GEOCHEMICAL STUDY OF SOME SPECIMENS OF STALACTITES FROM TOURKOVOUNIA CAVE, ATHENS

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The Tourkovounia cave or cave of Sotiros, is located at the Tourkovounia hill, in Athens. During a visit, on 25—3—1973, some specimens of the stalactites have been collected. In two specimens of stalactites, the successive zones of stalactite growth have been examined, (Fig. 1, 2), mineralogically and spectroscopically. Fluorescence and natural thermoluminescense have also been studied.

The successive zones of stalactite growth present different coloration. Their colour is white, reddish and yellowish. The yellowish tint is more common. The diadochic zones of stalactite growth have been separated and examined. A description of the successive zones is given :

1—The section of this stalactite is given in fig. 1. Its dimensions are : 4.5 cm length and 3 cm width. The external surface of the stalactite is coloured reddish-yellow. Four zones have been studied.

1—S—P1 : The external zone is yellowish, semitrasparent. Consists of calcite crystals.

1—S—P2 : The next zone is white - yellowish. In the limit with the external zone P1, a fair reddish coloration is appeared. This zone is semitrasparent.

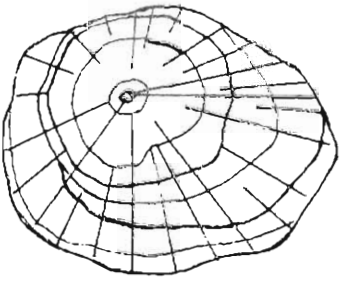

Fig. 1. Section of stalactite.

1—S—P3 : This zone presents a yellowish - brown coloration.

1—S P4 : A small internal zone, at the centre of stalactite, colored in yellowish tint.

The section of the second stalactite is given in fig. 2. The dimensions are 16.5 cm length and 1—1.5 cm width. In this specimen the stalactite growth do not form concentric zones, as in the first specimen, in fig. !, presents.

M—1 The external zone is white, semitrasparent and consists of calcite crystals.

M—2 The next zone is yellowish - brown. The calcite crystals are accompanied by microcrystalline aggregates of clay minerals.

M—3 A reddish zone, consists of calcite crystals with fair · coloured microcrystalline aggregates.

M—4 This zone consists of white calcite crystals.

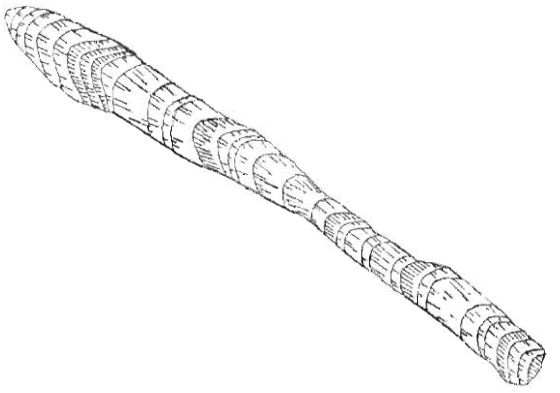

Fig. 2. Section of stalactite.

M - 5 A yellowish - brown zone, consists by calcite crystals with microcrystalline aggregates.

M—6 White calcite crystals form this zone.

M—7 This zone is coloured in yellowish - brown tint, the calcite crystals are accompanied by microcrystalline aggregates of clay minerals.

M—8 A white - yellowish zone.

M—9 This zone is coloured in yellowish - brown shade, the calcite crystals are accompanied by aggregates.

M—10 A thin white - yellowish zone.

M—11 A reddish - brown zone, the calcite crystals present impurities of iron oxides and clay minerals.

M—12 A white - yellowish zone.

M —13 A yellowish brown zone.

M—14 A narrow white zone.

M—15 A small yellowish - brown zone.

In the described samples, a qualitative spectroscopic analysis has been done Barium, iron, magnesium, manganese, sodium and strontium have been found in small quantities, as trace elements. The trace element content in samples is present in table 1.

