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Crystal structure of switzerite, $Mn_3(PO_4)_2 \cdot 7H_2O$, and its relationship to metaswitzerite, $Mn_3(PO_4)_2 \cdot 4H_2O$

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ABSTRACT

Switzerite, $Mn_3(PO_4)_2 \cdot 7H_2O$, is monoclinic, $P2_1/a$, with $a = 8.528(4)$ Å, $b = 13.166(5)$ Å, $c = 11.812(4)$ Å, $\beta = 110.05(3)°$, and Z = 4. A crystal sealed in a glass capillary tube was used to gather 1634 unique observed reflections, using a Philips PW1100 four-circle diffractometer. The structure was solved by direct methods with a final R of 0.089. The major structural unit in switzerite is a sheet of composition $Mn_4O_{10}(H_2O)_4$, which lies parallel to (001), and which is similar to the atomic sheet found in metaswitzerite, $Mn_3(PO_4)_2 \cdot 4H_2O$. $MnO_3(H_2O)_3$ octahedra are linked to this sheet by vertex-sharing, forming a complex slab of composition $[Mn_6O_{14}(H_2O)_{10}]_2$. Phosphate groups knit together the slabs internally to form a neutral layer with composition $Mn_6(H_2O)_{10}(PO_4)_4$, two per unit cell. Between these neutral layers are free water molecules, eight per unit cell, bonded to the layers by H bonds. Switzerite tranforms to metaswitzerite by expulsion of ¾ of the free water molecules and condensation of the neutral layers along **c** into a framework structure. Only minor changes occur within the layers, and the transformation of switzerite into metaswitzerite can be considered a typical topotactic reaction.

INTRODUCTION

In 1967, Leavens and White described the new mineral switzerite $[Mn_3(PO_4)_2 \cdot 4H_2O]$ from Kings Mountain, North Carolina. Its crystal structure was subsequently determined by Fanfani and Zanazzi (1979). However, it has recently been discovered that this mineral is the dehydration product of the heptahydrate, $Mn_3(PO_4)_2 \cdot 7H_2O$. The accompanying article (White et al., 1986) redefines switzerite as the heptahydrate and characterizes it. The tetrahydrate, formerly switzerite, is now metaswitzerite. These changes have been approved by the New Mineral Names Commission, IMA. This paper reports the results of the crystal structure determination of switzerite, as now defined, and discusses its relationship to metaswitzerite.

EXPERIMENTAL PROCEDURE

Since switzerite is not stable in air, a crystal (NMNH 120871) was sealed with water in a glass capillary tube and mounted on a Philips PW1100 four-circle diffractometer. Lattice parameters were determined by the least-squares method from the setting angles of 25 reflections, using graphite-monochromatized Mo$K\alpha$ radiation. Switzerite is monoclinic, with $a = 8.528(4)$, $b = 13.166(5)$, $c = 11.812(4)$ Å, and $\beta = 110.05(3)°$; from the systematic absences, the space group is uniquely determined as $P2_1/a$. Assuming a unit-cell content of $4[Mn_3(PO_4)_2 \cdot 7H_2O]$, the calculated density is 2.562 g/cm^3, and the absorption coefficient for Mo$K\alpha$ is 33.5 cm^{-1}.

Intensities were measured with the diffractometer operating in the $\omega/2\theta$ scan mode, with a scan width of 1.5° and a scan speed of 0.06°/s. To check the stability of the crystal during data collection, three standard reflections were measured every 180 min. In the range $6° \leq 2\theta \leq 60°$, 3571 unique reflections were collected, of which 1937 had intensities smaller than $3\sigma(I)$ and were considered "unobserved." The data were reduced to structure factors in the usual way; no absorption correction was applied.

