Luminescence applications in dosimetry, dating, natural sciences and engineering

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Luminescence in Cultural Heritage

Mainly

- Age assessment - dating
- Authenticity testing
- Forgery identification

Furthermore

- Provenance
- Technology – firing temperature of ceramics

Indirect dating methods

- Black Figured Cylica from Attica, type A
- Indirect dating is achieved due to:

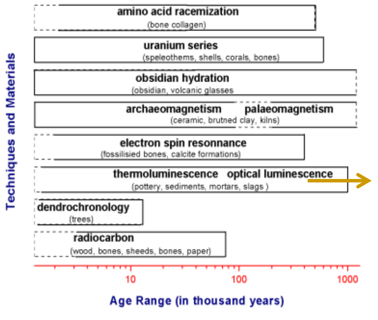
1. Type
2. Shape
3. Painting
4. Signature (Exikeias)

- 540-535 BC

Indirect dating methods??

No indication to be used towards dating.

Frequently used dating techniques & respective limitations



Among the main absolute techniques, luminescence:
-potentially dates all inorganic material
- up to 1 Ma (easily up to 300 ka)
- if organic material present: ideall combined use with radiocarbon

What can luminescence date?

- ✓ Ceramics
- ✓ Pottery
- ✓ Bricks
- ✓ Fired materials
- ✓ Burnt materials
- ✓ Volcaniclastic materials
- ➢ ***Thermal zeroing***

- ✓ Calcitic rocks (***$CaCO_3$:*** *TL only*)
- ✓ Granites
- ✓ Marbles
- ✓ Sediments of any type
- ➢ ***Optical zeroing***

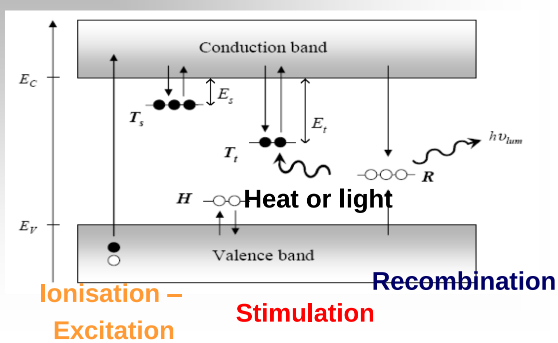
The impact of Environmental Radiation

- Radiation causes ionization to atoms and molecules into the materials, creating thus free electrons and (+) ions.
- These charged particles diffuse through the material until they finally get trapped in specific defects of the crystal lattice. Thus, the materials could store energy.
- The total number of trapped charges is proportional to the total radiation energy absorbed by the materials, and therefore to the time subjected to irradiation.
- Among these traps, some could be stable enough to store the electrons for extremely long time intervals, depending upon some physical characteristics of the material.

Luminescence Definition

- The electrons trapped in these stable (deep) traps could be released if they are externally stimulated to, in the lab.
- Released electrons once again diffuse through the material until they find (+) ions (holes) in the lattice and recombine. Each recombination results in the emission of one photon in the optical wavelength band. The light emitted is called *luminescence*.
- The intensity of the luminescence light is also proportional to the total radiation energy absorbed by the materials, and therefore to the time subjected to irradiation.
- Stimulation usually occurs either by heating or by the action of light. In the former case we have ***Thermoluminescence (TL)*** while in the latter ***Optically Stimulated Luminescence (OSL).***

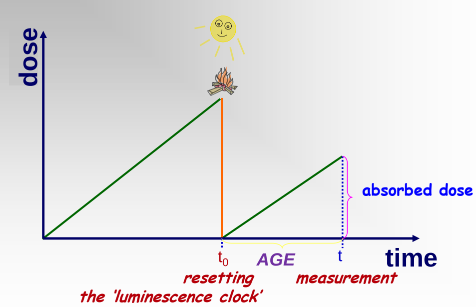
Energy band diagram

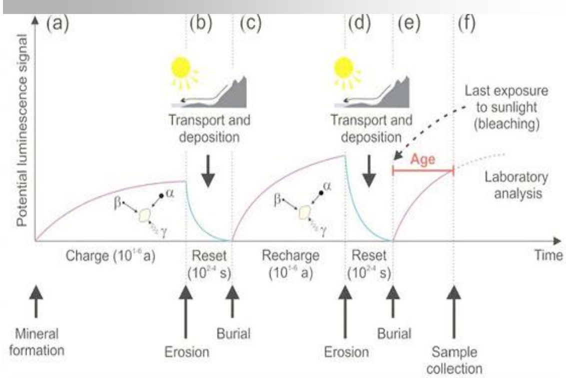


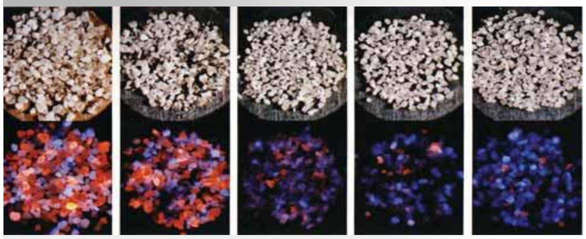
Luminescence Clock

- The number of trapped electrons is increasing as long as the material is irradiated. However, every time that the material is subjected to either prolonged heating (as in the case of firing) or intense light exposure (as in the case of sunlight), electrons are evicted and traps are emptied.
- In that case, the material is said to be totally zeroed. Afterwards, it could start accumulating energy in the form of trapped electrons in order to refill the empty traps once again.
- The total number of trapped electrons forms a luminescence "clock" which starts measuring time from the begging (zero) every time that these traps are zeroed.
- Therefore, light-exposed materials could be dated to their last exposure to light, while burnt materials to their last heating.

