

Luminescence of Speleothems

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SUMMARY - *Luminescence of Speleothems* - This paper discusses the advance of the speleothem luminescence research. Potential, resolution and limitations of high resolution luminescence speleothem proxy records of Paleotemperature, Solar Insolation, Solar Luminosity, Glaciations, Sea Level advances, Past Precipitation, Plants Populations, Paleosoils, Past Karst Denudation, Chemical Pollution, Cosmic Rays Flux variations, Cosmogenic Isotopes production and Supernova Eruptions in the Past, Advances of Hydrothermal Waters, and Tectonic Uplift are discussed. It is demonstrated that speleothems allow extremely high resolution (higher than in any other paleoclimatic terrestrial archives) and long duration of records. Some speleothems can be used as natural climatic stations for obtaining of quantitative proxy records of Quaternary climates with annual resolution.

RIASSUNTO - *La luminescenza degli speleotemi* - Il presente lavoro discute lo stato della ricerca degli studi di luminescenza negli speleotemi. In particolare vengono discusse le potenzialità, la risoluzione e limitazioni di record di luminescenza ad alta risoluzione, che possono essere utilizzati come proxy data di: temperatura, insolazione solare, luminosità solare, fluttuazioni glaciali e del livello marino, precipitazioni, vegetazione, evoluzione del suolo, denudamento carsico, inquinamento chimico, variazioni del flusso di raggi cosmici, produzione di isotopi cosmogenici, esplosioni di supernove, influenza di acque idrotermali e sollevamenti tettonici. È dimostrato che gli speleotemi consentono ricostruzioni ad alta risoluzione (più alta che in qualunque altro archivio paleoclimatico terrestre) che coprono intervalli temporali molto lunghi. Alcuni speleotemi particolari possono essere utilizzati quali stazioni naturali per ottenere dati proxy a risoluzione annuale del clima del Quaternario.

Key words: luminescence, speleothem records, paleoclimate, solar insolation

Parole chiave: luminescenza, speleotemi, paleoclima, insolazione

1. INTRODUCTION

Luminescence is the property of cave minerals most sensitive to depositional conditions (Tarashtan 1978). Therefore it can be used for determining these conditions.

Many speleothems exhibit luminescence when exposed to high energy beams. In dependence of the excitation source there are specific kinds of luminescence: "photoluminescence" (excited by UV and other light sources), "X-ray luminescence" (by x-rays), "Cathodoluminescence" (by electron beam), "Thermoluminescence" (by heat), "Candoluminescence" (by flames) and "triboluminescence" (by crushing). Different types of excitation may excite different luminescent centres- electron defects of the crystal lattice: admixture ions substituting ions in the crystal lattice or incorporated in cavities of that lattice; inclusions of other minerals; fluid inclusions, molecules, ions or radicals adsorbed

inside of the lattice. Some or all of them may exist in a single speleothem (Shopov 1997). Minerals contain many admixtures. Usually several centres activate luminescence of the sample and the measured spectrum is a sum of the spectra of two or more of them.

Absorption of excitation energy by a mineral leads to rising of electrons from ground state to an excited level. Sooner or later these electrons fall down to a lower level while emitting light. If the emission proceeds only during the excitation than it is called "fluorescence", if it proceeds later (usually seconds or minutes) than it is called "phosphorescence". In the later case falling of electrons from the excited state proceeds through intermediate levels (thus taking more time), so the energy of the emitted light is less than the energy of fluorescence (i.e. colour of the emitted light is shifted to red, Fig. 1). Some luminescent centres produce only fluorescence, but other both fluorescence and phosphorescence.

