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The High Pressure Form of Mn_2GeO_4, a Member of the Olivine Group

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Mn_2GeO_4 (olivine type) was compressed at 120 kilobars and 900°C into a new orthorhombic form, space group *Pbam*, with the lattice parameters $a=5{\cdot}257$, $b=9{\cdot}270$, $c=2{\cdot}951$ Å. Its structure was deduced from X-ray powder patterns, and the new phase is isomorphous with Sr_2PbO_4 and Ca_2SnO_4. Ge is octahedral, and Mn^{2+} has six oxygen atoms at the corners of a trigonal prism, the average Ge–O and Mn–O distances being 1·95 and 2·19 Å respectively. The density is 17·3% greater than that of the olivine form. The geochemical significance is evaluated.

The increase of seismic velocity with depth in the earth's mantle is believed to be due to the presence of denser modifications of common minerals. The transition of olivines into spinels, leading to density increases of the order of 10%, has been demonstrated with high pressure experiments in the laboratory by a number of minerals and compounds with the olivine structure, Fe_2SiO_4, Ni_2SiO_4, Co_2SiO_4, $(Mg_{0{\cdot}8}Fe_{0{\cdot}2})SiO_4$ and Mg_2GeO_4 (Ringwood, 1966; Ringwood & Major, 1966). This phase change results from the alteration of the oxygen packing from hexagonal to cubic, but the coordination of the metals is unchanged, silicon (or germanium) remaining tetrahedral and the divalent metal octahedral. Phases much denser than spinels can be expected when the coordination number of the tetravalent ion is increased to six, and we have been examining a number of compounds with the olivine structure in order to determine what their high pressure forms might be.

Mn_2GeO_4, with an orthorhombic unit cell $a=10{\cdot}70$, $b=6{\cdot}26$, $c=5{\cdot}04$ Å, density 4·85 g.cm^{-3} and space group *Pnma* belongs to the olivine group (Tarte, 1965). Ringwood & Seabrook (1963) subjected it to a pressure near 60 kilobars (kb) at 700°C, and noted the disproportionation into $MnGeO_3$ (ilmenite type) plus an additional phase. This transformation evidently had a restricted pressure–temperature field, for in the present study we found that above 90 kb and at 900°C Mn_2GeO_4 was altered to a finely-divided birefringent single phase with straight extinction and a mean refractive index of 2·04. The lower limiting transition pressure has not been established but probably exceeds 60 kb.

At first sight its X-ray powder diffraction pattern (Table 2), obtained with Fe $K\alpha$ radiation in a Debye–Scherrer camera 11·4 cm in diameter appeared to be derived from a spinel with the symmetry lower than cubic, but a system of indexing based upon the small unit cell given in Table 1 completely accounted for all of the observed reflexions. The dimensions were obtained by a least-squares fit. The calculated density, 5·69 g.cm^{-3} represents an increase of 17·3%.

Table 1. *Crystallographic data for high-pressure* Mn_2GeO_4

Symmetry: Orthorhombic
Unit-cell dimensions: $a=5{\cdot}257$, $b=9{\cdot}270$, $c=2{\cdot}951$ Å (all $\pm 0{\cdot}005$ Å)
$Z=2$
$D_x=5{\cdot}69$ g.cm^{-3}
Systematically absent reflexions: $h00$, $h\neq 2n$, $0kl$, $k\neq 2n$
Space group: *Pbam* (*Pba2**)

Atomic positions:	x	y	z	B
Ge in 2(a)	0	0	0	0·7(5) Å^2
Mn in 4(h)	0·069(6)	0·318(4)	½	1·9(6)
O(1) in 4(h)	0·245(22)	0·041(9)	½	−0·5(2·6)
O(2) in 4(g)	0·364(18)	0·314(14)	0	0·9(2·6)

* The non-centred alternative space group was not considered.

