A Simplified Scheme for Polymorphism in the Manganese Dioxides

By R. Giovanoli

Laboratory for Electron Microscopy of the University of Berne*

Dedicated to Professor Walter Feitknecht

Summary

In order to clarify how many MnO_2 modifications exist, the author has investigated the cryptocrystalline manganese dioxides and oxyhydroxides. He finds that only ramsdellite and pyrolusite (= polianite, β-MnO_2) are true MnO_2 modifications, and that the nsutite (γ-MnO_2) family includes a series of intergrowth structure varieties. While the nsutite family is structurally related to the true MnO_2 modifications, the birnessite and the hollandite families are distinctly differing in structure from one another as well as from ramsdellite, pyrolusite and nsutite. A simplified scheme of these compounds, finally, is proposed.

1. Introduction

There has been much confusion as to how many modifications of MnO_2 exist. Not less than 14 greek signs have been used, namely, $\alpha, \beta, \beta', \gamma, \gamma', \gamma'', \delta, \delta', \delta'', \varepsilon, \eta, \eta', \eta'', \varrho$[1,2]. In order to relate these products, most of which ar cryptocristalline, to some fully cristalline parent structures (mineral species), the author has

* Freiestraße 3, CH-3012 Berne (Switzerland).

1 O. Glemser *et al.*, *Z. anorg. allg. Chem. 309* (1961) 1, 18, 121.

2 R. K. Sorem and E. N. Cameron, *Econ. Geol. 55* (1960) 278.

investigated the disperse manganese oxides and oxy-hydroxides. Focusing X-ray technique, particularly with molybdenum radiation, electron microscopy, electron diffraction, thermoanalysis and classical analytical methods were used. Attention has been directed, moreover, not only at the appearance and structure but also on the *reactivity* of these products.

2. True MnO_2 modifications

Only two true modifications (mineral species) of MnO_2 exist, i.e., (i) ramsdellite (no greek sign attributed yet), and (ii) pyrolusite (= polianite, β-MnO_2). Ramsdellite[3,4] cristallises in the diaspore type, and pyrolusite[4] in the rutile structure. The two modifications differ in that ramsdellite consists of alternating *double* chains of $[MnO_6]$ octahedra while pyrolusite forms alternating *single* chains. Whereas ramsdellite is metastable and very rare in nature, pyrolusite is the thermodynamically stable phase MnO_2 and found wherever environment conditions favour thermodynamical equilibrium. The two structures have in common the hexagonal densest oxygen packing with the Mn^{4+} ions in half of the octahedral sites.

3. Disperse varieties of manganese dioxides

Some other mineral species claimed to be manganese dioxides have proved to be inclusion compounds $A_2Mn_8O_{16}$ of the hollandite type[5] (and may be found in nature fully cristalline, i.e. in mm size and fully ordered single crystals). Disperse varieties, synthetic or natural, of this mineral species often are called "α-MnO_2" since their analytical composition may approach the calculated value, and since the included cations such as K^+ and Ba^{++} may be present in an amount much below the figure expressed in the formula $A_2Mn_8O_{16}$[1]. It is, however, clear that such products are not true MnO_2 modifications but varieties of the hollandite parent structure.

Another series of natural or synthetic products claimed to be manganese dioxides may be derived from a third mineral species of the analytical composition Mn_7O_{13}, $5\,H_2O$ and will be treated in another section (see below).

Finally, we find a third series of natural or synthetic "manganese dioxides" which may be attributed to the two chain structures ramsdellite and pyrolusite but which, as a rule, are disperse and disordered. We shall deal first with this group in order to clarify what we mean by using the terms "parent structure", "mineral species", "modification" and "variety".

[3] A.M. Byström, *Acta Chem. Scand. 3* (1949) 163.
[4] A.F. Wells, *Structural Inorganic Chemistry*, Oxford 1962, p. 557.
[5] A. Byström and A.M. Byström, *Acta Crystallogr. 3* (1950) 146, *4* (1951) 469.

4. The nsutite family (γ-MnO_2)

It has been shown by de Wolff[6], Laudy and de Wolff[7], and ourselves[8] that structural intergrowth between ramsdellite and pyrolusite occurs, thus leading to products with X-ray powder patterns showing asymmetric and selective reflection broading. Such manganese dioxides have been named γ-MnO_2 by Glemser[9] when produced by oxidation and precipitation of Mn^{2+} by $(NH_4)_2S_2O_8$; electrolytically precipitated manganese dioxides are essentially the same.

Within these dioxides, the 021, 121, 221 and 002 reflections (with respect to the diaspore unit cell) are the more broadened the smaller the cristallites are. Some other reflections, particularly 110, are indicators for the degree of the structural intergrowth: In ramsdellite, 110 is in its fixed position, without broadening, while digesting synthetic products such as Glemser's[9] in hot diluted HNO_3 yields asymmetrical broadening of the 110 reflection though cristallite size increases by this procedure.

