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Luminescence of Speleothems in Italian Caves

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SUMMARY - *Luminescence of Speleothems in Italian Caves* - This paper studies luminescence of speleothems in ten Italian caves along a north-south transect. Using a Raman double spectrometer and excitation of luminescence of speleothem samples with multiline Ar-laser we measured 52 spectra of luminescence of samples from Grotta Doria (TS), Bus del Sasso (VI), Grotta del Vento (LU), two caves in gypsum in Gessi Bolognesi karst, Frassasi cave (AN) and Grotta di Carburangeli (PA).

RIASSUNTO - *La luminescenza degli speleotemi nelle grotte italiane* - Si presenta lo studio della luminescenza di speleotemi provenienti da 10 cavità italiane selezionate lungo un transetto nord-sud. Utilizzando un doppio stettrometro Raman ed eccitando gli speleotemi con un Ar-laser multilinea, sono stati misurati 52 spettri di luminescenza. I campioni studiati provengono da: Grotta Doria (TS), Bus del Sasso (VI), due grotte nei gessi del carso bolognese, Grotta di Frasassi (AN) e Grotta di Carburangeli (PA).

Key words: luminescence, Speleothem records, Paleoclimate, Solar Insolation
Parole chiave: luminescenza, speleotemi, paleoclima, insolazione

1. INTRODUCTION

Calcite speleothems frequently display luminescence that 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 by the roots of living plants and by the decomposition of dead vegetative matter. Root release is modulated by visible solar radiation via photosynthesis, while rates of decomposition depend exponentially upon soil temperature. The soil temperature depends mainly on solar infrared and visible radiation (Shopov *et al.* 1994), in case that cave is covered only by grass, or upon air temperatures, in case that 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 & Dermendjiev 1990; Shopov *et al.* 1991), but in the second case it can be used as a paleotemperature proxy (Shopov *et al.* 1996).

Luminescence organics in speleothems can be divided to 4 types: (1) Calcium salts of Fulvic acids, (2) Calcium salts of humic acids, (3) Calcium salts of huminomelanic acids and (4) Organic esters. All these four types are usually present in a single speleothem with hundreds of chemical compounds with similar chemical behavior, but of different molecular weights. Concentration distribution of these compounds (and their luminescence spectra) depends on type of soils and plants over the cave, so the study of luminescent spectra of these organic compounds can give information about paleosoils and plants in the past (White & Brennan 1989). Changes in visible color of luminescence of speleothems suggesting major changes of plant society are observed very rare.

Most known luminescent centers in calcite are inorganic ions of Mn, Tb, Er, Dy, U, Eu, Sm and Ce (Shopov 1997). Minerals contain many admixtures. Usually several centers activate luminescence of the sample and the measured spectrum is a sum of the spectra of two or more of them. Luminescence of minerals formed at normal cave temperatures is normally due mainly to molecular ions and sorbed organic molecules. But luminescence of uranil- ion is also very common in such speleothems. Sometimes it exhibits fine (even annual) lamination due to variations of the pH of the mineralizing waters or other geochemical factors. This luminescence has same color and zonality like organics, so may produce major confusions in the interpretation of all obtained luminescence data. Luminescence of uranil- ion is extremely difficult to distinguish from luminescence of organics. Before using a speleothem for any paleoenvironmental work it is necessary to determine that all luminescence of the sample is due to organics. This difficult task can be solved only by using complicated high precision Raman or luminescence spectrometers, with excitation of luminescence in 3 or more laser lines. Best devices for this purpose are Raman double spectrometers with excitation with multiline Ar- laser.

2. EXPERIMENTAL PART

To study the nature of the luminescent centers in the speleothem samples we used spectral equipment comprising of:

- a computer controlled high resolution 180 centimeter SPEX - Raman double spectrometer;
- a powerful (10.000 milliwatt) tunable Carl Zeiss ILA 120 Argonium laser, generating in 6 laser lines;
- a laser beam pre- monochromator.

On this equipment we measured 52 high quality spectra of luminescence of samples from cave Doria, Grotta del Vento, Sasso cave, a cave in gypsum in Gessi Bologniesi karst, Frasassi cave (Grotta di Fuime Vento) and of the Bedrock in the base of a flowstone from Frasassi cave.