The Fe film was supplemented with a pack of three films simultaneously exposed to Mo $K\alpha$ radiation in the powder camera, and intensities measured visually with a standard scale were reduced to structure factors, except for the lines arising from different reflexions in coincidence. The systematically absent reflexions (Ta-

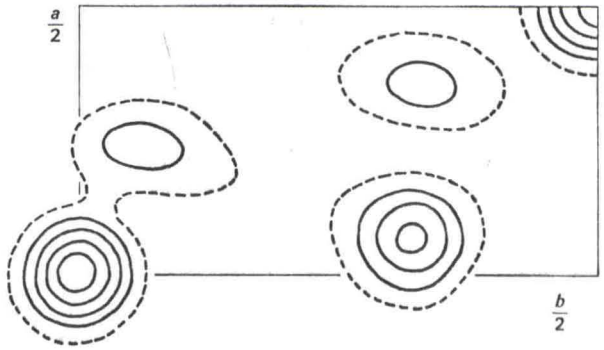

Fig. 1. Electron density projection $\varrho(x,y)$. Contours drawn at equal and arbitrary intervals.

Table 2. *X-ray powder diffraction pattern*

h	*k*	*l*	$\sin^2\theta$ (obs.)	$\sin^2\theta$ (calc.)	*I* (obs.)	*I* (calc.)
1	1	0	0·0450	0·0449	134	72
1	2	0	0.0778	0.0776	28	26
0	0	1	0.1079	0·1077	7	7
1	3	0	0·1322	0·1322	248	208
2	0	0	0·1359	0·1358	56	50
2	1	0	0·1469	0·1467	10	16
0	2	1	0·1526	0·1514	248	65
1	1	1		0·1526		227
0	4	0	0·1748	0·1747	28	17
1	4	0	0·2091	0·2086	49	41
1	3	1	0·2418	0·2399	7	8
2	0	1	0·2439	0·2436	7	4
2	1	1	0·2546	0·2544	56	64
0	4	1	0·2833	0·2825	17	14
2	2	1	0·2876	0·2871	113	115
2	4	0	0·3108	0·3103	7	5
1	4	1	0·3165	0·3163	14	9
3	1	0		0·3164		6
3	2	0	0·3497	0·3491	35	17
0	6	0	0·3932	0·3931	42	24
3	3	0	0·4038	0·4036	42	20
1	5	1	0·4146	0·4146	63	75
3	1	1	0·4239	0·4242	14	17
0	0	2	0·4313	0·4310	21	33
3	2	1	0·4575	0·4568	14	12
1	1	2	0·4777	0·4758	7	5
3	4	0	0·4798	0·4800	7	6
3	3	1	0·5119	0·5114	14	11
2	6	0	0·5286	0·5286	21	14
4	0	0	0·5421	0·5432	4	2
4	1	0	0·5528	0·5541	4	6
1	3	2	0·5633	0·5631	28	35
2	0	2	0·5652	0·5668	14	9
1	7	0		0·5688		6
4	2	0	0·5858	0·5867	21	14
3	4	1		0·5877		3
0	4	2	0·6051	0·6057	7	5
1	4	2	0·6392	0·6395	12	10
4	1	1	0·6620	0·6618	4	8
1	7	1	0·6752	0·6766	7	6
3	5	1	0·6854	0·6859	7	10
4	2	1	0·6975	0·6945	7	6
4	4	0	0·7175	0·7176	7	7
2	7	1	0·7775	0·7783	3	12
3	6	1	0·8057	0·8060	3	7
0	8	1		0·8066		20
0	6	2	0·8222	0·8241	28	25
3	3	2	0·8345	0·8346	17	25
5	1	0	0·8580	0·8596	14	10
1	9	0	0·9186	0·9182	17	18

ble 1) suggested the space group alternatives *Pbam* or *Pba*2, and two formula units Mn_2GeO_4 were appropriate for the unit cell. Ge was assigned to the point position 2(*a*) of *Pbam*, and the strongest lines 060, 130 and 111 could be due to reinforcement from Mn in 4(*h*), $x,y,\frac{1}{2}$ with $x\simeq 0$ and $y\simeq\frac{1}{3}$. An electron density projection $\varrho(x,y)$ calculated from 22 *hk*0 terms confirmed these positions, and contained two smaller peaks arising from the two oxygen atoms in the asymmetric unit (Fig. 1). One of these was placed in 4(*g*), the other in 4(*h*), and all reflexion data free from coincidences were refined by successive least-squares cycles to the final set of parameters in Table 1. A discrepancy index $R_{[F]}$ of 16·3% for 31 non-coincident reflexions and an overall value R_{I_0} of 24% were obtained for the complete diffraction pattern (Table 2). Bond lengths and standard deviations are given in Table 3.

