THE OCCURRENCE OF STRIPED CALCITES CONTAINING MANGANESE IN GYÖNGYÖSOROSZI

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A. Vidacs in his work dealing with the structure and mineral association of the mine of Gyöngyösoroszi mentions white and black striped calcites which occur as 5th phase. Our institute has collected a considerable amount of these calcites. The pink, sometimes glowing red luminescence of the crystalline white calcite appearing in broad band prompted S. Koch to study more closely the stripe formation of calcites.

As can be seen on *Fig. 1* and 2 the white and black calcites vary to a great extent. In some places they separate rhythmically in stripes the white and black stripes alternate and in some other places they cross each other, frequently the black calcite stripe forms a circle and surrounds white calcite. However, even within the black stripe one, but often two, white vein appears too.

Examining the pieces under UV light the white calcites occurring in broad stripes show everywhere pink and in some places in small patches and sometimes in stripes a glowing red luminescence. The thin white veins occurring in the black stripes showed everywhere a white colour also under UV light. Under the black stripes a quite thin (about 3 mm) stripe appeared which showed a yellowish luminescence and was limited sharply from the calcite extending in its vicinity and showing a pinkish luminescence. Under ultraviolet light at the borders of the black and white tiny crystalline stripes this band could everywhere be seen whereas under white light it could only be detected in certain places.

Under white light and partly under ultraviolet one the striped calcites could be separated into the following bands:

1. White finely granulated dense calcite. The crystal granules grow as they proceed towards the black stripe *(Fig. 3)*. It shows a pink luminescence.

2. A black band forming — as can be seen on the photomicrographs — by an extremely finely distributed dark substance settling on the white calcite crystals and forming inclusion rows in fine stripes in them, exhibiting their parallel intergrowth. Macroscopically it consists of small crystals — rombohedrons — looking like a dense black stripe. The size of the black rombohedrons also increases as we proceed from the dense small granular white calcite towards the wider white calcite band consisting of larger crystals. This is well illustrated on *Fig. 4* and *5* prepared with the same magnification only No. 4 was photo-

