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^{230}Th DATING OF THE SPELEOTHEMS FROM THE "GROTTA DEL FIUME -GROTTA GRANDE DEL VENTO" KARST SYSTEM IN FRASASSI (Ancona, Italy) AND PALEOENVIRONMENTAL IMPLICATIONS

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ABSTRACT

Chronological measurements have been carried out on speleothems from the «Grotta del Fiume-Grotta Grande del Vento» karst system in Frasassi (Ancona, Italy) by means of the ^{230}Th radiometric method in order to date hypogean karst levels and related geological events. Higher levels were found to be older than the lower ones according to standstills and sinkings of the water table.

The dated speleothems from the first and second level formed less than 10.000 years ago; the minimum ages of the third and fifth levels, which are respectively 130,000 and 200,000 years old, were correlated to climatic events.

Dating different portions of a spelothem allows the measurements of the radial and vertical accretion rates and their variation over time. Such data together with the $^{234}U/^{238}U$ activity ratio and the uranium content of the speleothems have been correlated with the climatic variations connected to the glacial cycles. The same data have been used to fit a hydrogeological model.

RIASSUNTO

[*Datazione col metodo del ^{230}Th di concrezioni provenienti dal sistema carsico «Grotta del Fiume - Grotta Grande del Vento» presso Frasassi (Ancona) e correlazioni paleoambientali*]

La cronologia di alcune concrezioni provenienti dal sistema carsico «Grotta del Fiume-Grotta Grande del Vento» è stata studiata datando col metodo del ^{230}Th i livelli carsici e gli eventi geologici ad essi correlati. I livelli superiori sono risultati più vecchi di quelli inferiori in accordo con i progressivi approfondimenti della falda freatica.

Le concrezioni datate provenienti dal primo e secondo livello si sono formate 10.000 anni fa; le età minime del terzo e quinto livello, che sono, rispettivamente, 130.000 e 200.000 anni, sono state correlate con gli eventi climatici.

La datazione di diverse porzioni di una stessa concrezione permette la determinazione del rateo di accrescimento radiale e verticale e la sua variazione nel tempo. Tali risultati insieme al rapporto di attività $^{234}U/^{238}U$ a ed alla concentrazione dell'uranio nelle concrezioni stesse sono state correlate con le variazioni climatiche connesse con i cicli glaciali. Gli stessi dati sono stati utilizzati per costruire un modello idrogeologico.

INTRODUCTION

Dating speleothems by ^{230}Th method (Gascoyne *et al.*, 1978) is a powerful tool for Earth Sciences to improve the knowledge on subjects such

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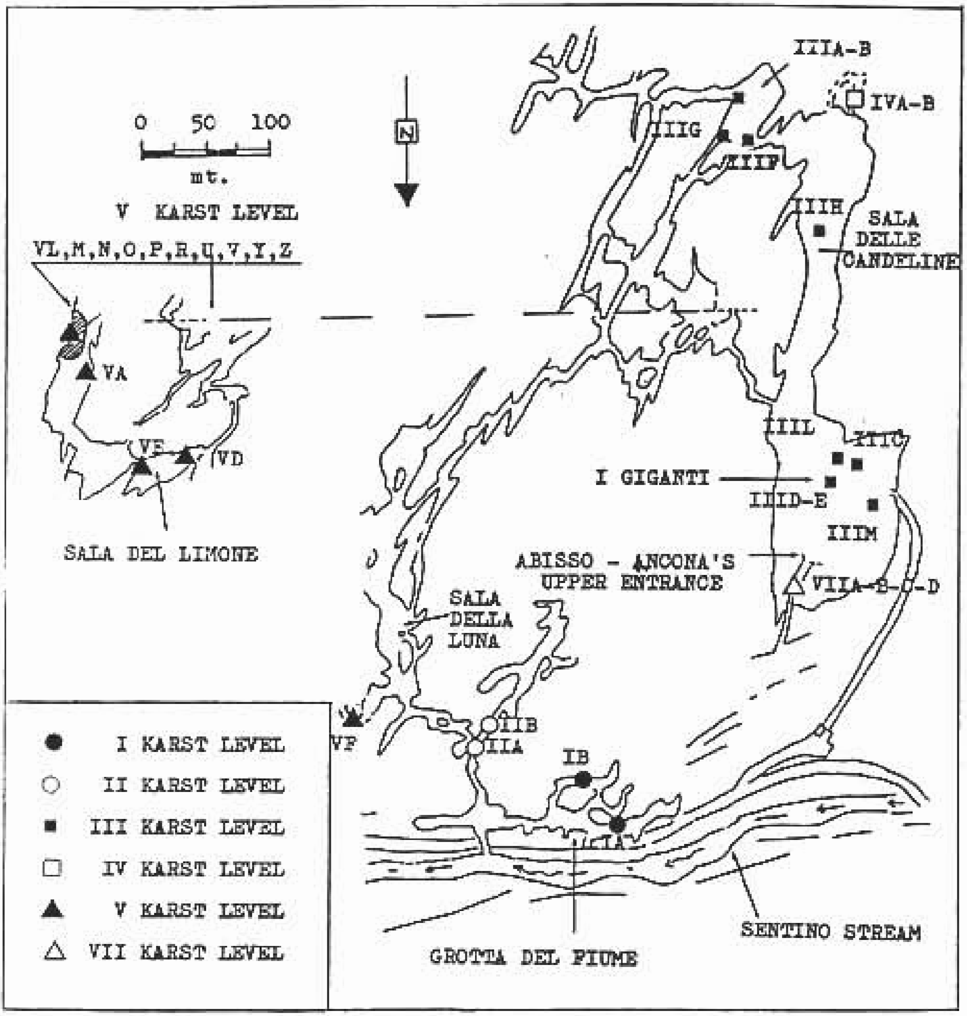

