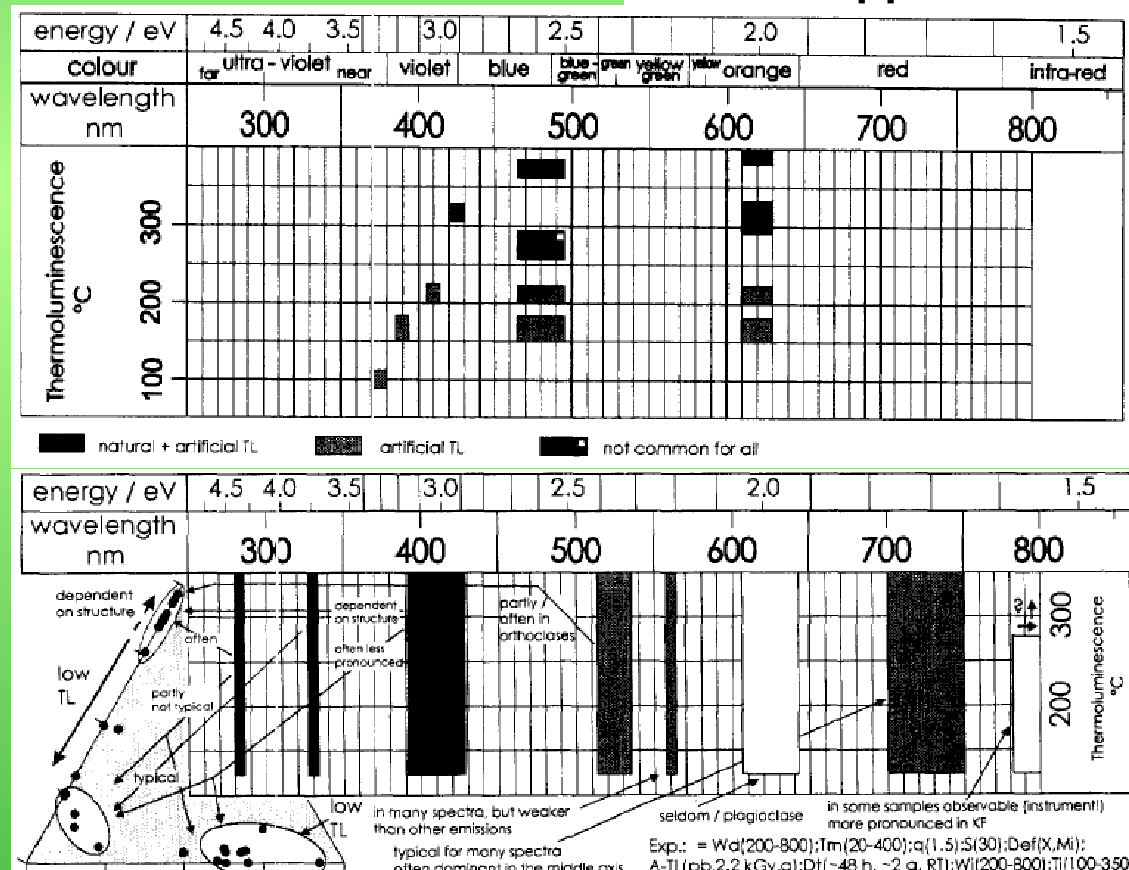


Bands in range
350 – 450 nm
most common
for dating
- TL: incandescence
- OSL: scattered light

Emission - Centre

Some more or less well known: e.g. Quartz "380" nm: AlO_4/M^+

Details hazy
Most have various proposals



Main emission bands of quartzes and feldspars
Krbetschek, M.R., Gotze, J., Dietrich, A., Trautmann, T., 1997. Radiat. Meas. 27, 695-748.

Thermally- and Optically- Stimulated Signals - Examples

- TSL: Different Rates, Stepped, Isothermal*
- OSL: Continuous, Ramped, Pulsed
- Preheating

Many techniques and as much jargon ...
*i.e. phosphorescence

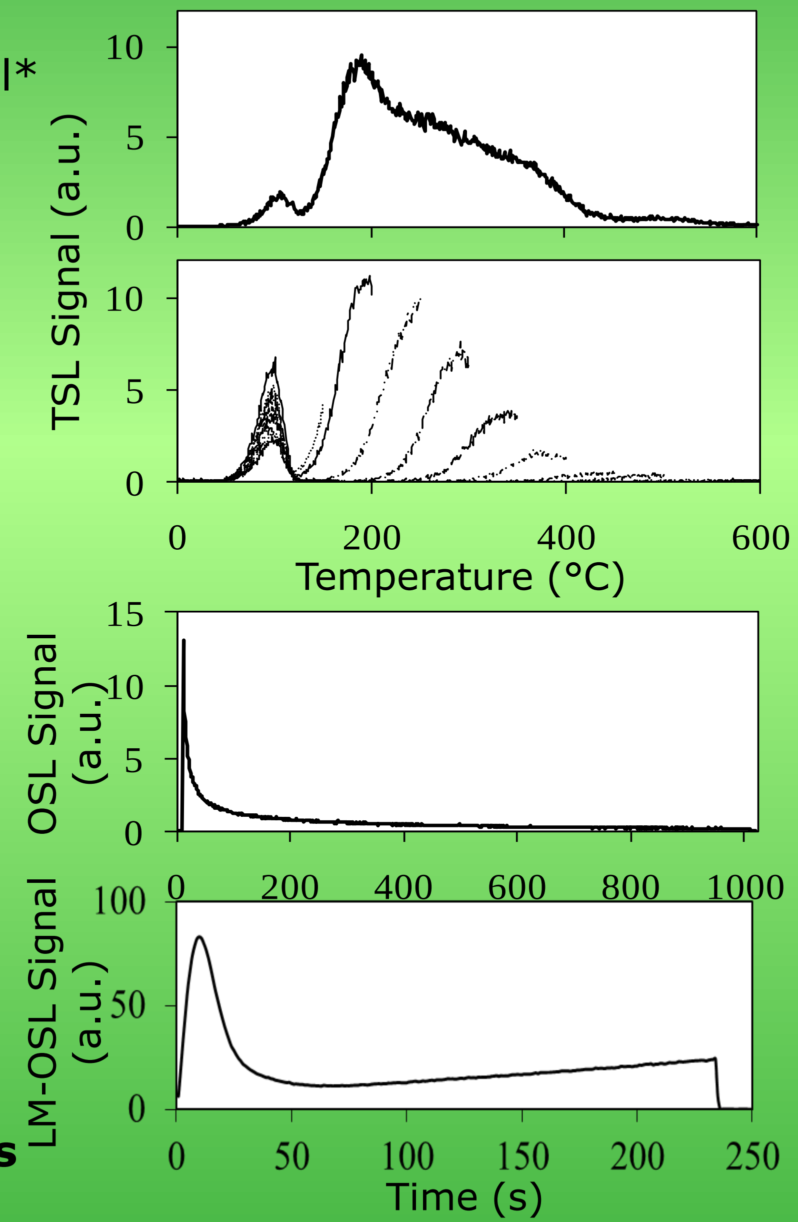
Some variants of interest:

Predose TSL: response to small test-dose, as a function of previous irradiation and annealing

LM-OSL: Ramped or "linearly modulated"

TT-OSL: "Thermally transferred", by measuring the normal OSL, then remeasuring after a higher preheat

- **All are transient signals**
-**Different trap types**
= different rates/temperatures



Dose Response and Evaluation of Absorbed Dose

1st order kinetics = exponential
(*i.e*. temperature dependence well described by the Arrenhius equation)

Thus, basic saturating exponential dose response:

$$I = I_0 + I_\infty (1 - e^{-D/\bar{D}})$$

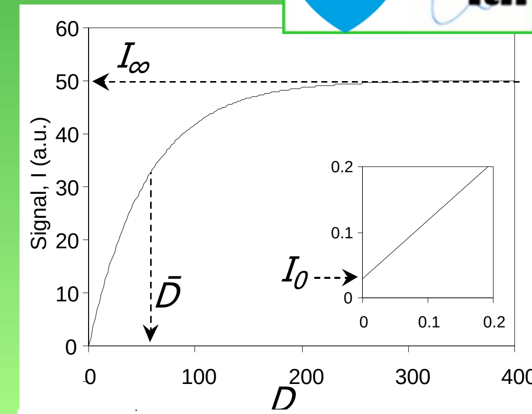
D in Gy (J/kg)

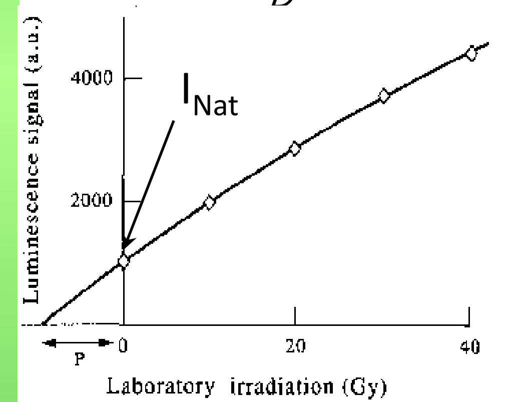
$\bar{D}$ "mean dose-life of signal saturation"
= inverse of rate constant

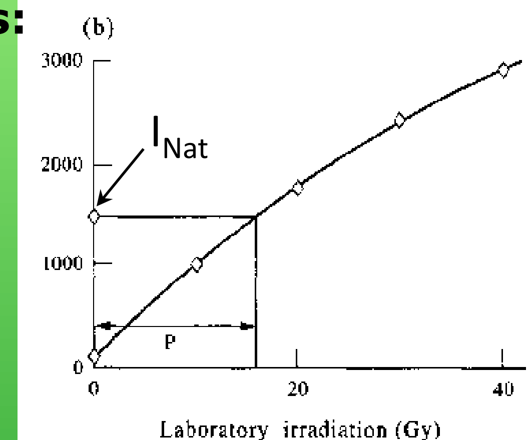
Calibrate as-found signal by generating a dose response characteristic (DRC) with controlled doses:

- additive (dose normalized)
- regenerative with sensitivity monitor
- predose sensitization

- Saturation defines useful dose range

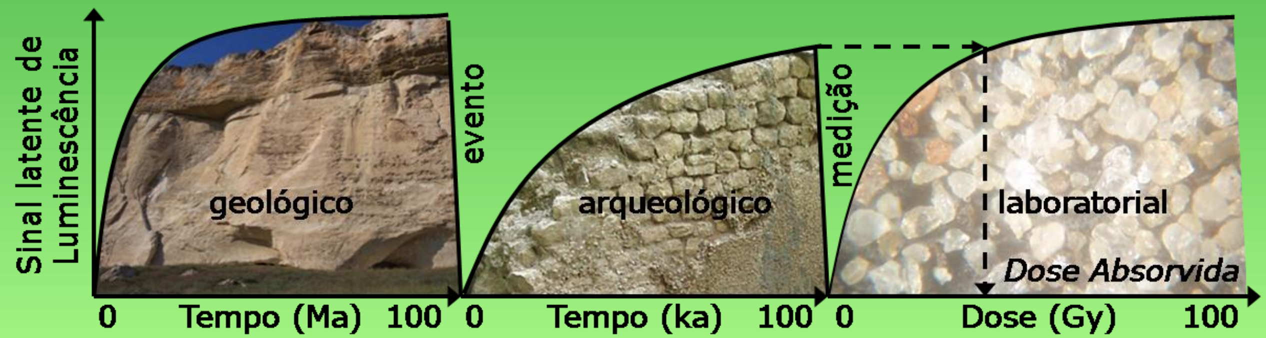






Wintle 1997, Radiat. Meas.

