

# ON THE GENESIS AND EVOLUTION OF MIRABILITE IN THE CAVE OF IZVORUL TĂUȘOARELOR (ROMANIA)

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Mirabilite was first noticed in the cave in 1976, but it is believed to have formed sometime between 1972 and 1976. It covers (as lush tufts) sandy floors and sand-covered boulders and cobbles. Since 1976 on it has showed a surprising wax and-waning behaviour, being presently on the brink of extinction. Natural electrical charges within mirabilite "nests" and air currents are considered to have played the main role in crystallization, by electrostatical fixing of airborne  $\text{Na}^+$  ions on  $\text{SO}_4^{2-}$  rich sandy sediments, within restricted air moisture conditions that seem to be recurrent every 11 years.

Mirabilite ( $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ ) is a rare cave mineral, described as individual speleothem in only two limestone areas so far: the Flint-Mammoth System (USA) and the cave Izvorul Tăușoarelor (Romania). It is present in Eastern Africa in lava caves too, where it is eaten by elephants having stomach troubles. Mirabilite, like all sulphate minerals (see Table 1) needs special conditions, mainly a relatively dry atmosphere, which is

Table 1  
Sulphate minerals in caves

Name	Formula	Crystal System
Bassanite	$2\text{CaSO}_4 \cdot \text{H}_2\text{O}$	Trigonal
Gypsum	$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$	Monoclinic
Kieserite	$\text{MgSO}_4 \cdot \text{H}_2\text{O}$	Monoclinic
Epsomite	$\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$	Orthorombic
Hexahydrate	$\text{MgSO}_4 \cdot 6\text{H}_2\text{O}$	Monoclinic
Mirabilite	$\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$	Monoclinic
Bloedite	$\text{MgSO}_4 \cdot \text{Na}_2\text{SO}_4 \cdot 4\text{H}_2\text{O}$	Monoclinic
"labile salt"	$\text{CaSO}_4 \cdot \text{Na}_2\text{SO}_4 \cdot 2\text{H}_2\text{O}$	Unknown
Anhydrite	$\text{CaSO}_4$	Orthorombic
Celestine	$\text{SrSO}_4$	Orthorombic
Baritine	$\text{BaSO}_4$	Orthorombic
Thenardite	$\text{Na}_2\text{SO}_4$	Orthorombic

(simplified after Ford and Cullingford, 1976 and Hill and Forth, 1986)

a highly particular case in caves. However, mirabilite is a special case itself, since it needs 10 water molecules for crystallization. It is yet a question to be answered, viz. what is the range of moisture mirabilite tolerates. Anyway, air moisture is a key factor in its formation.

## GEOLOGICAL BACKGROUND

The cave of Izvorul Tăușoarelor (Romania's deepest — 451.6 m: —356; +105.6) is located in the upper basin of Gersa Creek, on the western slope of the Rodnei Mountains. The Eocene limestones housing the

cave, are only 60 m thick, laying on and being covered by impervious rocks (crystalline schists and shales).

There are three distinctive facieses within the limestone pile (upwards: grey, diaclased; black, bituminous and white-greyish, richly fossiliferous). The cavity cuts all three facieses. The middle-section, within the bituminous limestone, has rich gypsum speleothems — crusts and flowers — obviously related to the sulphur contents of the limestone (Silvestru, 1984).

Mirabilite has been first noticed in 1976, though it surely pre-existed, but not before 1972. In 1976 it covered four distinctive areas of the floor in Sala de Mese (Dining Room) at —200 m (Fig. 1). The main "nest" (from hereon referred to as nest 1) measured approximately 0.8 square metres, with 55 to 60% of its sandy floor covered by mirabilite tufts.

#### SPECIFIC DATA

Megascopically, mirabilite mimics mould, reason for which it was long ignored. The very fine needles reach 5 cm in length, covering boulders, cobbles and sand all together.

The specific analyses were undertaken by the discoverers (Motiu et al., 1977) emphasizing the predominance of mirabilite associated with gypsum and epsomite. When taken into the outer atmosphere, mirabilite quickly turns into thenardite ( $\text{Na}_2\text{SO}_4$ ).

Microscopically, the needles show a prismatic habitus, transparent, white and rarely yellowish, with perfect cleavage by (100).

The sand in nest 1 proved to be quite rich in gypsum needles too, which often support finer mirabilite needles. Sometimes mirabilite is found independently "anchored" to sand grains which are, in order of frequency: quartz, feldspar, mica, mica-schist lithoclasts and rarely calcite. In other nests gypsum is not present however.

Our investigation outlined two compulsory factors for mirabilite occurrences in the cave:

— *the sand*; as previously mentioned, mirabilite occurs not only on sand but on boulders and cobbles too, but only when covered by a fine layer of sand. A simple, yet relevant experiment was undertaken by placing two slabs of the same nature into a fastly growing mirabilite nest. One of the slabs was cleared of sand, the other was left with its natural cover of sand. One year later, the former was mirabilite-free whilst the latter was covered with lush mirabilite tufts. Seemingly, on a cobble which had one third naturally free of sand, mirabilite occurred along the limits of the sand cover.

— *air currents*; all mirabilite nests are located in well-ventilated areas, where the air movement direction changes seasonally (unidirectional circulation). The above-mentioned experiment provided good evidence for air current influence on mirabilite crystallization: the slab on which mirabilite developed has only one side covered by the mineral, the side blown by air currents coming from the upper sections of the cave (see Fig. 1) during summer.

