

The transformation manganite \rightarrow pyrolusite

P. E. CHAMPNESS

Department of Geology, University of Manchester¹

SUMMARY. During the transformation of manganite to pyrolusite the *b*-axis must contract about 15 %. There is evidence that the shrinkage takes place partly by contraction of the whole crystal, but electron-microscope investigations of natural pyrolusites and of manganite oxidized in the laboratory show that the reaction also involves the formation of lamellar pores about 85 Å apart, parallel to (010) of the original manganite. Thus, although pyrolusite is tetragonal, the *a*- and *b*-axes are not microscopically identical, a fact which could explain why, when natural pyrolusite is treated hydrothermally at 200 and 300 °C and 1000 bars, only one orientation of manganite is formed (Dent Glasser and Smith, 1968). The pores and the accompanying distortion of the structure act as a 'memory' of the parent phase.

Two forms of pyrolusite occur in nature. Rare, well-formed crystals with a hardness greater than quartz are considered to be of primary origin (Strunz, 1943) but most pyrolusites are thought to be pseudomorphous after manganite and sometimes occur intergrown with it (Strunz, 1943; Davis 1967). Pseudomorphic pyrolusite usually occurs as a friable fibrous aggregate with relict (010) cleavage. It has a large surface area, which results in high chemical activity and absorption power.

Pyrolusite is tetragonal with *a* 4.44 Å and *c* 2.89 Å, $P4_2/mnm$, and its structure is similar to that of rutile. Manganite was once thought to be orthorhombic (Garrido, 1935) but Buerger (1936) showed that it is monoclinic,² $B2_1/d$ with *a* 8.86 Å, *b* 5.24 Å, *c* 5.70 Å, $\beta = 90^\circ$. The manganite and pyrolusite structures are similar; the lower symmetry and doubled *a* and *c* axes of manganite arise from the presence of hydrogen bonds.

Dasgupta (1965) made detailed X-ray single-crystal studies on manganite heated in air in the laboratory. At about 300 °C he found that pyrolusite was formed by loss of hydrogen from the structure: $\gamma\text{-MnOOH} + \text{O}_2 \rightarrow \text{MnO}_2 + \text{H}_2\text{O}$. The crystallographic axes of product and reactant were found to be parallel but the reflections from the pyrolusite were broad and diffuse.

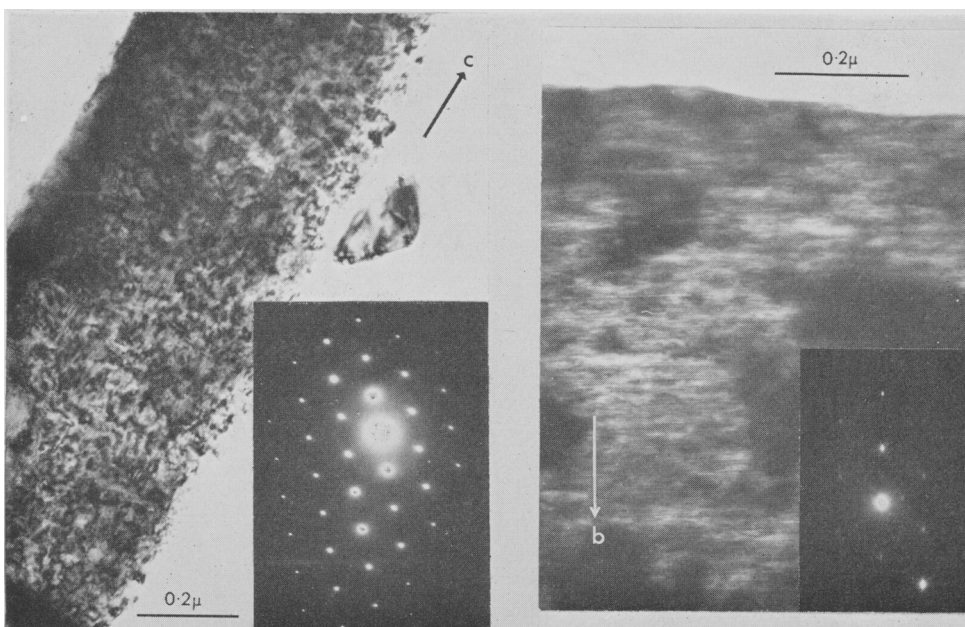
More recently Dent Glasser and Smith (1968) made extensive studies on oriented reactions in the system $\text{MnO}-\text{O}-\text{H}_2\text{O}$. In the reduction of pyrolusite to manganite by hydrothermal treatment at 200–300 °C and 1000 bars they encountered the surprising result that only one orientation of manganite was formed from the pyrolusite viz. $a_m \parallel a_p$, $b_m \parallel b_p$ whereas, because pyrolusite is tetragonal, one would expect there to be equal probabilities of *a* or *b* of pyrolusite becoming *a* or *b* of manganite.