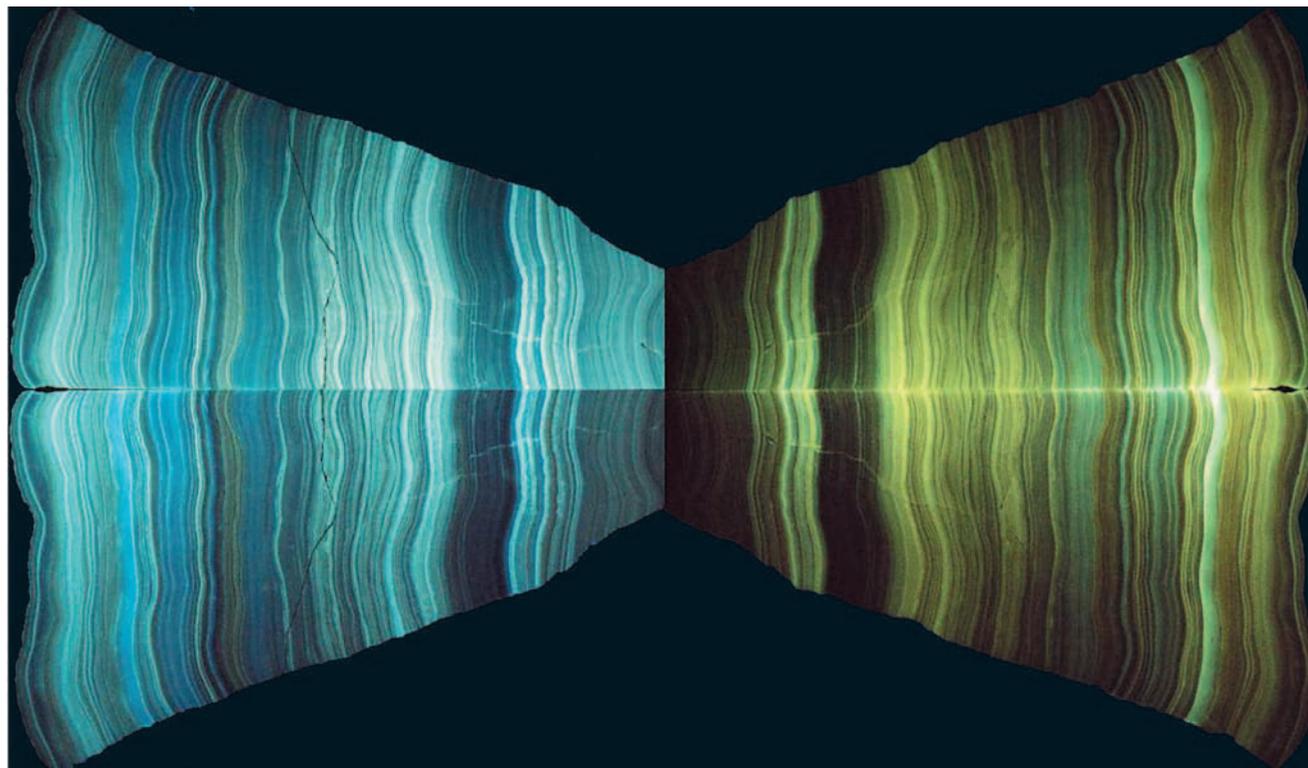


Fig. 1 - Luminescence of organics in a 7 cm long polished section of an infiltration cave calcite flowstone. Fluorescence (left) and phosphorescence (right). Variations of the colour of luminescence of organics are due to variations of the plant's society growing over the cave during transitions from glacial to interstadial climate.

Fig. 1 - Luminescenza dovuta a materia organica in una sezione lucida di colata calcitica. Fluorescenza (sinistra) e fosforescenza (destra). Le variazioni di colore nella luminescenza sono dovute alle variazioni delle associazioni vegetali al di sopra della cavità testimoniando la transizione da clima glaciale a interstadiale.

The type of luminescent centres determines the colour of luminescence. Colour may vary with changes of the excitation sources, because they may excite different luminescent centres existing in the mineral. Every luminescent center has its own excitation spectra, temperature dependence and conditions of excitation. One colour of luminescence sometimes may be produced by a single luminescent center or by combination of two or several centres.

