

## High-resolution luminescence speleothem records from Savi Cave, Trieste, NE Italy

Diana STOYKOVA<sup>1</sup>, Yavor SHOPOV<sup>1\*</sup>, Ugo SAURO<sup>2</sup>, Andrea BORSATO<sup>3</sup>, Franco CUCCHI<sup>4</sup> & Paolo FORTI<sup>5</sup>

<sup>1</sup>University Center for Space Research, Faculty of Physics, University of Sofia, 1164 Sofia (Bulgaria)

<sup>2</sup>Dipartimento di Geografia, Università di Padova, Via del Santo 26, I-35123 Padova

<sup>3</sup>Museo Tridentino di Scienze Naturali, Via Calepina 14, I-38100 Trento

<sup>4</sup>Dipartimento di Scienze Geologiche, Ambientali e Marine, Università di Trieste, Via Weiss 2, I-34127 Trieste

<sup>5</sup>Dipartimento di Scienze della Terra e Geologico-Ambientali, Università di Bologna

\*Corresponding author e-mail: [YYShopov@Phys.Uni-Sofia.BG](mailto:YYShopov@Phys.Uni-Sofia.BG)

**SUMMARY** - High-resolution luminescence speleothem records from Savi Cave, Trieste, NE Italy - We measured three luminescent records from the sample SV1, a stalagmite from Savi Cave (Trieste karst, Italy). The longest panoramic record (having the lowest resolution from the records) is a proxy of the solar influence on the climatic system and covers last  $14430 \pm 176$  years. The step of the record varies from 1.1 to 12.7 years. First composite record, which consists of 81000 data points, is compiled of 39 overlapping scans. It covers the last  $5005 \pm 140$  years. The time step of the record varies from 9.9 days to 33.9 days. The highest resolution record covers last  $2028 \pm 100$  years and allows precise determination of growth rate of the stalagmite. It consists of 40106 data points compiled of 16 overlapping scans. Its time step varies from 15.6 days to 19.9 days. We made a reconstruction of the annual growth rate variations for the last 2028 years, which represents annual precipitation for this region.

**RIASSUNTO** - *Record di luminescenza ad alta risoluzione di uno speleotema della Grotta Savi, Trieste, Italia* - Si presentano tre record di luminescenza della stalagmite SV1 proveniente dalla Grotta Savi nel Carso di Trieste. Il record panoramico più lungo (e con la risoluzione più bassa) è un dato proxy dell'influenza solare sul clima locale, e copre gli ultimi  $14430 \pm 176$  anni, con una risoluzione che varia da 1,1 a 12,7 anni. Il primo record composito, costituito da 81000 dati assemblati da 39 scansioni sovrapposte, copre gli ultimi  $5005 \pm 140$  anni con una risoluzione che varia da 9,9 a 33,9 giorni. Il record a maggior risoluzione, costituito da 40106 dati assemblati da 16 scansioni sovrapposte, copre gli ultimi  $2028 \pm 100$  anni con una risoluzione che varia da 15,6 a 19,9 giorni, e consente di determinare con precisione il tasso di crescita annuale della stalagmite. In base a questo record si è ricostruito il tasso di crescita annuale della stalagmite che rappresenta il valore di precipitazione media annuale per l'area in esame.

**Key words:** luminescence, speleothems, solar insolation, paleoclimate, Trieste Karst

**Parole chiave:** luminescenza, speleotemi, insolazione, paleoclima, Carso Triestino

### 1. INTRODUCTION

Calcite speleothems usually display luminescence produced by calcium salts of humic and fulvic acids derived from soils above the cave (Shopov 1989; White & Brennan 1989). These acids are released by the roots of living plants and by the decomposition of dead vegetative matter. Root release is modulated by the visible solar radiation via photosynthesis, while rates of decomposition depend exponentially on soil temperature. Soil temperature depends mainly on solar infrared and visible radiation in the case that the cave is covered only by

grass or upon temperature in the case that the cave is covered by forest or bush (Shopov *et al.* 1994). In the first case the zonality of luminescence can be used as a proxy of solar insolation (Shopov & Dermendjiev 1990) and in the second case it can be used as a paleotemperature proxy.