Thermally- and Optically- Stimulated Luminescence Dating



$$Age(a) = \frac{AbsorbedDose(Gy)}{DoseRate(Gy/a)} = \frac{D}{\dot{D}_\alpha + \dot{D}_\beta + \dot{D}_\gamma + \dot{D}_C}$$

D Ionizing radiation absorbed since event:
- crystallization, heating, light exposure, crushing, etc.
- 10^{-1}-10^{3} Gy (10^{-5}-10^{5} Gy +), >±3%@1σ

$\dot{D}$ Average rate of absorption of ionizing radiation by sample since event.
- NORMs, Cosmic, H_2O, Uniformitarianizm/Reconstruction
- Radiation Dosimetry & Spectrometry, Water retention tests, etc
- 10^{-4}-10^{-2} Gy/a, >±3%@1σ

Age Time since event: 10^{2}-10^{5} a (10^{-2}-10^{6} a +), >±4%@1σ
- stability, saturation & dose rate define useful age range

Prudêncio et al. 2009, Pedra & Cal 42, 10-12
Hutton J. 1785. Royal Society of Edinburgh.

Natural Radioactivity and Spatial Variability

Four major contributers:

1. Potassium: $^{40}K \rightarrow {}^{40}Ca + {}^{40}Ar$ (β,γ)

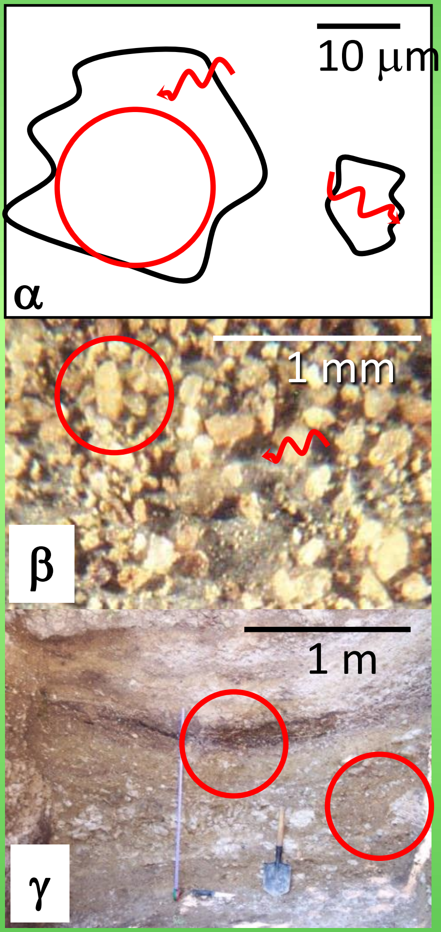
2. Uranium: $^{238}U \rightarrow {}^{208}Pb$ via series (α,β,γ)

3. Thorium: $^{232}Th \rightarrow {}^{206}Pb$ via series (α,β,γ)

- primordial radionuclides, long $T_{1/2}$
- oxides at different concentrations
- mix of emitters and absorbers
- gradients in dose rate at different scales:

α ~0.001 gcm^{-2}, β ~1 gcm^{-2}, γ ~100 gcm^{-2}

- E and hence attenuation/absorption varies with parent and through series



Principle of evaluation of dose rates from NORMs:

- Measure bulk K, Th, U ppms, or α, β, γ, dose rates
- Estimate silicate-equivalent infinite matrix dose rate
- Remove exterior of sample: some external contributions
- Correct for attenuation/absorption of remainder

4. Cosmic radiation (at/near earths surface):

- principally electron showers from relativistic muons
- ~100 gcm^{-2} & ~100000 gcm^{-2}
- time averaged dose rate calculated: lat., long., alt., depth.

Natural Radiation and Temporal Variability

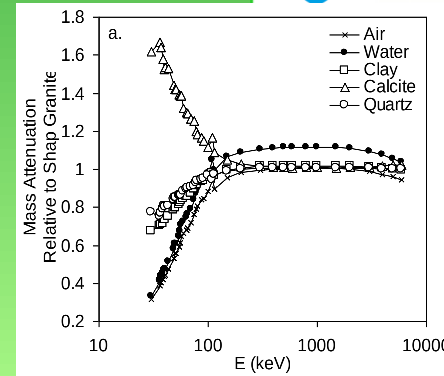
Changes in the sample's physical environment?
- e.g. museum pieces

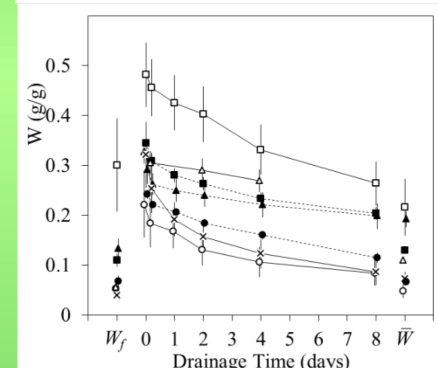
Water content:
- H_2O mass-attenuation differs from silicate matrix
- 1% H_2O mass fraction difference ~ 1% age difference
- water retention measurements to delimit likely range

Disequilibrium in the Th and U series:
- U & Ra relatively soluble in water…
potential for exchange where sample differs from surroundings
- Rn gaseous…