1.1. Origin of luminescence of Cave Minerals

Most known luminescent centres in calcite are inorganic ions of Mn, Tb, Er, Dy, U, Eu, Sm and Ce (Tarashtan 1978; Shopov 1986; Shopov *et al.* 1988a). Luminescence of minerals formed at normal cave temperatures (0-40 °C) is due mainly to molecular ions and sorbed organic molecules (Fig. 1). Luminescence of uranyl-ion is also very common in such speleothems. Before using a speleothem for any paleoenvironmental work it is necessary to determine that all luminescence of the sample is due to organics. This requires the use of a Raman or luminescence spectrometer, plus an Electron Spin Resonance (ESR) spectrometer or chromatograph (Shopov 1989a, 1989b). Lasers

and Raman spectrometers used for measurements of luminescent spectra allow also determination of the luminescent mineral in the speleothem, because the narrow Raman lines appearing in luminescence spectra at high resolution scanning are characteristic for different minerals (Tab. 1).

Easiest and most efficient method of excitation is irradiation by UV light sources producing photoluminescence and when luminescence is usually spoken about it is with this kind of excitation in mind. Visual Luminescent Analysis (VLA) has been widely used in caves, usually with a photographic flash but also with portable UV lamps with short wave UV (SWUV) and long wave UV (LWUV).

It is known that almost 50 cave minerals have the capacity for exhibiting luminescence, but only 17 had actually observed to be luminescent in speleothems so far.

2. MEASUREMENTS AND PHOTOGRAPHY OF LUMINESCENCE

Luminescence spectra of cave minerals have been measured by means of exciting them with nitrogen

Tab. 1 - Origin of luminescence of Cave Minerals

* - luminescence of Fe³⁺, Pb²⁺ and Rare earth elements in calcite is well described in Tarashtan 1978, Shopov 1986 and Shopov *et al.* 1988, so is not included in the table;

** - luminescence of Mn²⁺ and Rare earth elements in aragonite is well described in Tarashtan 1978 Shopov, 1986 and Shopov *et al.* 1988, so is not included in the table;

12 - Spectra of this luminescence is attributed by Tarashtan *et al.* 1978 to luminescence of clusters of the mineral magursilite sorbed in calcite;

14 - also in Shopov *et al.* 1988; White & Brennan 1989;

15 - hydrocarbons present only in fluid inclusions in calcite, formed 1 km below the surface by waters heated by Earth thermal gradient (epithermal solutions) in a cave in Carlsbad Caverns region. Guadeloupe Mts., New Mexico, US (Shopov *et al.* 1996).

Tab. 1 - Origine della luminescenza dei minerali di grotta.

	Luminescence center	Excitation	Color of emission	Phosphorescence	Origin	Reference
<i>Calcite*</i>						
1	Organics	Hg-lamp	blue	long	infiltration	Gilson <i>et al.</i> 1954
2	Organics	N ₂ -Laser	blue	long	infiltration	Shopov & Spasov 1983
3	Organics	SWUV	blue-green	long	infiltration	White & Brennan 1989
4	Organics	N ₂ -L., Xe,	blue-green	long	infiltration	Shopov 1989b
5	Organics	N ₂ -Laser	yellow-green	long	infiltration	Shopov 1989b
6	Organics	LWUV(Hg)	yellow	long	infiltration	Shopov 1989b
7	Organics	Ar-L., Xe,	yellow	long	infiltration	Shopov <i>et al.</i> 1989
8	Organics	SWUV, LWUV	yellow-orange	long	infiltration	White & Brennan 1989
9	CO ₃ ³⁻	N ₂ -Laser	blue		infiltration	Ugumory & Ikeya 1980
10	UO ₂ ²⁺	SWUV	green	no	infiltration	White & Brennan 1989
11	UO ₂ ²⁺	N ₂ -L., Hg	green	no	infiltration	Shopov 1989b
12	UO ₂ ²⁺	(magursilite?)	green-yellow	no	infiltration	Shopov 1989b
13	Organics	Hg, Xe	bluish	<15s	hydrot	Dublyansky (in press)
14	Mn ²⁺	Ar-L, N ₂ -L, Xe	orange-red	0.1s	h-t.	Mitsaki 1973; White 1974
15	Hydrocarbons	flash	violet	long	epithermal	Shopov & Buck p.c.
<i>Aragonite**</i>						
16	Organics	Hg-lamp	blue	long	infiltration	Shopov 1989b
17	Organics	Hg-lamp	blue-green	long	infiltration	Shopov 1989b
18	Organics	N ₂ -Laser	blue-green	long	infiltration	Shopov 1989b
19	Organics	N ₂ -Laser	green	long	infiltration	Shopov 1989b
20	Organics	Hg-lamp	yellow	long	infiltration	Shopov 1989b
21	Organics	SWUV, LWUV	blue-green	long	infiltration	White & Brennan 1989
22	UO ₂ ²⁺	SWUV	green	no	infiltration	White & Brennan 1989
23	?	Hg (LWUV)	orange	?	?	White & Brennan 1989
<i>Luminescence of Cave minerals at other excitations</i>						
<i>Cathodoluminescence of calcite</i>						
24	Mn ²⁺	electron beam	pink		?	White 1974
25	CO ₃ ³⁻	electron beam	blue		infiltration	Shopov p.c.
<i>Calcite Thermoluminescence</i>						
26	?	UV+ warming	glow at 105 K		infiltration	White & Brennan 1989
27	?	Xe+ heating	glow at 350, 500 K		?	Dublyansky (in press)
<i>X-Ray luminescence of calcite</i>						
28	CO ₃ ³⁻	X-rays	blue		infiltration	Shopov & Spasov 1983

