The transformation of groutite (α-$MnOOH$) into pyrolusite (MnO_2)

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Summary. The transformation of groutite (α-MnOOH) by heating has been studied at 300° C in air, by single-crystal and powder X-ray methods. At this temperature groutite transforms topotactically into pyrolusite (MnO_2), the *a*, *b*, and *c* axes of groutite becoming respectively the *a*, *b*, and *c* axes of pyrolusite (in pyrolusite $b = a$). At various stages of the transformation other weak and diffuse spots were observed on X-ray oscillation photographs, which could not be ascribed to pyrolusite. Some of these extra spots fit well to an α-Mn_2O_3 structure (isostructural with hematite), with *c* 14·3 and *a* 4·9 Å; the other few spots could not be identified.

The transformation of α-MnOOH into MnO_2 is explained by a homogeneous mechanism, with migration of protons and electrons to the crystal surface. A detailed interpretation of this mechanism is presented on the basis of the close-packing characteristics of these two structures.

GROUTITE (α-MnOOH) was studied by Gruner (1947) and by Collin and Lipscomb (1949), and it was concluded that it is orthorhombic (space group *Pbnm*, *a* 4·58, *b* 10·76, *c* 2·89 Å) and isostructural with goethite (α-FeOOH) and diaspore (α-AlOOH). The dehydration of goethite and diaspore has already been studied by several authors (e.g. Deflandre, 1932; Goldsztaub, 1935: Ervin, 1952; Francombe and Rooksby, 1959; Lima-de-Faria and Gay, 1962), and it was observed that they transform topotactically into hematite (α-Fe_2O_3) and corundum (α-Al_2O_3), respectively, with twinning developing during the transformations. Intermediate states in the process of these transformations have also been reported. The dehydration of groutite is more complex and not so well known. X-ray studies with a diffractometer, by Klingsberg and Roy (1959), have shown that groutite dehydrates to give several manganese oxides: ramsdellite at 130° C to 300° C, pyrolusite just above 300° C, and Mn_2O_3 at a higher temperature. The oxidation of groutite into ramsdellite was also pointed out by Feitknecht, Oswald, and Feitknecht-Steinmann (1960). These results, so

different from those corresponding to the goethite and diaspore dehydrations, are not entirely unexpected, firstly because no Mn_2O_3 isostructural with hematite has been reported up to the present, and secondly because of the various stable valencies of the manganese atom. The aim of the work described below was to obtain more knowledge about the dehydration of groutite, and so enable a more meaningful comparison to be made with the goethite and diaspore dehydrations.

X-ray study

The material used (cat. no. 19481), was kindly supplied by the Museum of the Department of Mineralogy and Petrology, University of Cambridge, England, and is from the Cuyuna range, Minnesota (U.S.A.), the type locality.

The thermal behaviour of groutite on heating in air was first investigated with a thermobalance (crushed material, $80+200$ mesh), and losses of weight at about $300°$ C, $500°$ C, and $1000°$ C were observed. X-ray powder photographs were taken of samples heated around these temperatures, which showed that groutite transforms at $300°$ C into pyrolusite (MnO_2), at $500°$ C into Mn_2O_3 (bixbyite structure), and at $1000°$ C into hausmannite (Mn_3O_4). The weight losses observed during the thermobalance study at these temperatures are in agreement with the formation of the compounds mentioned. These results are in fairly good agreement with those of Klingsberg and Roy (1959), except that the ramsdellite phase was not detected even for heat-treatments at $250°$ C for 1 hour, and $200°$ C for 23 hours, which showed a partial transformation of groutite into pyrolusite. The ramsdellite phase is possibly an unstable one, formed in very particular conditions of heating. Attention has previously been drawn to the unstable character of ramsdellite by Fleischer, Richmond, and Evans (1962). On partially dehydrating groutite into pyrolusite we observed no traces of ramsdellite. This shows that groutite transforms directly into pyrolusite, as had already been pointed out by Klingsberg and Roy (1959) for temperatures above $300°$ C. The transformation of groutite into pyrolusite was therefore considered to be the main dehydration process, and it was decided to study this transformation in detail.

