

*Topotaxy in the system MnO–O–H<sub>2</sub>O:  
groutite–ramsdellite–pyrolusite*

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*Summary.* X-ray and thermal studies in the system MnO–O–H<sub>2</sub>O show that the transformations groutite( $\alpha$ -MnOOH)–ramsdellite(MnO<sub>2</sub>)–pyrolusite(MnO<sub>2</sub>) are topotactic, with the *a*, *b*, and *c* directions of all three corresponding. The reactions proceed by migration of manganese atoms and, where appropriate, protons. Pure single crystals of ramsdellite could not be prepared by heating groutite, even though the two structures are very similar.

MANGANESE dioxide forms two well-crystallized polymorphs. The commoner, pyrolusite, has the tetragonal rutile structure (St. John, 1923), and appears to be the stable form. The other polymorph, ramsdellite, is orthorhombic and belongs to the diaspore–goethite group (Byström, 1949). Groutite,  $\alpha$ -MnOOH, is an oxyhydroxide isostructural with ramsdellite (Gruner, 1947; Collin and Lipscomb, 1949). Groutite and ramsdellite are generally described as being built of double chains of MnO<sub>6</sub> octahedra parallel to *c* (fig. 1*a*); pyrolusite has single octahedral chains parallel to *c* (fig. 1*b*). The unit cells and space groups of groutite, ramsdellite, and pyrolusite are:

groutite	<i>a</i> 4.58,	<i>b</i> 10.76,	<i>c</i> 2.89 Å; <i>Pbnm</i> ;
ramsdellite	4.533	9.27	2.886; <i>Pbnm</i> ;
pyrolusite	4.40	4.40	2.87; <i>P4<sub>2</sub>/mnm</i> .

Neither ramsdellite nor groutite has ever been synthesized, although excellent natural crystals have been found. Klingsberg and Roy (1959) studied the stability and interconvertibility of phases in the system Mn–O–OH. Although they did not succeed in synthesizing either groutite or ramsdellite, they found that the two were interconvertible. Powdered groutite heated in air at 130° C oxidized very slowly to ramsdellite; at 300° C it oxidized in a few hours. Above 300° C it changed directly to pyrolusite.

Ramsdellite is apparently metastable and transforms to pyrolusite at temperatures about 300° C (the exact temperature of inversion probably varies for natural specimens). Fleischer, Richmond, and Evans (1962)

noted that natural ramsdellite was pseudomorphic after groutite. They suggested that it was probably always formed by oxidation of the structurally similar groutite. The apparently universal presence of pyrolusite in parallel orientation with ramsdellite was attributed to a slower, reconstructive, alteration to the stable phase.

Because of the structural similarity of the three minerals it seems likely that they interconvert topotactically (i.e. a single crystal of one passes directly to a single crystal of another). This has not been completely checked in the laboratory although the study of Fleischer, Richmond, and Evans provides indirect evidence; Lima-de-Faria and Lopes-Vieira (1964) showed that groutite can be converted topotactically to pyrolusite at 300° C.

In the present work single crystals were used in an attempt to study the whole sequence groutite → ramsdellite → pyrolusite. By this means it was hoped both to gain information on the mechanism of the changes, and also to throw further light on the origin of natural ramsdellite.

*Starting materials.* Two samples of *groutite* were used; the first was supplied by Prof. J. W. Gruner of the University of Minnesota and came from Mahnomen Mine, Cuyuna Range, near Crosby, Minnesota; the second sample was simply labelled Cuyuna Range and was supplied by Dr. Roy Phillips of the Geology Department, Durham University. Both samples contained groutite intimately associated with manganite,  $\gamma$ -MnOOH. Handpicked portions of the specimens, previously shown by single crystal X-ray methods to contain only groutite, were ground to provide samples for preparing standard X-ray powder diffraction photographs and for heating experiments. The standard powder and single crystal X-ray photographs were prepared using samples from both localities. The data obtained agreed well with the literature values. The crystals consisted of flat, tabular laths, the thicker ones being opaque and the thinner ones reddish-coloured with parallel extinction.

Samples of *ramsdellite* from Lake Valley, Sierra County, New Mexico, and from Gavilan Mine, Lower California, Mexico, were supplied by Dr. Howard T. Evans, Jur., of the United States Geological Survey. These were part of the specimens described by Fleischer, Richmond, and Evans (1962). Most of the crystals contained an unidentified weak phase in parallel orientation, the cell dimensions of which correspond to that described by Fleischer, Richmond, and Evans (1962). Some of the Lake Valley crystals were found to show only ramsdellite reflections, and these were selected for the heating experiments. Although platy fragments separated from the bulk consisted of aggregates of perfectly

aligned very small needles, they yielded sharp single crystal X-ray photographs. Cell parameters and powder data agreed well with the literature values.