Tab. 2 - Special Speleothem Luminescence Research Methods.

Tab. 2 - *Metodi speciali di ricerca sulla luminescenza degli speleotemi.*

Method	Authors	Obtainable information
I Impulse Photography of Luminescence (IPL): 1. Photography of phosphorescence (IPP) 2. Photography of fluorescence & phosphorescence (IPFP)	Shopov & Tsankov 1986 Shopov & Grynberg 1985	Diagnostics of minerals; registration of colour & zonality of fluorescence, phosphorescence and its spectra; UV photography; extraction of single mineral samples; chemical changes of the mineral-forming solution; Climate and Solar Activity variations during the Quaternary.
II Laser Luminescent Microzonal Analysis (LLMZA)	Shopov 1987	Microzonality of luminescence; changes of the mineral-forming conditions; High Resolution Records of Climate & Solar Activity variations (with resolution up to 0.4 days). Reconstruction of annual rainfall and annual temperature in the past. Estimation of past Cosmic Rays (CR) and Galactic CR. Speleothem growth hiatuses.
III Color Slide Spectrophotometry (CSS)	Shopov & Georgiev 1989	Wide-band spectra of phosphorescence, fluorescence and diffuse reflectance of minerals; spectra of quick processes.
IV Autocalibration Dating (ACD)	Shopov <i>et al.</i> 1991	High Precision Speleothem Dating of Speleothems of any age, Climatic and Solar Activity cycles, variations of the Speleothem Growth Rate.
V Time Resolved Photography of Phosphorescence (TRPP)	Shopov <i>et al.</i> 1996d	Determination of the lifetime of the luminescent center. Uplift of the region. Past mixing of surface and epithermal or hydrothermal waters during mineral growth. Estimation of the temperature of the deposition, plus all information obtainable by IPP.

Lasers (Ugumori & Ikeya 1980; Shopov & Spasov 1983; Shopov 1988, 1989a, 1989b), Xe- or Hg-Lamp (Shopov *et al.* 1988; White & Brennan 1989), Argon Lasers (Shopov 1989b; White & Brennan 1989) or by He- Ne Lasers.

Conventional luminescent research methods have number of disadvantages, so several special speleothem research methods has been developed recently (Tab. 2). They allow considerable enlargement of kinds and quality of the obtainable information.

