Some manganese oxide pseudomorphs

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Summary. Pyrolusite pseudomorphous after manganite occurs at Serro do Navio, Amapa, Brazil. It consists of wedges, flattened on (100) and elongated along [010], twinned on (011) and showing forms *d*{210}, *b*{010}, and *f*{021} (all indices referred to manganite, in the setting of Dana, 7th edn). The difficulty of distinguishing between pyrolusite pseudomorphous after manganite and after groutite is discussed and also the possible existence of the latter. The distinction was made here by measuring the twinning angle between the pyrolusite lattices using (0*kl*) precession photographs. Specimens of manganite intergrown with pyrolusite are described and their relative orientations determined. On heating, manganite partly decomposes to a monoclinic phase, *a* 9·9 Å, *b* 5·73 Å, *c* 4·89 Å, *β* 98°, space group *I*2, *Im*, or *I*2/*m*.

On a recent visit to the Natural History Museum, Dr. V. Nayak generously presented to us a fine specimen of polianite from Serro do Navio (T6), Amapa, Brazil, now registered in our collection as B.M. 1965, 281. It consisted of spiky wedge-shaped crystals on a stalactitic matrix of pyrolusite with a little kaolinite and monoclinic cryptomelane (X-ray powder photographs; cf. Mathieson and Wadsley (1950), ASTM Card 4–0778). A drawing of a typical crystal is shown in fig. 1; the crystals appear to be pseudomorphous after a twinned orthorhombic or monoclinic mineral. X-ray powder photographs from them showed pyrolusite *a* 4·405±0·001 Å, *c* 2·876±0·001 Å, with a trace of a member of the tetragonal cryptomelane–hollandite–coronadite group; the evidence did not permit definite identification of the latter, but it is probably cryptomelane from the associations. Single crystal photographs showed that the pyrolusite was oriented, with (100) || to the plane of the wedge and [001] || to its edge; the twinned pyrolusite pseudomorphs have an *a*-axis exactly in common. The cryptomelane was oriented $[001]_C \| [001]_P$; $(100)_C \| (110)_P$; this orientation might reasonably be expected for an intergrowth of the two phases from their crystal structures (see, e.g., diagrams given by Bragg and Claringbull, 1965). Spectrographic examination of the crystals by Mr. C. J. Elliott showed about 0·2 % NiO as sole major impurity (alkalis would not have been detected).

Pyrolusite is commonly reported in the literature as pseudomorphous after manganite. However, the habit of these crystals is quite unlike any manganite that we have seen, and no similar habit is reported in Goldschmidt's Atlas (with the possible exception of fig. 41, pl. 121, vol. 5, due to Weisbach, 1858). I was led also to consider groutite as a parent mineral. The decomposition sequence: groutite → groutellite → ramsdellite → pyrolusite is known fully in the laboratory (see, e.g., Dent Glasser and Smith, 1965; Klingsberg and Roy, 1959), groutite and ramsdellite being known in nature. There seemed no obvious reason why pyrolusite pseudomorphous after groutite should not also occur. An objection is that the sides of the wedge would be indexed as (041) of groutite, a form that has not been recorded; it may equally be noted that the form (021) for manganite at the side of the wedge is normally rare and poorly developed, being noted only by Groth (1878, quoted in

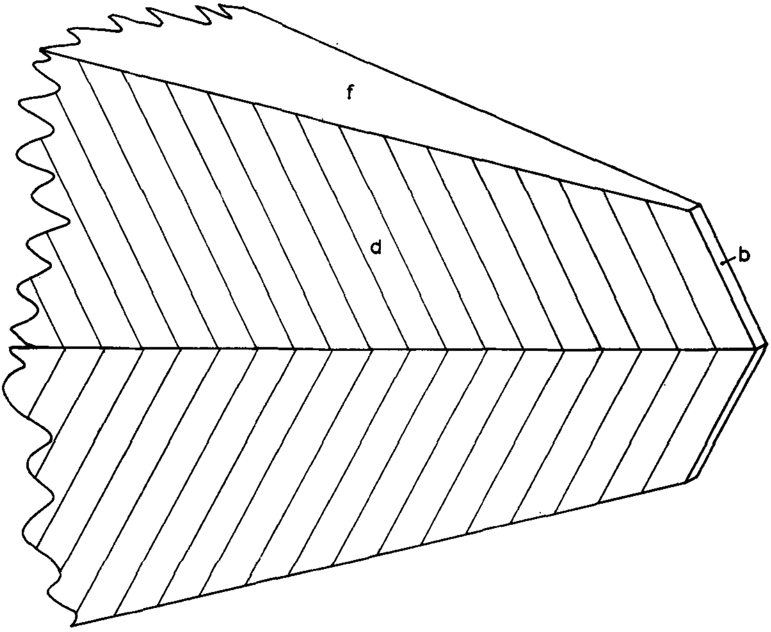

FIG. 1. Crystal of pyrolusite pseudomorphous after manganite from Amapa, Brazil, showing forms *d*{210}, *f*{021}, and *b*{010} of manganite.