To follow the transformation step by step, from the very early to the last stages, several single crystals of groutite were heated at $300°$ C for different times, and the corresponding X-ray oscillation photographs were taken. It was found that groutite transforms topotactically into pyrolusite (MnO_2), the a, b, and c axes of groutite becoming respectively

the a, b, and c axes of pyrolusite (in pyrolusite $b = a$) (fig. 1). Comparison
of the cell dimensions of groutite, a 4·58, b 10·76, c 2·89 Å, and pyrolusite,
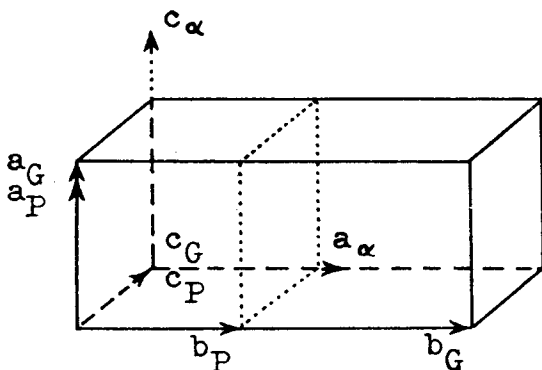a and b 4·38, c 2·85 Å (Vaux, 1937), shows that there must be contraction

FIG. 1. Orientation relationship of groutite (G), pyrolusite (P),
and α-Mn_2O_3 (α).

along the a and b axes of groutite, and practically no change in length
along the c direction. In fact two systems of cracks were observed in the
heated crystals, normal to the former directions.

Other weak and diffuse spots were observed on certain X-ray oscilla-
tion photographs, and could not be ascribed to pyrolusite. Some of
these extra spots (fig. 2a) appeared in positions similar to those in which
the main spots of hematite formed from goethite can be observed on the
corresponding oscillation photographs. This was verified for the main
orientations of the crystals. On further heating at 300° C these diffuse
spots disappeared, thus showing the unstable character of the compound
formed. From these facts, and from measurements, it was concluded
that these extra spots fitted well to a Mn_2O_3 structure isostructural
with hematite, with c 14·3 and a 4·9 Å, and in twinned orientation like
the twinned hematite formed from heated goethite. Support for this
conclusion was obtained by comparing a Weissenberg photograph of the
fourth layer of the reciprocal lattice normal to the c axis of the hematite
formed from goethite, with one of the corresponding planes of the
reciprocal lattice of heated groutite containing the diffuse spots (fig. 2 b
and c). The similarity between the photographs, and the 60° separation
of the main rows of spots on that of the heated groutite, provided
confirmation of the isostructural character of this compound with hema-
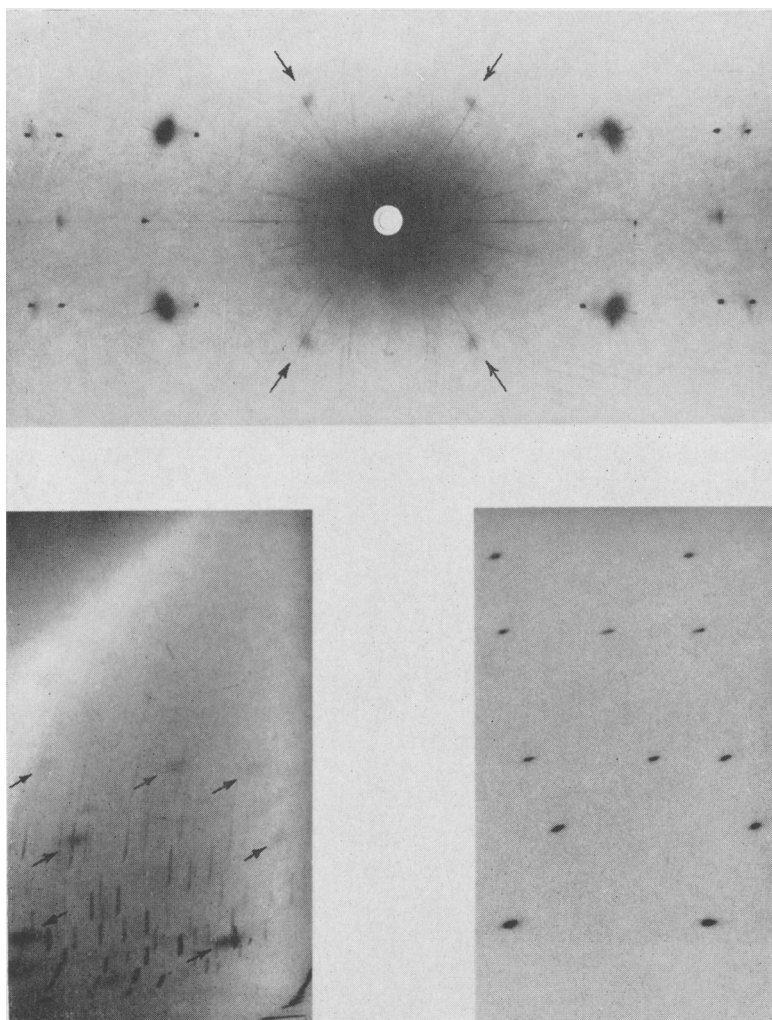tite and corundum. It has to be admitted that the diffuse spots could