Growth and Resetting of the Luminescence Signal







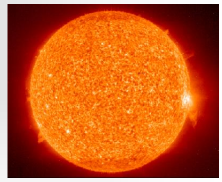
Blue: faint luminescence signal

Red: intense luminescence signal

Naturally occurring dosimeters

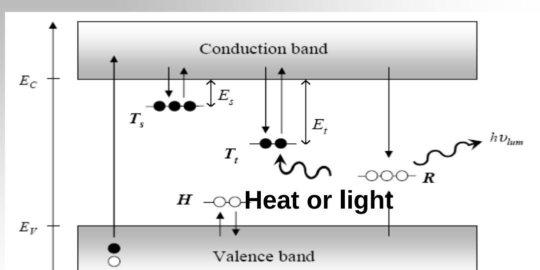
- Luminescence light is emitted ***mostly*** from specific crystal grains of

1. Quartz (SiO_2)
2. Feldspar (x[$AlSi_3O_8$] x = K, Na,Ca)
3. Calcite (in few cases)



- ALL INORGANIC SEMICONDUCTORS

Energy band diagram



Ionisation – Excitation

Stimulation

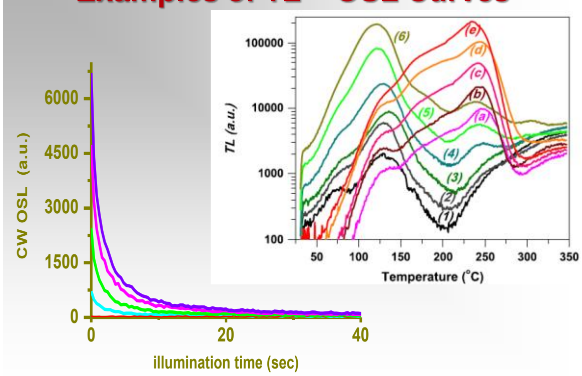
Recombination

Excitation and Luminescence Photon Energies Used in OSL Dating

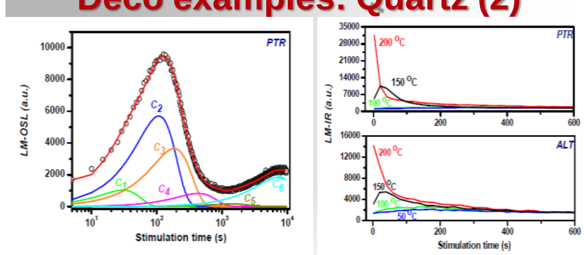
Mineral	*Energy (wavelength) of excitation photons*	*Energy (wavelength) of luminescence photons*	
Quartz (SiO_2)	**2.2 – 2.4 or 2.7 eV (510 – 560 or 470 nm) green-blue**	**3.35 eV (370 nm) ultraviolet**	**OSL**
Potassium Feldspar $KAlSi_3O_8$	**1.4 eV (880 nm) infrared**	**3.1 eV (400 nm) Violet**	**IRSL**

Appropriate detection filters required

Examples of TL – OSL Curves



Deco examples: Quartz (2)



→ Isolating fast OSL components towards studying the impact of IRSL stimulation to the fast OSL components.

(*Polymeris et al., Geochronometria 32, 79–85, 2008*)

Handling Requirements

- All samples submitted for dating should not be treated with any chemical nor exposed to temperatures greater than 100 °C, artificial ultraviolet, infrared or ionizing radiation (including x-rays) after sampling.
- Handling inside the laboratory should take place under strict red dim light conditions.
- The outer 2 mm thick layer of the sample, which was probably exposed to light, is removed. This thickness depends strongly on the opacity of the material.
- Pottery samples should ideally have a minimum of 8 mm thickness and minimum area of 4X4 cm.

Handling Procedures I

1. Gentle crushing and smashing
2. Estimation of water content for dose rate corrections (heating at 50-70 °C until mass stabilization)
3. Grain size selection by sieving, depending on the grain size of interest according to the following alternatives:

Fine grains (4-12 μm)

- ✓ Selection of grains with size <20 μm.
- ✓ Acetone suspension for 2 and 20 minutes for refinement.

Coarse grains (90-140 mm)

Handling Procedures II

1. Removal of carbonates (10% HCl, 24 hours)
2. Removal of organic component for dose rate corrections (15% H_2O_2, 24 hours at least)
3. Disaggregation by agitation in sodium oxalate solution
4. Removal of non-quartz components (35% H_2SiF_6, 36 hours → optional)
5. Suspension in acetone – deposit on disks via evaporation (case of Fine grains only)
6. Etching to remove outer layer of grains (40% HF, 60 mins, followed by washing using HCl and distilled water, only in case of Coarse grains)

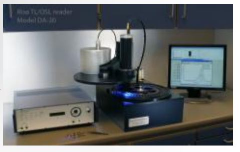
Luminescence Age

$$\text{Age [a]} = \frac{\text{ED [Gy]}}{\text{DR [Gy/a]}}$$

measured parameters:

- ➢ ED dose (correction of the natural signal (TL, OSL):

plateau test, growth, sensitivity changes, anomalous fading



- ➢ estimation of the dose-rate: cosmic dose, accurate U, Th, K concentrations estimation, a-efficiency, humidity, porosity

Annual Dose Rate Estimation

Natural U = ^{235}U AND ^{238}U

^{232}Th

SPECTROSCOPY, THICK SOURCE ALPHA COUNTING

^{40}K

XRF, Flame Photometry, Scanning Electron Microscopy

TL Dating

Inside the laboratory, every time that a sample is heated, the traps are getting empty from electrons.