The luminescent index has high resolution as in the case when the step of a record is less than one month the signal contains mainly climatic modulation. But in the case of the step bigger than one year, the climatic modulation of signal is in the range of the experimental error. And the luminescent record turns to proxy of solar insolation.

## 2. EXPERIMENTAL PART

We used impulse photography of phosphorescence (Shopov & Grynberg, 1985) to perform Luminescent Zonal Analysis (LZA) of the speleothem. The equipment consists of an UV-source (impulse Xe-lamp emitting in the entire UV and visible spectra); photo-camera with a shutter delayer, which opens the shutter several thousands of second after flash emission ends. Obtained pictures are scanned by precise professional scanner EPSON 1650 with step of 8  $\mu\text{m}$ . We chose a string with width of 200  $\mu\text{m}$  from scans and transform the string into luminescent curve by a computer program specially made for this aim. The program integrates pixels contained in a window of 20 x 200  $\mu\text{m}$  that is moving along the string with step of 10  $\mu\text{m}$ . This digital procedure is equal to the scanning of negatives by a scanning microdensitometer (PDS or Joyce Loebel 6). So this way is obtained a record of distribution of the optical density luminescence (decimal logarithm of the intensity of luminescence) of the speleothem along it's growth axis. It is linearly proportional to the concentration of the luminescent compounds in the calcite. Such records are proxies of the solar radiation or paleotemperature in the past if all these compounds are only organic (Shopov 1997).

Luminescent records may be transformed into luminescent time series by using absolute dating.

High-resolution fluorescence records are obtained using LLMZA analysis equipment described in (Shopov 1987) with excitation wavelength from 200 to 240 nm.

## 3. RESULTS AND DISCUSSION

Studied sample is a 27 cm long, 5 mm thick polished section of an active calcite stalagmite along its growth axis. It has been removed from Grotta Savi, in the Trieste Karst, NE Italy, and dated by means of 18 U/Th MC-ICPMS analyses (Tab. 1; cfr. Borsato *et al.* 2004). The whole stalagmite consists of translucent, columnar calcite, and is characterized by visible growth laminae.

We composed 3 paleoluminescence records from the measured luminescence of this stalagmite. After identification of positions of U/Th dates along the luminescent scans we transformed them into luminescent time series.

The longest luminescent record (Fig. 1) covers the last  $14430 \pm 176$  years ( $2\sigma$  error) with a time step from 1.11 to 12.70 years. It suggests higher soil temperature from 8.7 to 4.6 ka BP.

This luminescent record is obtained from the panoramic scan of the sample (Fig. 2). This photo is a negative photograph of the integral phosphorescence of the stalagmite under excitation by impulse Xe-lamp

Tab. 1 - Results of U/Th MC-ICPMS analyses (data from Borsato *et al.* 2004).

Tab. 1 - Risultati delle analisi isotopiche U/Th MC-ICPMS (dati in Borsato *et al.* 2004).

Sample	distance from top	Age corrected
	mm	ka ( $\pm 2\sigma$ )
SV1-B1	14.5	1.325 $\pm 0.13$
SV1-21	18.5	1.838 $\pm 0.10$
SV1-22	27.5	2.496 $\pm 0.13$
SV1-B4	52.5	4.452 $\pm 0.17$
SV1-23	62.3	4.795 $\pm 0.13$
SV1-B5	83.8	5.709 $\pm 0.13$
SV1 122	103.0	7.587 $\pm 0.17$
SV1-B6r	127.0	8.337 $\pm 0.28$
SV1-172	172.0	9.375 $\pm 0.19$
SV1-207	207.0	10.584 $\pm 0.20$
SV1-24	214.0	10.676 $\pm 0.23$
SV1-25	215.0	10.670 $\pm 0.21$
SV1-26	230.0	13.493 $\pm 0.26$
SV1-238	238.0	14.613 $\pm 0.20$
SV1-27	239.2	14.642 $\pm 0.22$
SV1-249	249.0	15.484 $\pm 0.43$
SV1-28	250.0	15.347 $\pm 0.20$
SV1-258	257.5	16.799 $\pm 0.51$

in the entire UV and visible spectra. So darker parts of the image correspond to brighter luminescence, higher concentration of humic and fulvic acids, and to warmer climate (Shopov 1997). Large number of very fine hiatuses is observed in the sample under microscope.