Manganese dioxides precipitated by O_3 from nitrate solutions do not show the 110 reflection at all, thus indicating a particularly high lattice disorder. *Any* intermediate MnO_2 may be produced within this family, except ramsdellite itself.

While the lattice disorder mentioned (the structural intergrowth) and the cristallite size thus give rise to an infinite number of possible X-ray powder patterns, we use the word *variety* to refer to exactly such minor structural differences in a parent structure (= modification or mineral species). It is, from this point of view, not justified or perhaps even misleading to pick out any particular preparation and attribute to it some greek sign.

The matter is yet more complicated by the possibility of substitution of part of the Mn^{4+} by Mn^{3+} and of O^{2-} by OH^-. This substitution does not only cause an overall shift of X-ray reflections towards lower Bragg angle (due to the larger Mn^{3+} ions), but introduces a distortion of the $[MnO_6]$ octahedron due to the d^4 electron configuration[10].

The entire family of these products, whether exactly $MnO_{2.000}$ or not, are all derived from the two parent structures ramsdellite and pyrolusite. They should nevertheless all be distinguished from the two parent structures, and should, thus, be named γ-MnO_2 or nsutite (after the large deposits found in Nsuta, Ghana[2,11]).

[6] P.M. de Wolff, *Acta Crystallogr. 12* (1959) 341.
[7] J.H.A. Laudy and P.M. de Wolff, *Appl. Sci. Res. B 10* (1962) 157.
[8] R. Giovanoli, R. Maurer and W. Feitknecht, *Helv. Chim. Acta 50* (1967) 4, 1073–80.
[9] O. Glemser, *Ber. dtsch. chem. Ges. 72* (1939) 1839.
[10] R. Giovanoli and U. Leuenberger, *Helv. Chim. Acta*, in press.
[11] W. Zwicker *et al.*, *Amer. Mineral. 47* (1962) 246.

5. The birnessite family

The oxidation of an $M(OH)_2$ suspension with O_2 under certain conditions yields platelets of the analytical composition $Na_4Mn_{14}O_{27}$, $9\,H_2O$[12]. This mineral species (defined by its unit cell) leads to a related but sodium-free compound of the analytical composition Mn_7O_{13}, $5\,H_2O$ when digested in HNO_3. Both are relatively well cristallised and differ distinctly from ramsdellite, pyrolusite, the hollandite and the nsutite families.

When occurring in smaller cristallites and especially when lattice disorder is prevailant, these two mineral species give rise to another series of possible X-ray powder patterns. Some of the members of this family approach, incidentally, the analytical composition $MnO_{\approx 2}$. They have been called hitherto "δ-MnO_2" or birnessite (after their occurrence in Birness, Scotland[1,13]).

As is the case for the nsutite family, the influence of, (i) cristallite size, (ii) lattice disorder, and (iii) partial substitution of Mn^{3+} by Mn^{4+} makes it difficult to recognise particular members of the birnessite family. *None* of its varieties, however, is a true MnO_2 modification.

While disperse Mn_7O_{13}, $5\,H_2O$ as well as disperse $Na_4Mn_{14}O_{27}$, $9\,H_2O$ may approach the formal composition $MnO_{\approx 2}$ (the X-ray powder patterns, then, being difficult to be recognised and distinguished from one another), the former is considerably less stable in reactivity towards, e.g., organic reducing agents, or thermal decomposition, or when subject to a vacuum[12,14].

6. Conclusion

All evidence yields that only ramsdellite and pyrolusite are true modifications of the phase MnO_2. There is, however, a series of varieties (called here the nsutite or γ-MnO_2 family) of intergrowth structure, and another series (called here the birnessite family) differing entirely from the two structures mentioned. The hollandite family, finally, gives rise to yet more products of the formal composition close to $MnO_{\approx 2}$ but is, as a family of inclusion compounds, not a true MnO_2 modification as well.

We therefore propose the following simplified scheme for polymorphism in the manganese dioxides:

True MnO_2 modifications	Nsutite family (γ-MnO_2)	Birnessite family (formerly "δ-MnO_2")	Hollandite family (formerly "α-MnO_2")
Pyrolusite (β-MnO_2) = Polianite. Stable modification Rutile type	Structural intergrowth of pyrolusite in a ramsdellite matrix or vice versa.	$Na_4Mn_{14}O_{27}$, $9\,H_2O$ and Mn_7O_{13}, $5\,H_2O$ and disperse and disordered varieties.	$A_2Mn_8O_{16}$ including K^+, Ba^{2+}, Pb^{2+}, a.s.o. in channels, and disperse and disordered varieties
Ramsdellite Metastable modification. Diaspore type	Partial substitution of Mn^{4+} by Mn^{3+} frequent.	Partial substitution of Mn^{3+} by Mn^{4+} frequent.	

A comprehensive study will appear in this journal later.

[12] R. Giovanoli, E. Stähli and W. Feitknecht, *Chimia 23* (1969) 264.
[13] L. H. P. Jones and A. A. Milne, *Min. Mag. 31* (1956) 283.
[14] F. Fischer, Lizentiatsarbeit, Bern 1969.