What is the respective phenomenon in nature?

Fires, Annealing, Firing generally, volcanic activity…

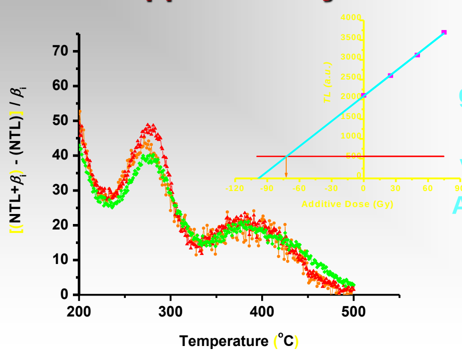
After each one of these effects, the materials have their traps totally emptied (=no TL signal).

This provides with a luminescence clock that is re-set every time that some material is heated to high temperatures → TL dating of pottery, volcanic materials, kilns….

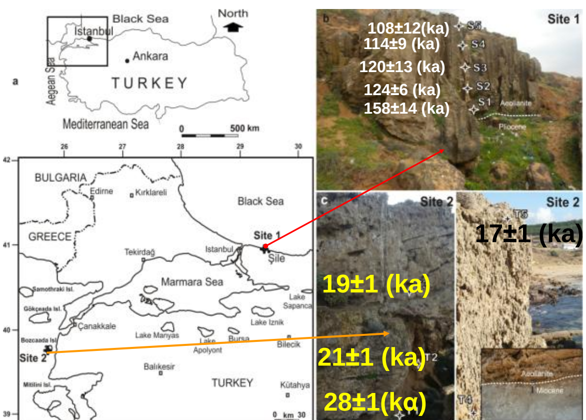
ED Estimation approaches

- There are two basic approaches, applied in both TL and OSL
1. Additive Dose Method
2. Regeneration Method
- In both cases the Natural TL or OSL signal accumulated is compared to the luminescent signal induced after artificial irradiation of well known doses in the lab.
- Frequently used: ***Multiple Aliquot Additive Dose (MAAD) TL*** & ***Single Aliquot Regenerative Dose (SAR) OSL*** methods.

T.B.M. Application: Şile Eolianites

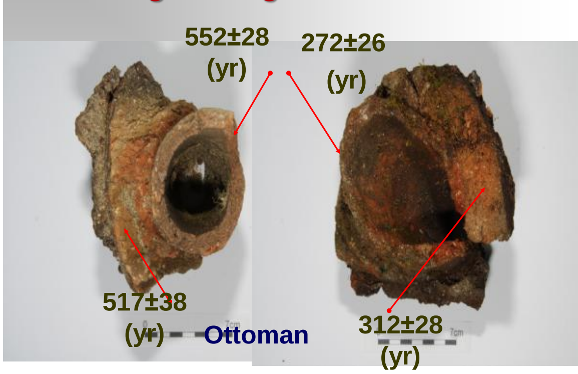


Linear growth of TL Versus Additive doses is required!

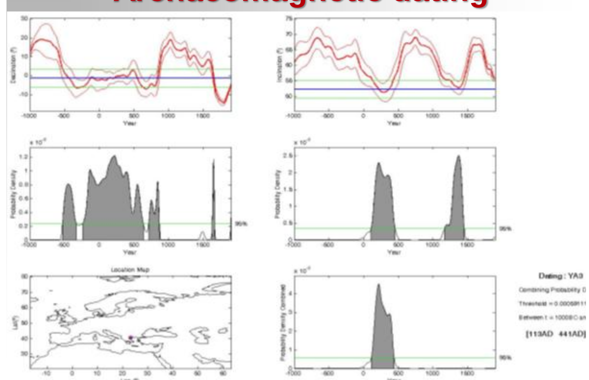


(*Polymeris et al., MAAJ 12 (2), 117 – 131, 2012*)

Metallurgical slags from North Greece



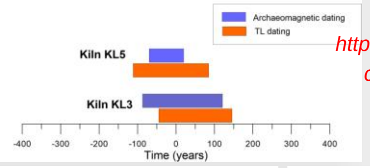
Archaeomagnetic dating



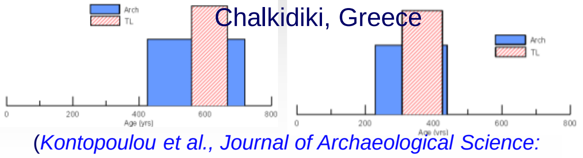
TL versus Archaeomagnetic dating; kilns

Kato Achaia, Western Greece

(*Tema et al., http://dx.doi.org/10.1016/j.culher.2014.09.013*)



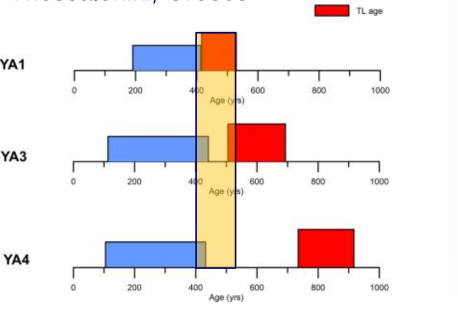
Chalkidiki, Greece



(*Kontopoulou et al., Journal of Archaeological Science: Reports 2 (2015) 156–168*)

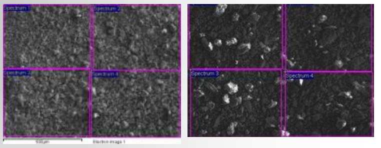
Not consistent results

Thessaloniki, Greece



Microstructure - Microdosimetry

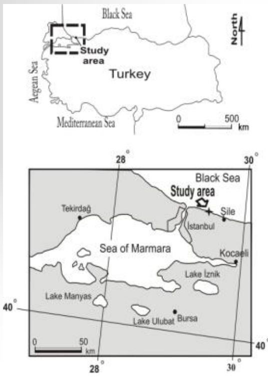
In order to demonstrate the heterogeneity of the samples, SEM measurements were performed . 4 different areas were scanned in order to get SEM-EDS elemental analysis.