STRUCTURE DETERMINATION AND REFINEMENT

The structure of switzerite was solved by direct methods with the program SHELX-76 (Sheldrick, 1976). By multisolution sign expansion, phases were found for 661 reflections with $E > 1.1$, and from the most probable E map, 3 Mn, 2 P, and 8 O atoms were located in the asymmetric unit. The structure was completed from successive Fourier and difference Fourier maps. Four cycles of full-matrix least-squares refinement with isotropic temperature factors reduced R to 0.14. Anisotropic temperature factors for Mn and P atoms were then introduced and after three cycles, all calculated shifts were less than $\frac{1}{2}\sigma$. The refinement was considered ended, with an R of 0.089 for the 1634 observed reflections. The quantity minimized was $\Sigma w(|F_o| - |F_c|)^2$; the weighting scheme was $w = a/[\sigma^2(F) + bF^2]$, with $a = 1.7816$ and $b = 0.0061$ in

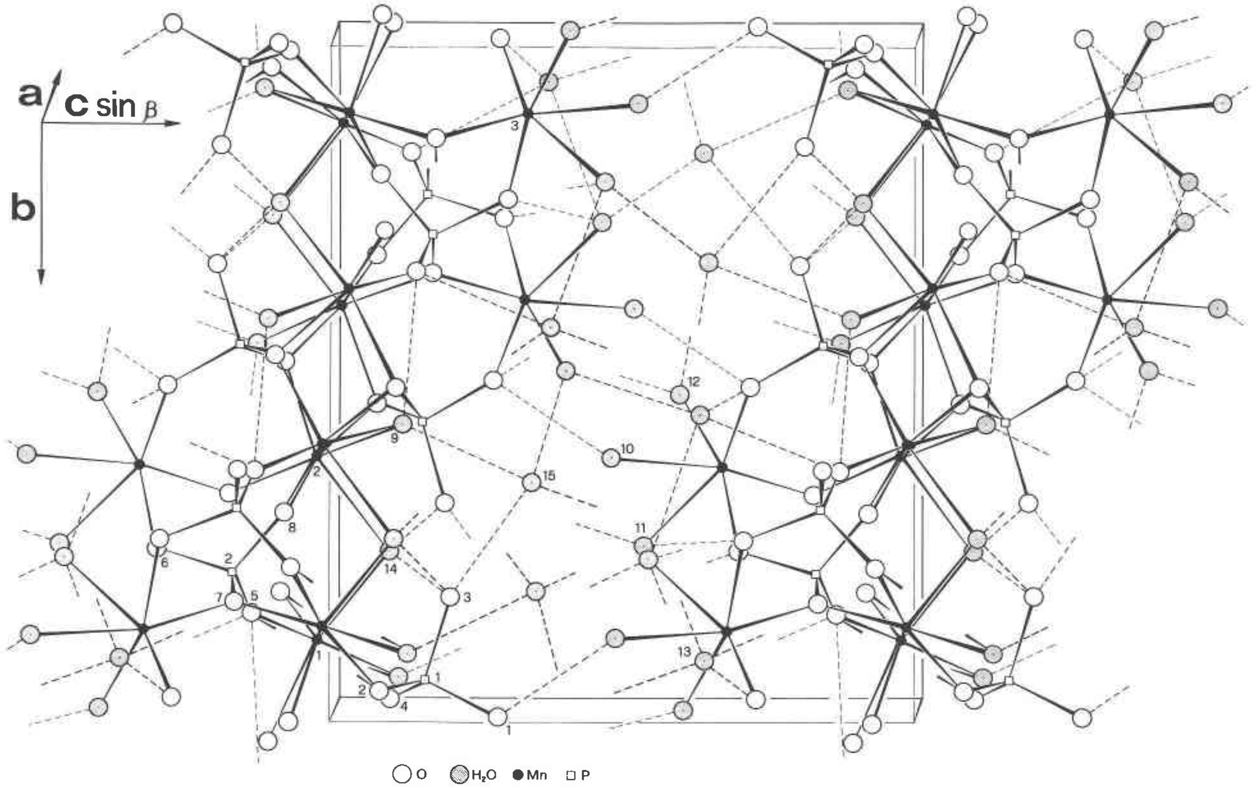

Fig. 1. Clinographic view of the crystal structure of switzerite.

the last cycle. Neutral-atom scattering factors from the *International Tables for X-ray Crystallography* (1974) for Mn, P, and O were used in structure-factor computations. The value for Mn was corrected for the Fe content shown by chemical analysis, as given in the accompanying paper (White et al., 1986). A correction was also applied for the real and imaginary parts of anomalous dispersion.

Table 1[1] lists the observed and calculated structure factors, and the final atomic coordinates and thermal parameters are listed in Table 2.