Table 1.— Trace element content in successive zones of stalactites

No	Ba	Fe	Mg	Mn	Na	Sr
S—P1	+	+	+	+	+	+
S—P2			+	—		+
S—P3		—		+	++	+
S—P4		—	+	+	++	+
M—1	+	+	+	+	++	++
M—2	+	+	++	+	—	+
M—3	+	++	++	+	+	++
M—4	+	++	++	+	+	+
M—5	+	+	++	+	++	++
M—6	+	+	++	+	+	++
M—7	+	+	++	+	+	++
M—8	+	+	+	+	++	+
M—9	+	+	++		+	+
M—10	+	+	++	+	+	+
M—11	+	++	+	+	+	+
M—12	+	+	+		++	+
M—13		+	+	+	+	+
M—14	+	+	++	+	++	++
M—15	+	+	++	+	++	++

The distribution of these minor elements, in examined samples, is not connected with the colour of the zones. Iron content is not high. It is believed, that iron is not in substitution for calcium in these stalactites, because it is known that the presence of ferric and ferrous iron, in calcite, gives to the mineral a bluish, green colour (Veudl Mandy, 1958). The presence of iron may be due to iron oxides, visible microscopically, in some specimens, and to microscopic aggregates of clay minerals. Magnesium content may be, also, connected with the presence of clay minerals,

Strontium and barium may be in diadochy with calcium in calcite, sodium too. The substitution of these elements for calcium, has been done, during the formation of calcite. Calcium carbonate is deposited when a hanging drop of the saturated solution begins to evaporate, becoming strongly supersaturated (Betekhtin).

Manganese content is almost similar in all zones. Calcite usually contains

manganese in substitution for calcium The entry of appreciable manganese in the structure of calcite usually introduces a pale pink to rose - red colour. (Dear—Howie—Zussman, 1967). However, there is no difference in manganese concentration in the white and reddish zones of stalactite growth. The reddish tint is not due to the presence ef manganese.

Natural thermoluminescence has been studied in all the examined samples. Thermoluminescence is the result of the release of energy stored as electron displacements. These electron displacements are commonly associated with lattice defects. Irradiation and impurities of the crystal, usually, are the cause of thermoluminescence.

A description of the thermoluminescence study is given :

I – S – PI Thermoluminescence has been observed, at 138° C. It is very weak.
I – S - P2 Very weak thermoluminescence at 120° C.
I – S – P3 Very weak thermoluminescence at 125° C.
I – S – P4 Very weak thermoluminescence at 170° C.
M - I No thermoluminescence has been observed.
M – 2 No thermoluminescence has been observed.
M 3 No thermoluminescence has been observed.
M—4 Very weak thermoluminescence, at 160° C.
M – 5 Very weak thermoluminescence at 145° and 248° C.
M—6 No thermoluminescence has been observed.
M—7 No thermoluminescence has been observed.
M – 8 Very weak thermoluminescence at 135° C.
M – 9 Very weak thermoluminescence at 120° — 130° and 180° C.
M – 10 Very weak thermoluminescence at 60° C.
M – 11 Very thermoluminescence from 126° C to 170° C.
M – 12 Very weak thermoluminescence from 150° C to 260° C.
M – 13 Very weak thermoluminescence from 105° C to 162° C.
M – 14 Very weak thermoluminescence at 90° C and from 210° C to 274° C.
M—15 Very weak thermoluminescence from 160° C to 240° C.

Thermoluminescence presents strong intensity in calcites, formed at high temperature. Calcites formed at low temperatures, in sedimentary deposits, and in caves, do not present strong thermoluminescence, (Mc Dougall, 1969).

In examined samples, thermoluminescence was absent in some specimens. In the other specimens, a very weak white light appears, on heating. There is no relation between thermoluminescence and colour of specimens In the internal

zones of the second stalactite, a persistence of the thermoluminescence is observed.