Standard photographs of *pyrolusite* were prepared using a sample from Ilmenau, Thuringia (sample G. 1544 of the Gordon Collection) supplied by the Geology Department, Aberdeen University. Powder data and cell parameters corresponded to the literature values.

TABLE I. Heating experiments on groutite and on ramsdellite

Starting material	Crystal no.	Temp.	Time	Result
Groutite Cuyuna Range	1	136° C	14 days	Groutite
	2	165	24 hrs	Groutite
	3	175	72 hrs	Groutite
	4	225	16 hrs	Groutite
	5	250	24 hrs	Groutite + Pyrolusite + trace Ramsdellite + 'Weak Phase'*
	6	250	52 hrs	Groutite + Pyrolusite + trace Ramsdellite + 'Weak Phase'*
Groutite, Mahnomon Mine, Cuyuna Range	7	220	29½ hrs	Groutite
		220	66 hrs	Groutite
		255	23 hrs	Groutite + Pyrolusite + 'Weak Phase'*
	8	220	68 hrs	Groutite
Ramsdellite, Lake Valley, New Mexico	9	300	24½ hrs	Ramsdellite + trace Pyrolusite
		300	51½ hrs	Ramsdellite + Pyrolusite
	11	300	26 hrs	Ramsdellite + Pyrolusite
		300	26 hrs	Pyrolusite

\* Identical to that mentioned on p. 328.

X-ray methods showed that, for all three minerals, the longest dimension of the crystals corresponded to the *c*-axis.

*Experimental results.* Selected single crystals of groutite and ramsdellite were heated in air at various temperatures for differing lengths of time. The results are summarized in table I. All changes were topotactic, the *a*, *b*, and *c* axes of all three minerals corresponding.

Crystals that contained both ramsdellite and pyrolusite also showed a pronounced streaking of reflections parallel to *b*\*. Contrary to expectation it proved impossible to produce single crystals of ramsdellite by heating groutite. Prolonged heating at temperatures similar to those given by Klingsberg and Roy did not change groutite crystals (table I, crystals 1-4). With rising temperature, a slow reaction began about 250° C, but the principal product was pyrolusite, with only small amounts of ramsdellite being formed (table I, crystals 5-8). The results

of Klingsberg and Roy's heating experiments on powdered groutite differed somewhat from the present results and it was thought that, because the escape of water is possibly more difficult from single crystals, a localized hydrothermal reaction might be occurring. Accordingly the experiments were repeated using powdered samples of groutite from both localities. The results are summarized in table II. The products of the thermal transformation, especially at the lower temperature, gave very

TABLE II. Heating experiments on powdered groutite

Starting material	Sample no.	Temp.	Time	Result
Groutite Cuyuna Range	1	185° C	29½ hrs	Groutite
	2	185	29½ hrs	Groutite
	3	185	29½ hrs	Groutite + possibly trace Ramsdellite
	4	220	29½ hrs	Groutite + Pyrolusite + possibly trace Ramsdellite
	5	220	29½ hrs	Groutite
	6	220	29½ hrs	Groutite + Pyrolusite
Groutite, Mahnomen Mine, Cuyuna Range	7	185	25 hrs	Groutite + possibly trace Ramsdellite
	8	185	29½ hrs	Groutite + possibly trace Ramsdellite
	9	185	29½ hrs	Groutite + possibly trace Ramsdellite
	10	220	25 hrs	Groutite + Pyrolusite
	11	220	29½ hrs	Groutite + Pyrolusite + possibly trace Ramsdellite
	12	220	29½ hrs	Groutite + Pyrolusite + possibly trace Ramsdellite

poor photographs that were difficult to interpret. Nevertheless, the results agreed well with those obtained using single crystals, except that water was lost at slightly lower temperatures. The powder photographs occasionally showed extra lines that could not be attributed to any of the three expected compounds. These lines do not correspond to the weak phase mentioned above and have so far not been explained.

When the starting material was ramsdellite (table I) the change to pyrolusite began at about 300° C and was fairly slow.