Table 2. Atomic coordinates and thermal parameters for switzerite

Atom	x/a	y/b	z/c	U or U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Mn(1)	−0.0495(2)	0.8831(2)	−0.0218(2)	48(8)	30(8)	305(12)	−12(8)	82(8)	−3(9)
Mn(2)	0.0561(2)	0.6165(2)	−0.0172(2)	45(9)	19(8)	318(12)	6(7)	111(8)	7(9)
Mn(3)	0.5827(3)	0.1243(2)	0.3363(2)	117(10)	101(10)	306(13)	−5(9)	94(8)	18(9)
P(1)	0.3346(4)	0.9442(3)	0.1667(3)	22(14)	56(14)	269(21)	−4(11)	86(13)	18(14)
P(2)	0.1859(4)	0.7886(2)	−0.1746(3)	24(14)	56(14)	230(19)	2(11)	66(12)	−1(14)
O(1)	0.4013(13)	0.0088(9)	0.2783(10)	205(23)					
O(2)	−0.0635(12)	0.5325(7)	0.0856(8)	136(19)					
O(3)	0.8479(13)	0.6696(8)	0.1964(9)	183(22)					
O(4)	0.6486(11)	0.5262(7)	0.1002(8)	94(18)					
O(5)	0.0895(12)	0.8708(7)	−0.1374(9)	147(20)					
O(6)	0.0832(13)	0.7499(9)	−0.2995(9)	205(23)					
O(7)	0.6485(12)	0.1651(8)	0.1751(8)	125(19)					
O(8)	0.2246(11)	0.6997(7)	−0.0841(8)	109(18)					
O(9)	0.3135(12)	0.5698(8)	0.1174(8)	127(19)					
O(10)	−0.0463(17)	0.6111(11)	−0.5191(12)	417(29)					
O(11)	−0.2715(19)	0.7280(12)	−0.4574(13)	492(37)					
O(12)	−0.2909(19)	0.5156(12)	−0.4036(13)	452(35)					
O(13)	−0.1552(18)	0.9346(12)	0.6287(12)	410(33)					
O(14)	0.0537(12)	0.7477(8)	0.0943(8)	135(20)					
O(15)	0.4303(21)	0.6651(14)	0.3397(15)	568(42)					

Note: Anisotropic thermal parameters are in the form $\exp -2\pi^2(h^2a^{*2}U_{11} + k^2b^{*2}U_{22} + l^2c^{*2}U_{33} + 2hka^*b^*U_{12} + 2hla^*c^*U_{13} + 2klb^*c^*U_{23})$. Estimated standard deviations (in parentheses) refer to the last digit.

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[1] To obtain a copy of Table 1, order Document AM-86-312 from the Business Office, Mineralogical Society of America, 1625 I Street N.W., Suite 414, Washington, D.C. 20006. Please remit $5.00 in advance for the microfiche.