Under ultraviolet light, at 2535 A wavelegth, all specimens have been studied An orange - red fluorescence appears. However zones of violet - blue fluorescence in the stalactite mass, have been observed.

A detailed study, under the ultraviolet light, using microscope, showed that these zones of violet - blue fluorescence are limited in certain zones of the stalactite growth. These zones are these darkened by impurities. The intensity of the violet - blue fluorescence is strong in very limited zones of the reddish specimens. A shadow of the violet - blue fluorescence is presented in the neighbourhood of these limited zones.

Experimental works of Fonda (1940) on artificial precipitated calcite, demostrated that the fluorescence increase in intensity with increasing manganese content (max. 3.3 mol % $MnCO_3$), and that with more manganese the fluorescence decreases. Brown (1934) has also reported that the reddish - yellow fluorescence of calcite increases in intensity, with increasing manganese.

It have been shown that some elements give different fluorescence spectra in calcite. So the presence of stannous ion give a white fluorescence, lanthanum and neodymium give pale yellow, magnesium bluish green.

Manganese content is almost similar in all zones, as is shown in table 1, It has been observed that violet - blue fluorescence is presented in the dark colour zones . In the white zones, an orange - red fluorescence always appears. But these zones consist of pure calcite, meanwhile in the coloured zones, iron oxides and clay minerals are presented.

The difference of fluorescence of stalactite zones is due to the presence of mineralogical impurities of the calcite crystals. Orange - red fluorescence is due to the presence of manganese ion, and the violet - blue to the concentration of the mineralogical impurities.

Manganese is an activator for fluorescence, as also for thermoluminescence. Is has been known that the presence of manganese in crystals increase the intensity of thermoluminescence not only in calcite (Zeller, 1953, 1954, and others . . .) but also in other minerals.

Manganese gives an orange thermoluminescence in calcites. Is is believed that manganese content is independent of thermoluminescence. Its presence may be connected to other causes, in the examined stalactites.

The conclusion of this study in the following :

1. The examined stalactites, from the Tourkovounia Cave, consist of calcite. In some

zones of the stalactite growth, iron oxides and clay minerals are enriched. These zones are of reddish - brown colour.

2. Barium, strontium, sodium, manganese, iron and magnesium are found in trace amounts in all zones of the stalactite growth. Strontium, barium, sodium and manganese, are in diadochy with calcium, in calcite. Iron and magnesium presence due to the mineralogical impurities, There is no relation of the distribution of these elements in the zones (ixternal or external zones).

3. A very weak whitish thermoluminescence has been observed in some zones. Thermoluminescence was more persistent in the internal zones.

4. In ultraviolet light, an orange - red fluorescence with zones of violet - blue fluorescence appears, in the stalactite mass. In a detailed study of these zones, is demostrated that violet - blue fluorescence is limited at the impurities zones of the stalactite growth. The orange - red fluorescence of the stalactite is due to manganese content.

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ΓΕΩΧΗΜΙΚΗ ΜΕΛΕΤΗ ΜΕΡΙΚΩΝ ΔΕΙΓΜΑΤΩΝ ΣΤΑΛΑΚΤΙΤΩΝ ΕΚ ΤΟΥ ΣΠΗΛΑΙΟΥ ΤΟΥΡΚΟΒΟΥΝΙΩΝ, ΑΘΗΝΩΝ

Ὑπὸ ΒΑΣΙΛΙΚΗΣ ΜΗΤΣΑΚΗ

Τὸ σπήλαιον Τουρκοβούνια, εἶναι περισσότερον γνωστὸν ὡς σπήλαιον τοῦ Σωτῆρος. Κατὰ τὴν διάρκειαν μιᾶς ἐπισκέψεως εἰς τὸ σπήλαιον τοῦτον, τὴν 25 - 3 - 1973, συνελέγησαν μερικὰ δείγματα σταλακτιτῶν. Εἰς τὰ δείγματα ταῦτα, ἐγένετο κάθετος τομὴ πρὸς τὸν ἄξονα ἀναπτύξεως τῶν σταλακτιτῶν, καὶ ἐμελετήθησαν αἱ ζῶναι ἀναπτύξεως τοῦ σταλακτίτου (εἰκ. 1 καὶ 2).