*Discussion.* The structures of groutite and ramsdellite are so similar that they can be represented by the same diagram (figs. 1a and 2a). They differ only in small variations in the oxygen positions and in the fact that some of the oxygen atoms in groutite form part of hydroxyl groups. The change groutite → ramsdellite could therefore be accomplished by the migration of protons and electrons only.

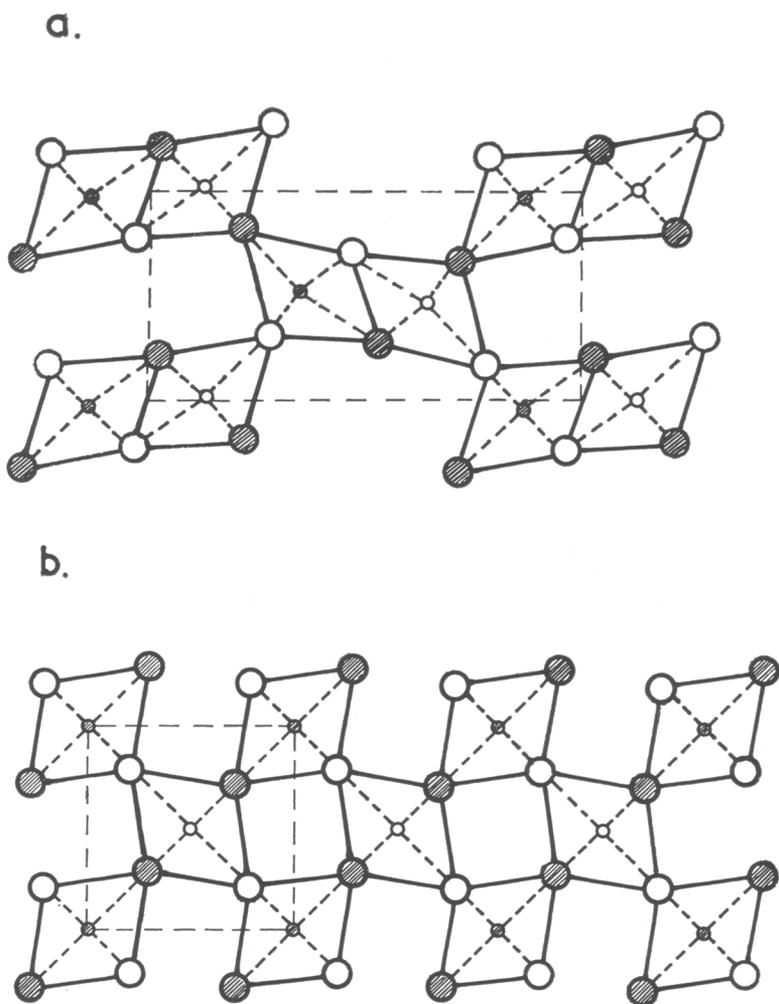


FIG. 1. Structures of: (a), ramsdellite (or groutite) and (b), pyrolusite, looking along the chains of octahedra parallel to  $c$ . Axes  $a$  and  $b$  are in the plane of the paper,  $a$  vertical and  $b$  horizontal; the relative orientation shown is that observed experimentally. Large circles: oxygen (or hydroxyl). Small circles: manganese. Open circles at height zero; filled circles at height one-half.