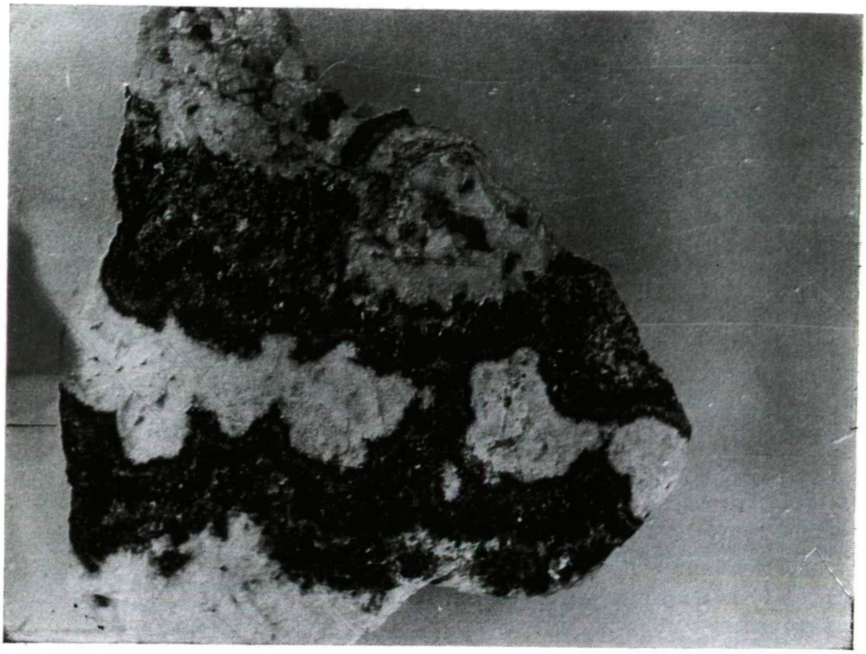

Fig. 1. White-black banded calcite. $1/2$ natural size

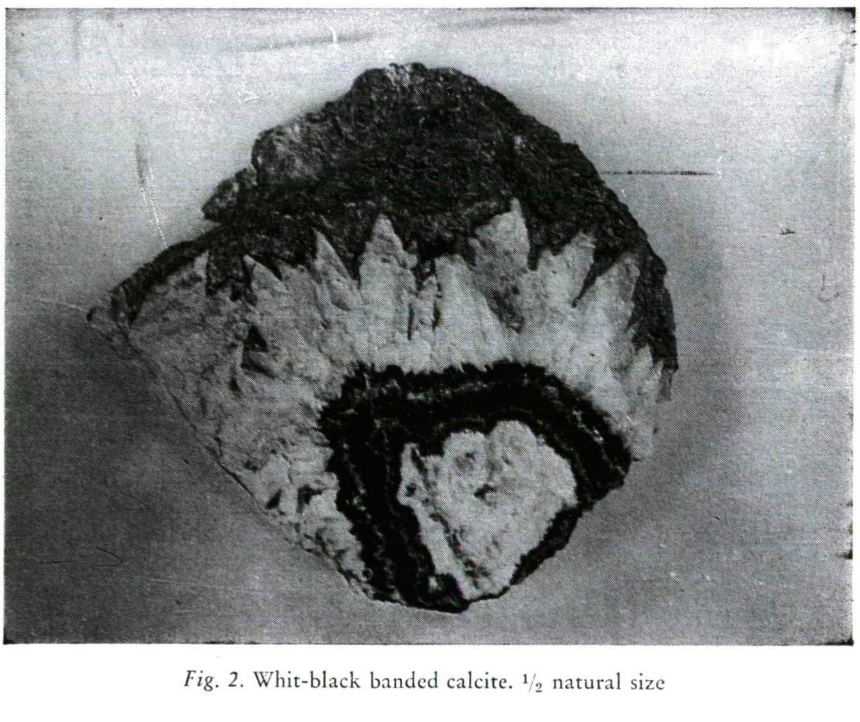

Fig. 2. Whit-black banded calcite. $1/2$ natural size

graphed on the side of the dark band which is situated nearer to the small white calcite granules and No. 5 on that one situated nearer to the larger white calcite granules.

The inclusions are composed of dark-alternating sharp, and blurred-lines. Nowhere one can see a homegeneous dark band. *Fig. 6* shows the structure of a dark band under higher magnification.

The band rich in dark inclusions dces not really adjoin the crystalline calcite along a sharp border line, but by crystal granules containing few inclusions *(Fig. 7.)*.

Already here along the dark rombohedrons in some places a thin pyrite vein appears, in some other places this vein limits only the white crystalline band (Fig. 2.).

3. In the black band a white calcite stripe without inclusions extends everywhere *(Fig. 8.)*. It does not show fluorescence.

4. On the black rombohedrons increasing in size a well developed stripe of white rombohedrons settles. On Fig. 9 it can be seen that the white band limited from the black calcite by a pyrite vein consists of considerably larger crystals than the calcite of band 1. On the Fig. 9. the twin lamellae and cleavage directicns of the calcite crystals are well visible. This white band shows everywhere a pink fluorescence and this band contains the spots luminescing glowing red.

5. As 5th type may be mentioned that is composed of a thin band which can only be separated under ultraviolet light from the small granular calcite and probably only differs from it in its structure.

Although it does not belong to the white and black striped calcites we mention that these striped white and black calcites are associated with a reddish brownish calcite where the white calcite is bordered by pyrite. (Upper part on Fig. 2.).

The data of chemical analyses of the single bands are summarized in Table 1. The first part of the Table contains the analytical data, and the second one the mineral composition calculated on the basis of the analytical data. The denotations and numbers respectively used at the analysis correspond to the numeration of the above five bands. 1' etc. and 1" etc. means that similar bands were separated from a quite different sample.

From the analytical data the following conclusions can be drawn:

1. Samples 3, 3' and 3", thus the white vein extending in the black band proved to be everywhere ideally pure calcite, which did not contain manganese even in traces.

2. Of the selected substance only 1 and 1" samples contained SiO_2 as insoluble residue which was composed of the thin quartz veins occurring in some places in the small granular dense white calcite.

3. The pyrite vein associated with the bands points to the fact that FeO and $FeCO_3$ occurs everywhere except in the white vein extending in the black band. The reddish brown colour of the calcite appearing above the pyrite vein limiting the white broad band is caused by the greater amount of iron content of this calcite as compared to the other ones.

4. With the exception of calcite No. 3 which is ideally pure, manganese can be found in every band, the white calcites contain $MnCO_3$ the black ones probably MnO.

