

EXSOLUTION GROWTHS OF ZINCITE IN MANGANOSITE AND OF MANGANOSITE IN PERICLASE

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ABSTRACT

Manganosite from Franklin, New Jersey, contains exsolved plates of zincite oriented with zincite {0001} [10 $\bar{1}$ 0] parallel to manganosite {111} [011]. Periclase from Långban and Nordmark, Sweden, contains exsolved octahedra of manganosite oriented with periclase {111} [011] parallel to manganosite {111} [110]. The structural relations expressed in the orientations and the solid solubility of Zn in MnO and of Mn in MgO are discussed.

ZINCITE INTERGROWTHS IN MANGANOSITE

Manganosite, MnO, occurs at Franklin, New Jersey, as irregular masses up to 3 or 4 inches in size, associated with willemite, franklinite, coarse zincite, and calcite.¹ A pronounced octahedral parting is present in the larger masses, in addition to the cubical cleavage proper to the mineral. The parting surfaces are covered by a more or less continuous film or plate of zincite, about 0.05 to 0.25 mm. in thickness. Optical examination proves that the zincite plates are single individuals over their entire extent, and that they are flattened on {0001}. A series of cleavage cracks arranged at 60° are seen in the plates, together with rod-like and hexagonal plate-like inclusions arranged parallel to the cleavage directions. An *x*-ray Laue photograph verified the plane of flattening as {0001} and the cleavage as {10 $\bar{1}$ 0}. The law of orientation of the two minerals was found to be zincite {0001} [10 $\bar{1}$ 0] parallel to manganosite {111} [011].

ISOMORPHOUS SUBSTITUTION OF ZN IN MnO AND MN IN ZnO

Experimental data bearing on the substitution of Zn for Mn in MnO are lacking. Analyses² of the natural manganosite from Franklin show 3.41 and 4.89 per cent ZnO, but it is possible that the Zn is due to impurities. Co, Ni, Cd and Ca have been found³ to substitute to varying extents for Mn in artificial MnO. The oxides of these metals, like MnO, form crystals of the NaCl-type. On the other hand, the isometric form of ZnO, although its predicted (ionic) radius ratio is within the range of the NaCl structure-type, forms crystals of the sphalerite-type.⁴ This is apparently due to the relatively great tetrahedral bond-forming tendency of Zn. For this reason Zn would not be expected to enter, or at least be

¹ Palache, C.: *U. S. Geol. Survey, Prof. Paper* **180**, 37 (1935).

² Analyses cited in ref. 1, *loc. cit.*

³ Natta, G., and Passerini, L.: *Gazz. chim. Ital.*, **59**, 129 (1929); see also ref. 11.

⁴ Bragg, W. L., and Darbyshire, J. A.: *Trans. Faraday Soc.*, **28**, 522 (1932).

stable, within the 6-fold coordination of oxygen ions obtaining in MnO, in spite of the fact that its apparent ionic radius ratio does not differ from Mn as much as do Co, Ni, Cd and Ca. Nevertheless, Zn is present in natural MgO (periclase) from Nordmark, Sweden, in amounts ranging from 1.6 to 2.5 per cent ZnO,⁵ although here again possibly due to admixture.

Divalent Mn enters zincite up to an apparent maximum of 6.5 per cent MnO, and divalent Fe is commonly present in small amounts.² Hexagonal, wurtzite-type, modifications of MnO and FeO are not known. Trivalent Mn also has been reported (<0.7 per cent Mn₂O₃) in zincite and is thought to cause the red color.⁶

The characters of the zincite growths as seen in polished sections⁷ and in hand specimens exclude an origin other than by exsolution. A small solubility of Zn in MnO is thus indicated. This is estimated, from the relative volumes of the two minerals and assuming complete unmixing, at most as 15 weight per cent ZnO.