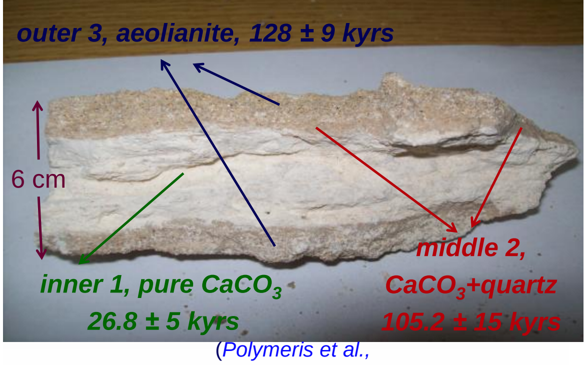
Code	Na	% error	Mg	% error	Si	% error	K	% error	Fe	% error
ya3-7	1.55	34.19	2.20	16.36	52.39	3.66	5.75	12.87	14.05	7.26
ya3-6	1.99	22.11	2.54	9.06	52.53	2.23	5.57	12.75	13.40	10.82
ya3-5	1.3	24.62	1.78	12.36	63.77	2.62	4.93	10.75	11.69	12.32
ya3-4	1.08	19.44	1.74	16.09	61.01	2.07	5.82	20.79	12.25	14.45
ya3-8	1.34	5.22	2.41	10.79	53.55	1.77	5.45	6.06	13.15	10.27
ya3-10	1.77	31.64	2.45	16.33	53.85	2.49	5.15	19.61	13.12	10.52
ya4-7	1.51	35.10	2.07	28.50	56.03	3.68	5.17	17.02	11.64	13.40
ya4-3	1.71	23.98	2.08	20.19	50.90	3.20	5.48	12.59	13.42	4.92
ya4-6	1.77	14.69	2.20	28.64	54.10	5.16	3.32	22.29	11.72	7.51
ya4-4	1.99	7.54	2.41	24.48	53.43	1.95	4.02	13.43	14.01	10.28
ya4-2	0.94	38.30	2.09	21.05	56.45	3.10	5.38	10.78	12.54	11.08
ya4-8	1.17	33.33	2.03	23.15	52.61	4.41	3.66	24.04	13.96	6.73
Ya4-11	1.71	29.24	2.21	6.79	49.67	1.01	3.85	16.36	13.75	2.40

Mean values and their std was yielded for all major elements. Even thought Si is uniformly distributed, Na, K, show large heterogeneity. An arbitrary level of 20% was selected as typical of heterogeneity. YA4 almost 30% heterogeneity in feldspar content.

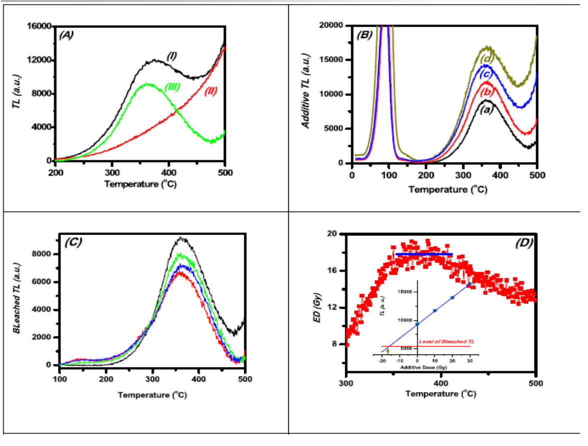
Dating rizoliths



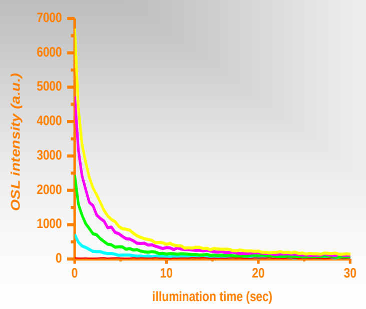
Dating rizoliths



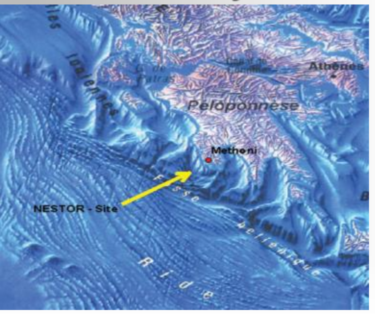
(*Polymeris et al., http://dx.doi.org/10.1016/j.quaint.2015.05.060*)



Regeneration Method: OSL Curves

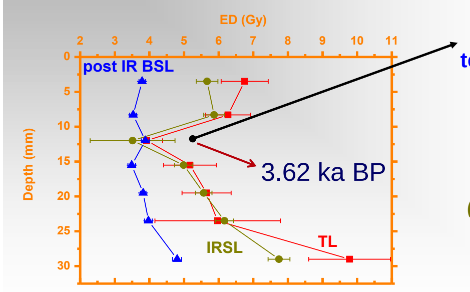


SAR Application; underwater sediment from Pylos, Greece



(*Polymeris et al., Quat. Geo. 4, 68 – 81, 2009*)