Fig. 3. ×20

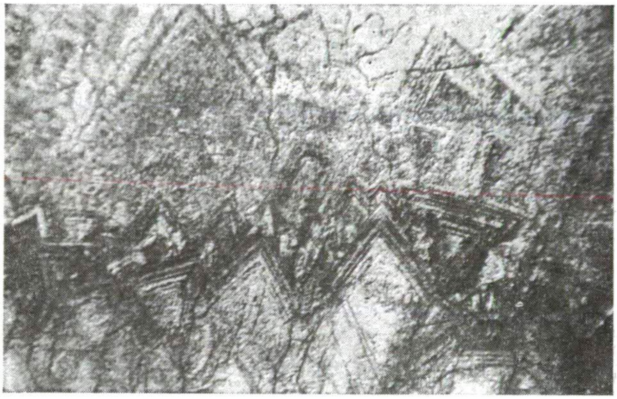

Fig. 4. ×20

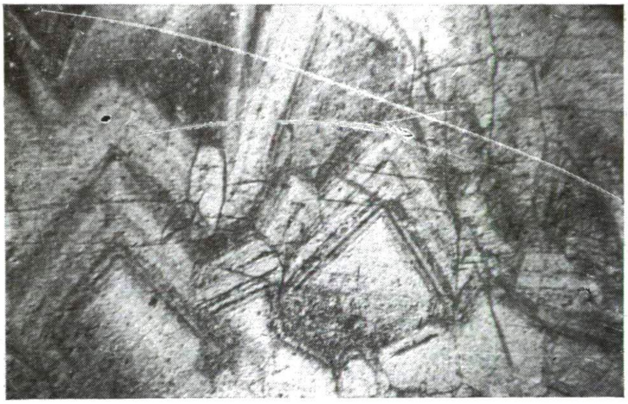

Fig. 5. ×20

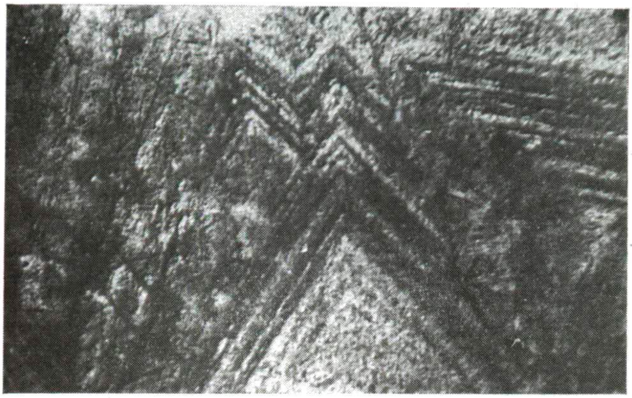

Fig. 6. ×70

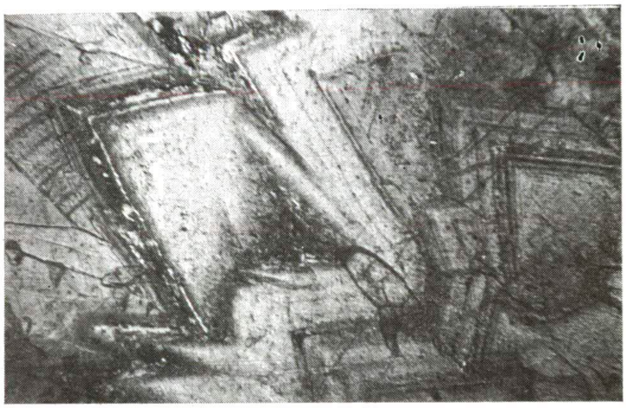

Fig. 7. ×20

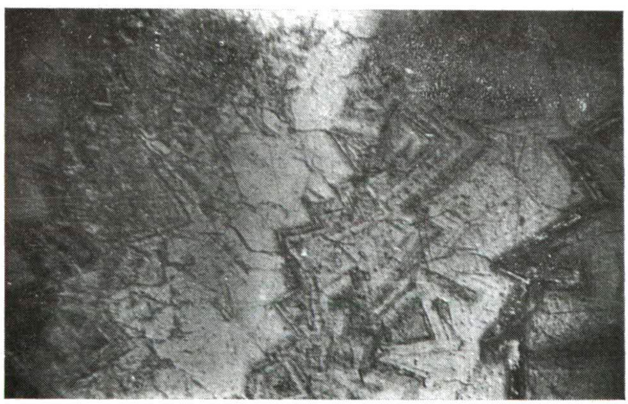

Fig. 8. ×12

Table 1.