U-series post-Rn dose rate:
c. 60 % of α & β
c. 99 % of γ

Contextual information, reconstruction, and evaluation of potential variability

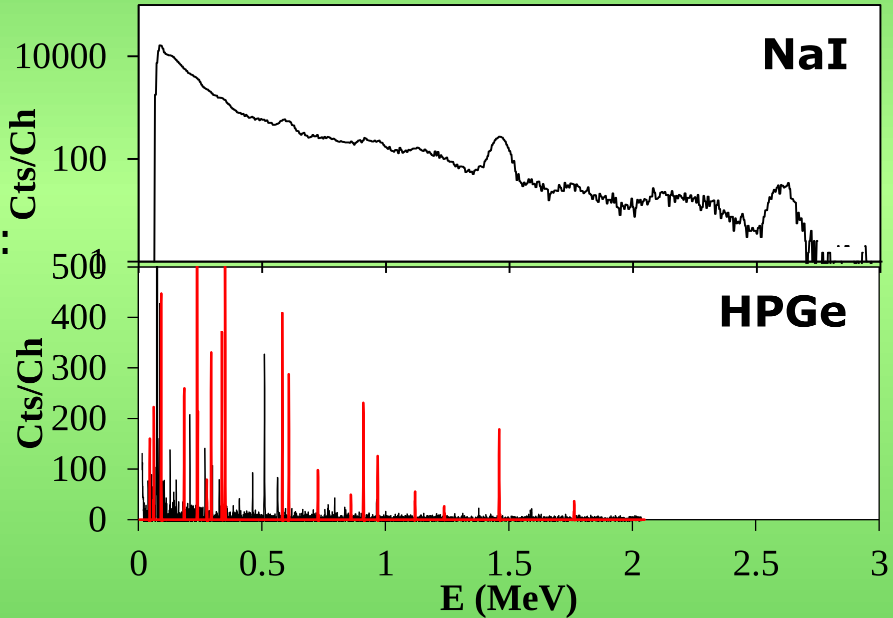




Isotope	$T_{1/2}$	γ Emission (keV)	Intensity
^{238}U	4470 Ma		
^{234}Th	24,1 d	62	0,040
		93	0,054
^{226}Ra	1599 a	186†	0,033
^{214}Pb	26,8 m	242*	0,075
		295	0,191
		352	0,369
^{214}Bi	19,9 m	609	0,468
		1120	0,154
		1238	0,061
		1765	0,162
		2204	0,052
^{210}Pb	22 a	45	0,045

Dose Rate Evaluation

NaI field gamma spectrometers
- Radioluminescence
- Low energy resolution: ^{40}K, ^{214}Bi, ^{208}Tl
- Spatially averaged field to ca. 500 kg



HPGe lab' gamma spectrometers
- 'Radioconductivity'
- High energy resolution
- Large 'natural' samples or subsamples: 20 - 400 g
- 17 different emissions through K, Th and U series

INAA: Portuguese Research Reactor & HPGe lab' gamma spectrometers
- Small neutron activated subsamples: 0.2 g
- Up to 30 different parent isotopes including ^{39}K, ^{232}Th and ^{238}U

If all agree then all is well…
If not, certain spatial/temporal effects can be constrained

Dose Rate Evaluation: VADOSE project

Reevaluate accuracy of environmental dose rate estimates in soils and sediments

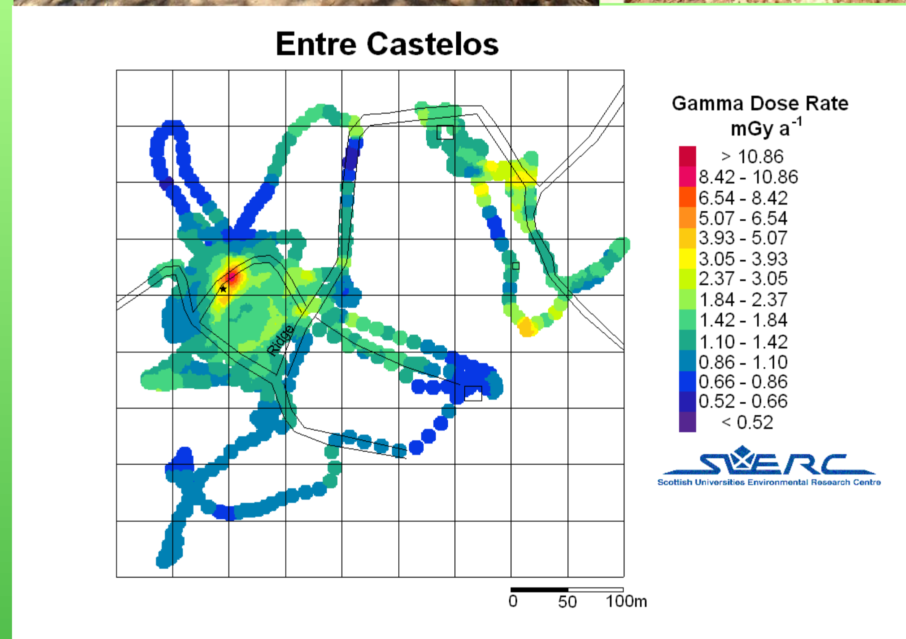
- evaluate radioactivity and absorption characteristics at different spatial scales (μm-km)
- contrasting soils and sediments
- transport models tailored to each
- assess accuracy of predictions from routine measurements
- develop simple improved models

So far:

Sampling (100 kg each site)

- sediments: clay, sand, mixed
- soils: granite, schist, limestone
- uraniferous

Field gamma spectrometry survey and 4pi measurements in sampling locations



Luminescence dating of soils, sediments and ceramics

Example:
ex-Palácio dos Lumiares, Bairro Alto
- Rescue excavation ERA S.A.
- Hillslope near ex-water course

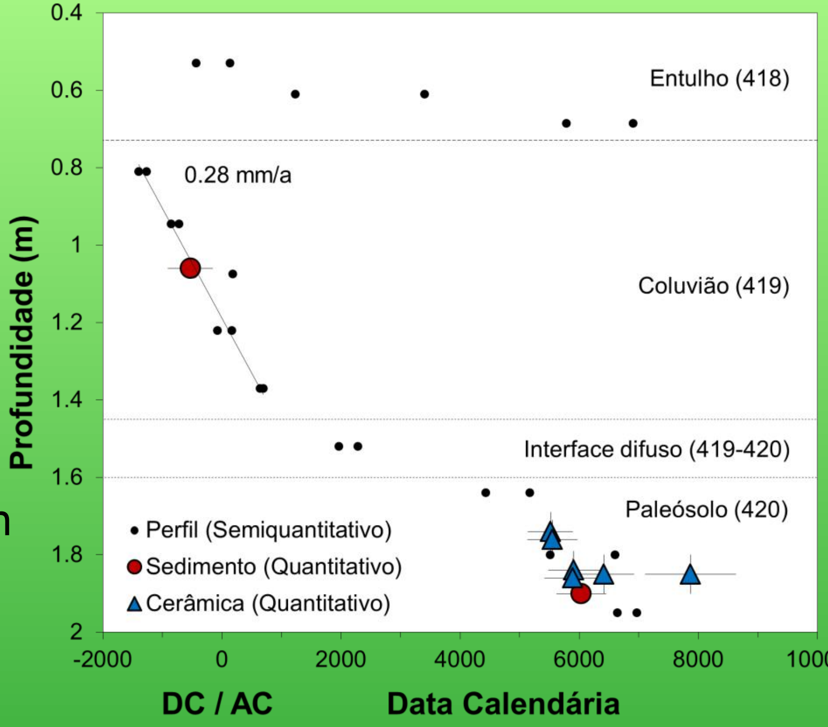
OSL absorbed dose evaluation
- sand-sized quartz grains
- soils/sediments and ceramics