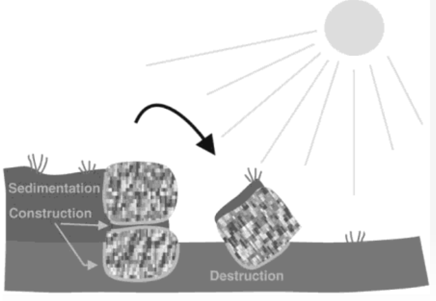
SAR Application; underwater sediment from Pylos, Greece



Layer Contains tephra from the Santorini Volcano eruption *(1606 BC).* Verified also By SEM analysis

(*Polymeris et al., MAAJ 11 (2), 107 – 120, 2011*)

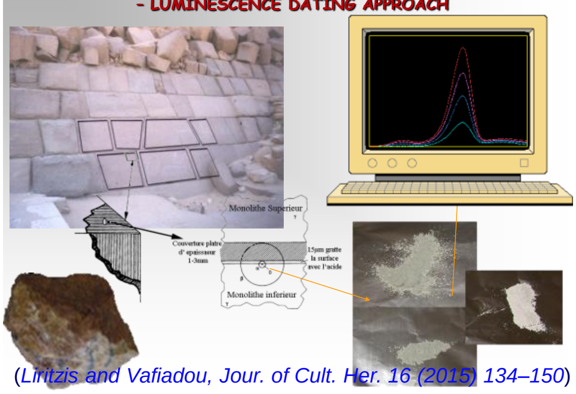
Surface Dating



Applied to masonry as well as Megalithic structures. Requires Accurate sampling (first mm's of each stone)

(*Liritzis, Geochronometria, 38(3) 292–302, 2011*)

MONUMENTS - MATERIALS - INSTRUMENTATION - LUMINESCENCE DATING APPROACH



(*Liritzis and Vafiadou, Jour. of Cult. Her. 16 (2015) 134–150*)

Surface Dating Applications

Gate of Dragon House's Complex
1140 ± 240 BC

Dragon House's
1200 ± 200 BC or ROMAN (166±115)

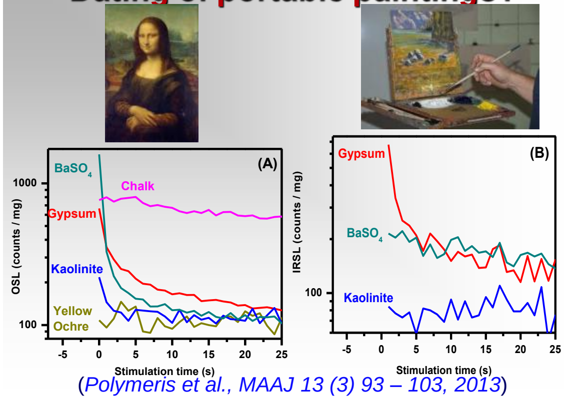
Range of occupational phases

(*Liritzis et al., MAAJ 10 (3), 65 – 81, 2010*)

Surface Dating Applications

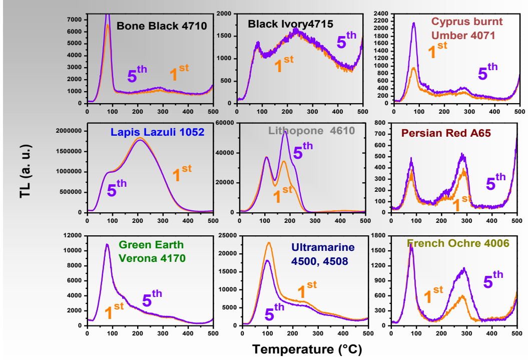
(*Liritzis et al., MAAJ 13 (3) 105 – 115, 2013*)

Dating of portable paintings?



(*Polymeris et al., MAAJ 13 (3) 93 – 103, 2013*)

Dating of portable paintings?



Authenticity

- In art and antiques, a common problem is verifying that a given artefact was produced by a certain famous person, or was produced in a certain place or period of history. The word Authentication (coming from the Greek word: *αυθεντικός*; real or genuine) defines the act of establishing or confirming something (or someone) as authentic, i.e. genuine.
- This is usually performed by either comparing the attributes of the object itself to what is known about objects of this specific origin, or applying a number of physico-chemical techniques to the materials used.
- The age of a ceramic object (terracotta or porcelain) stands usually as the most significant information towards authenticity. Among the various dating techniques, (TL) stands as the most effective technique towards the age assessment and, consequently, authenticity testing of ancient fired ceramic materials.

Authenticity Testing - Sampling

- **5000 fake art objects are sold every year to the art market.**
- **40% of the objects that were tested by TL were found to be not genuine.**

Forgery

- Archaeological forgery is the manufacture of supposedly ancient items that are sold to the antique market and may even end up in the collections of museums.
- It is related to Art forgery, which refers to creating and, in particular, selling works of art that are falsely attributed to a famous artist.
- Most of the Archaeological forgery is made for reasons similar to Art forgery - for financial profit, since both are extremely lucrative.
- The monetary value of an item that is thought to be thousands of years old is much higher than the similar one sold as a souvenir. In this context forgery must of course be clearly distinguished from copies produced with no intent to deceive.