FIG. 2. (a) (top): Oscillation photograph (15°, Fe-Kα radiation) of groutite crysta
(α-MnOOH) after heating at 300° C in air for 10 minutes; oscillation along the a-axis,
looking down the c-axis. Sharp spots correspond to residual groutite, and the main
diffuse spots correspond to formed pyrolusite. The four diffuse spots indicated by
arrows correspond to α-Mn$_2$O$_3$. (b) (bottom left): Part of a Weissenberg photograph
of the same groutite crystal, for the reciprocal lattice plane containing the diffuse
spots of α-Mn$_2$O$_3$ (indicated by arrows). Axis of rotation, a of groutite (or c of α-
Mn$_2$O$_3$), fourth layer of α-Mn$_2$O$_3$; Fe-Kα radiation. (c) (bottom right): Correspond-
ing part of a fourth-layer Weissenberg photograph of formed hematite (α-Fe$_2$O$_3$)
from heated goethite (300° C); rotation along the c-axis of hematite, Fe-Kα
radiation.

have come from some very small portion of hematite or corundum formed from a very small iron or aluminium content of groutite. This appears very improbable, however, because the measured cell dimensions, c 14·3 and a 4·9 Å, are appreciably different from those of hematite, c 13·749, a 5·0345 Å, (Bernal, Dasgupta, and Mackay, 1959), or corundum, c 12·97, a 4·75 Å (Deflandre, 1932), because Gruner's chemical analysis of groutite (Gruner, 1947) showed a Fe_2O_3 content of only 0·02 % and no Al_2O_3, and because hematite and corundum are very stable, and once formed would remain unchanged and not disappear on further heating. The remaining few spots could not be identified.

The stable cubic form of Mn_2O_3 is described by Wells (1962) as the α-form, possibly to distinguish it from the γ-form of Mn_2O_3, which was so called by structural analogy with γ-Fe_2O_3. Such a structural analogy obviously does not exist for the cubic Mn_2O_3 and α-Fe_2O_3 (hematite) or α-Al_2O_3 (corundum). There is no unique criterion for denoting the different polymorphs; these are named either in chronological order, or according to structural analogies. Although the choice of an irreproachable criterion is difficult, the one based on structural analogies appears to us to be the more useful. In the particular case when manganese, iron, and aluminium compounds are compared there is an implication of isostructural relationship when the same Greek letter is used for two polymorphs. We therefore propose that the very unstable compound studied here be called α-Mn_2O_3, and the cubic form, which is the more stable, be known simply as Mn_2O_3, or distinguished by a more suitable Greek letter.