The sand seems to play a special, probably double role. First, one would suspect that it is the source of  $\text{Na}^+$  (the  $\text{SO}_4^{2-}$  source is not a reason for debate since, as already mentioned, gypsum is common in the cave because of bitumena in the limestones). However, chemical analyses showed no higher  $\text{Na}_2\text{O}$  contents to justify mirabilite formation. It is thus quite probable that the  $\text{Na}^+$  source is somewhere else. Sand, however, is important because of its specific porosity which favours retention of moisture and, by creating both a favourable microclimate in the pores and a lattice for crystal growth, initiates crystallization. Within such a scenario, the role of the air current is implicit.

From the 1976 initial nest, mirabilite rapidly spread, covering ever larger sections of the Dining Room's floor, entering then the Sasca System (Fig. 1) where the farthest nest lies 150 m away from nest 1.

This spectacular evolution halted abruptly sometime between 1986 and 1987 and reversed, the retreat velocity doubling the advancement one. Presently, mirabilite in the cave is on the brink of extinction.

#### GENETIC HYPOTHESES

Previous authors considered that  $\text{Na}^+$  came from the feldspars and  $\text{SO}_4^{2-}$  was water-borne, raising by capillarity through sand deposits and thus forming mirabilite on the surface of the alluvia (Moțiu et al., 1977).

As we previously mentioned,  $\text{Na}^+$  seems to have no connection with cave sediments; as for the underground streams, the chemical analyses revealed that the  $\text{SO}_4^{2-}$  contents do not significantly differ from urban drinkable water. Given these facts, we consider the above-mentioned crystallogenesis mechanism quite improbable.

Domșa (1988) proposed a different scenario: seepage water penetrating in to the Dining Room's ceiling, loses  $\text{Ca}^{++}$  by speleothem crystallization and thus enriches in  $\text{Na}^+$ . Once this water reaches the sandy floor (by dripping) it meets  $\text{SO}_4^{2-}$ -rich water in sediments (as in the previous hypothesis). Moreover, this author proposes a solution for a difficult question: why did mirabilite occur only after 1972? He believes that this was due to the digging of a new entrance in the Sasca System (Fig. 1) in 1975, when air currents changed patterns, moisture diminished and mirabilite could crystallize.

However, facts rather deny such a mechanism: if seepage water carries  $\text{Na}^+$ , there should be dripping signs on the floor where it hits the sand. No such signs have been found so far, on the contrary, mirabilite nests are located in areas with no apparent dripping. As for the  $\text{SO}_4^{2-}$  in the underground streams, the question was already discussed. The opening of the new passage in the Sasca System had no significant role in changing air current patterns, since this labyrinthic section had (and still has) another, wider opening in the Dining Room (Fig. 1); in the new (very narrow) passage, the air current is quite feeble. Moreover, nest 1 lies upstream the entrance to the Sasca System and, whatever the change in air current patterns, that could possibly occur downstream only.

Our research focussed on air currents and sediments. Testing natural electric charges in the sand, values up to 81.9 mV were measured within nest 1 (natural electric charges in sediments may occur because of the diffusion-absorption potentials, Airinei, 1977). Other values (within mirabilite nests) ranged between 1.5 and 13.5 mV. Measurements in other sand deposits where mirabilite is not present, revealed charges up to 45.1 mV. This strongly suggests that natural electric charges may be prior to mirabilite formation. Furthermore, since all mirabilite nests are located in well-ventilated areas and electrical charges revealed in areas with poor air circulation are not associated with mirabilite, it is obvious that the air current-electrical charges association is a *sine qua non* of mirabilite genesis in the Cave of Izvorul Tăușoarelor.

We assume two possible ways this association could work out a crystallogenesis:

a. The cations and anions are present in the sand and need special moisture conditions to get fixed by 10 crystallization water molecules, conditions provided by air currents. Within such a frame, one may assume that the speed and water content of the air are subject to very fine tuning, in which electrical charges may act like a catalyst.

b.  $\text{Na}^+$  is air-borne and electrostatically fixed in the electrically charged areas rich in  $\text{SO}_4^-$ . The anions come from the water circulating through the bituminous limestone in which the Dining Room and the Sasca System are carved.

The pattern followed by the mirabilite spreading reveals an advancement from nest 1 downward and northwestward. This is a secondary track of air currents (which follow the main passage through the Ball Room, see Fig. 1) by a unidirectional circulation (that changes direction seasonally). If we accept hypothesis b., this spreading pattern strongly suggests the  $\text{Na}^+$  source must be in the Dining Room or upstream the Kilometre Passage.

At this point, the following questions are to be further answered:

1. What is actually the source of  $\text{Na}^+$ ? Is it in the cave or in the outer atmosphere?
2. What causes the wax-and-waning of mirabilite?
3. Why did mirabilite appear only recently (as compared with gypsum)?

The answers lay ahead. Fine and detailed analyses are to be made with equipment still not available for the author. However, several assumptions can be fairly proposed:

1. The source may lie:— in the limestones (a specific sedimentary sequence opened by speleogenesis) in sediments (of unknown location) in the outer atmosphere.

2. Air moisture variations. Since the range of mirabilite stability is restricted, slight variations of water contents in the cave atmosphere may either solve mirabilite or arrest its formation.

3. The registered wax-and-waning of mirabilite in the Cave of Izvorul Tăușoarelor roughly covers 11 years (1976—1987) which corresponds

to a basic atmospheric cycle. If the  $\text{Na}^+$  source is long active, mirabilite formation could be cyclic. That implies that it might have been present 11 years ago (1964–65) but given its striking resemblance to mould, it might have passed unnoticed. Before that (1954–55) the cave was not yet explored.

There is also the possibility that in the previous periods the meridematic conditions were not favourable, or, in other words, not every 11 years the climatic oscillations would induce favourable conditions for mirabilite formation in the cave.

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