Forgery

- A string of Archaeological forgeries have very often followed news of prominent archaeological excavations in sites e.g. in ancient Egypt or China, resulting in the appearance of a number of forgeries supposedly spirited away from the sites. In recent times, forgeries of pre-Columbian pottery have also been very common. These forged objects are usually offered in the free market but some have also ended up in museum collections and as objects of serious historical study.
- Forgers use artificial irradiation by gamma ray to age modern productions. Besides fraudulent action, objects can be exposed to various sources of X-rays (e.g.radiography, security control at airports). For all these reasons, the determination of artificial irradiation is an important topic for dating art objects.

Dealing with forgery

It is very likely that the TL signal characteristics can potentially provide useful indications as well as arguments towards forgery identification. Therefore, a comparative study of the glow curve details between genuine and forged artifacts could provide preliminary hints.

De-convolution as well as ***dose-rate dependent*** effects could be very useful towards this direction.

The main technique to identify artificial irradiations is the subtraction technique. It is based on the fact that alpha efficiency varies according to the luminescence technique (fine grain, coarse grains, TL, OSL). Studying of alpha to beta efficiency becomes important.

(*Zink et al., Rad. Meas. 45, 649 – 652, 2010*)

Firing Temperature: the rationale

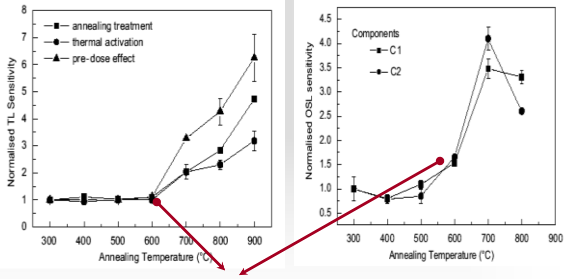
- The firing temperature of ancient pottery provides a basis for understanding many aspects of ancient technology such as manufacturing techniques and functional relationships between specific resource manufacturing combinations.
- Pottery is made by firing clays, which contain 40–80% silica. Most of it is in the crystalline form of quartz, the luminescence properties of which undergo certain changes during firing.
- The luminescence output of these quartz grains is increased as the firing temperature also increases. This is the well established phenomenon of pre-dose sensitization.
- In order to evaluate the firing temperature in a reliable way, it is necessary for the quartz to (i) register it, (ii) remember it and (iii) manifest it in one form or another.

(*Sunta & David, PACT 6, 460, 1982*)

Firing Temperature: the technique

- The ceramic sample should be divided into seven segments. Each segment should be annealed to a different temperature between RT and 900 °C, in steps of 50-100 °C in order to bracket the firing temperature.
- After the annealing, each segment should be crushed and grains of dimensions 4–11 mm should be selected and deposited on aluminum discs.
- Subsequently, the initial sensitivity, as well as the thermal and pre-dose sensitizations were recorded for both TL and OSL at room temperature as a function of the annealing temperature.
- The luminescence is expected to remain constant until the re-firing reaches the firing temperature. Thereafter, it is expected to rise appreciably.

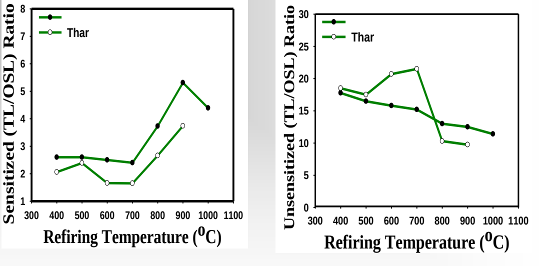
Application to known firing temperature (600 °C)



Firing Temperature

(*Polymeris et al., NIM A 50, 747 – 750, 2007*)

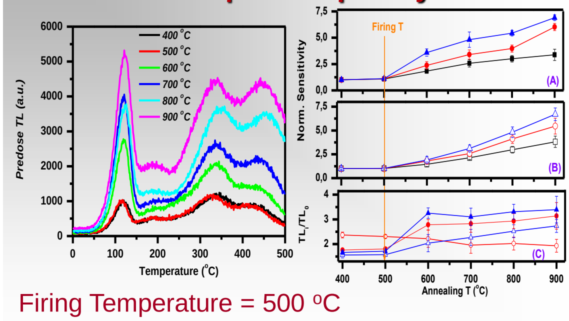
Application to unknown firing temperature: Indian pottery



Firing Temperature = 700 °C

(*Koul and Chougaonkar, Geo\tria, 38(3) 303–311, 2011*)

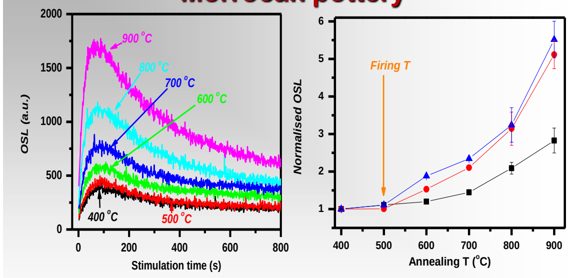
Application to unknown firing temperature: Mesopotamia pottery



Firing Temperature = 500 ºC

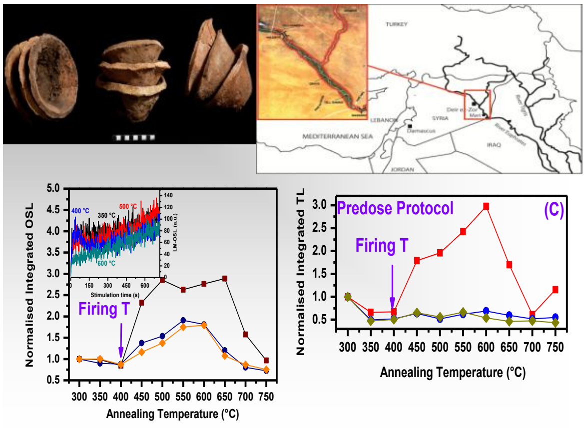
(*Polymeris et al., Archaeometry In Press, 2013*)