The simplest method for luminescent research is Impulse Photography of Phosphorescence (IPP) (Shopov & Grynberg 1985; Shopov 1989a, 1991). Photographic slides obtained by using this method can be developed by Colour Slide Spectrophotometry (CSS) for the preparation of spectra of diffuse reflec-

tance, phosphorescence or fluorescence (Shopov & Georgiev 1987, 1989). It is intended for research of wide-line spectra, such as luminescence of most speleothems formed at normal cave conditions (at temperature below 40 °C) (Shopov 1989a). It allows easy non-destructive determination of objective information of mineral composition and speleothem luminescence.

3. PALEOENVIRONMENTAL APPLICATIONS OF SPELEOTHEM LUMINESCENCE

Before using of a speleothem for any luminescence paleoenvironmental records, is necessary to determine that all luminescence of the sample is due to organics. Otherwise a subsequent research may produce major

confusions. To prove that all speleothem luminescence is due to organics is a very complicated task (Shopov 1997).

3.1. *Paleoluminescence, Paleotemperature and Paleo- Solar Activity*

Calcite speleothems frequently display luminescence, which is produced by calcium salts of humic, and fulvic acids derived from soils above the cave (Shopov 1989a, 1989b; White & Brennan 1989). These acids are released (i) by the roots of living plants, and (ii) by the decomposition of dead matter. Root release is modulated by visible (650-710 nm) solar insolation (SI) via photosynthesis, while rates of decomposition depend exponentially upon soil temperatures that are determined primarily by solar infrared radiation (Shopov *et al.* 1994) in case that the cave is covered only by grass or upon air temperatures in case that the cave is covered by forest or bush. In the first case, microzonality of luminescence of speleothems can be used as an indirect Solar Activity (SA) index (Shopov *et al.* 1990c), but in the second as a paleotemperature proxy. So, in dependence on the cave site we may speak about "solar sensitive" or "temperature sensitive" luminescent speleothem records like in tree-ring records, but in our case record may depend only on temperature either on solar irradiation.

Time series of a Solar Activity (SA) index "Microzonality of Luminescence of Speleothems" (Shopov *et al.* 1990c) are obtained by Laser Luminescence Microzonal analysis (LLMZA) of cave flowstones described by Shopov (1987). This technique uses relatively simple device, but the quality of results is as good as high is the experience of the researcher, because every sample require a different approach. Many restrictions for samples for LLMZA apply (Shopov 1987). LLMZA allow measurement of luminescence time series with duration of hundreds of thousands years, but time step for short time series can be as small as 6 hours (Shopov *et al.* 1994) allowing resolution of 3 days (Shopov *et al.* 1988a). IPP and LLMZA devices (Shopov & Grinberg 1985; Shopov & Tsankov 1986; Shopov 1987) are the only ones allowing reliable measurements of the intensity of luminescence of speleothems. The wide range of devices used for measurement of speleothem annual growth by annual bands of luminescence do not produce reliable intensity of luminescence of speleothems, so can not be used for any other luminescent paleoenvironmental reconstructions.

3.2. *Paleoluminescence Reconstructions of the Solar Insolation*

Basically all solar sensitive raw paleoluminescence records (if measured properly using IPP or LLMZA de-

vices) are solar insolation records (Stoykova *et al.* 1998; Shopov *et al.* 2000). Other proxies can be derived from such records using different types of digital analysis.

3.3. *Paleoluminescence Reconstructions of the Solar Luminosity*

NASA used a record of luminescence of a flowstone from Duhlata cave, Bulgaria, to obtain a standard record of variations of the Solar Irradiance ("Solar constant") in [W/m²] for the last 10000 years (D. Hoyt, personal communication) by calibration of the luminescence record of (Shopov *et al.* 1990b) with satellite measurements.

Paleoluminescence solar insolation proxy records contain not only orbital variations, but also solar luminosity self variations, producing many cycles with duration from several centuries to 11500 years with amplitude ranging respectively from 0.7 to 7 % of the Solar Constant (Stoykova *et al.* 2002). Solar luminosity variations can be obtained from paleoluminescent records by extracting of the orbital variation from them using band-pass filtration with frequencies of the orbital variations.