Fig. 1 - Locations of the speleothems sampled from the karst levels

as karst evolution, neotectonics, palaeoclimatology. The «Grotta del Fiume-Grotta Grande del Vento» karst system in Frasassi (Ancona, Italy) offers a unique situation: it covers a rather wide area (several square kilometers) well known from a geological point of view, interested by seven karst levels (Bocchini & Coltorti, 1978a, b) over 210 meters of vertical spread; an efficient management allows a quite good preservation of the environment and offers facilities to the interested scientists.

On this basis we carried out a research in order to improve the knowledge of the karst evolution in terms of dates related to the concretionary stages. Moreover, the rate of accretion can be measured for the speleothems, giving indications on the palaeoclimate; finally, the data on U content and its isotopic composition can be used for speculations on palaeo-hydrogeology. All analyses have been performed by means of alpha spectrometry.

SAMPLING

This research deals with more than 20 stalagmites (and a stalagmitic flowstone) from the 1st to the 5th karst level (Fig. 1).

The base and the top of some stalagmites have been dated; one has been sampled along its vertical axis by collecting 11 subsamples; others have been horizontally drilled to obtain a 2.5 cm diameter core reaching generally the nucleus of the stalagmite at its base; 10 cm long portions of such cores have been dated.

ANALYTICAL DATA

Elemental, isotopic (activity ratio) and age data are displayed in Tab. 1. It is very important to point out right now that the interpretation of the age data must be carried out only after a very careful evaluation of their validity. In fact, at least two kind of situations can occur to unvalidate the measured ages.

The first one depends on the sampling direction related to the conditions of accretion. Two examples are shown in Fig. 2. If the speleothem accreted as a sequence of vertical (Fig. 2a) or horizontal (Fig. 2b) concretionary sheets, it is quite evident that a set of subsamples along an horizontal core can give the same age, or that an inner subsample can appear to be younger than the outer ones. This can be the case of sample FRS 3H and FRS 3E respectively.

The second situation probably occured during the accretion of sample FRS III B; in this case, it is very probably correct to assume a uranium mobilization responsible for the modification of the $^{230}Th/^{234}U$ activity ratio. Consequently, the basic assumption of the method which requires a chemically and isotopically closed system since the deposition of the speleothem, could not be fulfilled.

Anyway, it must be emphasized that if a cluster of subsamples, large of circulating water and the consequent lower amount of dissolved carbonate could have been compensated by the longest residence time of the seepage water in the wall-rock due to the deepening of the base level.

PALEOHYDROGEOLOGY

The climatic factors as temperature and precipitation, together with the pedology and the lithology of the region interested by the percolation water affect the dissolved uranium concentration and its isotopic composition. In fact, the interaction of carbon dioxide-rich waters with the carbonate wall rocks will result in their dissolution with the enrichment of the water in uranium with a $^{234}U/^{238}U$ activity ratio close to the unity. On the other side, during the interaction of less acid water with the carbonate wall-rocks, the leaching will prevail over the dissolution: the water will contain a smaller amount of uranium characterized by higher $^{234}U/^{238}U$ activity ratio, due to the easier leacheability of ^{234}U lying in «hot» sites (Fleischer, 1980). The leaching of non-carbonate rocks will result in waters richer in uranium, with a higher isotopic ratio (Taddeucci *et al.* 1987).