Field Gamma Spectrometry
- points of sampling and representative

Instrumental Neutron Activation Analysis
- soils/sediments and ceramics

…also profiling…

Chronostratigraphy and process
- Early Neolithic occupation of Lisbon
- Hiatus/erosion late prehistory
- Colluviation: Roman to C16-construction
- Residuals in rubble



Profiling of archaeosediments

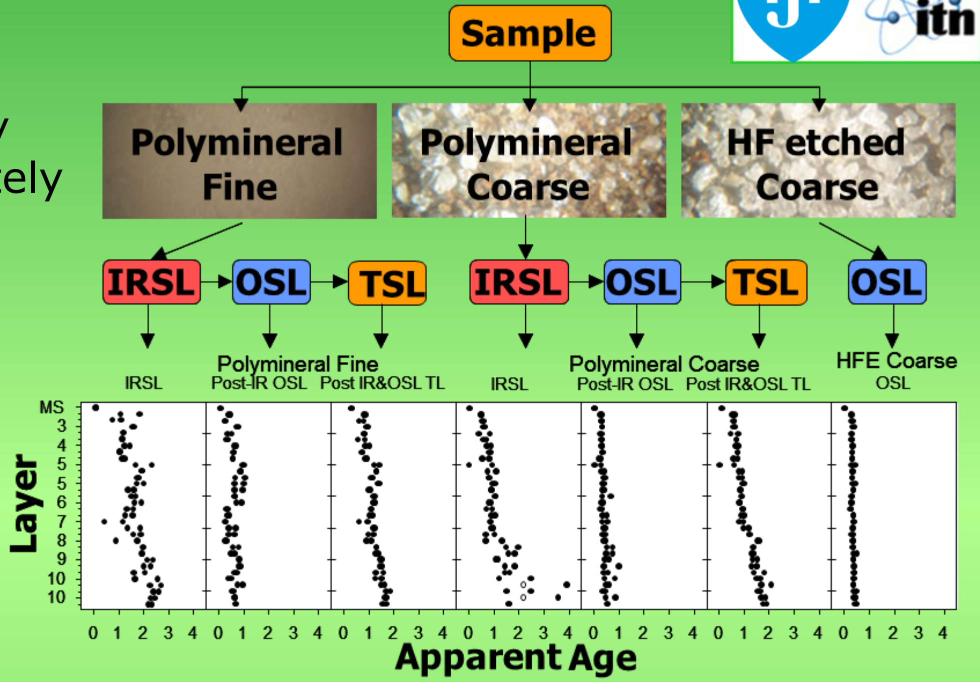
Sediments ubiquitous, but potentially complex: success in dating is intimately linked to sedimentary process.

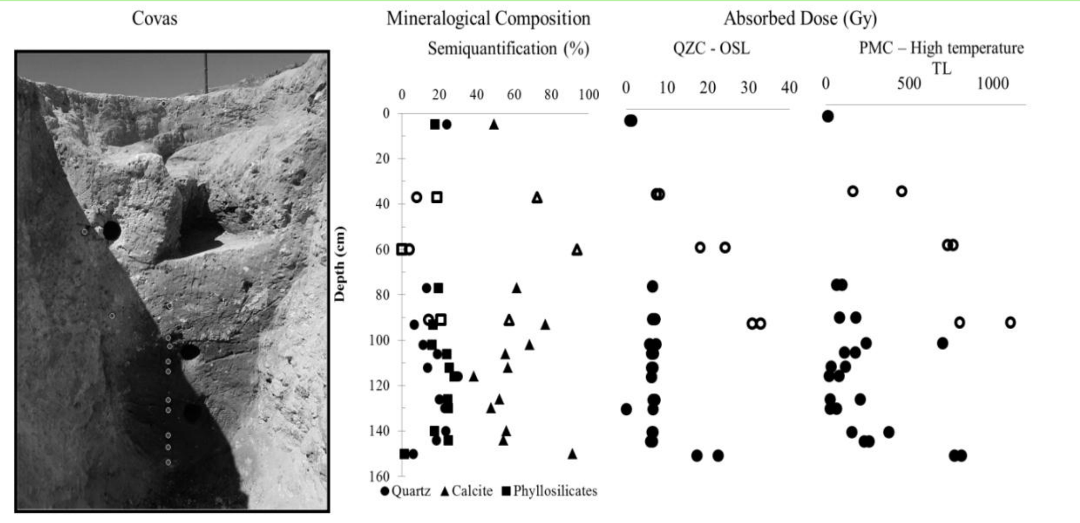
Assess datability and contextualise absolute dating results

- Basic, rapid survey
- Many samples ~5g down section
- Fractions: PMF, PMC, HFC
- Measurement: IRSL, OSL, TSL
- 1 calibration dose

Range ca. 0-100 Gy

Phases of accumulation
Identification of residuals
Semiquantitative ages
Relate to mineralogy: XRD





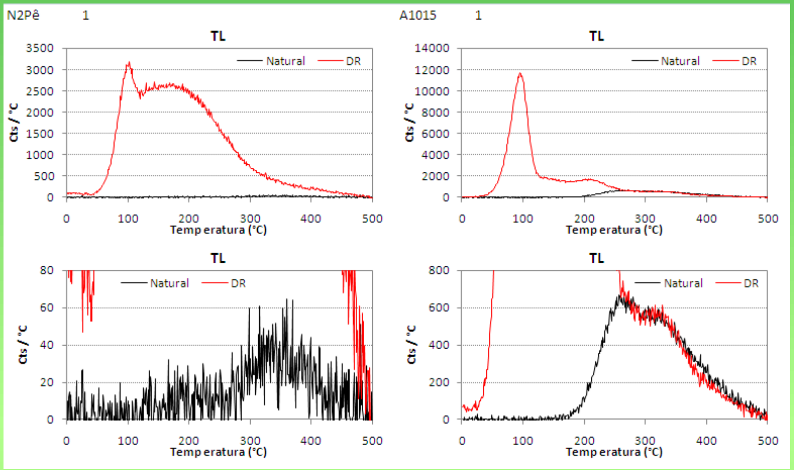
Burbidge et al., 2007. Quat. Geochron. 2, 296-302.
Rodrigues et al. In Prep