¹ This paper was read at the Mineralogical Society meeting 'Order-Disorder Effects in Minerals' held in Aberdeen on 18–19 September 1969.

² Non-standard space group adopted by Buerger (1936) to preserve pseudo-orthorhombic axes.

© Copyright the Mineralogical Society.

Dent Glasser and Smith could offer no specific explanation of this phenomenon but they suggested that, as pyrolusite is commonly found pseudomorphic after manganite, a 'memory effect' such as that found in the non-structurally controlled polymorphic transition in *p*-dichlorobenzene (Kitaigorodskiy *et al.*, 1965) might be operating.



FIGS. 1 and 2: Fig. 1 (right). Electron micrograph and diffraction pattern of a pyrolusite grain formed by oxidation of manganite, showing lamellar pores parallel to (010). Fig. 2 (left). Electron micrograph and diffraction pattern of pseudomorphic pyrolusite from Amapa, Brazil, showing a high dislocation density.

Strunz (1943) pointed out that during the transformation manganite \rightarrow pyrolusite the equivalent repeat distances along the *a*- and *c*-axes alter very little, but a contraction of about 15 % must take place along the *b*-axis. He concluded that because the morphological angle (110):(1 $\bar{1}$ 0) of the pseudomorph was larger than $80^{\circ} 20'$, the value for manganite (it varies from $84^{\circ} 30'$ to $85^{\circ} 30'$), contraction of the bulk crystal takes place during the transformation. However, he admitted the possibility that submicroscopic cracks parallel to (010) could also be present.

Electron microscope study. The microstructure of natural pyrolusites pseudomorphous after manganite supplied by the British Museum (Natural History) (nos. BM 1965, 281, from Amapa, Brazil, and BM 91106 from Elgerburg, Thuringia, cf. Davis, 1967) and a pyrolusite produced by heating a manganite (no. 415 from Ilfeld, Harz Mountains, supplied by the Museum of the Department of Mineralogy and Petrology,

University of Cambridge) for three hours in air at 300 °C were studied in the transmission electron microscope. The instrument used was an A.E.I. EM6G equipped with high-resolution dark-field facilities and a goniometer stage, and was operated at

