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The Crystal Chemistry of Dense M_3O_4 Polymorphs: High Pressure Ca_2GeO_4 of K_2NiF_4 Structure Type

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Ca_2GeO_4 of olivine form has been found to transform at 900°C and 110 kbars to K_2NiF_4 type, with $a = 3.70$, $c = 11.88$ Å, and with a corresponding density increase of 25%. The geochemical significance of this transformation is discussed, and a comparison of the molar volumes of olivines, spinels and other structure type with the volumes of their isochemical mixtures of simple oxides or fluorides is used to obtain relative molar volumes for a large number of dense M_3O_4 structure types.

Introduction

The crystal chemistry of the dense M_3O_4 structure types is of great importance to chemical theories of the earth's mantle, which is believed (*1*) to contain the high pressure forms of the olivine compositions Mg_2SiO_4–Fe_2SiO_4, together with significant amounts of CaO, MgO and Al_2O_3 in combination with one another and with SiO_2. Although transformations of A_2SiO_4 compounds to spinel form (2), (3), (4), and (5), and of $ASiO_3$ compounds to garnet form (*6*), can account in part for the sudden density increases which seismic data have shown to exist in the earth's mantle, the density of the lower mantle can only be attributed to compounds in which silicon is bonded to six rather than to four oxygen atoms. Although few such compounds have as yet been obtained experimentally, the behaviour of individual compounds containing the small 4+ ions Ge^{4+} or Mn^{4+} provide many useful analogies for high pressure silicate systems containing either four or six-coordinate silicon. Among numerous examples are rutile type GeO_2, β-MnO_2 (*7*) and the rutile form of SiO_2 (stishovite) (*8*), the hollandite isotypes $KAlGe_3O_8$ (*9*), $K_xMn_4O_8$ (*10*), (*11*) and high pressure $KAlSi_3O_8$ (*12*), and the transformations (*2*) of silicates of olivine type to the spinel form exhibited at zero pressure by the corresponding germanates. $CaGeO_3$ and $CaGeO_3$–$CaSiO_3$ solid solutions of wollastonite ($CaSiO_3$) type have been shown to transform to perovskite type at high temperature and pressure (*13*), while $CaMnO_3$ has the perovskite structure at zero pressure. In the present work we have examined the high pressure behaviour of the germanium olivine Ca_2GeO_4 (*14*), (*15*). The results, briefly reported elsewhere (*16*), are pertinent to the high pressure behaviour of Ca_2SiO_4, and the observed transformation of Ca_2GeO_4 demonstrates the K_2NiF_4 structure type as an olivine polymorph considerably more dense than spinel.

The insights obtained by examining germanate or manganate systems for analogues of the silicates can be greatly strengthened by considering the crystal chemistry of the entire structural class to which an individual dense germanate or manganate belongs. In addition to discussing the polymorphism of Ca_2GeO_4, we shall also present a more general discussion of the molar volumes of the denser M_3O_4 structure types, and provide a simple method of predicting the molar volumes of M_3O_4 polymorphs of given composition.

Experimental

Ca_2GeO_4 of olivine structure (*14*), (*15*) was prepared by heating a finely ground 2:1 molar mixture of $CaCO_3$ and GeO_3 at 1200°C followed by further grinding and heating at 1200°C for 20 h.

A small quantity of this compound was reacted for 3 to 5 min at 100–120 kbars and 900°C in a high pressure opposed anvil apparatus (*17*) and cooled to room temperature before release of pressure. The X-ray pattern of the product was obtained using CuKα radiation with a Debye-Scherrer camera of 114 mm diameter. Line spacings were measured with a travelling microscope, and film shrinkage corrections were made in all cases. Where appropriate, reflection intensities were obtained by visual comparison with a calibrated scale.

Results

The powder diffraction pattern of high pressure Ca_2GeO_4 was readily indexed in terms of a body-centred tetragonal unit cell with $a = 3.70$ Å, $c = 11.88$ Å, Table I. Final lattice parameters were obtained by a least squares fit of data corresponding to $2\theta > 60°$.

The unit cell dimensions suggested that Ca_2GeO_4 was isostructural with K_2NiF_4 (*18*), (*19*) and a comparison of the observed and calculated reflection intensities showed that this was indeed so, Table I. For this calculation atoms were placed in the positions:

$$0,0,0;\ \tfrac{1}{2},\tfrac{1}{2},\tfrac{1}{2}\ +$$

$$2\mathrm{Ge}\ \text{at}\ 0,0,0$$

$$4\mathrm{Ca}\ \text{at}\ \pm\, 0,0,z;\ z_{\mathrm{Ca}} = 0.35$$

$$4\mathrm{O}_1\ \text{at}\ \tfrac{1}{2},0,0;\ 0,\tfrac{1}{2},0$$

$$4\mathrm{O}_2\ \text{at}\ \pm\, 0,0,z;\ z_{\mathrm{O}} = 0.163$$

The fractional coordinates z were taken as similar to those for K_2NiF_4, but adjusted to allow the average octahedral Ge-O distance to remain at 1.88 Å as found in rutile type GeO_2 (*20*). Temperature factors B were fixed at 1 Å^2 for all atoms. A least-squares refinement of structure factors derived from 26 noncoincident reflections, Table I, gave $z_{\mathrm{Ca}} = 0.353 \pm .005$ and $z_{\mathrm{O}} = 0.162 \pm .015$, in good agreement with these assumptions. The corresponding R_{F_0} factor was 21.8%, while the R_{I_0} factor for the intensity data of Table I was 26%.