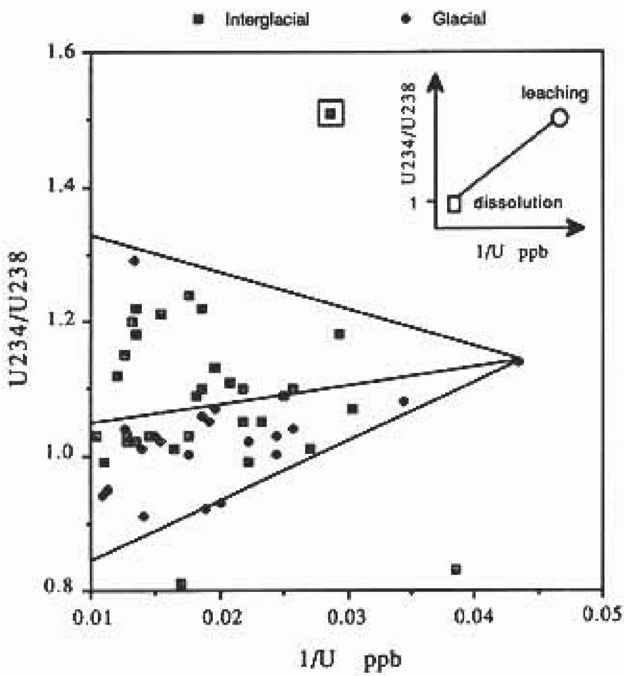

Fig. 4 - Initial uranium isotopic composition of the speleothems versus the reciprocal value of their uranium content.

In Fig. 4, the initial uranium isotopic composition of the speleothems, corresponding to that of the deposition water, is plotted versus the reciprocal value of their uranium elemental content (black circles refer to material deposited during glacial periods, and open squares to the interglacials). «Cold» samples seem to lye on an array that can be explained in terms of mixing between two end members; the first one (square in the insert) refers to «dissolved uranium» water and the second one (circle in the insert) refers to «leached uranium» water interacting in a lithologically homogeneous reservoir; the low uranium content of the «leached» end member (extreme right valve in the figure) agrees with the existence of a carbonate reservoir.

By taking into account the «warm» samples, a third end member must be considered, represented by waters leaching (more than dissolving) uranium-rich rocks, different from carbonates (marls and clayey marls). This is compatible with an interglacial warm-wet climate, when the abundant rainfall was responsible for a better hydrologic connection among lithologically different reservoirs.

Double square in Fig. 4 represents a very interesting case dealing with a small stalagmite from the 5th karst level (FRS VF) only 5 centimeters high, overlying a cherty archaeological artefact and connected to a palaeolithic fireplace with bones. The ^{230}Th age integrated over the whole stalagmite (due to its small size) turned out to be 1,500±400 years; the same speleothem has been dated by means of ^{14}C method by Prof. G. Calderoni (Earth Science Department, University of Rome «La Sapienza») and gave the age of 1 ,700±100 years. The ^{14}C age of fire carbons and bones is 13,000±100 years, that can therefore be assumed as the age of the artefact.

It is worthwhile to note that the ^{230}Th and the ^{14}C ages agree within the limit of the errors; that means that no carbon exchange occurred between the seepage water and the «infinite age ^{14}C» carbonate wall-rock. This conclusion is in agreement with the low uranium content and the very high isotopic ratio shown by the depositing water that had to be a typical «leaching» one.

CONCLUSIONS

The work that has been carried out identifies at least two dates within the whole evolution of the karst system: 130,000 and 200,000 years respectively for the end of the formation of the 3rd and 5th karst levels. Also the variations over time of the speleothems accretion rate agree with the palaeoclimatic conditions. The uranium content and its isotopic composition calculated for the carbonate-depositing waters have been used to figure out a hydrogeologic model involving a mixing among three end-members:

i) «dissolving» waters in a carbonate reservoir
ii) «U-leaching» waters in the same carbonatic reservoir
iii) «U-leaching» waters in a non-carbonate reservoir.