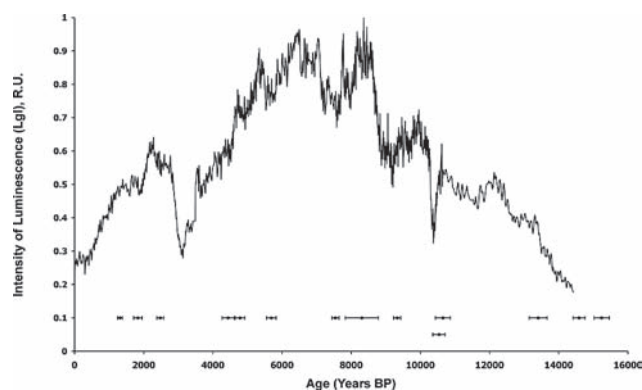


Fig. 1 - Luminescent composite record from SV1 stalagmite, covering the last  $14430 \pm 176$  years, the step of the record varies from 1.11 to 12.7 years.

Fig. 1 - Record composito di luminescenza della stalagmite SV1, che copre gli ultimi  $14430 \pm 176$  anni. La risoluzione del record varia da 1,11 a 12,7 anni.

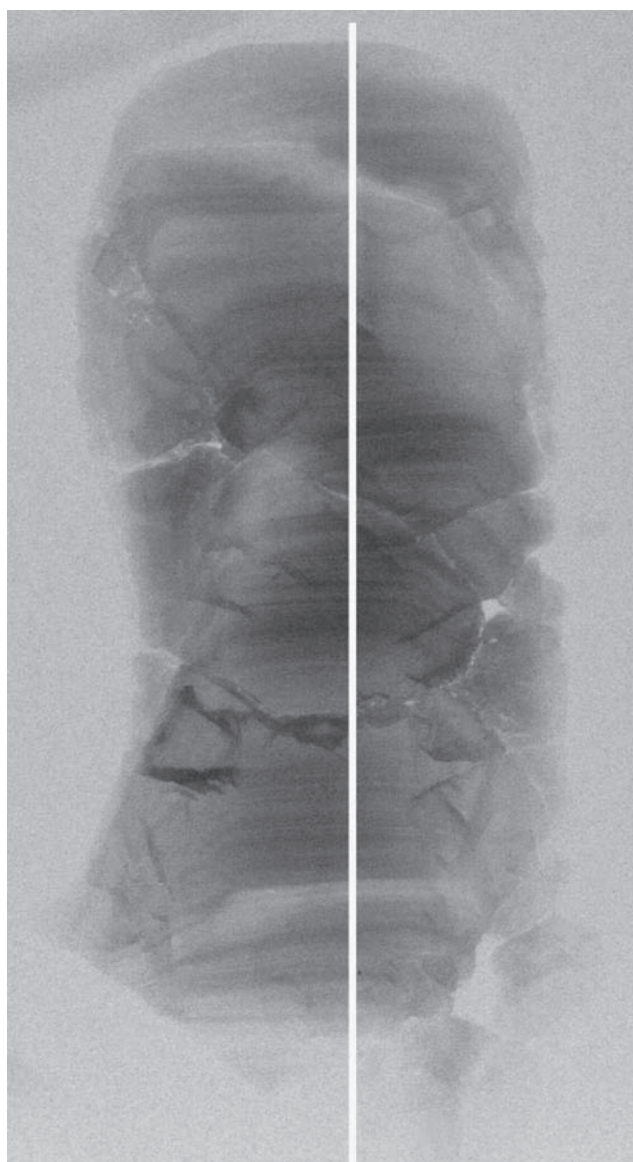


Fig. 2 - Negative photograph of the integral phosphorescence of the stalagmite from Savi cave under excitation by impulse Xe-lamp, in the entire UV and visible spectra. The white line shows one of the scanning paths.