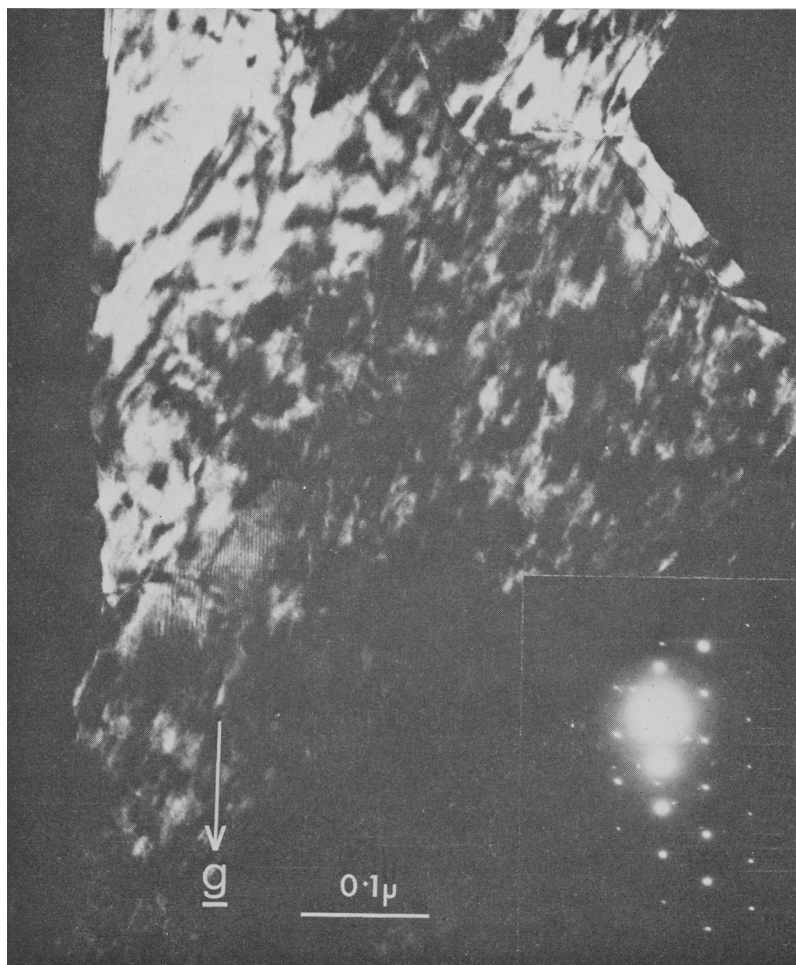


FIG. 3. A grain of pseudomorphic pyrolusite from Elgerburg, Thuringia. The moiré pattern indicates a relative rotation of (010) lattice planes. Dark field micrograph from a 101 reflection.

100 KV. The specimens were ground in absolute alcohol and a drop of the suspension was deposited on a carbon-coated electron-microscope grid. The natural pyrolusite and that produced by oxidation in the laboratory gave comparable results.

Fig. 1 is an electron micrograph of an oxidized manganite which shows fine lamellar pores about 85 Å apart parallel to (010). Because of their good relict cleavage, most of the grains lie on (010) (figs. 2 and 3). They are extensively buckled and show an extremely high dislocation density (fig. 2).

Micrographs often show moiré patterns, which are of the rotation type (the fringes are parallel to the operating g -vector), i.e. they are produced by a relative rotation of the (010) lattice planes. The moiré fringes in fig. 3 have a spacing that varies from about 27 Å to about 40 Å, which correspond to lattice rotations of about 5° and $3\frac{1}{2}^\circ$ respectively. Further evidence of the disordered nature of the structure along b is shown by the diffraction pattern which remains essentially the same when the specimen is tilted through 30° .

The present study has revealed that the a - and b -axes of pseudomorphous pyrolusite are not equivalent on the submicroscopic scale due to the presence of lamellar micropores parallel to (010). The pores and the accompanying strain probably constitute the 'memory' of the parent manganite, which leads to the original orientation of the manganite being reproduced during reduction of the pseudomorph.

Acknowledgements. The author wishes to thank Drs. S. O. Agrell and R. J. Davis for providing specimens and Professor J. Zussman and Dr. G. W. Lorimer for critically reading the manuscript. N.E.R.C. provided the electron microscope for the Department of Geology, University of Manchester.

REFERENCES

- BUERGER (M. J.), 1936. *Zeits. Krist.* **95**, 163.
DASGUPTA (D. R.), 1965. *Min. Mag.* **35**, 131.
DAVIS (R. J.), 1967. *Ibid.* **36**, 274.
DENT GLASSER (L. S.) and SMITH (I. B.), 1968. *Ibid.* **36**, 976.
GARRIDO (M. J.), 1935. *Bull. Soc. franç. Min.* **58**, 224.
KITAIGORODSKIY (A. I.), MNYUKH (YU. V.), and ASADOV (YU. G.), 1965. *Journ. Phys. Chem. Solids*, **26**, 463.
STRUNZ (H.), 1943. *Naturwiss.* **31**, 89.

[Manuscript received 8 June 1970]