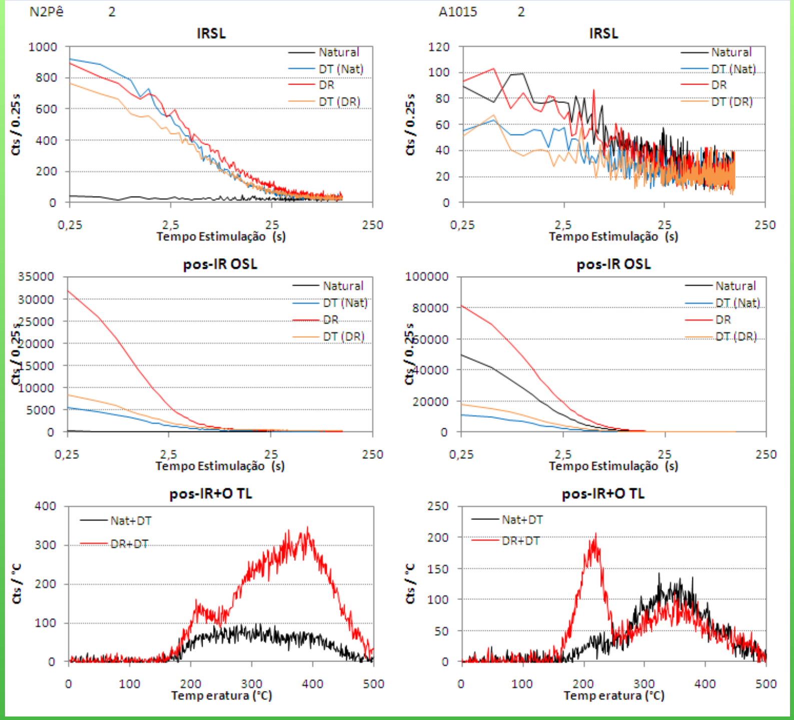
Authenticity testing of ceramics

Terracotta
– A rich source of silicate minerals
- Fired between 400 and 700 °C

Drill < 1 g powder
Simple preparation (acid wash): PM
Similar measurements to profiling

Is as-found dose as large as expected large for stable signals? (1-10 Gy)





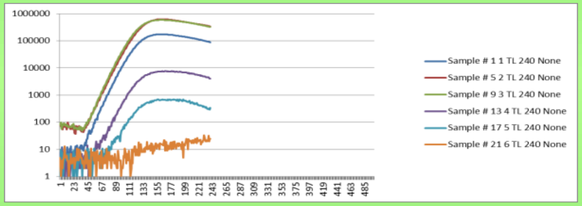
Dias, et al., 2010. Instituto Tecnológico e Nuclear.

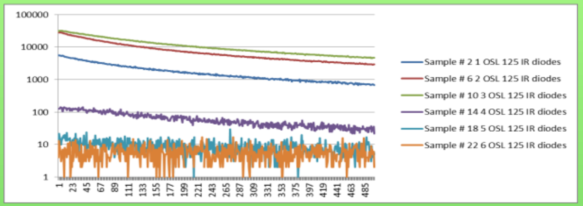
Detection of multi-kGy doses to ceramics

IAEA TC Project RER/0/034
Regional Training Course on Radiation Technology for Cultural Heritage Preservation Theme IV.
Retrospective evaluation of absorbed dose within objects using stimulated luminescence

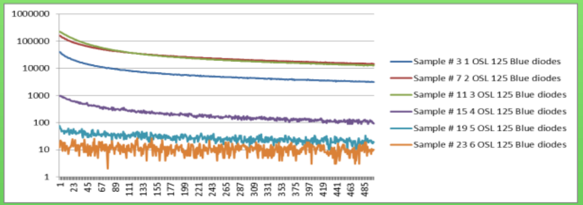
Introduce non specialists from a range of backgrounds to luminescence-dosimetric methods applied to cultural heritage materials.

Lab. exercise: 2 hrs inc. data processing
- Micro-invasive sampling by drilling
- Preparation of silicates by acid washing
- IRSL, OSL and TSL measurement

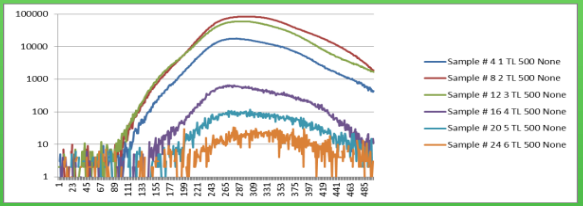




Terracotta – Roman amphora:
- lots of well behaved minerals
- One subsample irradiated, 10kGy
- Other contains only archaeological dose

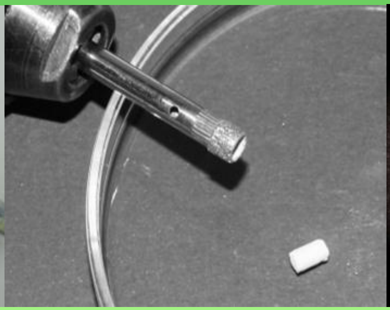


Objective: distinguish between the irradiated and un-irradiated subsamples.