*Fig.2 - Fotografia negativa della fosforescenza della stalagmite SV1 sotto eccitazione di impulsi di lampada allo Xe, nell'intero spettro UV e visibile. La linea bianca rappresenta una delle scansioni effettuate.*

This suggests that they may be caused by temporary change in the feed water saturation. It can become aggressive from time to time (due to bigger saturation time at lower temperatures). So speleothem will be dissolved rather than growing during such episodes. This mechanism looks more reliable than lack of feed water for few years. There are several much thicker hiatuses in the sample, which are visible with necked eye due to precipitation of dust or clay on the surface of the speleothem during longer periods without growth.

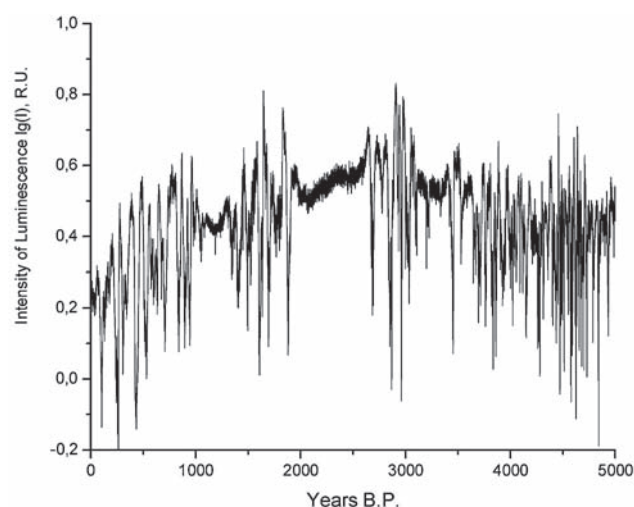


Fig. 3 - The composite SV1 stalagmite record consisting of 81000 data points compiled with 39 overlapping scans. It covers the last  $5002 \pm 140$  years. The time step of the record varies from 9.9 days to 33.9 days.

*Fig. 3 - Record composito della stalagmite SV1 costituito da 81000 dati assemblati da 39 scansioni sovrapposte. Il record copre gli ultimi  $5005 \pm 140$  anni con una risoluzione che varia da 9,9 a 33,9 giorni.*

As a result of a strong sea influence the  $\delta^{18}\text{O}$  record from Savi (Borsato *et al.* 2004) exhibits distinct anti-correlation with the paleotemperature as represented by the luminescent record. The  $\delta^{13}\text{C}$  record exhibits even more distinct anti-correlation with the luminescence record because of the fact that higher soil temperature lead to higher production of  $\text{CO}_2$  by decomposition of the humus. This  $\text{CO}_2$  has lower concentration of  $\delta^{13}\text{C}$  relatively to the atmospheric one. For that reason more intensive production of  $\text{CO}_2$  leads to lower concentration of  $\delta^{13}\text{C}$  in the soil air and in the soil carbonate solutions precipitating calcite speleothems in the caves. It means, that production of  $\text{CO}_2$  from decomposition of the soil (which is depleted to  $\delta^{13}\text{C}$ ) dominates over emission of  $\text{CO}_2$  in the soil from respiration of plants. Respiratory  $\text{CO}_2$  is always enriched with  $\delta^{13}\text{C}$ . This isotopic behavior is representative for regions covered by grass (as the case of Grotta Savi). Stable isotope records from the same sample (Borsato *et al.* 2004) have a systematic lag of about 500 years relatively to the paleoluminescence record. This suggests that  $\delta^{18}\text{O}$  record represent climatic response to the solar forcing (recorded by the luminescent record), while  $\delta^{13}\text{C}$  record represents the ecosystem response to the solar forcing.

We prepared also a composite record consisting of 81000 data points which has been compiled from 39 overlapping scans (of 4800 data points each). It covers the last last  $5005 \pm 140$  years ( $2\sigma$ ) (the upper 80 mm of the sample) with several hiatuses. The resolution of the record varies from 9.9 days to 33.9 days (Fig. 3).

