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The Role of CO_2 in Gypsum Speleogenesis: 1° contribution

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SUMMARY

Starting from direct observations carried out inside gypsum caves around Bologna (Italy), the authors develop a new theory about the role played by CO_2 in gypsum karstification.

Such a theory agrees with the presence of calcite sinters inside gypsum caves without any source of calcium carbonate (cover or interbedding layer).

Moreover, starting from this theory, gypsum speleogenesis has to be always considered as a hyperkarstic phenomenon (more than 3 components at the equilibrium).

INTRODUCTION

The opinion that gypsum speleogenesis is a parakarstic phenomenon (Cigna, 1978), to be ascribed only to the solution of calcium sulphate by percolating water, and therefore quite independent from the CO_2 content of the waters (Picknett, 1976), is generally accepted.

Such an opinion, despite its diffusion, does not agree at all with the direct observations, which day by day are carried out in gypsum karst around Bologna (Italy).

It is common here to see in caves which have no source (cover or interbedded) layers of calcium carbonate, water can cause at the same time the deposition of calcite sinter and the simultaneous dissolution of gypsum.

Starting from this fact, which is impossible to explain with the current theory of gypsum speleogenesis, we decided to analyse critically the genetic hypothesis for gypsum caves.

In the present work, we started from the description of direct

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observations carried out in the gypsum caves of Bologna, and then we analysed the physico-chemical conditions present when gypsum dissolution and calcite deposition can occur. We found that the role played by CO_2 in gypsum speleogenesis is a very important one, not only in the particular case of the caves of Bologna, but also in the most general field of gypsum karstification.

DIRECT OBSERVATIONS

A few kilometers from Bologna in the gypsum formation of the Messinian, there are over 150 caves, half of which contain calcareous concretions. Frequently concretions are represented by small areas of thin wall crusts, but sometimes (as in Novella, Coralupi, Pisoliti caves) the calcite flows reach a length up to 20 meters and a thickness up to more than 30-50 centimeters.

The largest of such calcareous formations are actually found in caves within outcropping gypsum, so that it is impossible for meteoric waters to dissolpe calcium carbonate in some overlying formations (cover) and then to bring this into the caves Therefore, to explain the genesis of such calcareous concretions, a statistical analysis of the physico-chemical conditions, in which the calcite deposition occurs, has been carried out: we found

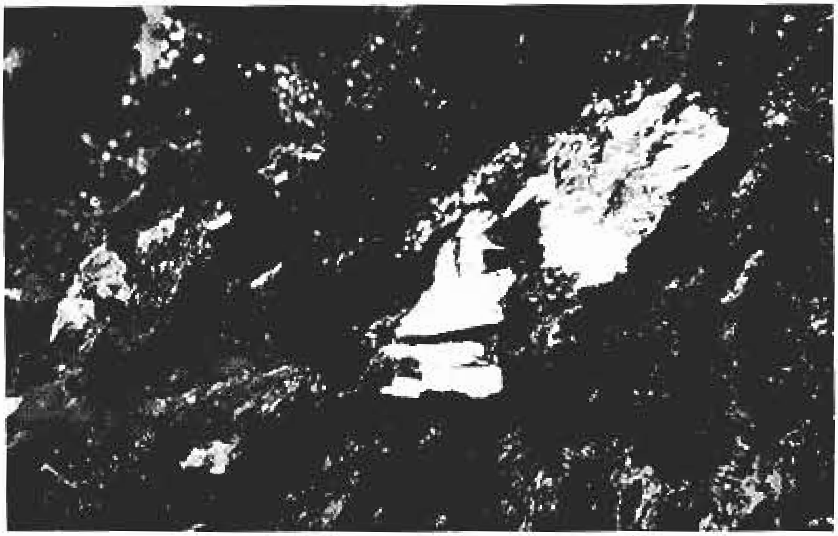

Fig. 1 - Novella cave: eroded gypsum crystals of the floor with overlying calcite sinter by the same dripping water.

that there are 4 common features for all the concretions to be taken into account.

Such conditions are to be regarded as necessary if the calcium carbonate deposition is to be present. They are:

1) All the caves, which have calcite sinter, are developped under a ground surface covered which woodland, with a soil layer which is from 20 to 150 centimeters thick and lying directly on gypsum rocks. On the other hand, none of the caves have any calcite sinter inside, if they are developped in gypsum without soil cover.