It may also be remarked that some grains of manganosite in transmitted light exhibit still further kinds of oriented microscopic inclusions, probably formed by exsolution: (1) an unidentified black lath-like mineral (Fig. 1) possibly identical with a gray mineral seen in polished section,⁷ (2) hexagonal plates of hematite (?) (Fig. 1), and (3) prismatic crystals of a colorless anisotropic mineral that may be willemite. The zincite and willemite from Franklin also contain abundant oriented microscopic inclusions.

Structural Interpretation of the Orientation. The observed orientation between the zincite and the manganosite marks a position of complete coincidence of the crystal structures of the two minerals. Manganosite has a NaCl-type structure with $a_0 = 4.436 \text{ \AA}$, and zincite has a wurtzite-type structure with $a_0 = 3.242 \text{ \AA}$ and $c_0 = 5.176 \text{ \AA}$. Manganosite viewed along [111] is composed of alternate layers of Mn and O ions stacked in cubic close packing, and zincite viewed along [0001] is composed of alternate layers of Zn and O ions stacked in hexagonal close packing.

⁵ Sjögren, H.: *Geol. För. Förh.*, **9**, 527 (1887).

⁶ Dittler, E.: *Zeits. anorg. Chem.*, **148**, 332 (1925).

⁷ Ramdohr (*Zbl. Min.*, p. 133, 1938) has also described manganosite from Franklin in polished section. He notes a minute oriented exsolution growth of an unidentified gray mineral (which is not zincite), and rims of zinc-hausmannite (=hetaerolite) on the manganosite grains. These features were also observed by the writer. Megascopic amounts of the so-called zinc-hausmannite were found on some specimens along the manganosite margins, and as penetrations along the partings on the sides of the zincite lamellae. X-ray powder pictures taken in comparison with hausmannite from Ilmenau and type hetaerolite proved the mineral to be hausmannite.

The actual O—O distances in MnO {111} and ZnO {0001} are 3.14 Å and 3.24 Å, respectively.

A mechanism of formation of the oriented growths is suggested by these facts. If, during the growth of a {111} face of MnO, Zn atoms occupy the positions adjacent to an O plane intended for Mn ions, a two-dimensional surface ZnO layer is formed on which are imposed the structural and dimensional characters of zincite. If growth continues by the deposition of additional layers of Zn and O ions, in the fashion of hexagonal close packing proper to zincite, an overgrowing three-dimensional zincite crystal is formed which is oriented by the law observed to the underlying MnO crystal. This mechanism may proceed upon the faces of a preformed MnO crystal (*oriented overgrowth*) or intermittently during the growth of a MnO crystal (*oriented syncrystallization*). Similarly, a MnO crystal containing Zn in isomorphous substitution for Mn may undergo environmental or other changes bringing a concentration and ordering of the Zn atoms, with the crystallization of ZnO as an exsolved phase again oriented upon the {111} planes.

A further illustration of the relation between packing scheme and orientation in ZnO and MnO is afforded by the films of (hexagonal) ZnO formed upon sphalerite when the latter is heated in air. Electron diffraction study⁸ proves that the two substances are oriented with ZnO {0001} [10 $\bar{1}$ 0] parallel to ZnS {111} [011]. This law is identical with that of ZnO—MnO, as would be expected since sphalerite along [111] is composed of alternate layers of Zn and S (=O) atoms essentially in cubic close packing. The ZnO film presumably is formed by the surface thermal dissociation of the ZnS with the substitution of O for S.

In all of these cases, the essential circumstance for the orientation of the one substance to the other is an identity or near-identity in structure between them. The identities tend to be shared, since the later-formed crystal can thus obviate the expenditure of energy in generating a free surface of its own kind.⁹

MANGANOSITE INTERGROWTHS IN PERICLASE

Periclase, MgO, occurs at Långban, Sweden, as uniformly colored grass-green irregular grains associated with hausmannite in a dolomitic marble.¹⁰ The grains have brucite rims. Cleavage fragments examined in transmitted light under moderate magnification are seen to contain hosts of minute octahedra of manganosite (Fig. 2). The manganosite octahedra

⁸ Aminoff, G., and Broomé, B.: *Nature*, **137**, 995 (1936). See also Seifert, H.: *Zeits. Kryst.*, **102**, 183 (1940).