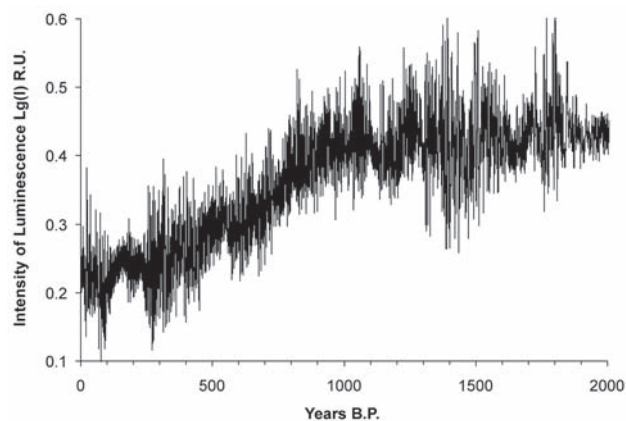


Fig. 4 - The highest resolution composite record of SV1 covers the last  $2028 \pm 100$  years. It consists of 40106 data points compiled of 16 overlapping scans. Its time step varies from 15.6 days to 19.9 days.

*Fig. 4 - Il record composito a maggior risoluzione della stalagmite SV1 copre gli ultimi  $2028 \pm 100$  anni ed è costituito da 40106 dati assemblati da 16 scansioni sovrapposte. La risoluzione varia da 15,6 a 19,9 giorni.*

The highest resolution composite record covers the last  $2028 \pm 100$  years ( $2\sigma$ ) (the upper 20 mm of the sample) with several hiatuses. This composite record consists of 40106 data points and has been compiled of 16 overlapping scans (of 4800 data points each). It has resolution from 15.6 days to 19.9 days (Fig. 4). It allows precise measurements of the annual growth rate of the speleothem. It varies from 2.2 to  $45.4 \pm 0.5$  microns/year from its mean value of 6.36 microns/year.

We used this record to measure a long record of the annual growth rate of the speleothem. It covers 2028 years taking into account hiatuses in the record (Fig. 5). This record represents mainly the annual rainfall at

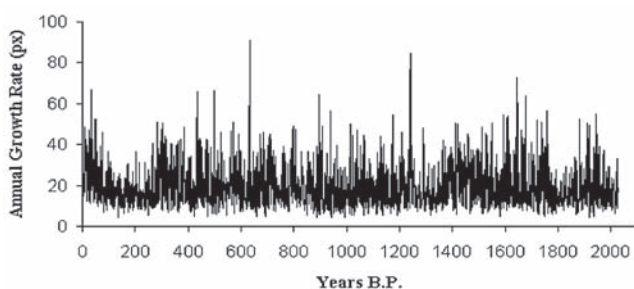


Fig. 5 - The annual growth rate of SV1 stalagmite. The mean value is 6.36 microns/year and it varies from 2.2 to  $45.4 \pm 0.5$  microns/year. This record represents mainly the annual rainfall at the cave site.

*Fig. 5 - Il tasso di crescita annuale della stalagmite SV1, che rappresenta principalmente la precipitazione media annua al di sopra della cavità. Il valore medio è di 6.36 micron/anno e varia da 2,2 a  $45,4 \pm 0,5$  micron/anno.*

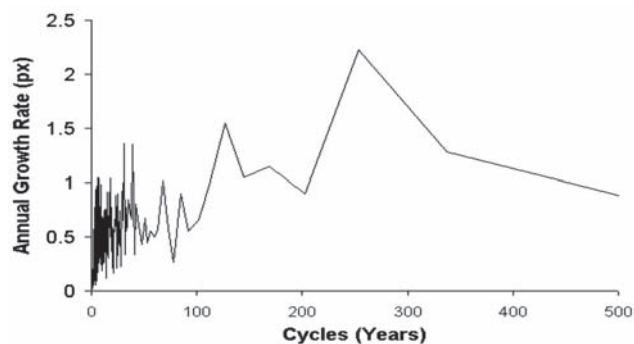


Fig. 6 - A periodogramme of the annual growth rate of SV1 stalagmite from cave Savi. It represents the cycles of the annual rainfall in the region of Trieste, Italy.