2) All calcite sinters are found a few meters within the cave, that is extremely near to the surface; moreover they grow in those places, which the percolating water reaches rapidly: this is certified by small leaves, twigs and other materials introduced from the surface by the water.

3) All calcite sinters rest upon eroded or washed gypsum crystals, or over a thin clay layer, which, in turn, rests on eroded or washed gypsum crystals; moreover, most of the concretions are free from gypsum substratum, being connected only in a few places in areas far from the direct circulations of the water. Besides, it is common to see that water dissolves gypsum and forms calcite sinter in the same place.

Fig. 2 - Novella cave: eroded gypsum crystal inside calcite sinter: it is evident that calcium carbonate growth has followed the dissolution of gypsum.

4) The pH of the concreting waters is always in the range 7.8-8.2, while those of the water unsaturated with respect to calcite vary from 7.0 to 7.4.

DISCUSSION

The first condition which seems to be needed for producing calcite sinter is the presence of woodland cover, which causes a notable increase in CO_2 content of the water, and at the same time the presence of a humic basis and acids, so that the resulting solutions can be buffered within pH of 7.8 to 8.2, which are the values we measured in the concretioning zones of gypsum caves.

Owing to the increase of the $CO_3^=$ ions, caused by the presence of a high concentration of dissolved CO_2 along with a slightly alkaline pH, calcium carbonate deposition is obviously favoured.

The second observed condition is the closeness to the surface of all calcite concretions, which means that the water becomes

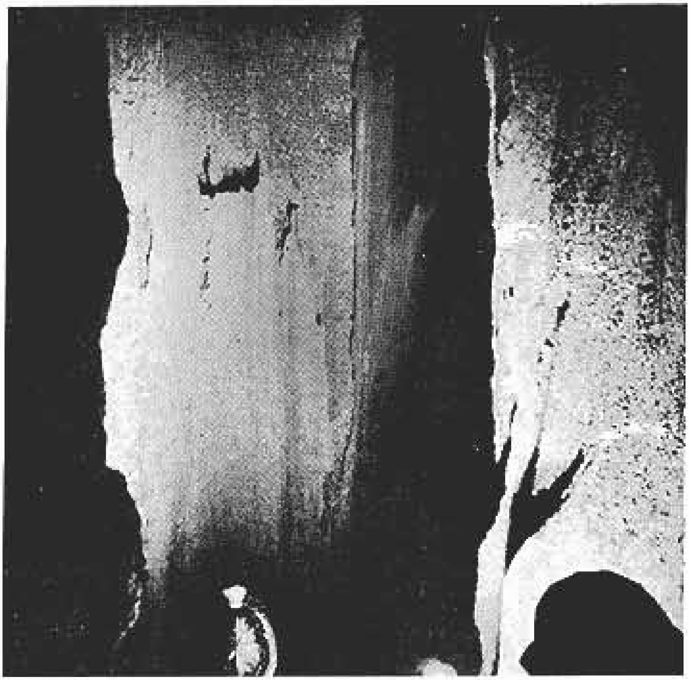

Fig. 3 - Tempio Cave: on the right there are some calcite crusts almost completely datached from gypsum; on the left and at the bottom of the photo we can see three parallel calcite blades.

oversurated with respect to $CaCO_3$ a few meters inside gypsum rocks. This fact clearly indicates that as soon as the water starts dissolving gypsum, i.e. as soon as a given concentration (lower than the saturation one for gypsum) of Ca^{++} (before entirely absent in the solution) is reached, the calcium carbonate deposition immediately occurs and such a process stops after a few (10-20) meters.

Therefore a direct relation has to exist between gypsum solutions and calcite deposition in gypsum caves. The dissolution features of the gypsum beds below all calcite sinters are in agreement with such a direct relation: in fact the starting step of the concretioning process always is the gypsum dissolution together with calcite deposition made by the same water (see fig. 1-2). Owing to this double action it is easy to explain the genesis, on quite vertical walls, of calcite crusts, which are almost completely detached from gypsum substrata (see fig. 3), and also of the calcareous parallel blades, which during their growth practically follow the progressive withdrawing of the gypsum walls, dissolved by percolating water (see fig. 4).