The first and second end-members prevail during the glacial period while the third one prevails during the interglacial period.

The high accretion rate of the speleothems occurring over the last thousands of years can be regarded as an index of the good «state of health» of the cave, at least from the tourist point of view. Because of the intense anthropization now occurring, we think that it should be easy and quite inexpensive to survey the accretion rate of carbonate concretions simply by periodically weighting some standard concretioning objects, appropriately located within the cave.

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Table 1 - Analytical data. Roman numerals refer to the karst level, letter to the speleothem and arabic numerals to its parts. All speleothems are stalagmites except FRS 4 which is a stalagmitic flowstone. For each sample in the first row are reported the values while in the second row are reported the errors.

Sample	Subsample	Period (Glacial or Interglacial)	U ppb	^{234}U / ^{238}U	^{234}U / ^{238}U	^{230}Th / ^{232}Th (initial)	^{230}Th / ^{234}U	Age k•years
FRS I A2	top	I	96	0.99	1.03	1	0.05	10
			3	0.04	0.04	0.1	0.02	
FRS II A1	base	I	78	1.03	1.03	1	0.07	10
			3	0.03	0.03	0.1	0.02	
FRS II A2	top	I	33	1.06	1.07	3	0.08	10
			2	0.08	0.08	0.2	0.02	
FRS II B1	base	I	74	1.22	1.22	2	0.03	10
			4	0.06	0.06	0.1	0.01	
FRS III A1	base	I	79	1.11	1.15	24	0.60	93
			5	0.06	0.06	4	0.05	+13-11
FRS III A3	top	G	50	0.94	0.93	inf.	0.40	55
			3	0.02	0.02		0.03	5
FRS III B1	base	I	55	1.06	1.09	32	0.70	130
			4	0.07	0.07	5	0.04	+15-14
FRS III B2	4.5-9 cm	G	65	1.01	1.02	14	0.47	68
	(upwards)		3	0.04	0.04	2	0.03	6
FRS III B5	18-22.5 cm	I	57	1.03	1.03	inf.	0.49	74
	(upwards)		2	0.03	0.03		0.11	+26-21
FRS III B6	22.5-27 cm	I	45	0.99	0.99	inf.	0.62	104
	(upwards)		2	0.05	0.05		0.04	+13-11
FRS III B7	27-31.5 cm	I	43	1.04	1.05	99	0.56	88
	(upwards)		1	0.06	0.06	26	0.03	8
FRS III B8	31.5-36 cm	I	34	1.12	1.18	65	0.70	132
	(upwards)		2	0.07	0.07	20	0.05	+18-16
FRS III B9	36-40.5 cm	G	41	1.03	1.03	inf.	0.26	33
			2	0.05	0.05		0.02	3
FRS III B10	40.5-45 cm	G	72	1.01	1.01	inf.	0.40	55
			4	0.06	0.06		0.02	5
FRS III B11	top	G	39	1.04	1.04	inf.	0.13	15
			3	0.09	0.09		0.03	+4-3
FRS III C1	75-85 cm	G	45	1.02	1.02	15	0.09	10
	(inwards)		2	0.05	0.05	2	0.01	3