*Fig. 6 - Periodogramma del tasso di crescita annuale della stalagmite SV1 della Grotta Savi che rappresenta la ciclicità delle precipitazioni annuali nella regione di Trieste.*

the cave site. More precipitation leads to dissolving of more  $\text{CaCO}_3$  by the carbonate rocks and its precipitation in cave speleothems.

We used the special real-space periodogramme analysis algorithm described in Shopov *et al.* (2002) to calculate the intensity of the cycles of the annual precipitation at the cave site. Resulting periodogramme shown on figure 6 demonstrates that the strongest cycle of the annual rainfall in the region of Trieste, Italy, is with duration of about 300 years.

#### 4. CONCLUSIONS

Stable isotope records from the same sample have a systematic lag of about 500 years relatively to the paleoluminescence record. This suggests that  $\delta^{18}\text{O}$  record represents climatic response to the solar forcing (recorded by the luminescent record), while  $\delta^{13}\text{C}$  record represents the ecosystem response to the solar forcing.

Strongest cycle of the annual rainfall in the region of Trieste, Italy, is with duration of about 300 years.

#### ACKNOWLEDGEMENTS

This research has been funded by COFIN 2000 “Ricostruzione dell’evoluzione climatica e ambientale ad alta risoluzione da concrezioni di grotta lungo una traversa N-S in Italia con particolare riferimento all’intervallo Tardiglaciale-attuale”, coordinated by U. Sauro

#### REFERENCES

Borsato A., Cucchi F., Frisia S., Miorandi R., Paladini M., Piccini L., Potleca M., Sauro U., Spötl C., Tuccimei P.,

- Villa I. & Zini L., 2004 - Ricostruzione climatica degli ultimi 17.000 anni da una stalagmite della Grotta Savi (Trieste, Italia) (in this volume).
- Shopov Y.Y., 1987 - Laser Luminescent MicroZonal Analysis- A New Method for Investigation of the Alterations of the Climate and Solar Activity during Quaternary. In: "Problems of Karst Study of Mountainous Countries" (Proceedings of the International Symposium of Speleology 5-1 2 Oct. 1987), MEISNIEREBA, Tbilisi: 228-232.
- Shopov Y.Y., 1989 - Spectra of Luminescence of Cave Minerals. *Expedition Annual of Sofia University*, 3-4: 80-85.
- Shopov Y.Y. & Grynberg M.A., 1985 - A New Method for Direct Photography of Luminescence. *Exp. Ann. Sofia Univ.*, 1: 139-145.
- Shopov Y.Y. & Dermendjiev V., 1990 - Microzonality of Luminescence of Cave Flowstones as a New Indirect Index of Solar Activity. *Comptes rendus de l'Academie bulgare des Sci.*, 43, 7: 9-12.
- Shopov Y.Y., Ford D.C. & Schwarcz H.P., 1994 - Luminescent Microbanding in speleothems: High resolution chronology and paleoclimate. *Geology*, 22: 407-410.
- Shopov Y.Y., 1997 - Luminescence of Cave Minerals. In: Hill C. & Forti P. (eds), *Cave Minerals of the world*. 2<sup>nd</sup> edition, NSS, Huntsville, Alabama, USA: 244-248.
- Shopov Y.Y., Stoykova D.A., Tenchov G., Tsankov L., Sanambria M., Georgiev L.N. & Ford D.C., 2002 - Correlation Between Luminescent Speleothem Records of Solar Insolation and Paleotemperature Records. In: Daoxian Y. & Cheng Z. (eds), *Karst Processes and the Carbon Cycle*. Geological Publishing House, Beijing, China, IGCP379: 136-144.
- White W.B. & Brennan E.S., 1989 - Luminescence of speleothems due to fulvic acid and other activators. *Proceedings of 10<sup>th</sup> International Congress of Speleology*, 13-20 August 1989, Budapest, 1: 212- 214.