Table 3. *Interatomic distances*

Ge	–O(1)	4 × 2·00(8)	Å
	–O(2^{I})	2 × 1·86(9)	
O(1)	–O(2^{I})	8 × 2·83(13)	
	–O(1^{I})	2 × 2·70(12)	
	–O(1^{II})	2 × 2·95	*
Mn	–O(1)	1 × 2·14(9)	
	–O(1^{I})	1 × 2·29(9)	
	–O(2)	2 × 2·20(10)	
	–O(2^{I})	2 × 2·14(10)	
O(1)	–O(2)	2 × 3·00(13)	
	–O(1^{I})	1 × 2·78(12)	
	–O(1^{II})	2 × 2·95	*
O(2^{I})	–O(2)	2 × 2·89(13)	
	–O(1^{I})	2 × 2·63(13)	

* *c*-axis length.

Description

The structure is illustrated by Fig. 2. It is the same as that reported earlier for Sr_2PbO_4, Ca_2PbO_4 (Trömel, 1965), Ca_2SnO_4 and Cd_2SnO_4 (Trömel, 1967) whilst Na_2CuF_4 (Babel, 1965) is also closely related to it.

In the present instance Mn has six oxygen ligands situated at the corners of a somewhat distorted trigonal prism with the average Mn–O distance of 2·19 Å. A seventh oxygen at a distance of 2·73 Å through the centre of one prism is probably unbonded. While this is an unusual coordination for Mn^{2+}, it has also been found in Mn_5O_8 (Oswald, Feitknecht & Wampetich, 1965; Oswald & Wampetich, 1967). In Mn_2GeO_4 the Mn polyhedra join by common edges, forming a three-dimensional network in which there are octahedral positions occupied by Ge, with bonds to oxygen averaging 1·95 Å.

This trigonal prismatic coordination, which may be supplemented by one, two or three additional oxygen atoms bonded through one or more of the three prism faces, is more commonly found for Na^+ and Ca^{2+}, which play similar roles in mixed oxide systems. An example of this is provided by the calcium ferrite structure adopted by a number of oxides of Ca with the trivalent metals, by the sodium-containing phases $NaA^{3+}B^{4+}O_4$ (Reid, Wadsley & Sienko, 1968) including high-pressure $NaAlGeO_4$ (Reid, Wadsley & Ringwood, 1967*a*), as well as by a number of mixed oxides with divalent metals other than Ca, for instance Mg in $MgSc_2O_4$ (Müller-Buschbaum, 1966). The bond distances between Na, Ca, Mn^{2+} or Mg and oxygen are much the same as for octahedral coordination.

Geochemical significance

The geochemical significance may well be encompassed by Fig. 3, containing graphs of the two *average* metal–oxygen distances for each phase plotted against unit-cell volume, and summarizing the stereochemical rela-

tions between all known compounds isomorphous with high-pressure Mn_2GeO_4. An oxy-compound with this structure will presumably be stable only when the two different metal–oxygen bond lengths intercept the two curves *at the same unit cell volume*, with due regard to uncertainties. The average trigonal pyramid distances for Fe–O, Co–O, Mg–O and Ni–O can be assumed to be the same as the octahedral in the corresponding monoxides with the NaCl structure, respectively 2·14, 2·13, 2·10 and 2·08 Å, while the average Si–O octahedral bond length will be close to 1·77 Å as in stishovite (Chao, Fahey, Littler & Milton, 1962), all ±0·05 Å. The likelihood of natural siliceous olivines forming the Mn_2GeO_4 structure under pressure is therefore expected to increase in the order Fe_2SiO_4–Co_2SiO_4–Mg_2SiO_4–Ni_2SiO_4, corresponding to decreasing average divalent metal–oxygen distances.