Obtained spectra demonstrated, that 100% of luminescence of samples 1-6 is due to organics. Therefore this samples are appropriate for luminescence paleo-reconstructions. In luminescence spectra of these samples we observed gradual shift of the maxima of luminescence (Fig. 1) with the change of the wavelength of the excitation laser line (Fig. 2). Such phenomena cannot be observed if the luminescence of the samples was due to any inorganic excitation center, because the wavelength of maxima of luminescence does not depend on the excitation wavelength. Observed phenomena happened only when luminescence is due to a broad fraction of numerous organic compounds. In such case when we change the excitation wavelength we excite luminescence of different compounds with different molecular weight and different maxima of luminescence. Broad spectra result from superposition of the luminescence lines of these compounds. Samples, which have only such luminescence, can be used for luminescence paleo-reconstructions. Some samples exhibit such luminescence together with luminescence of inorganic compounds. Such samples cannot be used for luminescence paleo-reconstructions under any circumstances. Their spectrum exhibits one or more lines, which position do no depend on the excitation wavelength, superposed over the broad luminescence band of organics (Fig. 3). Such

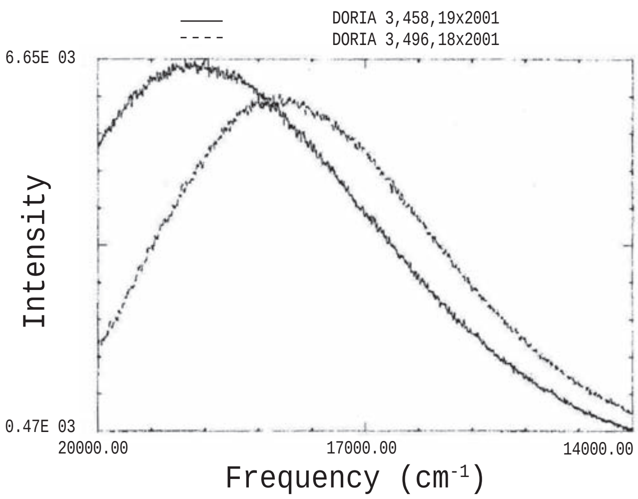

Fig. 1 - Comparison between luminescence spectra of sample Doria-3 from Doria cave under excitation by Ar-laser line at 458 nm (solid curve) and 496 nm (dashed curve).
Fig. 1 - Confronto tra gli spettri di luminescenza del campione Doria-3 della Grotta Doria con eccitazione di Ar-laser a 458 nm (linea continua) e 496 nm (linea tratteggiata).

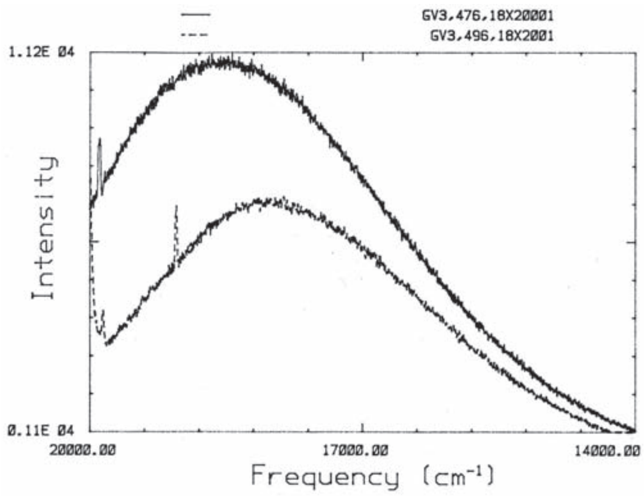

Fig. 2 - Comparison between luminescence spectra of sample GV3 from Grotta del Vento cave under excitation by Ar-laser line at 476 nm (solid curve) and 496 nm (dashed curve). Narrow lines are lines of Raman scattering of calcite. They are always located on equal distance from the excitation line (Raman shift), so the right Raman line indicates the position of the excitation line in both spectra.
Fig. 2 - Confronto tra gli spettri di luminescenza del campione GV3 della Grotta del Vento con eccitazione di Ar-laser a 476 nm (linea continua) e 496 nm (linea tratteggiata). I due picchi stretti che caratterizzano gli spettri sono linee dello scattering Raman della calcite. Queste sono posizionate ad eguale distanza dalla linea di eccitazione (Raman shift), cosicché la linea Raman sulla destra indica la posizione della linea di eccitazione in entrambi gli spettri.

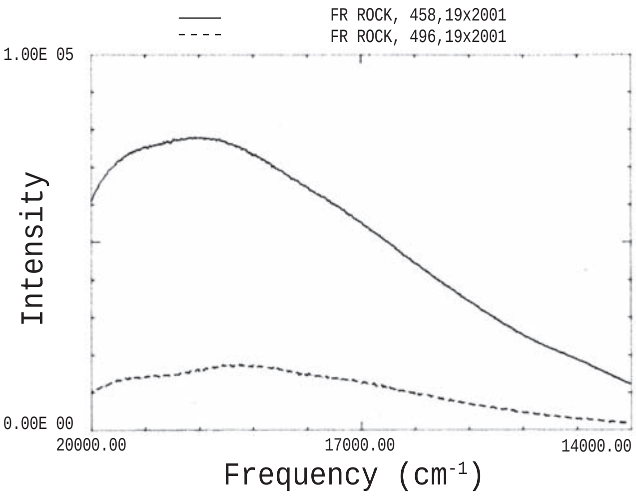

Fig. 3 - Comparison between luminescence spectra of sample FR3-4 bedrock from Grotta di Frasassi (Grotta di Fuime Vento) cave under excitation by Ar-laser line at 458 nm (solid curve) and 496 nm (dashed curve).
Fig. 3 - Confronto tra gli spettri di luminescenza del campione FR3-4 bedrock della Grotta di Frasassi con eccitazione di Ar-laser a 458 nm (linea continua) e 496 nm (linea tratteggiata).