Moreover the presence of a thin clay layer beneath the con-

Fig. 4 - Novella Cave: The largest isolated calcite blade: it is over 16 meters high and over 3 meters long, but only 10-15 centimeters thick. Ist distance from gypsum wall is now about 2 meters.

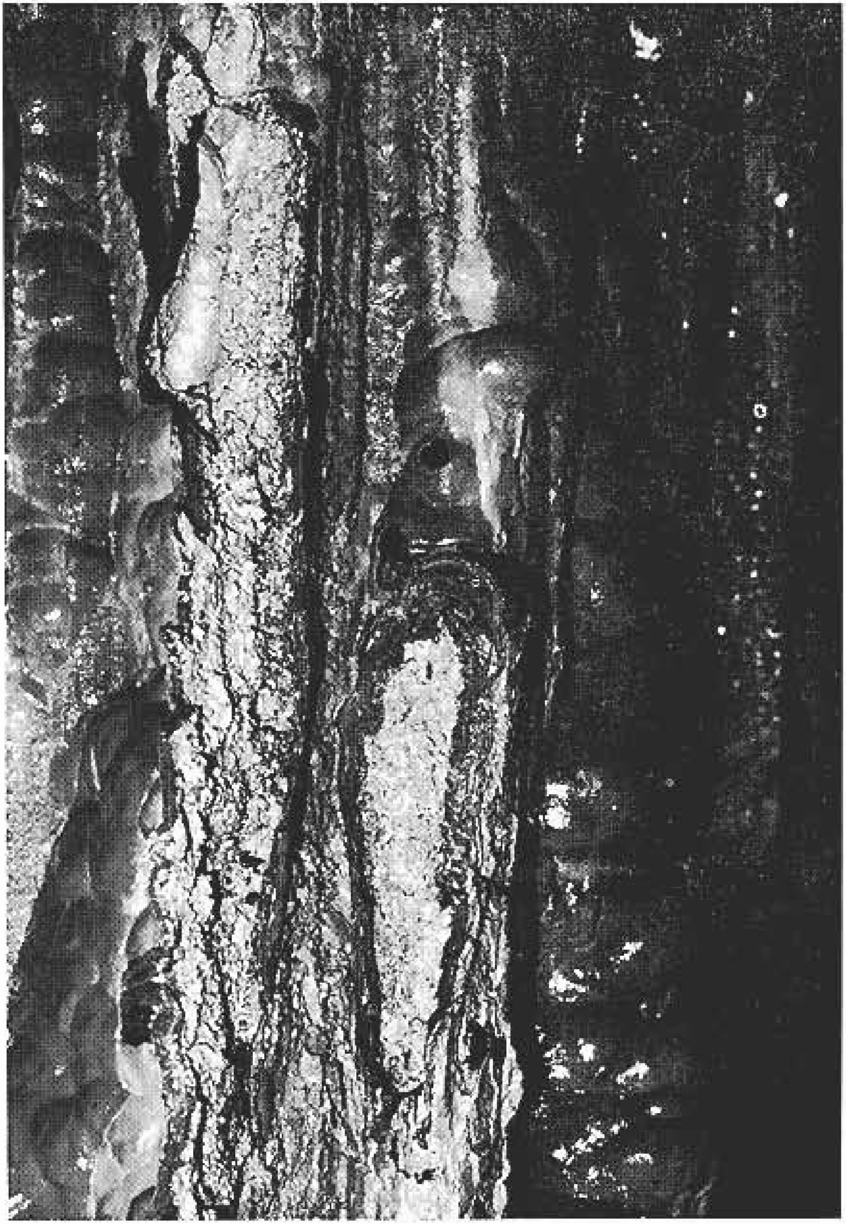

Fig. 5 . Novella Cave: Broken calcite flows showing clay layers inside.

Fig. 6 - Novella cave: cross section of a calcite blade with clay layer inside as nucleus.

cretion and over the gypsum substratum is to be expected starting from our theory.

In fact when the gypsum rock is dissolved, a small quantity of clay remains, and if the water circulates slowly enougth, the clay forms a thin layer between the gypsum and the calcite sinter. Successively when the solution of the rock proceeds the clay deposit is not enough to fill the void produced and therefore we observe the growth of a calcite crust quite unattached to the gypsum.