These millennial solar luminosity cycles can produce climatic variations with intensity comparable to that of the orbital variations. Known decadal and even century solar cycles have negligible intensity (100 times less intensive) relatively to these cycles. Solar luminosity (SL) and orbital variations both cause variations of solar insolation affecting the climate by the same mechanism.

Luminescence time series has been used to solve number of problems of solar physics (Dermendjiev *et al.* 1989, 1990, 1992).

3.4. *Luminescence and Cosmic Rays Flux (CRF)*

Cosmic rays produce cosmogenic isotopes (¹⁴C, ¹⁰Be, etc.) in the upper atmosphere by nuclear reactions. As it is known, the ¹⁴C record represents the Cosmic Ray Flux (CRF) and modulation of the CRF by the solar wind (representing solar activity). We have obtained a striking high correlation (with a correlation coefficient of 0.8) between the calibration residue delta ¹⁴C record and a luminescent speleothem record (Shopov *et al.* 1994). It is as high as the best correlation ever obtained between a direct Solar index (inverted annual Wolf number) and the CRF (Beer 1991, r = 0.8). Obviously luminescence records can be used as a CRF proxy. To reconstruct the past CRF the luminescent record should be inverted.

3.5. *Luminescence and supernova explosions*

Galactic CRF have some short-term variations due to supernova explosions. These variations of the GCRF

can be determined only by comparison of a record of production of cosmogenic isotopes (CI) with an independent on CRF solar activity record. The luminescence microzonality is the only independent SA index with such length of record. It was used to reconstruct GCRF variations for the last 6500 years with 20-yr. resolution by subtracting of an inverted luminescent SA record from the residual ^{14}C record (Shopov *et al.* 1996b). Obtained record represents self-variations of the GCRF (due to supernova eruptions) beyond Solar system (where solar modulation does not exist).

3.6. Luminescence and Paleosoils

Luminescence organics first detected in speleothems by Gilson & Macarthey (1954) are humic and fulvic acids accordingly White & Brennan 1989, but accordingly Shopov (1997) more precisely they can be divided to 4 types:

1. Calcium salts of fulvic acids, soluble in water;
2. Calcium salts of humic acids not soluble in water and acids, but mobile in karst in form of colloid solutions;
3. Calcium salts of huminomelanic acids not soluble in waters and acids, but soluble in alcohols. They are mobile in karst in form of colloid solutions.
4. Organic esters not soluble in water but soluble in ether.

Each of these classes is usually presented in a single speleothem with hundreds of chemical compounds with similar chemical behaviour, but different molecular weights. Superposition of luminescence bands of all this compounds gives the broadline spectra of speleothem luminescence. Distribution of concentration of these compounds (and their luminescence spectra) depends on type of soils and plants society over the cave. So study of luminescence spectra of this organics can give information about paleosoils and plants in the past (White & Brennan 1989). Changes in visible colour of luminescence of speleothems suggesting major changes of plants society are observed very rarely only in speleothems growing hundreds of thousands years through glacial and interglacial periods (Shopov 1997) (Fig. 1).

3.7. Luminescence and Annual Growth Rates of Speleothems

Speleothem growth rate may vary up to 14 times within a single sample, resulting in non-linear time scale of the records (Shopov *et al.* 1992, 1994). These variations represent rainfall variations in case that there are no growth interruptions (hiatuses) in the studied part of the speleothem. In this way annual precipitation was reconstructed for last 280 years at



Fig. 2 - Annual banding of luminescence of organics in a flowstone crosssection (base of the picture = 0.8 mm). Dark parts are clay inclusions. Fluid inclusions are visible as bubbles and some crystal surfaces are also visible.