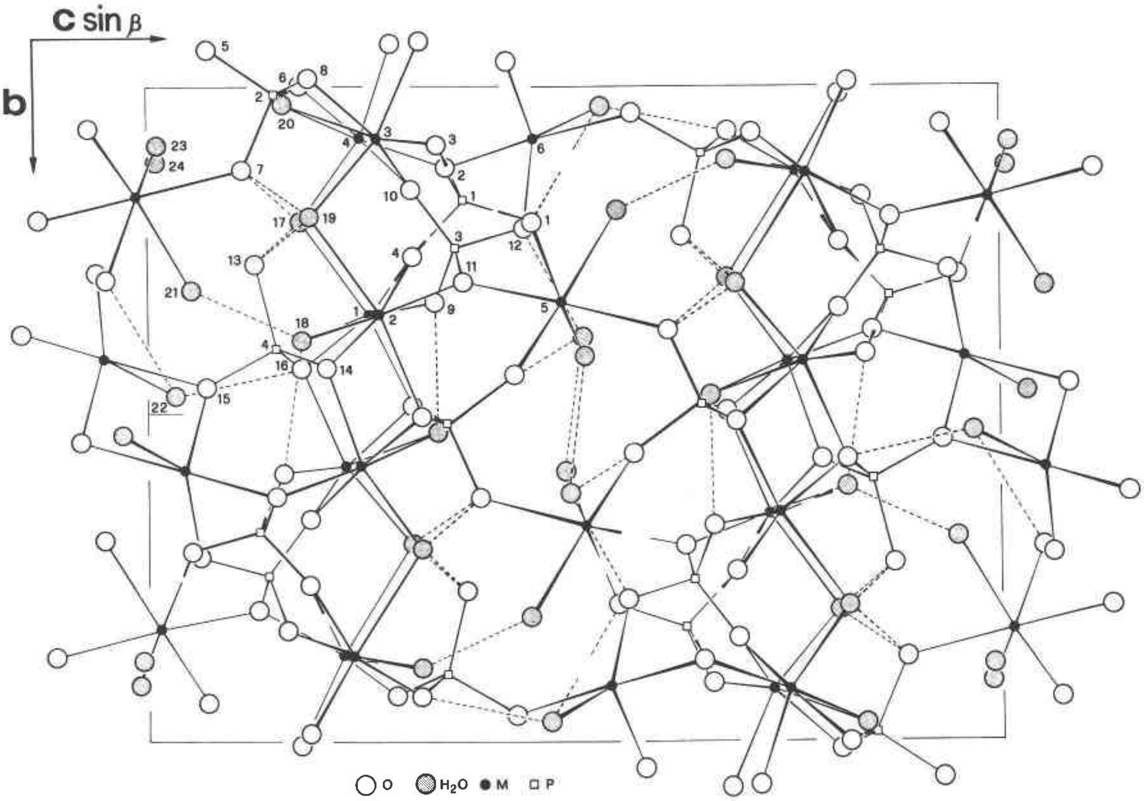

Fig. 2. Clinographic view of the crystal structure of metaswitzerite, redrawn from Fanfani and Zanazzi (1979).

Results and discussion

Figure 1 shows a view of the unit cell of switzerite. Bond lengths and angles are given in Tables 3 and 4, respectively. The coordination of all Mn^{+2} ions in the structure is sixfold in the form of distorted octahedra. The Mn(1) and Mn(2) atoms are each coordinated by four O atoms and two water molecules in a *cis* configuration. The Mn(3) atom is coordinated by three O atoms and three water molecules. The average Mn–O distance is 2.19 Å, with values in the range 2.10–2.40 Å.

Table 3. Bond lengths (Å) in switzerite

P(1)–O(1)	1.507	Mn(3)–O(1)	2.109
P(1)–O(2)	1.529	Mn(3)–O(6)	2.122
P(1)–O(3)	1.534	Mn(3)–O(12)	2.206
P(1)–O(4)	1.559	Mn(3)–O(11)	2.219
		Mn(3)–O(7)	2.227
P(2)–O(5)	1.512	Mn(3)–O(10)	2.290
P(2)–O(6)	1.522		
P(2)–O(7)	1.540	O(9)–O(5)	2.734
P(2)–O(8)	1.543	O(9)–O(15)	2.769
		O(10)–O(1)	2.772
Mn(1)–O(5)	2.099	O(11)–O(15)	2.952
Mn(1)–O(8)	2.114	O(11)–O(13)	2.955
Mn(1)–O(4)	2.142	O(12)–O(13)	2.753
Mn(1)–O(4)′	2.165	O(12)–O(15)	2.874
Mn(1)–O(14)	2.238	O(13)–O(1)	2.783
Mn(1)–O(9)	2.402	O(13)–O(5)	2.956
		O(14)–O(3)	2.619
Mn(2)–O(2)	2.131	O(14)–O(3)′	2.654
Mn(2)–O(2)′	2.142	O(15)–O(3)	2.699
Mn(2)–O(8)	2.160	O(6)–O(11)	2.585
Mn(2)–O(7)	2.168		
Mn(2)–O(14)	2.177		
Mn(2)–O(9)	2.308		

Note: Maximum estimated standard deviations are 0.013 Å for Mn–O distances, 0.015 Å for P–O distances, and 0.020 Å for O–O distances.

P shows the usual tetrahedral coordination, with P–O distances in the range 1.51–1.56 Å and a mean value of 1.53 Å. As in metaswitzerite (Fanfani and Zanazzi, 1979), one of the O atoms of the P(1) tetrahedron is not linked to any other cation, but functions as an acceptor in three H bonds. Probable H bonds in the switzerite structure were located by structural geometry and electrostatic bond-valence calculations. Distances between H-bonded O atoms are listed in Table 3. Bond-valence sums, computed by the method of Brown and Shannon (1973), are listed in Table 5. The H bond valence was divided between acceptor and donor atoms according to the values proposed by the same authors and reported by Donnay and Donnay (1973).