Moreover this theory explains the presence, otherwise very difficult to justify, of clay layers, which we commonly find as nuclei of calcite flows or of calcite parallel blades (see figs. 5,6).

In fact when the gypsum rock is dissolved, a smoll quantity of tion and clay layer erosion; along with calcium carbonate deposition and gypsum dissolution; this process builds up a single isolated calcite blade or many parallel blades.

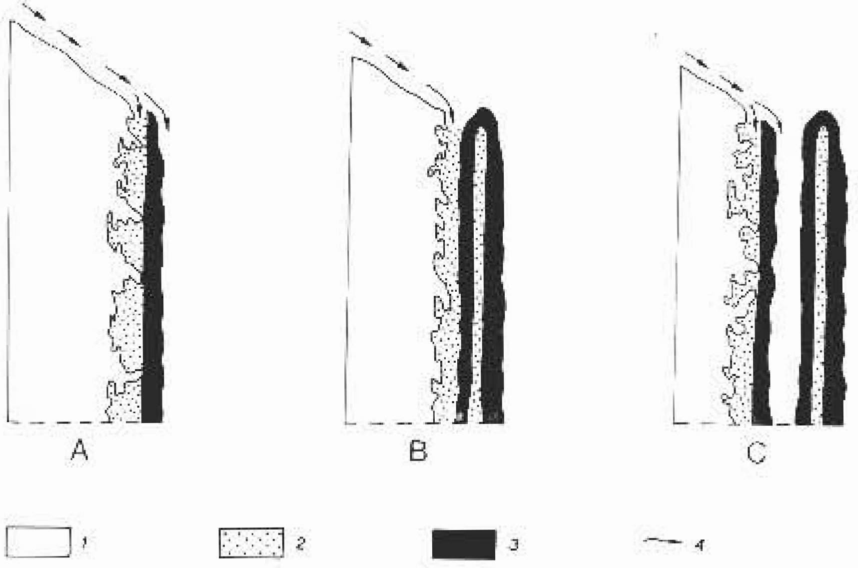

Fig. 7 - Evolutionary steps in the formation of calcite sinter blades inside gypsum caves:

1 - Gypsum/2 - Clay/3 - Calcite sinter /4 - Waler flow.

Step A: water flow dissolves gypsum wall and deposees calcium carbonate,, with the creation of a thin clay layer between gypsum and calcite sinter.

Step B: the clay produced by the solution of gypsum is not enough to fill the void fomed the progressive withdrawing of the gypsum wall leaves isolated calcite blade, with or without cly layer inside (this due to vater stifness)

Step C: the same situation of step A is obtained: a new calcite blade is now growing to form parallel blades.

Moreover the difference in pH existing between concretioning and unconcretioning waters of the same cave agree perfectly with the present theory. In fact the lower the value of pH, the lower the CO_3= concentration has to be and therefore it is more difficult for supernaturation to occur with respect to $CaCO_3$.

In the concretioning waters, during the time that Ca++ ions are removed from equilibrium by calcite deposition, solution of gypsum takes place, so that the concentration of SO_4= is increased while that of CO_3= is lowered and that of Ca++ remains quite the same. Owing to the fact that CO_3= ion can cause hydrolysis while the SO_4= can not, the developing of calcite deposition leads to a lowering of pH, until an equilibrium is reached and calcite deposition stops.

All the experimental data agrees with the hypothesis of a direct relation between gypsum solution and calcite deposition. We decided, therefore, to evaluate the influence of CO_2 concentration in gypsum speleogenesis by means of theoretical calculations, starting from the experimental data found in gypsum caves near Bologna.

The system is well defined if the gypsum solution equilibrium ($K_{ps} = 3.922 \times 10^{-5}$ at 10° C; Marshal and Slusher, 1966) is added to those necessary to define the $CaCO_3$ - H_2O - CO_2 system (Picknett, 1976).