Fig. 2 - Laminazione annuale dovuta a materia organica in una sezione di colata calcitica perpendicolare all'asse di crescita (base della fotografia = 0,8 mm). Le parti più scure sono inclusioni di argilla. Sono visibili inclusioni fluide a forma di bolla e alcune superfici di cristalli.

the cave site, with precision of 80 mm/year (Shopov *et al.* 1996a, 1996c). Speleothem luminescence visualises annual microbanding, not visible in normal light (Shopov 1987; Shopov *et al.* 1988a) (Fig. 2). This peculiar banding had been called "Shopov bands" by Lauritzen (1996). If this banding is visible in normal light or the luminescent curve have sharp profiles or jumps like in Baker *et al.* (1993), it suggests that speleothem growth stopped for a certain period during the year and such time series can not be used for obtaining of rainfall proxy records.

3.8. Using of Paleoluminescence for Determination of the Origin of Glacial Periods and Improvement of their Dating

We measured a luminescent solar insolation proxy record in a speleothem (JC11) from Jewel Cave, South Dakota. This record exhibits a very rapid increasing in solar insolation at 139 kyrs +/- 5.5 kyrs (2 sigma error) responsible for the termination II. This increasing is preceding the one suggested by the Orbital theory with about 10 kyrs and is due to the most powerful cycle of the solar luminosity with duration of 11.5 kyrs superposed on the orbital variations curve. Solar luminosity variations appear to be as powerful as orbital variations of solar insolation and can produce climatic variations with intensity comparable to that of the orbital variations (Shopov *et al.* 2000, 2002). So paleoluminescence speleothem records may serve as a reliable tool for studying the mechanisms of formation and precise timing of glaciations.

3.9. *Paleoluminescence and Sea Level Variations*

Using speleothem luminescence solar insolation proxy records it has been demonstrated, that solar luminosity variations are responsible for almost 1/2 of the variations in high-resolution solar insolation experimental records. Solar luminosity variations are responsible for the short time variations of the sea level (Shopov *et al.* 2000).

3.10. *Luminescence Reconstructions of Past Karst Denudation*

Reconstructions of past carbonate denudation rates has been made using the quantitative theory of solubility of karst rocks (Shopov *et al.* 1991) (in dependence of the temperature and other thermodynamic parameters) and quantitative paleoluminescence reconstructions of the annual precipitation rates for the last 280 years and of the annual temperature for the last 1200 years (Shopov *et al.* 2001).

3.11. *Pollution and migration of toxic compounds indicated by speleothem luminescence*

In many samples all or a significant part of the luminescence is produced by ions of uranium and Pb. Sometimes they even have annual banding due to variations of acidity of the karst waters, causing variations of the solubility of some pollutants or toxic compounds (Shopov 1997). Uranium compounds have such migration behaviour.

4. LUMINESCENCE OF HYDROTHERMAL MINERALS

Luminescence of the high-temperature hydrothermal minerals is due mainly to cations because molecular ions and molecules destruct at high temperatures. Luminescence of cations can be used as an indicator of hydrothermal origin of the cave mineral (Shopov 1989a, 1989b). Calcites formed by low-temperature hydrothermal solutions have short-life fluorescence due to cations and long phosphorescence of molecular ions (Gorobetz 1981). Minimal temperature of appearance of this orange-red luminescence was estimated by Dublyansky (in press) by fluid inclusion analysis in hydrothermal cave calcites to be about 40 °C, but our direct measurements of luminescence of calcites in hot springs show that even at 46 °C such luminescence did not appear. It probably appears at over 60 °C. Such luminescence data are comparable with the stable isotope data used conventionally for this purpose (Bakalowicz *et al.* 1987; Ford *et al.* 1987).