The mechanism of the transformation of groutite into pyrolusite

In interpreting phase transformations of inorganic materials it has been shown in recent years that the close-packing characteristics of the compounds involved in the transformations are of fundamental importance (e.g. Ervin, 1952; Ball and Taylor, 1961; Lima-de-Faria, 1962). The groutite structure, like those of goethite and diaspore, is based on a hexagonal close-packing of oxygen ions, with Mn^{3+} occupying half of the octahedral holes, in alternate pairs of rows (fig. 3). Again, the pyrolusite structure is based on a hexagonal close-packing of oxygen ions, with Mn^{4+} occupying also half of the octahedral holes, but in alternate single rows (fig. 3). The transformation does not involve loss of oxygen, but just loss of hydrogen and change in valence of the manganese ion. It is therefore natural to assume that the close-packing of the oxygens will not change during the transformation, and that only movement of

protons, electrons, and manganese ions will take place. The protons and electrons will gradually migrate to the surface, where water is probably
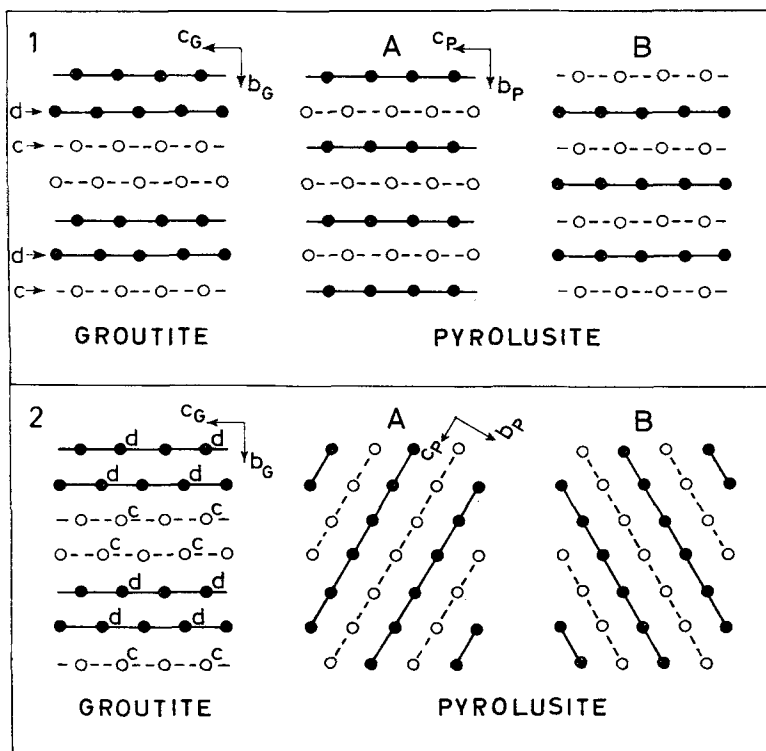

FIG. 3. Schematic representation of the possible mechanisms of the transformation of groutite (α-MnOOH) into pyrolusite (MnO_2). Octahedral holes of the groutite and pyrolusite layers are represented, the occupied ones (in respect of manganese ions) by filled circles, and empty ones by open circles; the positions of the hydrogen ions are not represented. The movement of the manganese ions is supposed to take place along the channels linking the octahedral holes; they move out from positions marked d, and come in, from adjacent layers, to positions marked c. On the second mechanism the two other variants A' and B', parallel to the A and B variants, are not represented.

formed on contact with the air; the manganese ions will move through the oxygen framework to form the pyrolusite structure.