FRS III C2	65-75 cm (inwards)	I	48 1	1.11 0.02	1.11 0.02	inf.	0.07 0.01	8 2
FRS III C8	0-10 cm (inwards)	I	46 7	1.05 0.04	1.05 0.04	inf.	0.02 0.01	3 1
FRS III E1	100-110 cm (inwards)	I	40 5	1.09 0.07	1.09 0.07	inf.	0.08 0.01	9 1
FRS III E2	90-100 cm (inwards)	I	54 2	1.10 0.03	1.10 0.03	inf.	0.06 0.01	7 2
FRS III E1O	0-10 cm (inwards)	G	23 1	1.13 0.07	1.14 0.07	inf.	0.14 0.04	16 1
FRS III F1	75-85 cm (inwards)	G	88 1	0.96 0.04	0.95 0.04	inf.	0.51 0.03	76 6
FRS III G1	100-110 cm (inwards)	I	59 3	0.93 0.04	0.81 0.04	inf.	0.55 0.05	82 10
FSR III H1	100-110 cm (inwards)	I	76 3	1.19 0.04	1.20 0.04	inf.	0.08 0.01	9 1
FRS III H2	90-100 cm (inwards)	G	51 3	1.07 0.03	1.07 0.03	inf.	0.10 0.02	12 2
FRS III H4	73-85 cm (inwards)	I	74 2	1.18 0.03	1.18 0.03	inf.	0.07 0.01	7 1
FRS III H5	60-73 cm (inwards)	I	65 2	1.21 0.03	1.21 0.03	inf.	0.07 0.01	7 1
FRS III H6	47-60 cm (inwards)	G	75 4	1.27 0.06	1.29 0.06	11 2	0.19 0.01	23 1
FRS III H7	35-47 cm (inwards)	I	54 2	1.22 0.05	1.22 0.05	inf.	0.08 0.01	9 1
FRS III H8	23-35 cm (inwards)	I	51 2	1.13 0.05	1.13 0.05	inf.	0.05 0.01	6 1
FRS III H9	10-23 cm (inwards)	I	57 2	1.24 0.05	1.24 0.05	inf.	0.05 0.01	8 1
FRS III H1O	0-10 cm (inwards)	I	26 2	0.83 0.09	0.83 0.09	inf.	0.07 0.01	8 1
FRS III L1	100-110 cm (inwards)	I	74 4	1.02 0.05	1.02 0.07	inf.	0.49 0.04	73 +9-8
FRS III L5	55-65 cm (inwards)	G	52 2	1.05 0.03	1.05 0.03	inf.	0.38 0.02	52 4
FRS III L10	0-10 cm (inwards)	I	37 1	1.01 0.04	1.01 0.04	inf.	0.08 0.01	9 1
FRS III M1	20-30 cm (inwards)	I	39 2	1.10 0.05	1.10 0.05	inf.	0.01 0.01	1 1

FRS 2 (III)	nucleus	G	53	0.92	0.92	inf.	0.10	12
			2	0.05	0.05		0.01	1
FRS 4 (III)	flowstone	I	91	0.99	0.99	1	0.02	4
			5	0.18	0.18	(*)	0.03	2
FRS IV A2	top	G	67	1.02	1.03	12	0.10	11
			2	0.03	0.03	3	0.01	1
FRS IV B1	base	G	71	0.91	0.91	1	0.11	13
			3	0.04	0.04	0.1	0.01	
FRS IV B2	top	G	29	1.07	1.08	1	0.11	10
			1	0.06	0.06	0.1	0.01	
FRS V A1	base	I	61	1.01	1.01	40	0.53	82
			3	0.04	0.04	9	0.03	8
FRS V A2	top	G	54	1.06	1.06	10	0.30	39
			1	0.03	0.03	1	0.02	3
FRS V D1	base	G	57	1.00	1.00	11	0.44	64
			3	0.04	0.04	1	0.03	+6-5
FRS V D2	top	G	79	1.03	1.04	18	0.19	22
			3	0.03	0.03	7	0.26	+3-2
FRS V E1	base	I	83	1.07	1.12	inf.	0.93	199
			5	0.07	0.07		0.06	+22-20
FRS V E2	top	G	92	0.95	0.94	12	0.37	50
			4	0.03	0.03	2	0.02	4
FRS V F1	integrated (see text)	I	35	1.51	1.51	inf.	0.01	2
			3	0.13	0.13		0.01	1
FRS 3a (V)	nucleus	I	78	1.02	1.02	12	0.48	71
			5	0.02	0.02	2	0.04	+8-7
FRS 3b (V)	external	I	46	1.10	1.10	23	0.05	6
FRS IIID1 (VII)	100-110 cm (inwards)	G	41	1.00	1.00	inf.	0.76	157
			1	0.04	0.04		0.04	+21-18
FRS 1 (VII)	external layer of III D1	I	69	1.02	1.03	inf.	0.69	124
			2	0.03	0.03		0.03	+12-11

* Age corrected for detrital thorium.

Tab. 2 - Ages of the speleothems in relation to the evolution of the karst process.

Karst level	Height above water table (m)	N° of sampled speleothems	N° of measured samples	Karst level minimum age (k•years)	Related climatic event
VII	+ 210	4	5	> 200	> Mindel-Riss
VI	+ 65	-	-	> 200	> Mindel-Riss
V	+ 52	16	21	200	Mindel-Riss
IV	+ 35	2	3	200 - 130	Riss
III	+ 25	12	34	130	Riss-Würm
II	+ 12	2	2	10	Post-Würm
I	+ 2	2	1	10	Post-Würm