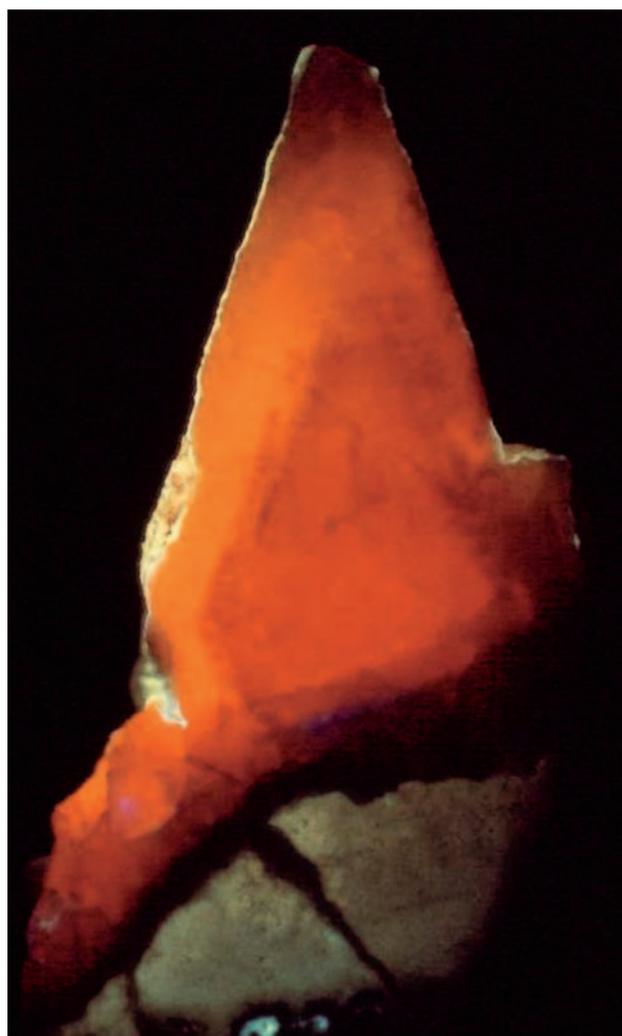


Fig. 3 - Characteristic red luminescence of hydrothermal calcite due to Mn-Pb couple incorporated isomorphically in the crystal lattice. The internal red part of this calcite from Carlsbad cave has been formed at epithermal conditions, few hundred meters below Earth's surface. When rapid uplift of the region happened, infiltration waters from the surface start to deliver organics. They have green phosphorescence, which together with Mn-Pb couple produce orange luminescence in the outer part of the crystal.

Fig. 3 - Caratteristica luminescenza rossa in calcite idrotermale dovuta all'incorporazione isomorfa di Mn e Pb nel lattice cristallino (Carlsbad Cave, USA). La parte interna della concrezione si è formata in condizioni epitermali alla profondità di 1 km. Il successivo rapido sollevamento della regione ha causato l'infiltrazione di acque meteoriche arricchite in materia organica. Questa ha una fosforescenza verde che, a causa della presenza di Mn e Pb, produce la luminescenza color arancio nella parte esterna del cristallo.

4.1. *Luminescence and Tectonics*

The tectonic uplift of an area (i.e. uplift of bedrock) can be deduced by luminescence in combination

with absolute dating methods. For example some speleothems from Carlsbad Cavern, New Mexico exhibit luminescence originated by epithermal mineralizing solutions in the older part of the speleothem (Fig. 3). Mixing of these waters with surface waters containing organics appear in younger parts of the speleothem, thus suggesting a time of uplift during the duration of speleothem deposition (Shopov *et al.* 1996d). The boundary layer (so the uplift) can be dated by U/Pb dating methods (Ford 2002).

5. LUMINESCENCE AND DATING OF SPELEOTHEMS

Finally, speleothem's luminescence may be used to determine the age of the speleothem itself. Shopov *et al.* (1991) and Dermendjiev *et al.* (1996) developed Autocalibration dating, which is shown to be the most precise speleothem dating method for samples younger than 2000 years (Shopov *et al.* 1994).

Although Ugumori & Ikeya (1980) first suggested Optically Stimulated Luminescence (OSL) dating method on speleothem calcite, further attempts were not successful due to interference of luminescence of organics. So OSL- dating can not be used for speleothems.

6. CONCLUSIONS

In conclusion, speleothem luminescence of organics can be used for obtaining of broad range of paleoenvironmental information (Shopov 1999).

Some speleothems can be used as natural climatic stations, for obtaining of proxy records of Quaternary climate with annual resolution.

ACKNOWLEDGEMENTS

This research was funded by Bulgarian Science Foundation by research grant 811/98 to Y. Shopov

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