Although a number of olivine compositions containing Ge or Si in the tetrahedral site can be compressed to spinels in the laboratory with a characteristic density increase of 10%, the formation of high pressure Mn_2GeO_4 shows that at least one structure, denser than spinel by 7%, can be obtained when Ge or Si goes into an octahedral site. The formation of other dense structures in which the coordination number of silicon is six or even more may be sequential or alternative to spinel formation.

The occurrence of these additional AB_2O_4 phases could be predicted from graphs similar to Fig. 3 constructed for other isostructural families. From Fig. 3 one can already exclude certain combinations of elements from the high pressure Mn_2GeO_4 structure type. The Ca–O and Ge–O intercepts on the two lines are very widely separated, and it is significant that Ca_2GeO_4 (olivine type) transforms at high pressures and temperatures to the K_2NiF_4 type (Reid, Wadsley & Ringwood, 1967*b*).

It is clearly fallacious to assume a simple mineralogy for the mantle. A considerable number of different structures with the stoichiometry A_2BO_4 are known where the coordination of both metals *A* and *B* is greater than four, and transformations involving them will most likely occur successively at different depths. Whatever phase forms will be governed by the effects *in situ* of high pressures and temperatures on the internuclear distances.

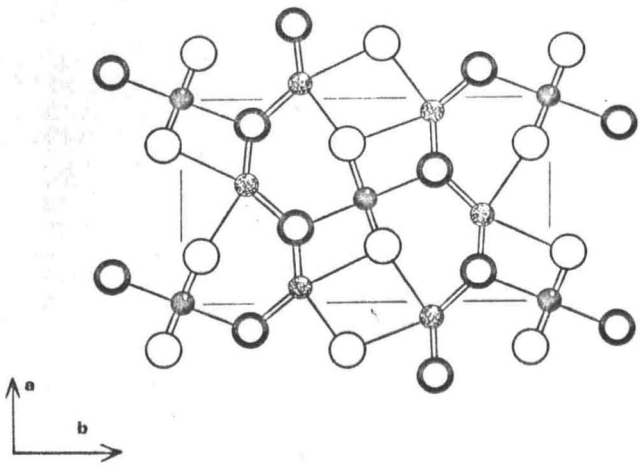

Fig. 2. The structure of Mn_2GeO_4 in projection on to (001). Small black circles Ge; stippled circles Mn; largest circles oxygen appearing at two levels.

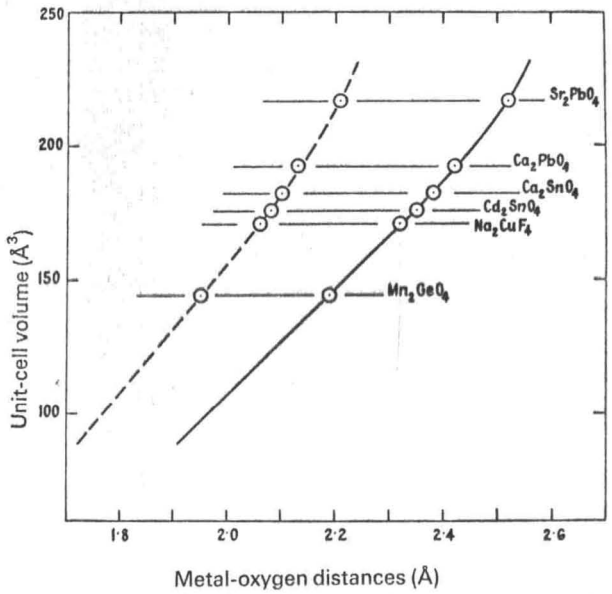

Fig. 3. Volume of unit cell *versus* the average octahedral (dashed line) and trigonal prismatic (full line) bond distances in Mn_2GeO_4 and isomorphous compounds. Verticals drawn from 1·77 Å (average Si–O bond length) and 2·10 Å (average Mg–O length), ±0·05 Å, should intersect the dashed and full lines at the same unit-cell volume if Mg_2SiO_4 is to form the Mn_2GeO_4 structure.

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