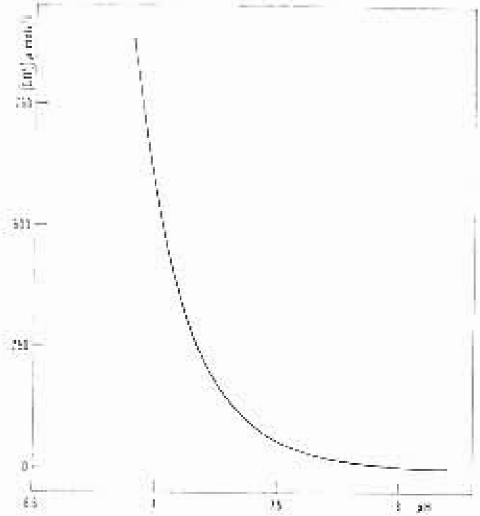

Fig. 8 . The equilibrium pattern for the system CO_2 - H_2O - $CaCO_3$. $CaSO_4.2H_2O$ at 10° C and with respect to CO°_2 and pH.

Table 1 - Calculated concentrations for solutions saturated with respect to $CaCO_3$ and $CaSO_4.2H_2O$ at 10° C

$[CO_2]^1_{init.}$	$[Ca^{++}]$	$[HCO_3^-]$	$[CO_2^\circ]$	$[SO_4^=]^2$	$[\dot{H}_2CO_3]$	$[CO_3^=]$	$[CaHCO_3^+]$	$[CaCO_3^\circ]$	$[H^+]$	$[OH^-]$	P mAt	pH
m mole/l					μ mole/l							
9,8180	13,492	5,9432	3,5340	13,818	7,1684	1,4093	292,23	40,000	0,29507	0,01442	67,18664	6,6
5,3616	13,443	3,7308	1,4026	13,666	2,8449	1,3938	184,02	40,000	0,18595	0,02280	26,66453	6,8
3,0617	13,409	2,3460	0,55722	13,565	1,1303	1,3835	115,95	40,000	0,11722	0,03608	10,59345	7,0
1,8135	13,387	1,4770	0,22154	13,500	0,44937	1,3769	73,096	40,000	0,07392	0,05713	4,21180	7,2
1,1065	13,377	0,93068	0,088122	13,463	0,17875	1,3731	46,099	40,000	0,04663	0,09050	1,67532	7,4
0,6921	13,372	0,58651	0,035052	13,432	0,071100	1,3699	29,076	40,000	0,02941	0,14338	0,66639	7,6
0,4436	13,364	0,36990	0,013952	13,417	0,028299	1,3683	18,341	40,000	0,01856	0,22718	0,26524	7,8
0,2919	13,359	0,23339	0,005555	13,413	0,011267	1,3680	11,572	40,000	0,01171	0,36002	0,10560	8,0
0,1981	13,359	0,14720	0,002211	13,403	0,004484	1,3670	7,3004	40,000	0,00739	0,57053	0,04203	8,2
0,1397	13,359	0,09284	0,000880	13,396	0,001785	1,3662	4,6059	40,000	0,00466	0,90415	0,01673	8,4

1) The concentration of $CO_{2\,iniz.}$ is fixed as $CO_{2\,iniz.} = HCO_3^- + CO_2^\circ + H_2CO_3 + CO_3^= + CaHCO_3^+ + CaCO_3^\circ$ owing to the absence of any source for $CaCO_3$ (cover or interbedded)

2) The concentration of $SO_4^=$ is fixed as $[SO_4^=] = [Ca^{++}] + [CaHCO_3^+] = + [CaCO_3^\circ]$
because we started from the hypotesis that Calcium has to be quite absent before gypsum solubilization.

Now we used the constants and the method outlined by Picknett (1973, 1976), to compute the concentrations of the various ions at the equilibrium for the system $CaCO_3$ - H_2O - CO_2 - $CaSO_4.2H_2O$ at 10° C (which is very close to the actual temperature of the gypsum caves of Bologna) and at values of pH varying from 6.6 and 8.4. Moreover we imposed the starting value for CA++ to be the square root of the solubility constant for gypsum and also that the SO_4= to be always equal to the sum of concentrations of CA++, $CaCO_3$. This was because the starting hypothesis was that all the calcium present has to derive from gypsum solution.

