A comparative luminescence study on several limestone samples of various origins

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Abstract

Limestone is a sedimentary rock composed largely of the minerals calcite and aragonite, which are different crystal forms of calcium carbonate ($CaCO_3$). Many limestones are composed from skeletal fragments of marine organisms such as coral or foraminifera. Limestone makes up about 10% of the total volume of all sedimentary rocks.

Limestone is very common in architecture, especially in Europe and North America. Many landmarks across the world, including the Great Pyramid and its associated complex in Giza, Egypt, are made of limestone.

Dating of monuments constructed by limestones as well as sedimentary rocks consisting of limestones is restricted to applying thermoluminescence (TL) (Liritzis, 2000, 2010, 2011, Liritzis et al., 1997, 2008) since there is a strong disbelief regarding whether limestone does show useful optically stimulated luminescence (OSL, Galloway, 2002).

In the present work several properties of different limestone samples of various origins are studied and compared. Subsequent collection, the samples were kept in the dark and measured after several months using mostly TL. Several properties, such as the response to artificial beta irradiation, the shape of TL curves and the number of the TL peaks, repeatability, sensitivity changes, anomalous fading were studied. There is also an attempt to retrieve OSL signal from the limestone samples; while natural OSL is almost flat and useless for dating, OSL following artificial irradiation indicates a decaying shape. The structure of all samples was studied by XRD. For some among the samples the XRD showed the presence of quartz minerals, which would yield the 110°C peak in TL and the fast component in OSL, characteristics identifiable in the curves.

Introduction

Since limestone is one of the most used building material in the ancient word, it is of great importance to reevaluate and enrich the old dating protocols by exploiting properties of the material that there were not possible to exploit using the old instrumentation. In a first attempt, eight samples were chosen from different archaeological sites in the Eastern Mediterranean basin, samples which were already dated in previous publications, based on their geochemical content, four of them consist of traces of quartz (Table 1), due to compare the TL signals and to evaluate the OSL signals in order to be used in the dating protocols and study their dose response.

Table 1: Code names and origin of the samples, XRD analysis results and component resolved sensitivity changes for the TL/OSL signals.

A/A	CODE/NAME	ORIGIN	MONUMENT	Quartz Content	Geochemical content	Sensitivity changes TL (% per cycle)	Sensitivity changes OSL (% per cycle)
1	MTL3 (Liritzis, 1994)	Mycenae, Greece	Mycenae, Greece	Traces (<0.5%)	99 % Calcium Carbonate	1%	<1% for the fast component
2	L.LIG (Theocharis, et al 1996)	Ligourio, Hellinikon, Argolid	pyramidal structures	-	>99 % Calcium Carbonate	Ongoing measurements	Ongoing measurements
3	Koumoula (Liritzis et al, 2015)	Koumoula hill, Parnassus Mountain, Delphi, Greece	Koumoula site, Parnassus Mountain	-	>99 % Calcium Carbonate	11% for the 275 °C TL peak, <5% for the 350 °C TL peak	<0.7% for the fast component
4	BTL1 (Liritzis, 1994, Liritzis, et al. 2010)	Fichtia near Mycenae, Peloponnese, Greece	megalithic block house	3%	>99 % Calcium Carbonate	Ongoing measurements	Ongoing measurements
5	SETI I (Liritzis and Vafiadou, 2015)	Egypt	Seti's I Temple, Abydos	Traces (<0.5%)	86% Calcium Carbonate, 7% ankerite, <7% montmorilonire, halite (<0.5%)	12% for the 325 °C TL peak	Ongoing measurements
6	VT3	Egypt	Valley Temple, Giza	Traces (<0.5%)	~90 % Calcium Carbonate, > 9.5% halite, dolomite (<0.5%)	13% for the 240 °C TL peak, <3% for the 310 °C TL peak	~2% for the fast component
7	VT7	Egypt	Valley Temple, Giza	-	99 % Calcium Carbonate	8% for the 240 °C TL peak	<0.7% for the fast component
8	ITH-4	Ithaca, Greece	School of Homer	Ongoing measurements		Ongoing measurements	~1.5% for the fast component

TL Measurements

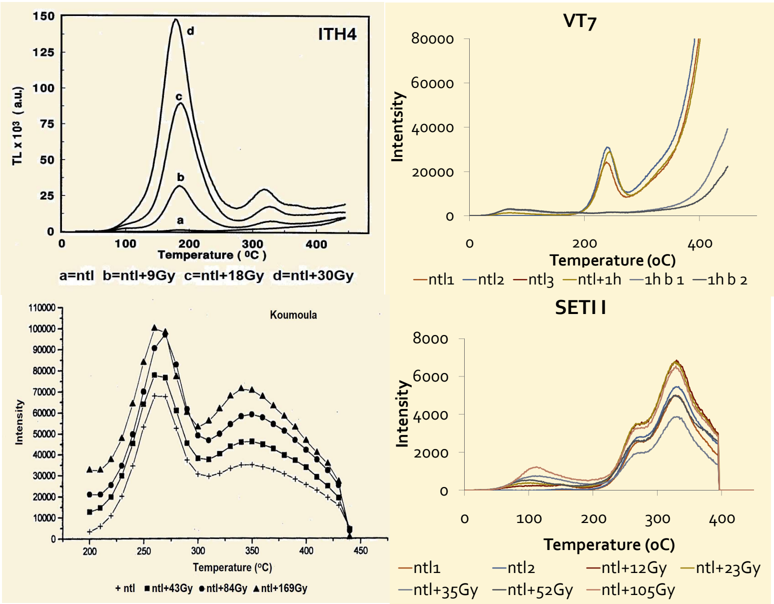

Fig. 1: TL glow curves of the natural TL signal (ntl), the additive dose procedure (ntl + extra dose) and the bleached sample (hb) for a selection of samples.