Cave name	Vegetation above
Grotta Savi	bush, growing to forest (probably pasture in most of the historical times)
Grotta del Vento	forest (probably pasture in the historical times)
Grotta di Frasassi	scarp with submediterranean forest (partly bush in the past)
Grotta di Carburangeli	Mediterranean bush in the past – now strongly artificial (houses, roads, etc.)

Tab. 2 - Vegetation over Italian carbonate caves.
Tab. 2 - Copertura vegetale al di sopra di alcune grotte italiane studiate.

are spectra of luminescence of our sample 7, which exhibits luminescence of both organic and inorganic activators.

We studied visual luminescence of 42 speleothems from 11 Italian caves. This way we choose 15 speleothems for study of their paleoluminescence variations (Tab. 1). Vegetation above Italian carbonate caves is given in table 2. Geographic data about these caves are presented in table 3. The best sample for preparation of high resolution luminescence paleoclimatic

Tab. 1 - Luminescence of sections of calcite speleothems from Italian caves.
Tab. 1 - Luminescenza di sezioni di speleotemi calcitici delle grotte italiane studiate.

Sample	Active top	Luminescence	Total length (cm)	Visibile lamination
		GROTTA DEL VENTO - Alpi Apuane		
GV1	yes	low luminescence with coarse banding	26,5	coarse
GV3	yes	low luminescence with coarse banding	13,5	coarse
		GROTTA DI FRASASSI		
FR3	yes	luminescence with coarse banding and many fractures	~80	faint
FR5	yes	luminescence with coarse banding and strong clivage	~80	yes
		GROTTA SAVI - Carso Triestino		
SA1	yes	luminescence with very fine (annual) banding and fine hiatuses	27,5	yes
		GROTTA DORIA - Carso Triestino		
Doria3	yes	luminescence with coarse banding and many pores	5	no
Doria8	yes	low luminescence with very coarse banding and very big pores	5	faint
		BUS DEL SASS - Prealpi vicentine (VI)		
Sass8	no	fine banding and extremely strong luminescence in the middle part	~15	faint
		GROTTA DI CARBURANGELI (Carini - PA)		
CR1	no	fine banding at the top but many pores below	106	coarse
		GROTTA DI SANTA NINFA (S. Ninfa - TP)		
SN4	yes	some banding and extremely strong luminescence	3	yes
		SPIPOLA ACQUAFREDDA KARST SYSTEM - Gessi Bolognesi		
SP1	yes	many luminescence bands, changes in growth axis direction	15,5	faint
		GROTTA NOVELLA - Gessi Bolognesi		
NO1	yes	many bands with stable luminescence and hiatuses	5,5	yes

Tab. 3 - Geographical, climatic and physical characteristics of several Italian studied caves.
Tab. 3 - Caratteristiche geografiche, climatiche e fisiche di alcune grotte italiane studiate.

Cave	Coordinates	Elevation (m a.s.l.)	Climate	Mean annual rainfall (mm)	Cave temp (°C)	Mean annual temp. (°C)	Host rock	Depth of cave passage (m)	Cave Physics
Grotta Savi	45°37′05″N 13°53′10″E	358	intermediate Mediterranean-continental	1350	11,8	12,5	bioclastic limestones	15-65	3 km from the northern Adriatic coastline
Grotta del Vento	44°02′07″N 10°21′31″E	650	Mediterranean mountain type	2400	10,7	11,4	metamorphic dolomite	50-60	Presence of air current in the gallery
Grotta di Frasassi	43°23′53″N 12°58′01″E	212	Mediterranean	1060		14,3	massive limestones	200-400	Cave developed from mixing of low temperature hydrothermal waters. It has several entrances. Presence of oxidizing and reducing bacteria.
Grotta di Carburangeli	38°10′57″N 13°09′36″E	22	Mediterranean	678	19.4	19,4	Calcarenites and dolomitic limestones	10-20	Very shallow cave, near the coastline

reconstruction appears to be stalagmite Savi-1 from Grotta Savi - Carso Triestino (see the paper in this volume).