Prudêncio, M.I. IAEA TC Project RER/0/034.
Enhancing the Characterization, Preservation and Protection of Cultural Heritage Artefacts

Luminescence analysis of high fired ceramics

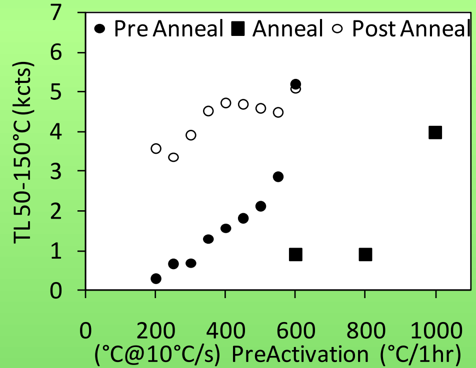


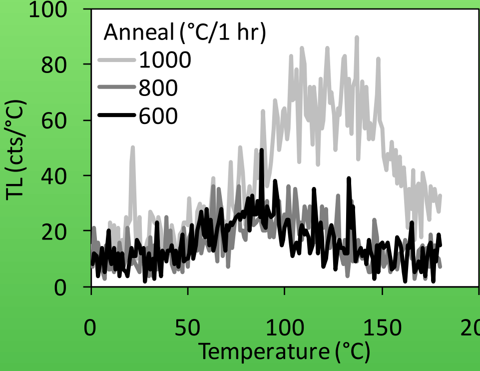
Faience and Porcelain trade in Lisbon, 1500-1750AD
- P: Mullite: firing > ~1050 °C
- F: Gehlenite+Diopside > ~900 °C
- Quartz grains: mg quantities

Predose response of 110 ºC TSL
- Irradiate, measure and 'activate' to 500 °C, repeat…
- Non-linear DRC: new protocol to reduce extrapolation errors resets sensitivity by annealing
- Anneal induces different changes in predose sensitization:

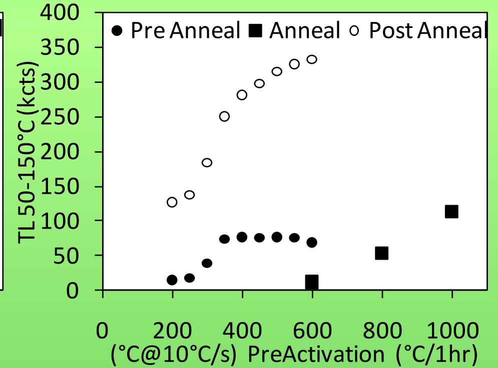
Firing temperature
Phase changes
Ionic mobility

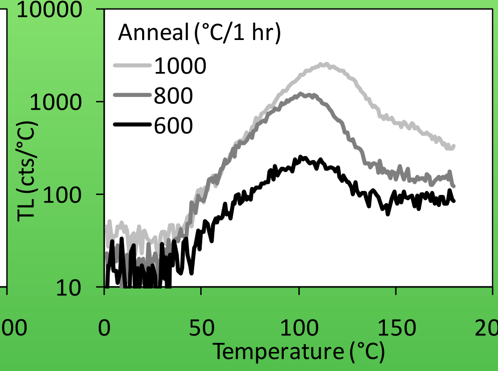
Porcelain





Faience





Burbidge, 2012. Spectroscopy Letters 45, 118–126
Burbidge et al., 2010. Mediterranean Archaeology and Archaeometry 10, 53-60

Luminescence-dosimetric processes in quartz

Quartz grains prepared from:
- Pegmatite: milky, strongly etched, Li rich
- Granite: transparent, well crystallized, resistant

Examine differences/changes in emissions and radiation sensitivity following phase changes

RL Spectra – CUDAM, UNIMIB
- Measure during irradiation, repeat: 300-1000 nm
- Etched surface vs. 'fresh' interior

TSL Bands – GeoLuC, IST/ITN
- Anneal: rt, 600, 800, 1000, 1100 °C/1hr
- Irradiate & Activate: 500 °C
- Irradiate & Measure: NUV, B, G-Y, O-R

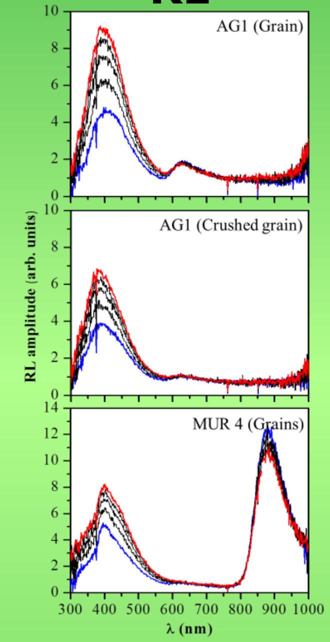
B emission common
NUV & O-R strong in pegmatitic quartz
NIR from granitic quartz
Max. sensitization: <200°C TSL in NUV, similar for O-R in pegmatite
O-R emission related to surface defects

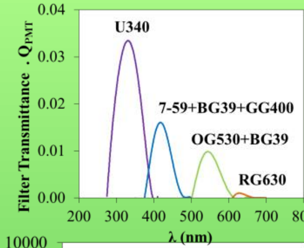
Approx. 3 mm

AG1, from Pegmatite

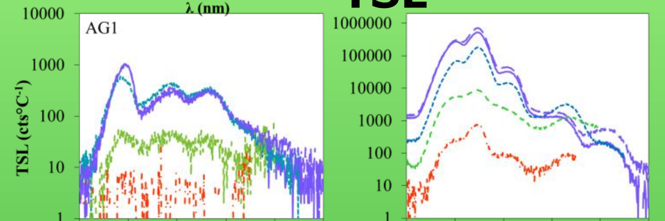
MUR4, from Granite

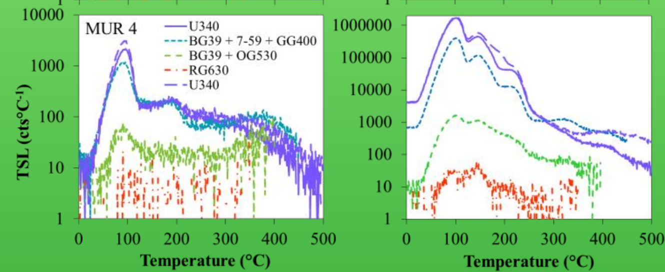
RL





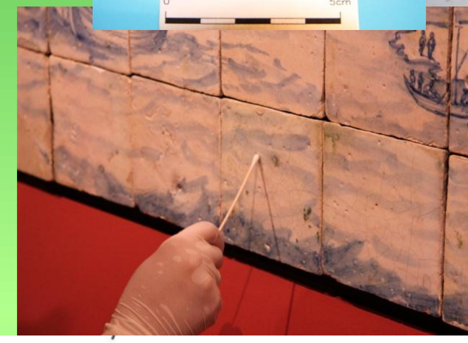
TSL





Burbidge, Martini, et al., italia12858468220330. Convénio Portugal(FCT) / Itália(CNR) 2011-2012

