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TODOROKITE AND PYROLUSITE FROM VERMLANDS TABERG, SWEDEN

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During the course of an examination of the soft iron ore of Vermlands Taberg in western Sweden (P. Ljunggren, 1958) manganese mineralization was found to have taken place both in the goethitized iron ore and in the argillized wall-rock. The manganese oxides are found as veins in the soft iron ore, as impregnations in the argillized wall-rock and in secondary calcite veins. A formation of dendrites of manganese oxides is also very common. This manganese mineralization is mainly concentrated to the border zone between the soft iron ore and the argillized skarn and leptite rocks. The width of the manganiferous veins hitherto found, often less than ten centimetres, is too small to allow any profitable mining of manganese ore.

The quite predominating manganese oxide mineral in these veins is pyrolusite. In a secondary calcite vein cutting the soft iron ore another manganese oxide mineral was found and identified as todorokite (T. Yoshimura, 1934; C. Frondel, 1953). An examination of the pyrolusite and the todorokite is given in the present paper.

TODOROKITE

The todorokite is found as black aggregates in a 5 cm. wide secondary calcite vein in the soft iron ore. The aggregates consist of small needle-shaped crystals (maximum size 0.2×0.01 mm.) arranged spherulitically or dendritically in the calcite vein.

The mineral was found upon *x*-ray examination to be identical with todorokite (Mn, Ba, Ca, Mg) $Mn_3O_7 \cdot H_2O$, as described by C. Frondel in 1953 and T. Yoshimura in 1934. The d-values of todorokite from Todoroki and from Vermlands Taberg are given in Table 1. The DTA curve of todorokite from Vermlands Taberg is given in Fig. 1. It shows endothermic peaks at 105°, 330°, 660°, 730°, 810°, and a small deflection at 965° C. The sample upon which this DTA was performed was extremely pure, and the endothermic reactions recorded are typical of the todorokite of this locality. No other minerals have been identified in the sample by microscopic or *x*-ray methods.

A spectrochemical analysis of the todorokite was carried out in order to discover the content of some of the trace elements which are of most interest for the geochemistry of manganese (cf. P. Ljunggren, 1958b):

Zn = 0.001%	V < 0.001%
Ni < 0.001%	Ba = 0.01 %

TABLE 1. *X*-RAY POWDER SPACINGS FOR TODOROKITE FROM TODOROKI (C. FRONDEL, 1953, p. 766) AND FROM VERMLANDS TABERG. —Fe RADIATION, Mn FILTER, CAMERA DIAMETER 114.83 MM.

Todoroki d (in Å)	I	Vermlands Taberg d (in Å)	I
9.65	10	9.67	vs
7.2	.5		
4.81	8	4.78	m
4.46	3	4.47	vw
3.20	4	3.22	vw
2.45	3	2.43	vw
2.40	4	2.39	vw
2.216	4	2.21	vw
2.150	1		
1.981	1	1.97	vw
		1.74	vvw
		1.68	vvw
1.419	4	1.42	vw
1.392	1		
1.331	5		

Pb = 0.001% Rb < 0.001%
Bi < 0.001% K = 0.1 %

The spectrographic analysis shows furthermore small amounts of Ca and Mg (less than one per cent), but it is not possible to state whether this is due to a small admixture of Ca-Mg-bearing minerals, whether these elements are included in the todorokite structure or whether they were possibly adsorbed upon the surface of the todorokite aggregates.

PYROLUSITE

The pyrolusite is found as more or less earthy aggregates, both in the soft iron ore and in the argillized skarn and leptite. No crystals are seen upon macroscopic examination. An *x*-ray powder analysis gave the following cell dimension:

$$a = 4.40 \text{ Å}$$
$$c = 2.87 \text{ Å}$$
$$c/a = 0.652$$

these values being identical with those given by A. M. Byström in 1949 (p. 171).

A spectrochemical analysis of the pyrolusite of this locality gave the following trace element composition:

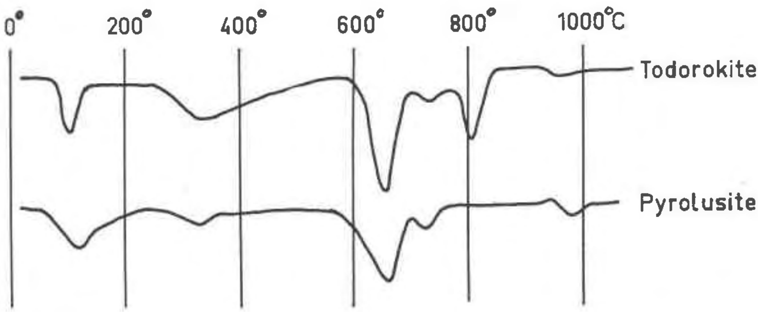

FIG. 1. DTA curves of todorokite and pyrolusite from Vermlands Taberg.

Zn $\leq$ 0.001%	V < 0.001%
Ni = 0.01 %	Ba < 0.001%
Pb < 0.001%	Rb < 0.001%
Bi < 0.001%	

These figures demonstrate that the pyrolusite is unusually pure. The very low value of Ba is especially remarkable as Ba is strongly adsorbed by MnO_2.

A DTA curve of the pyrolusite of Vermlands Taberg is given in Fig. 1. It shows endothermic peaks at 120°, 330°, 665°, 730°, and 980° C., and one exothermic peak at 940° C. The two peaks at 940° and 980° C. are unusually strong when compared with the curves of pyrolusites given by J. L. Kulp and J. N. Perfetti in 1950 (p. 244).

CONCLUSIONS

The similarity between the todorokite and the pyrolusite from Vermlands Taberg is striking. The DTA curves are almost identical as is also the chemical composition. Typical for both the minerals examined is the unusually low content of trace elements, which in itself must give some clue to the formation of these manganiferous veins and impregnations.

The soft iron ore of Vermlands Taberg is known to have arisen through a weathering of magnetite ore in Preglacial time. The magnetite was altered into hematite, which eventually changed into goethite; the goethite was the final stage of the alteration. Contemporaneously, the magnesium-dominant skarn minerals changed into antigorite and the feldspar-bearing rocks into kaolinitic masses. These transformations meant a complete change in mineralogical composition, resulting mainly in a formation of (OH)-bearing minerals. The iron of the iron ore was not removed from the rock system as is evident from the present features of the ore bodies. The manganese of the original iron ore seems to have become somewhat enriched during the transformation into soft iron ore (cf. Table III, P. Ljunggren, 1958a). It is therefore probable that the manganese of the manganiferous veins, now to be found as pyrolusite and todorokite, originated in the wall-rock in connection with the transformation of the latter. A possible source is the skarn minerals which underwent a thorough rebuilding upon their alteration into antigorite.

The remarkably low content of some of the trace elements in the pyrolusite and the todorokite may be explained through the conditions under which these minerals were formed. These veins cut both the soft iron ore and the argillized wall-rock; this indicates that they were formed during a late phase of the alterations. The physical condition of the argillized rocks and of the soft iron ore bodies prevented any further considerable transport of waters which could carry suitable cations to the manganese dioxide. It is a well-known fact that manganese dioxides strongly absorb certain cations, amongst them those given in the above spectrochemical analyses (P. Ljunggren, 1955). The most plausible explanation for the purity of the manganese oxide minerals of Vermlands Taberg is not the presence of very pure waters in the rock system but the very low permeability of the enclosing argillaceous rocks which prevented water containing these trace element cations from reaching the MnO_2 minerals.

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