OSL Measurements

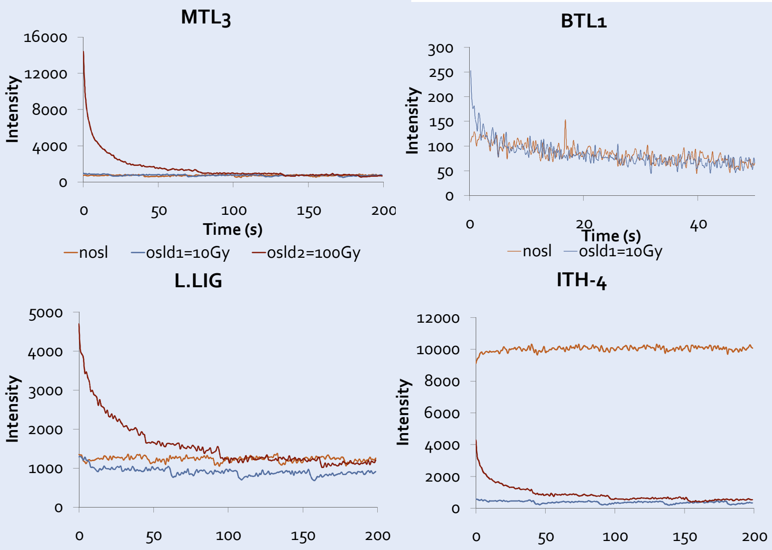

Fig. 2: OSL decay curves of the natural OSL signal (nosl), the additive dose procedure (nosl + extra dose) for a selection of samples.

Conclusions:

The diversity in the TL glow curve shapes and the pattern of the sensitivity changes in the TL signal is obvious, even for limestone samples in close proximity.

The natural OSL signal in the samples is not useful for OSL dating, since a fast component is missing from the NOSL signal even when there is a small presence of quartz. On the contrary, following artificial irradiation in the laboratory, a fast component is prominent. Moreover, the OSL signal seems to yield a straightforward dependence on the given dose.

Both aforementioned features of the luminescence signal could be attributed to the different contents of calcite and aragonite inside the samples.

References:

Galloway, R.B., 2002. Does limestone show useful optically stimulated luminescence?, *Ancient TL*, 20, 1-7.

Liritzis, I., Guilbert, P., Foti, F. and Schvoerer, M., 1997. The Temple of Apollo (Delphi) strengthens new thermoluminescence dating method, *Geoarchaeology International*, 12(5), 479-496.

Liritzis, I, Kitis, G., Galloway, R.B, Vafiadou, A., Tsirliganis, N. and Polymeris., G., 2008. Probing luminescence dating of archaeologically significant carved rock types, *Mediterranean Archaeology & Archaeometry*, 8(1), 61-79.

Liritzis, I, Drivaliari, A., Polymeris, G.S. and Katagas, Ch., 2010. New quartz technique for OSL dating of limestones, *Mediterranean Archaeology & Archaeometry*, Vol.10, No.1, 81-87.

Liritzis, I., Aravantinos, V., Polymeris, G.S., Zacharias, N., Fappas, I., Agiamarniotis, G., Sfampa, I.K., Vafiadou, A. and Kitis, G., 2015. Witnessing prehistoric Delphi by Luminescence dating, *Comptes Rendus PALEVOL*, Vol.14, 219-232.

Liritzis, I., 1994. A new dating method by thermoluminescence of carved megalithic stone building, *Comptes Rendus (Academie des Sciences)*, t. 319, serie II, 603-610.

Liritzis, I., 2000. Advances in thermo- and opto- luminescence dating of environmental materials (sedimentary deposits): part II: applications, *GLOBALNEST*, 2(1), 29-49.

Liritzis, I., 2010. Strofilas (Andros Island, Greece): new evidence for the cycladic final Neolithic period through novel dating methods using luminescence and obsidian hydration, *Journal of Archaeological Science*, 37, 1367–1377.

Liritzis, I., 2011. Surface dating by luminescence: An Overview, *Geochronometria*, 38(3), 292-302.

Liritzis, I. and Vafiadou, A., 2015. Surface luminescence dating of some Egyptian monuments, *Journal of Cultural Heritage*, 16, 134-150

Theocaris, P., Liritzis, I., Lagios, E. and Sampson, A., 1996. Geophysical prospection and archaeological test excavation and dating in two Hellenic pyramids, *Surveys in Geophysics*, 17, 593-618.

7th Balkan Symposium on Archaeometry

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