Monitoring of multi-kGy doses to historic tiles



Doses to deactivate microorganisms in ceramics are expected to be "quartz equivalent" and might be retrospectively evaluated using small samples from the ceramics themselves

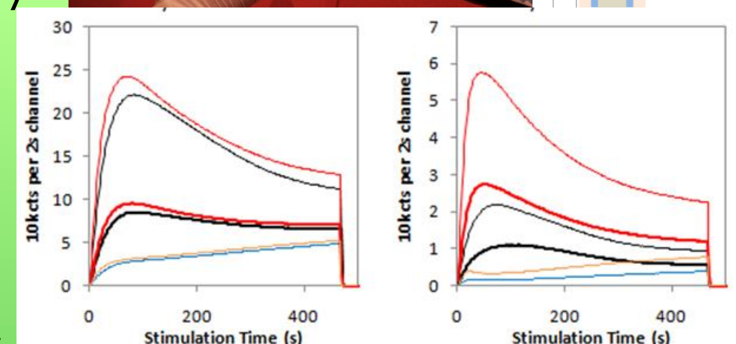
Evaluate 'high growth' OSL signals: e.g. 'TTOSL' = Preheat, OSL, preheat higher, OSL again

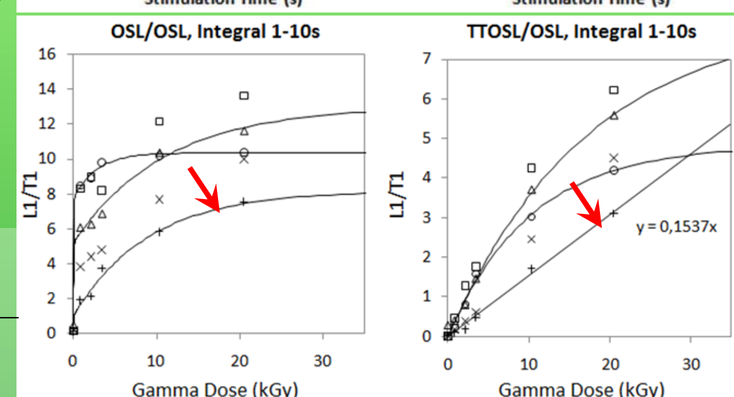
- Gamma irradiation of ceramic sherds 0-22 kGy
CHIP, S.A. IST/ITN Campus. 250 kCi ^{60}Co.
- LMOSL to limit max. count rates
- Generate beta DRC in lab' and attempt to recover gamma doses

Approximately linear growth in TTOSL to multi kGy doses following higher preheats

13% underestimates of gamma doses – not a bad start

Signal		Preheat	Range	Mean % Residual
OSL	1-10s	280 300	>1 kGy	-35
TTOSL	1-10s	280 300	>1 kGy	**-13**





Burbidge et al., 2011. Radiat. Meas. 46, 860-865.

Monitoring of multi-kGy doses to ceramics

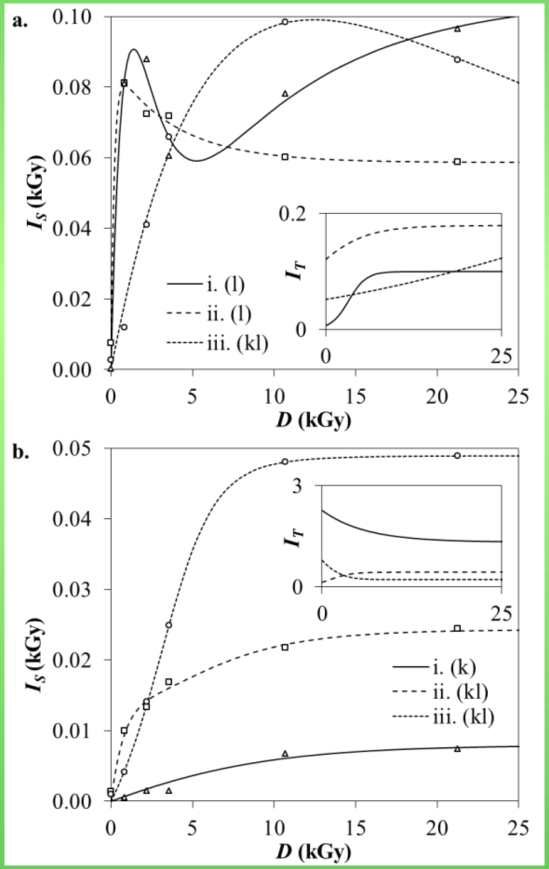
Recent re-analysis:

- Complex DRCs can be explained simply by differences and changes in the relationship between the signal and the test/normalization signal.

- TT-OSL DRCs appear to relate to greater dose dependent relative supralinearity in the test/normalization response.

- If truly dose dependent, such effects do not make absorbed dose evaluations inaccurate, they merely complicates analysis of the DRC.

A relatively simple general form has been developed for fitting DRCs to help evaluate such effects



Burbidge, C.I., Submitted. Radiat. Meas.

Conclusions

Luminescence dating and dosimetry at GeoLuC, UCQR, IST/ITN:
- Combination of retrospective and environmental dosimetry
- Applied principally to cultural heritage and geological materials
- Dating human history and the quaternary
- Authentication and evaluation of high and low radiation doses
- Environmental dose-rate evaluation by radioactivity surveys

development of applications, methods and basic understanding

- Studies complex natural systems
- Has a strong and relevant basis across physics disciplines
- Has much scope for further basic research

In IST/ITN we have a good and growing base in Luminescence Dosimetry and related analyses:
- GeoLuC, UCQR: dating, retrospective, environmental dosimetry, cultural heritage, geology …
- UPSR: personnel, environmental, medical dosimetry …
- RPI: personnel (neutron), medical dosimetry …
- UFA: IL spectrometry …

Aim: further this through current submissions and integration in IST