The major structural unit in switzerite is a rather compact sheet of composition $Mn_4O_{10}(H_2O)_4$. This sheet, which is parallel to (001), is similar to that found in metaswitzerite, as shown by the similar *a* and *b* translations in the lattices of these two compounds (Fig. 2). The sheet is built up of Mn(1) and Mn(2) octahedra, which share edges and vertices to form six-sided rings. The Mn(3) octahedra, which have composition $MnO_3(H_2O)_3$, are linked to this sheet by vertex-sharing. In this way a complex slab of

Table 4. Bond angles (°) in switzerite

O(1)–P(2)–O(2)	108.0	O(2)–Mn(2)–O(2)′	79.7
O(1)–P(1)–O(3)	112.1	O(2)–Mn(2)–O(8)	102.6
O(1)–P(1)–O(4)	108.2	O(2)–Mn(2)–O(7)	93.8
O(2)–P(1)–O(3)	109.0	O(2)–Mn(2)–O(14)	165.4
O(2)–P(1)–O(4)	109.4	O(2)–Mn(2)–O(9)	82.6
O(3)–P(1)–O(4)	110.0		
O(5)–P(2)–O(6)	109.4	O(2)′–Mn(2)–O(8)	167.1
O(5)–P(2)–O(7)	107.9	O(2)′–Mn(2)–O(7)	103.9
O(5)–P(2)–O(8)	110.5	O(2)′–Mn(2)–O(14)	87.8
O(6)–P(2)–O(7)	110.6	O(2)′–Mn(2)–O(9)	89.8
O(6)–P(2)–O(8)	109.4		
O(7)–P(2)–O(8)	108.9	O(8)–Mn(2)–O(7)	88.6
		O(8)–Mn(2)–O(14)	87.9
		O(8)–Mn(2)–O(9)	78.0
O(5)–Mn(1)–O(8)	112.6		
O(5)–Mn(1)–O(4)	90.8	O(7)–Mn(2)–O(14)	96.6
O(5)–Mn(1)–O(4)′	89.4	O(7)–Mn(2)–O(9)	164.9
O(5)–Mn(1)–O(14)	98.4	O(14)–Mn(2)–O(9)	89.9
O(5)–Mn(1)–O(9)	168.8		
O(8)–Mn(1)–O(4)	97.2	O(1)–Mn(3)–O(6)	97.6
O(8)–Mn(1)–O(4)′	157.8	O(1)–Mn(3)–O(12)	93.4
O(8)–Mn(1)–O(14)	85.5	O(1)–Mn(3)–O(11)	160.5
O(8)–Mn(1)–O(9)	76.9	O(1)–Mn(3)–O(7)	105.5
		O(1)–Mn(3)–O(10)	86.0
O(4)–Mn(1)–O(4)′	84.5		
O(4)–Mn(1)–O(14)	168.6	O(6)–Mn(3)–O(12)	167.7
O(4)–Mn(1)–O(9)	81.7	O(6)–Mn(3)–O(11)	86.4
O(4)′–Mn(1)–O(14)	88.8	O(6)–Mn(3)–O(7)	89.0
O(4)′–Mn(1)–O(9)	81.6	O(6)–Mn(3)–O(10)	87.5
O(14)–Mn(1)–O(9)	88.2		
		O(12)–Mn(3)–O(11)	81.4
		O(12)–Mn(3)–O(7)	93.3
		O(12)–Mn(3)–O(10)	87.9
		O(11)–Mn(3)–O(7)	93.6
		O(11)–Mn(3)–O(10)	75.1
		O(7)–Mn(3)–O(10)	168.3

Note: Range of estimated standard deviations is 0.2–0.5°.