Application to unknown firing temperature: Morrocan pottery

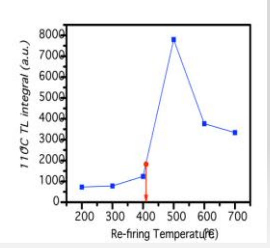


Firing Temperature = 500 ºC

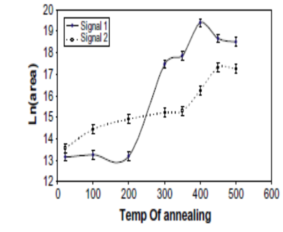
(*Polymeris et al., Archaeometry In Press, 2013*)



Similar Applications



Identification of fires in the past; Castle in Spain (*Sanjurjo-Sanchez et al., LAIS 2 Conference, Lisbon, 2012*)



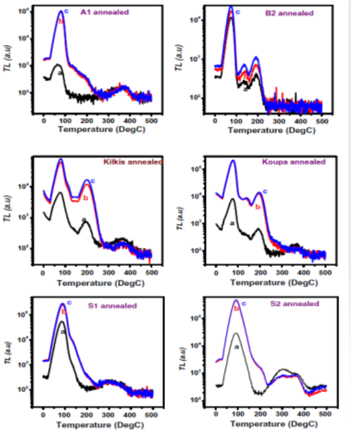
Palaiothermometry using Indian salt (*Gartia, NIM B 267, 290 – 2907, 2009*)

Provenance vs Universality

- Among the several luminescence properties and features that are commonly studied in luminescence materials, some indicate prevalent nature, namely they are present for all similar and same materials independent on origin and provenance. These are universal properties and could be easily taken advantage towards dating. Quartz yields many prevalent or universal features; this is why it has been established as the most widely used naturally occurring luminescent material for dosimetry and dating purposes. Similar features are:

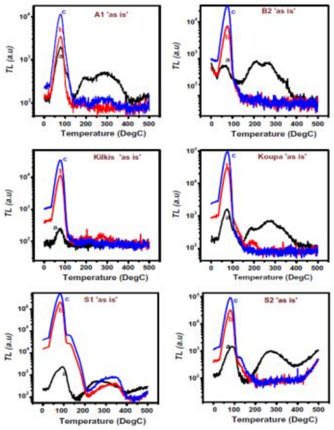
1. 110 ºC and 325 ºC TL peaks
2. Fast OSL component
3. Sensitization of TL/OSL signal
4. Thermal quenching

(*Subedi et al., MAAJ 10 (4), 69 – 75, 2010*)



Fired

A1→ Nepal
B2→ India
Kilkis → Greece
Koupa → Brazil
S1 → Nigeria
S2 → Turkey



Un-fired

A1→ Nepal

B2→ India

Kilkis → Greece

Koupa → Brazil

S1 → Nigeria

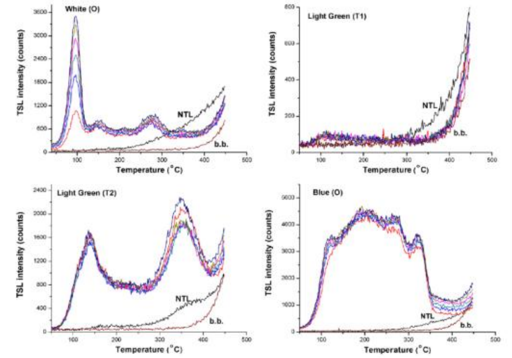
S2 → Turkey

Provenance vs Universality

- However, there are numerous cases of materials which exhibit luminescence properties that are not of prevalent values. On the contrary, specific properties show strong dependence on the geographical origin as well as on the provenance of each material. In all those cases, TL could be effectively used in order to identify their provenance. Some among these materials are the following:

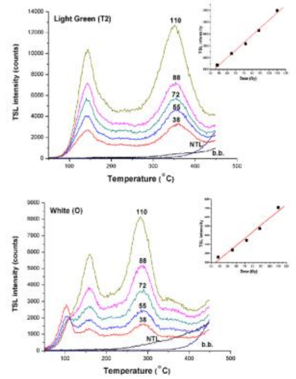
1. Obsidian (*Goksu & Turetken, PACT 3, 356, 1979; Polymeris et al., MAAJ 10 (4), 83 – 91, 2010*)
2. Turquoise (*Crespo-Feo et al., Rad. Meas. 45, 749–752 2010; Subedi et al., MAAJ 10 (4), 61 – 67, 2010*)
3. Archaeological glass (*Galli et al., Appl. Phys. A 79, 253–256, 2004; Sfampa et al., LAIS 2 Conference, Lisbon, 2012*)

Ancient Glass technology; Color



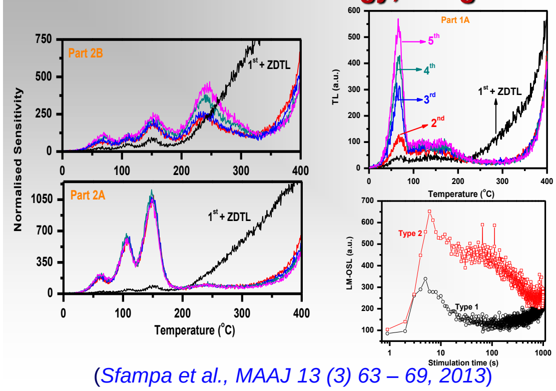
(*Zacharias et al., J. Non Crys. Sol. 354, 761– 767, 2008*)