Τὸ χρῶμα τῶν ζωνῶν ἀναπτύξεως δὲν ἦτο ὁμοιόμορφον. Παρετηρήθησαν ἐναλλαγαὶ λευκῶν καὶ ἐρυθρωπῶν ζωνῶν. Ὀρυκτολογικὴ μελέτη τῶν ζωνῶν ἔδειξεν ὅτι εἰς τὰς ἐρυθρωπὰς ζώνας, ὁ ἀσβεστίτης συνοδεύετο ὑπὸ ἀργιλικῶν ὀρυκτῶν καὶ ὀξειδίων τοῦ σιδήρου.

Τὰ στοιχεῖα βάριον, στρόντιον, νάτριον, μαγγάνιον, σίδηρος καὶ μαγνήσιον ἀνευρέθησαν εἰς ἴχνη, εἰς ὅλας τὰς ζώνας. Τὰ στοιχεῖα σίδηρος καὶ μαγνήσιον, ἀνευρίσκονται ὡς προσμίξεις τῶν ἀσβεστιτῶν, ἐνῶ τὰ ὑπόλοιπα ἔχουν ἀντικαταστήσει τὸ ἀσβέστιον εἰς τὸ πλέγμα τῶν ἀσβεστιτῶν. Δὲν παρετηρήθη συγκέντρωσις τῶν στοιχείων τούτων εἰς τὰς ἐξωτερικὰς ἢ ἐσωτερικὰς ζώνας ἀναπτύξεως τοῦ σταλακτίτου.

Ἀκολούθως, τὰ δείγματα τῶν σταλακτιτῶν ἐξητάσθησαν διὰ θερμοφωταύγειαν. Λίαν ἀσθενὴς λευκὴ θερμοφωταύγεια ἐνεφανίσθη εἰς τὰ πλεῖστα τῶν δειγμάτων. Εἰς ὡρισμένα δείγματα δὲν παρετηρήθη θερμοφωταύγεια. Ἂν καὶ τὸ μαγγάνιον, θεωρεῖται ὡς ἐνεργὸν στοιχεῖον διὰ τὴν ἔντασιν τῆς θερμοφωταυγείας εἰς τοὺς ἀσβεστίτας, δὲν θεωρεῖται, εἰς τὴν προκειμένην περίπτωσιν, ὅτι τὸ στοιχεῖον τοῦτο σχετίζεται μὲ τὴν ἐμφάνισιν τῆς θερμοφωταυγείας, εἰς τοὺς ἐξετασθέντας σταλακτίτας.

Οἱ ἐξετασθέντες σταλακτῖται, παρατηρούμενοι εἰς ὑπεριῶδες φῶς, δεικνύουν πορτοκαλλόχρουν φθορισμὸν γενικῶς, εἰς ὡρισμένας μόνον ζώνας παρατηρεῖται ἰώδης φθορισμός. Μία λεπτομερὴς ἔρευνα, ἔδειξεν ὅτι ὁ ἰώδης φθορισμὸς συνιστᾶται μόνον εἰς περιωρισμένας ζώνας ἀναπτύξεως τοῦ σταλακτίτου, εἰς τὰς ζώνας, ὅπου εἶναι συγκεντρωμέναι αἱ προσμίξεις τῶν κρυστάλλων τοῦ ἀσβεστίτου, εἰς τὰς ἐρυθρωπὰς ζώνας. Τὸ μαγγάνιον θεωρεῖται ὅτι προκαλεῖ τὸν πορτοκαλλόχρουν φθορισμόν.