The results of such an analysis, listed in table 1, were used to trace out the equilibrium curve for the system with respect to CO_2 and pH (see fig. 8). In this diagram the zone under the curve represents solutions in which the CO_2 concentration is lower than the equilibrium one, so that, if calcite sinter is present, the water will dissolve it and so cause gypsum deposition.

On the other hand, water with a composition in the region over the curve, will deposit calcium carbonate and so will dissolve more gypsum than that stated for pure water.

Now, if we consider pH values in the range of our measurements and pCO_2 values not too far from normal, we can immediately deduce from the diagram of fig. 8 that in gypsum caves water could never be aggressive with respect to calcite, and this perfecly agrees with all the observations made in gypsum caves near Bologna, where we never have seen redissolution features over active or fossil calcite sinters.

Moreover, starting from table 1, it is possible to evaluate the behaviour of water with a given value for CO_2 and pH, then it comes in contact with gypsum; each time the quantities of $CaCO_3$ and of $CaSO_4.2H_2O$ which are to be dissolved or deposited to reach the condition of equilibrium can be computed.

It is obvious that a large error would affect the simple transposition of the data obtained by these theoretical calculations to the real cases of all the caves, because a cave water always contains many dissolved salts beside calcite and gypsum, and so its behaviour is often quite different from the expected one obtained starting from the considered equilibria.

But it is important to emphasize that our results are effective not only for gypsum caves, but also for all the cases in which the system $CaCO_3$ - H_2O - CO_2 - $CaSO_4.2H_2O$ is present. Consequently, keeping in mind that natural water always contains some dissolved CO_2, every time natural water comes in contact with gypsum rocks, the equilibria outlined before have to take place.

Therefore, if we start from Cigna's classification of karstic phenomena (Cigna, 1978), gypsum speleogenesis has to be classified not has a parakarstic one (2 components in equilibrium: gypsum and water), but always as a hyperkarstic phenomenon (more than 3 components in equilibrium: gypsum, calcite, water, carbon dioxide).

Owing to the fact that gypsum speleogenesis is an hyperkarstic phenomenon, it is obvious therefore that the explanation of all the genetic mechanism could be quite complicated. And this fact justifies why in gypsum caves it is still possible to see morphologies and formations not well known or not yet completely explained.

RIASSUNTO

La presenza di concrezioni calcaree all'interno di grotte gessose del Bolognese, che sono del tutto prive di una sorgente qualsiasi (copertura od interstrato) di questo minerale, ha spinto gli autori a rivedere criticamente le teorie speleogenetiche per il gesso.

Dall'analisi delle osservazioni sperimentali condotte in tutte le principali grotte concrezionate del Bolognese e dai calcoli teorici fatti risulta evidente il ruolo importante giocato dalla CO_2 nella carsificazione dei gessi.

Tali risultati poi sono del tutto generali e quindi possono essere applicati non solo nel particolare caso delle Grotte Bolognesi, da cui si era partiti, ma alla generalità dei casi di speleogenesi gessosa.

Inoltre, grazie a questa teoria, è facile spiegare la genesi fino ad oggi ancora non spiegata, di alcune concrezioni calcaree delle grotte Bolognesi: quali le lame isolate o parallele e la presenza al loro interno di argilla.

Quale conseguenza logica di questa teoria si ha poi che i fenomeni speleogenetici in gesso debbono sempre esser considerati ipercarsici (più di 3 componenti all'equilibrio: gesso, calcare, acqua e anidride carbonica) e non paracarsici (2 componenti all'equilibrio: gesso e acqua), come è stato fatto fino ad oggi.

BIBLIOGRAPHY

CIGNA, A.A. 1978. A classification of Karstic phenomena. Int. J. of Spel. 10 (1): 3-10.

MARSHALL, W.L., SLUSHER, E., 1966. Thermodynamics of calcium sulphate dihydrate in acqueous sodium chloride solutions, 0-110°. J. Phys. Chem. 70:4015-4027.

PICKNETT, R.G. 1973. Saturated calcite solutions from 10 to 40° C: a theoretical study evaluating the solubility product and other constants. Trans. Cave Res. Grp. G.B. 15(2):67-80.

PICKNETT, R.G. 1976. The chemistry of cave waters. In: The science of speleology. Ford T.D. and Cullingford C.H.D., Eds. Acad. Press, London: 213-266.