Number of the types	CaO	MgO	FeO	MnO	CO_2	SiO_2	$CaCO_3$	$FeCO_3$	$MnCO_3$
1	52,58	—	1,71	1,39	42,79	1,50	93,84	2,38	2.25
2	54,23	—	1,25	1,36	43,20	—	96,77	1,91	
3	56,07	—	—	—	43,98	—	100,05	—	—
4	54,18	—	1.12	0,89	43,74	—	96,68	1,80	1,45
5	55,02	—	—	1,03	43,82	—	98,20	—	1.67
1'	53,05	—	1,80	1,50	43,64	traces	94,65	2,91	2,43
2'	54,00	—	1,59	1.03	43,37	—	96,40	2,57	—
3'	56,08	—	—	—	43,88	—	99,96	—	—
4'	54,80	—	traces	1,29	43,82	—	97,91	—	2,09
5'	55,19	—	—	1,00	43,81	—	98,38	—	1,62
1''	52,72	—	1,00	1,42	41,86	3,02	93,20	1,61	2.30
2''	54,32	—	1,02	1,45	43.22	—	96,91	1,64	—
3''	56,00	—	—	—	43,94	—	99,94	—	—
4''	54,13	—	1,09	0,97	43,73	—	96,59	1,76	1,57
5''	53,88	—	1,02	1,38	43,80	—	96,13	1,64	2,23
reddish brown	52,68	—	3,12	0,89	43,17	—	94,00	4,35	1,45
reddish luminescent	56,09	—	—	traces	43,92	—	100,01	—	—

5. The substance prepared under ultraviolet light from the part luminescenting glowing red proved on the basis of the analysis to be pure calcite with manganese traces. It is known from the literature that the presence of manganese ions in minimal amounts may induce the strong red luminescence of the substance, it is therefore probable that the strong luminescence of the striped calcites from Gyöngyösoroszi is also due to this fact.

Thus according to the analysis the white-black band of the striped calcites is caused by the manganese occurring in various forms in the different stripes, i. e. the dark colour of the band which seems to be black is due to the manganese content of the extremely fine inclusions present possibly as MnO in the calcite.

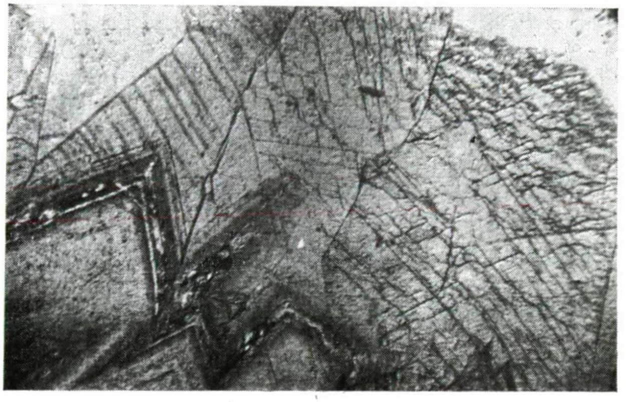

Fig. 9. ×20

We prepared the DTA curves of the single bands too, however, under the experimental conditions a peak corresponding to either $MnCO_3$ or MnO did not appear. Presumably the apparatus was not sensitive enough to record the relatively small quantity.

Unfortunately the X-ray pattern did not either show lines corresponding to MnO, however, this is not only due to the small quantity, but also to the fact that most probably this MnO which appears in extremely finely distributed stripes does not separate in crystals. Thus conclusions could only be drawn on the basis of the analytical data so that the analyses were performed very carefully, the components in the parallels were determined by various methods.

When we began to investigate striped calcites and prepared the first analyses about 15 per cent $MnCO_3$ was found in the white calcite. Then the question arose whether mangano-calcite or kutnahorite is involved, however, in the course of the systematic examinations (determinations of the manganese content were still carried out from numerous other places which are not illustrated on the Table) we did not succeed in finding calcite containing such large amounts of manganese.

Examinations are in progress to determine why and under what conditions $MnCO_3$ separate beside each other or subsequently. Presumably the pH, the redox-potential and last but not least, or just in accordance with the above, the CO_2 content and the CO_2 atmosphere over the crystallizing solution play a role.

Experiments were carried out according to which in the course of an hour in a CO_2 current heated to 600° and at 300—400° C in 4 hours, artificial $MnCO_3$ transformed in MnO. It may be that at lower temperature this change may also take place in the course of a longer period and possibly the occurrence of calcites containing $MnCO_3$ and MnO in alternating stripes showed also be attributed to the CO_2 atmosphere, or just to its absence, at the separation, this question requires, however, further investigation.

REFERENCES

VIDACS, A.: Structure and Mineral Association of the Veins of the Mine of Gyöngyösoroszi. Acta Min. Petr. Tom. X. p. 77. 1957.