Luminescence of the stalagmite CR1 from Grotta di Carburangeli (Carini - Pa) exhibits fine banding (Fig. 4, A), but this sample is extremely porous in the older parts. This obstructs paleoluminescence measurements.

Photos on figure 4 are negative photographs of integral phosphorescence of 2-5 mm thick polished sections of calcite speleothems, under excitation by impulse Xe- lamp 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 perhaps to warmer climate (Shopov 1997).

Luminescence of the flowstone Sasso-8 from Bus

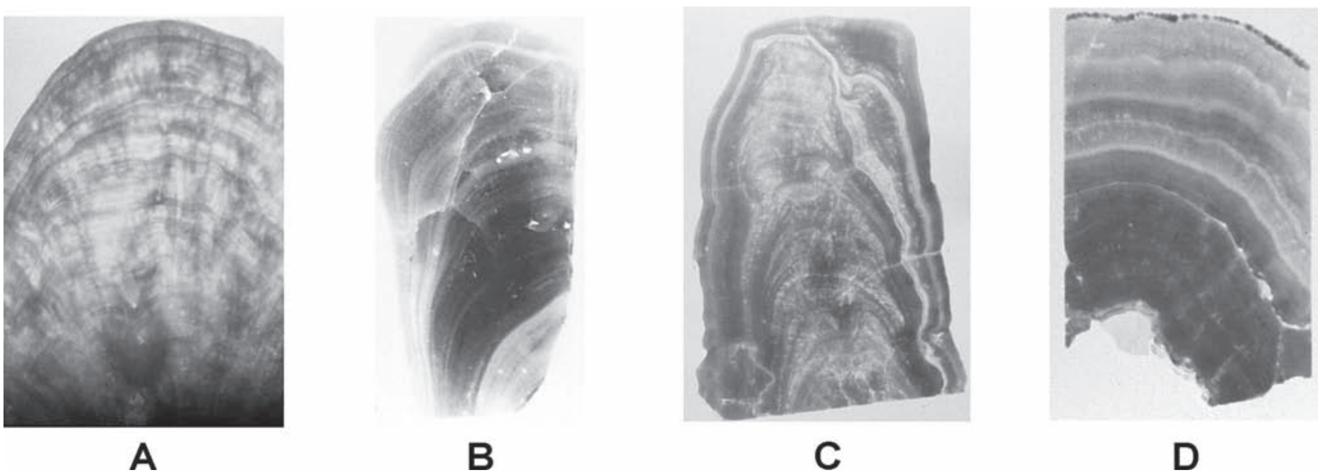

Fig. 4 - Luminescence of some samples (A. top of sample CR-1 from Grotta di Carburangeli; B. sample Sasso-8 from Bus del Sasso cave, Prealpi Vicentine; C. sample from the Spipola Acquafredda karst system; D. sample from Grotta Novella, Gessi Bolognesi gypsum karst).
Fig. 4 - Luminescenza di alcuni campioni (A. top del campione CR-1, Grotta di Carburangeli; B. campione Sasso-8, Bus del Sasso cave, Prealpi Vicentine; C. campione proveniente dal sistema carsico Spipola Acquafredda; D. campione proveniente da Grotta Novella, Gessi Bolognesi).

del Sasso cave, Prealpi Vicentine, exibits extremely strong luminescence in the middle part of the speleothem and very fine banding in the outer part.

Most interesting are calcite samples from caves in gypsum (Fig. 4, C and D). Most unique is the calcite stalagmite SP1 (Fig. 4, C) from the Spipola Acquafredda karst system, Gessi bolognesi gypsum karst. Its carbonate is believed to be formed only from active CO_2 from the air, because the bedrock of the cave consist of gypsum and do not contain CO_2. Luminescence of this sample is very strong and exhibits many luminescence bands. They exhibit many variations in the direction of the growth axis of the speleothem, so this speleothem has been utilised for detailed reconstruction of past earthquakes. It was taken from the cave about 50 years ago (1950-1955). At that time the speleothem was active. The cave is covered by thin layer of soil and for large portion by an oak forest. The location of the main entrance is Lat. 44°26′41″ Long. 1°04′22″.

Calcite flowstone NO1 (Fig. 4, D) was taken from Grotta Novella some 1 km far from Spipola about 30 yrs ago when it was active. Luminescence of this sample is strong and exhibits several thick luminescence bands with relatively stable intensity of luminescence. They are separated by hiatuses. This suggests that this flowstone was growing relatively fast, but for short periods of time (with stable climate). Such growth pattern suggests that the speleothem growth was possible only in a very small range of climatic conditions, so it did not grow most of the time. The location of the main entrance of the cave is at 44°25′35″ long. 1°02′13″. The situation of this cave is similar to that of Spipola: completely covered by an oak forest. The average temperature inside the two caves is about 10-11 °C. Both caves are developed in Messinian gypsum.

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