⁹ Frondel, C.: *Am. Jour. Sci.*, **30**, 51 (1935).

¹⁰ Sjögren, H.: *Geol. För. Förh.*, **17**, 288 (1895); **20**, 25 (1898).

are all oriented to the periclase so that manganosite $\{111\}$ $[011]$ is parallel to periclase $\{111\}$ $[011]$.

An identical occurrence at Nordmark, Sweden, has been described.⁵ Bulk analyses of this intergrowth show 7.0 to 9.1 per cent MnO.

It has been found¹¹ experimentally that MnO can enter MgO up to about 26 mol per cent MnO, and that Mg can enter MnO up to about 31 mol per cent MgO. An origin by exsolution of the present occurrences

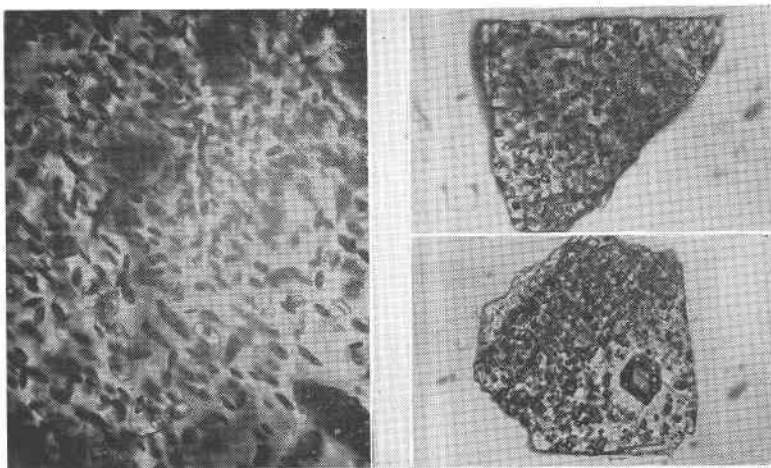


FIG. 1 (left). Oriented lath-like exsolution growths of an unknown black mineral and of hexagonal plates of hematite (?) in manganosite. Section parallel $\{111\}$ of manganosite. Oil immersion, 425 \times .

FIG. 2 (right). Oriented exsolution growths of manganosite octahedra (some distorted by elongation) in periclase. Note clear area around the large manganosite crystal; this is characteristic. Periclase grains are resting on $\{100\}$ cleavages. 140 \times .

would indicate that the (quenched) artificial preparations were in unstable equilibrium. The periclase from Långban probably still contains some Mn in solid solution, for it has $n_{Na} = 1.7425 \pm 0.0005$ while pure MgO has $n_{Na} = 1.7360$. Assuming that the increase is due to MnO and that the index varies linearly between $n_{Na} = 1.7360$ for MgO and $n_{Na} = 2.18$ for MnO,¹² then the observed index corresponds to about 2 mol per cent MnO. This may be a saturation value for ordinary conditions.

A complete structural and close dimensional resemblance exists between manganosite and periclase. Both have a NaCl-type structure,

¹¹ Passerini, L.: *Gazz. chim. Ital.*, **60**, 535 (1930).

¹² Ford, W. E.: *Am. Jour. Sci.*, **38**, 503 (1914); calculated from the measured indices, n_{red} 2.16 and n_{green} 2.19.

with periclase $a_0=4.203 \text{ \AA}$ and manganosite $a_0=4.436 \text{ \AA}$. Manganosite hence may crystallize from a periclase environment without regard to the habit of the exsolved crystals, since any habit would maintain a structural coincidence with the MgO host crystal. Zincite, on the other hand, by reason of its only partial resemblance to manganosite, is forced to develop a particular habit when crystallizing within MnO in order to make contact with the particular plane of the MgO in which the structural resemblance exists. A similar geometrical control of nucleation is found in certain types of oriented adsorption layers on the surface of crystals.¹³

¹³ Frondel, C.: *Am. Mineral*, **25**, 338 (1940).