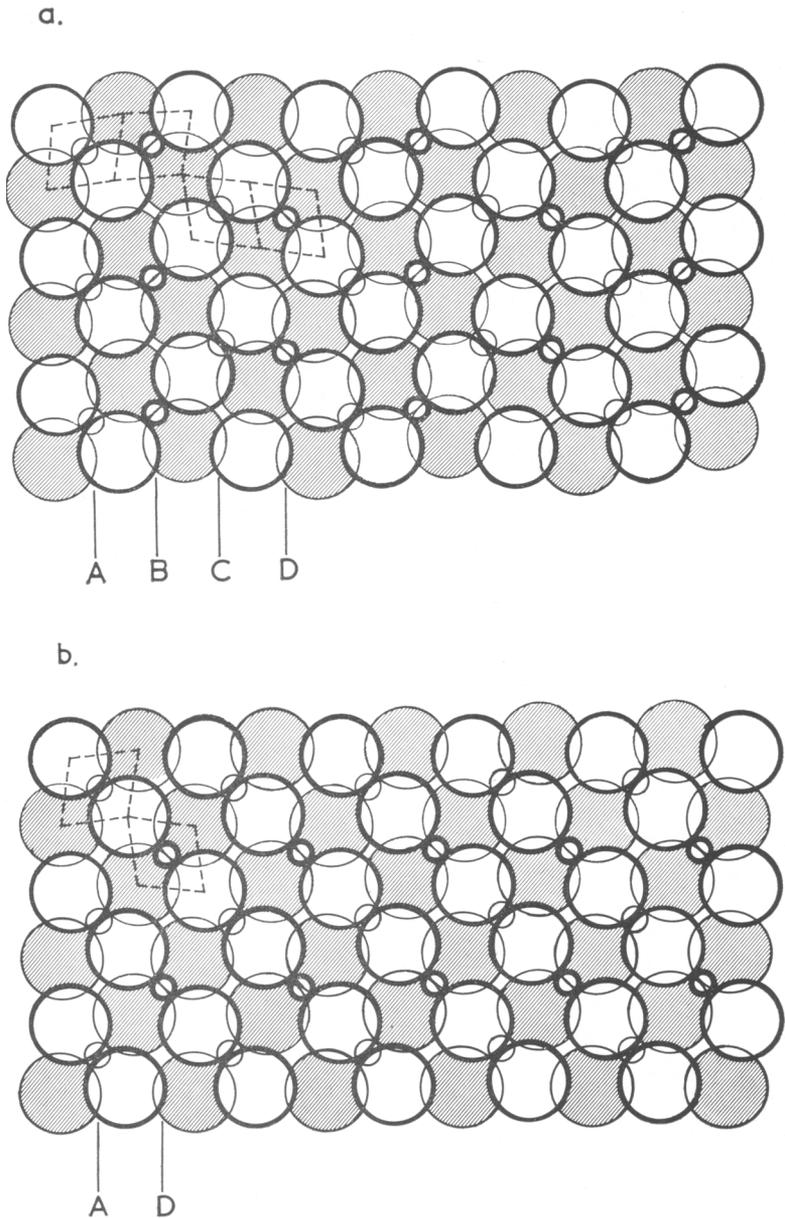


FIG. 2. Structures of: (a) ramsdellite (or groutite) and (b) pyrolusite; orientation as in fig. 1, showing the oxygen packing. Vertical chains of octahedra are outlined by broken lines. In (a) A, B, C, D, indicate the four different arrangements of manganese atoms; only two different arrangements (A, D) occur in (b). Large circles: oxygen (or hydroxyl); open circles at height zero, filled circles at height one-half. Small circles: manganese; lightly drawn at height zero, heavily drawn at height one-half.

The oxygen packing in pyroslusite is similar to that of ramsdellite and groutite (fig. 2*b*). Ramsdellite can thus change to pyroslusite by migration of manganese ions; only small adjustments to the oxygen positions are required.

The streaking of reflections parallel to  $b^*$  is readily explained. Ramsdellite and pyroslusite can both be regarded as being built up of layers parallel to (010); these layers have similar arrangements of oxygen atoms, but differ in the way in which the manganese ions are arranged between them. Ramsdellite contains manganese in layers that repeat every fourth layer parallel to (010) (ABCD, fig. 2*a*); pyroslusite contains only two such layers (AD, fig. 2*b*). It can be seen that crystals examined at an intermediate stage in the reaction, before the manganese ions are completely rearranged, will probably possess a certain amount of disorder in the arrangement of the layers. This 'stacking' disorder explains the streaking of reflections parallel to  $b^*$ . (For a fuller discussion of disorder in manganese dioxides see de Wolff (1959).)

The small quantity of ramsdellite formed when groutite crystals were heated was in the expected orientation. It is very difficult, however, to explain why the major product formed was pyroslusite, especially as crystals 5-8 were heated well below the usual ramsdellite-pyroslusite inversion temperature. The ramsdellite formed may represent an intermediate stage, or may merely be a minor product. It should be noted that crystals 5-7 contain unchanged groutite along with the pyroslusite. This shows that if the ramsdellite is an intermediate stage, it must convert very rapidly to pyroslusite.

Klingsberg and Roy's results differed from the present ones possibly because their sample was from a different locality. Their results, together with the evidence of natural ramsdellite pseudomorphic after groutite, show that it must be possible to form ramsdellite from groutite. The conditions under which natural ramsdellite was formed from groutite are apparently not the ones used in the present work, i.e. slow heating of single crystals in air. Under such conditions it seems that as soon as sufficient energy is available to cause the groutite to oxidize, the change proceeds right through to the stable dioxide.

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