If we admit that the oxygen close-packed framework is maintained, then the relative orientation of the two structures (groutite and pyrolusite) can be derived from an analysis of the mechanism of the

transformation. The a-axis of groutite is normal to the hexagonal close-packed layers and must therefore coincide with the a-axis of pyrolusite, which is also normal to these layers in the pyrolusite structure (rutile type of structure). For the orientation relationship of the other two pairs of axes we have to consider now the movement of the manganese ions. In fig. 3 the octahedral holes of a hexagonal close-packed layer of the groutite structure are represented, the occupied ones shown as full circles, and the empty ones as open circles. Each layer is composed of alternate pairs of occupied and unoccupied (in respect of manganese ions) rows of octahedral holes; successive layers are similar but occupied rows are superimposed on empty ones; the positions of the hydrogen ions are not represented. When the transformation takes place and protons start migrating, the stability of this distribution is broken, and the occupied rows tend to alternate forming the pyrolusite structure. The ions in the rows marked d tend to move into the rows marked c, but there are various possibilities to achieve this final state. The manganese ions could be imagined to move along the plane of the layers, through the oxygen framework, but movement normal to the layers seems more probable along the channels connecting the octahedral holes. Restricting the analysis to the movement of manganese ions along these channels, two main mechanisms appear possible. In a first one the manganese ions would move out of alternate rows (marked d), whilst rows marked c would be filled up by manganese ions coming from adjacent layers. This mechanism has two variants according to the starting rows, and the pyrolusite crystals formed could be of types A or B, parallel to each other, not giving rise to twinning. In a second mechanism, which is schematized in fig. 3, alternate pairs of manganese ions (marked d) would move out, and other pairs (marked c) would come in from adjacent layers. The pyrolusite structure would then be derived in an inclined orientation in relation to the groutite structure, the two variants, A and B, and the two additional parallel variants A' and B' (according to the starting pairs), giving rise to twinning. The first mechanism is the simplest one and appears also to be more consistent with an equilibrium between the structures of the original groutite and the pyrolusite forming; therefore, it is considered the more probable, and in fact is the one that leads to the orientation relationship observed in the X-ray study.

References

BALL (M. C.) and TAYLOR (H. F. W.), 1961. Min. Mag., vol. 32, p. 754.

BERNAL (J. D.), DASGUPTA (D. R.), and MACKAY (A. L.), 1959. Clay Min. Bull., vol. 4, p. 15.

COLLIN (R. L.) and LIPSCOMB (W. N.), 1949. Acta Cryst., vol. 2, p. 104.

DEFLANDRE (M.), 1932. Bull. Soc. franç. Min., vol. 55, p. 140.

ERVIN (G.), 1952. Acta Cryst., vol. 5, p. 103.

FLEISCHER (M.), RICHMOND (W. E.), and EVANS (H. T.), 1962. Amer. Min., vol. 47, p. 47.

FEITKNECHT (W.), OSWALD (H. R.), and FEITKNECHT-STEINMANN (U.), 1960. Helv. Chim. Acta, vol. 43, p. 1947.

FRANCOMBE (M. H.) and ROOKSBY (H. P.), 1959. Clay Min. Bull., vol. 4, p. 1.

GOLDSZTAUB (S.), 1935. Bull. Soc. franç. Min., vol. 58, p. 6.

GRUNER (J. W.), 1947. Amer. Min., vol. 32, p. 654.

KLINGSBERG (C.) and ROY (R.), 1959. *Ibid.*, vol. 44, p. 819.

LIMA-DE-FARIA (J.), 1962. Ph.D. thesis, Cambridge.

—— and GAY (P.), 1962. Min. Mag., vol. 33, p. 37.

VAUX (G.), 1937. *Ibid.*, vol. 24, p. 521.

WELLS (A. F.), 1962. Structural inorganic chemistry. Oxford, Clarendon Press, third edition.