Ancient Glass technology; firing atm



(*Zacharias et al., Optical Materials 30 (2008) 1127–1133*)

Ancient Glass technology; firing atm



(*Sfampa et al., MAAJ 13 (3) 63 – 69, 2013*)

Dealing with two major drawbacks

Time-consuming chemical pre-treatment in dark conditions

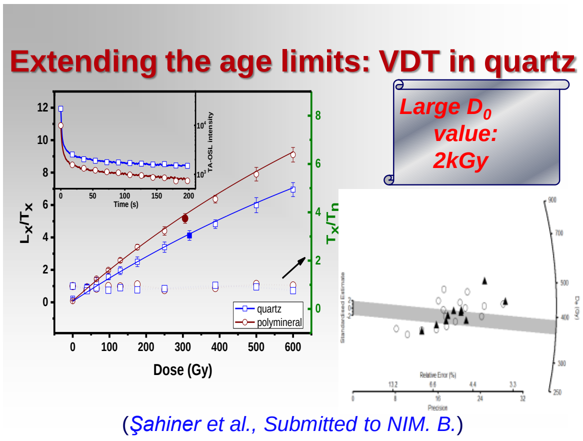
+

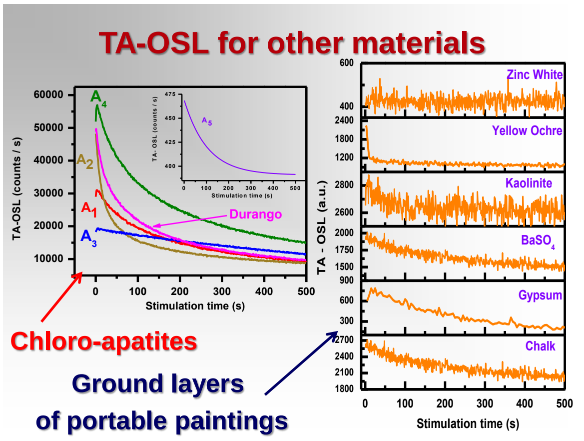
Relatively low upper age limit

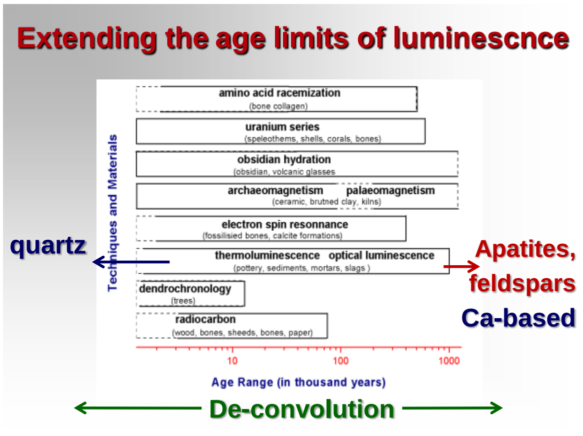
↓

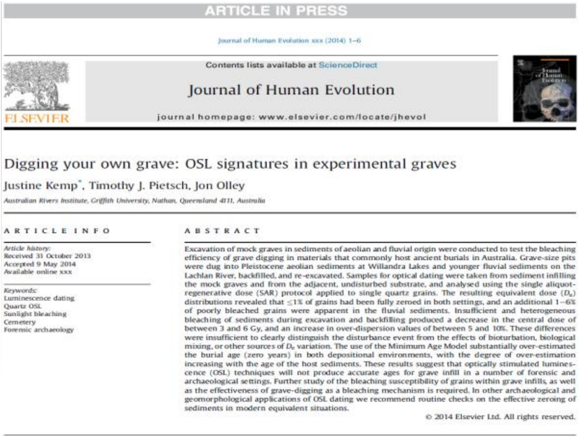
New dating protocols by luminescence

(*Şahiner et al., Radiation Measurements 68 (2014) 14-22.*)





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Digging your own grave: OSL signatures in experimental graves

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ABSTRACT

Excavation of mock graves in sediments of aeolian and fluvial origin were conducted to test the bleaching efficiency of grave digging in materials that commonly host ancient burials in Australia. Grave-size pits were dug into Pleistocene aeolian sediments at Willandra Lakes and younger fluvial sediments on the Lachlan River, backfilled, and re-excavated. Samples for optical dating were taken from sediment infilling the mock graves and from the adjacent, undisturbed substrate, and analysed using the single aliquot-regenerative dose (SAR) protocol applied to single quartz grains. The resulting equivalent dose (D_e) distributions revealed that ≤1% of grains had been fully zeroed in both settings, and an additional 1–6% of poorly bleached grains were apparent in the fluvial sediments. Insufficient and heterogeneous bleaching of sediments during excavation and backfilling produced a decrease in the central dose of between 3 and 6 Gy, and an increase in over-dispersion values of between 5 and 10%. These differences were insufficient to clearly distinguish the disturbance event from the effects of bioturbation, biological mixing, or other sources of D_e variation. The use of the Minimum Age Model substantially over-estimated the burial age (zero years) in both depositional environments, with the degree of over-estimation increasing with the age of the host sediments. These results suggest that optically stimulated luminescence (OSL) techniques will not produce accurate ages for grave infill in a number of forensic and archaeological settings. Further study of the bleaching susceptibility of grains within grave infills, as well as the effectiveness of grave-digging as a bleaching mechanism is required. In other archaeological and geomorphological applications of OSL dating we recommend routine checks on the effective zeroing of sediments in modern equivalent situations.

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