Goldschmidt's Atlas). Groutite is known to twin (Segeler, 1959) but the twinning plane is not recorded; the proposed plane here, (021), is structurally quite plausible. The over-all habit is unknown for manganite, but strikingly resembles fig. 2 of Fleischer, Richmond, and Evans (1962) for ramsdellite pseudomorphous after groutite.

Measurements of a portion of a crystal, set with pyrolusite [001] accurately vertical by X-ray methods, were kindly made for me by Mr. P. G. Embrey, and are given in table I. The faces were difficult to measure, giving very poor reflections, and the accuracy is about ±2°.

TABLE I. Goniometric measurements (P. G. Embrey)

Observed			Manganite*			Groutite†		
b	0°	91°	(010)	0° 00′	90° 00′	(010)	0° 00′	90° 00′
d	69°	91°	(210)	67° 07′	90° 00′	(110)	66° 55′	90° 00′
d	−65°	88°						
f	−6°	49°	(021)	0° 00′	47° 27½′	(041)	0° 00′	46° 48½′‡

* Palache *et al.* (1944) † Gruner (1947) ‡ Calculated

Even so, the faces show considerable distortion, and measurements of this and other crystals suggest they may depart by up to 6° from their expected positions. Measurements of a twinned crystal showed that the two c-axes were inclined at about 58° to each other.

The results can be interpreted equally well in terms of manganite or groutite, as shown in the table. This arises because manganite is pseudo-orthorhombic, $a{:}b{:}c = 0{\cdot}8441{:}1{:}0{\cdot}5448$, $\beta = 90^\circ\ 0'$ (Palache *et al.*, 1944; b-centred monoclinic lattice of Buerger, 1936), while for groutite the orthorhombic axial ratios may be written $a{:}b{:}c = 0{\cdot}8524{:}2{:}0{\cdot}5326$ (Gruner, 1947). Forms observed for manganite agree with corresponding ones for groutite with double k index to within less than 1° in all cases. Both minerals often show prism faces striated parallel to [001] with broadly similar patterns of striation on terminal faces; both cleave perfectly on (010) and well on (100) and in laboratory heating experiments both yield the same orientation of pyrolusite with axes parallel to the parent phase. Given the distortions due to the volume shrinkage involved in converting either form of MnOOH to pyrolusite (cf. Strunz, 1943), distinction of the parent phases by quantitative morphology seems impossible and one's decision must be a statement of probabilities based on the general habit. Type groutite has a unique habit and was first recognized in this way, but acicular groutite is known (Segeler, 1959; cf. Dent Glasser and Smith, 1965), and the best resemblance here is to the wedge-shaped ramsdellite pseudomorphs mentioned above.

In the present case the problem could be resolved by X-ray measurements of the twinning angle. Zero layer precession photographs of twinned crystals taken with Mo-$K\alpha$ radiation around their common a-axis showed two ($0kl$) lattices inclined at about 57° to each other. The reflections recorded were diffuse but nearly circular, showing no sign of orientation change while forming the pyrolusite. Accurate measurements of the sides and the diagonals of the quadrilateral formed by two pairs of equivalent reflections from the two lattices allowed more exact measurements of the inclination angle. Taking the lengths of the two diagonals and the sum of the lengths of one or the other pair of opposite sides yielded two independent estimates of the angle using the cosine formula. Assuming that the axes of the pyrolusite are exactly parallel to those of the parent MnOOH, half of this angle represents the angle (010):($0kl$) for the twinning plane in the parent. Measurements of this latter angle for three distinct reflections for each of two crystals are given in table II and clearly support manganite rather than groutite as the parent phase, twinned as usual on (011) but having quite a new habit.