Table 5. Bond-valence sums (v.u.) in switzerite

	P(1)	P(2)	Mn(1)	Mn(2)	Mn(3)	···H–O	–H···O	–H	Sum
O(1)	1.32				0.41	0.18 0.19			2.10
O(2)	1.26			0.36 0.37					1.99
O(3)	1.24					0.23 0.25 0.22			1.94
O(4)	1.18		0.35 0.37						1.90
O(5)		1.30	0.41			0.15 0.21			2.07
O(6)		1.27			0.40	0.27			1.94
O(7)		1.22		0.34	0.30				1.86
O(8)		1.21	0.39	0.35					1.95
O(9)			0.19	0.24			0.79 0.81		2.03
O(10)					0.26		0.81	1.00	2.07
O(11)					0.31	0.15	0.85 0.73		2.04
O(12)					0.32		0.80 0.83		1.95
O(13)						0.15 0.20	0.82 0.85		2.02
O(14)			0.29	0.33			0.75 0.77		2.14
O(15)						0.19 0.17	0.83 0.85		2.04

Mn octahedra with composition $[Mn_6O_{14}(H_2O)_{10}]_2$ is formed. Phosphate groups knit the slabs together internally to form a complex neutral layer with composition $Mn_6(H_2O)_{10}(PO_4)_4$. Two of these neutral layers are present in the unit cell; between them are the free water molecules, $O_w(13)$ and $O_w(15)$, of which there are eight per unit cell. Adjacent layers are linked via a network of H bonds, both directly by H bonds between water molecules in adjacent layers and indirectly through H-bonded interlayer molecules $O_w(13)$ and $O_w(15)$. The spatial distribution of chemical bonds in the structure is strongly anisotropic; i.e., strong cation–oxygen bonds occur in the **a**-**b** plane, but in the **c**-direction only weak H bonds hold the structure together. This layered arrangement accounts for the perfect {001} cleavage of switzerite.

TRANSFORMATION OF SWITZERITE INTO METASWITZERITE

Structurally, switzerite and metaswitzerite are closely related; in both structures, complex sheets of Mn octahedra and P tetrahedra with about the same configuration are present. However, in switzerite the structure is layered, whereas in metaswitzerite the condensation of these layers yields a three-dimensional framework.

The transformation of switzerite into metaswitzerite occurs irreversibly in the solid state according to the reaction

$$2Mn_3(PO_4)_2 \cdot 7H_2O \rightarrow Mn_6(PO_4)_4 \cdot 8H_2O + 6H_2O.$$

The atomic rearrangement and consequent dehydration during the tranformation can be understood by comparison of the two structures. Inspection of the structures of switzerite (Fig. 1) and metaswitzerite (Fig. 2) shows that water molecules lying in a layer parallel to (001) at about one-half *c* in switzerite are involved in the transformation. These include $O_w(10)$ and $O_w(11)$, which are coordinated to Mn(3), and the free water molecules $O_w(13)$ and $O_w(15)$. In the transformation, the neutral polyhedral layers condense along **c**. All of the $O_w(15)$ and one half of the $O_w(13)$ molecules are expelled; the other $O_w(13)$ become $O_w(24)$ in the metaswitzerite structure. The Mn(3) atoms in switzerite become Mn(5) and Mn(6) in metaswitzerite. Atom Mn(3) is transformed into Mn(5) by loss of $O_w(10)$ and formation of a bond to O(3), which is also coordinated to a P atom in the adjacent sheet. Only slight deformation of the shape of the coordination polyhedron around Mn(3) is involved in this transformation. The other half of the Mn(3) atoms in switzerite are transformed into Mn(6) in metaswitzerite by loss of $O_w(10)$ and formation of a bond with O(1), which is also bonded to P and Mn in the adjacent sheet. Atom $O_w(11)$ is also lost, and the other bond angles shift, changing the coordination of Mn(6) to trigonal dipyramidal.

Only minor changes occur inside the neutral layers. The [100] and [010] directions, lying in the plane of the layers, maintain the same periodicity in the two minerals, but the separation between two adjacent layers changes from

11.8 Å, which is *c* of switzerite, to 8.6 Å, one-half *c* of metaswitzerite. The conservation of the characteristic two-dimensional structural units of switzerite during its conversion to metaswitzerite minimizes the number of strong chemical bonds to be broken and the amount of movement during the transformation. The transformation reaction of switzerite into metaswitzerite can therefore be considered a typical topotactic reaction according to the definitions of Oswald and Gunther (1979).

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