TABLE II. Angle between twinning plane and (010) from $0kl$ precession photographs (Mo-$K\alpha$ radiation)

Measured from pyrolusite reflections	Crystal 3 Film X11829		Crystal 4 Film X11928	
002	28·61	28·73	28·62	29·17
200	28·77	28·60	28·68	28·12
400	28·23	28·48	28·87	28·85
Average	28·57°		28·72°	
(010):(011) Manganite	28·58°		Palache *et al.* (1944)	
(010):(021) Groutite	28·03°		Gruner (1947)	

To obtain standard photographs of manganite, by chance the specimen selected was B.M. 1926, 1210, from Dundas, Montagu County, Tasmania. The black-bladed acicular crystals yielded X-ray powder photographs showing a mixture of manganite and pyrolusite. [001] rotation and ($hk0$) precession photographs taken with Fe-K radiation showed that the lattices of the two phases were exactly parallel. This new observation finally confirms in natural material the relative orientations in intergrowth found by Dasgupta (1965) and others from laboratory studies of heated manganite (cf. e.g. Strunz, 1943).

Bannister and Vaux (unpublished work) have surveyed a number of pyrolusites by [001] Fe-K rotation photographs. One of the five samples studied, B.M. 37451, from Luisa, near Giessen, Hesse, Germany, could now be identified also as a parallel intergrowth of pyrolusite and manganite by comparison with photographs of B.M. 1926, 1210. This was confirmed by powder and additional rotation photographs, and the orientation finally confirmed by (*hk*0) precession photograph.

A second sample of the five, B.M. 91106, from Elgersburg, Thuringia, consisting of radiating fibrous spherical aggregates of pyrolusite, yielded pyrolusite X-ray powder photographs together with very weak diffuse extra lines of manganite. The strongest manganite line, (210) at 3·40 Å, is easily confused with a possible β line from the strongest pyrolusite reflection, the (110) reflection at 3·14 Å. The manganite reflections were thus overlooked initially on the rotation photograph, but were there, and were confirmed on new photographs around [001].

These results amply support the assumption that the pyrolusite crystal axes are accurately parallel to those of the parent manganite in natural pseudomorphs, thus confirming the interpretation of the results in table II. Moreover there is no reason to challenge the accepted view that much pyrolusite is pseudomorphous after manganite, notwithstanding the remarks above as to the ambiguity of morphological evidence. X-ray evidence has in several cases been decisive.

Crystals from B.M. 1926, 1210 were heated for various times in air at 340° C. After two hours some manganite had been destroyed, and besides pyrolusite and residual manganite reflections, the extra reflections noted by Dasgupta (1965) were observed. The destruction of the manganite was complete after 16 hours, and thereafter no change in the relative intensities of pyrolusite and extra reflections was observed up to 6 weeks heat treatment. Powder photographs of the heated crystals showed traces of the extra reflections as very weak lines at 4·9 and 2·83 Å; however, a specimen that had been finely powdered before heat treating as above for 1 week showed no extra reflections on the powder photograph.

[001] rotation and various precession photographs showed that any pyrolusite formed from the manganite in the crystals during heat treatment was oriented parallel to that present initially, and that the extra reflections were due to a phase with approximate cell dimensions: a 9·9 Å, b 5·73 Å, c 4·89 Å, β 98°, space group $I2$, Im, or $I2/m$. This had been formed topotactically in two twinned orientations, both having [010] parallel to the pyrolusite [001], and [001] inclined at 4° in β acute to either side of pyrolusite [100]. The two lattices together have orthorhombic symmetry and must therefore have been derived from the manganite (possibly twinned on (100)); Dasgupta has observed similar

extra reflections on heating pyrolusite at somewhat higher temperatures, but had they been so formed here they would have been present in two further orientations related to the present two by reflection across a pyrolusite (110) plane, in order to preserve the tetragonal symmetry of the parent lattice.

The above results suggest that the phase is formed directly from manganite in the core of the crystals, out of access to air, and may be a polymorph of Mn_2O_3. Dr. Dasgupta (*pers. comm.*) has prepared the phase in a nearly pure form by heating manganite in a neutral atmosphere. The new phase is formed at temperatures comparable to or less than the inversion temperature of ramsdellite to pyrolusite. In the cases discussed above, pyrolusite is observed in nature with manganite alone, and its formation thus occurred by (?aerial) oxidation, at temperatures below the thermal decomposition of manganite. These observations appear to accord with current views, that pyrolusite pseudomorphs are commonly formed within the stability range of ramsdellite. Pseudomorphs of pyrolusite, as opposed to ramsdellite, after groutite, are thus likely to be very rare, although Fleischer, Richmond, and Evans (1962) consider it possible.

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