Discussion

The transformation of Ca_2GeO_4 from olivine to K_2NiF_4 type is accompanied by a density increase of 25%, as compared with the 10% increase typically produced by olivine-spinel transformations. The olivines A_2BO_4 contain the two A ions in six-coordinate positions, with the B ions in tetrahedral sites. In spinels the same coordination obtains, but the oxygen lattice is more closely organized. In K_2NiF_4 isotypes however, the A ions are nine-coordinated, and the B ions six-coordinated in octahedral sites, so that the packing density is greatly increased. The K_2NiF_4 structure is closely related to the cubic perovskite type. In effect, one slab of the cubic ABX_3 perovskite, comprising a layer of corner-shared octahedra and the *two* layers of A ions coplanar with the octahedral apices on either face of the slab, is fitted to a second slab with octahedral apices placed opposite to A ions, Fig. 1. This arrangement places the adjacent layers of A ions and their almost coplanar layers of oxygen atoms in a correspondence which is only a slight distortion of the rocksalt lattice, and the structure

TABLE I

DIFFRACTION DATA FOR HIGH PRESSURE Ca_2GeO_4[a]
$a_0 = 3.700 \pm 0.005$ Å, $c_0 = 11.88 \pm 0.01$ Å; CuK_α
$\lambda = 1.5418$ Å

hkl	$\mathrm{Sin}^2_{\mathrm{obsd}}$	$\mathrm{Sin}^2_{\mathrm{calc}}$	I_{obsd}	I^b_{calc}
002	0.0168	0.0169	47	69
101	0.0476	0.0477	16	27
103	0.0815	0.0813	~100	100
110	0.0868	0.0869	~90	78
105	0.1492	0.1487	14	17
006 114	0.1515	0.1516 0.1542	14	24 6
200	0.1737	0.1737	47	48
202	0.1909	0.1906	9	9
211	0.2209	0.2213	5	5
116	0.2387	0.2385	21	20
213	0.2554	0.2550	40	31
008	0.2688	0.2695	5	4
206 215	0.3251	0.3254 0.3224	28	27 8
220	0.3475	0.3473	16	11
118	0.3567	0.3564	5	4
222	0.3643	0.3641	2	3
109	0.3849	0.3846	9	4
303	0.4287	0.4288	14	6
310	0.4341	0.4342	14	9
208	0.4429	0.4433	7	6
226	0.4984	0.4989	16	9
1.0.11	0.5493	0.5530	6	4
219	0.5562	0.5582	6	5
316	0.5851	0.5858	7	8
323	0.6003	0.6022	9	7
228	0.6148	0.6168	3	4
325	0.6674	0.6696	9	3
400 1.1.12	0.6930	0.6949 0.6933	3	4 1
318	0.7009	0.7037	2	3
2.1.11	0.7239	0.7267	9	6
413	0.7759	0.7761	14	7

[a] K_2NiF_4-type.

[b] Calculated intensities for the additional 25 possible reflections up to hkl = (4, 1, 3) were each less than 2 on the present scale, corresponding to intensities below the weakest observed.

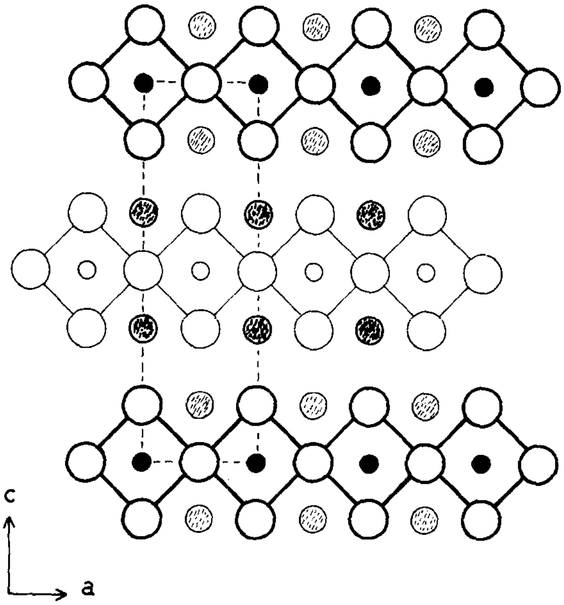

FIG. 1. The K_2NiF_4-type structure of Ca_2GeO_4, projected on the x–z plane. Heavily shaded atoms at $y = 0$, lightly shaded atoms at $y = \frac{1}{2}$. The GeO_6 octahedra are outlined, heavily for Ge at $y = 0$, lightly for Ge at $y = \frac{1}{2}$. The oxygen atoms above and below each Ge atom have been omitted. Small circles Ge, large circles O, stippled circles Ca. The unit cell is shown with dashed lines.

can be formally described as being made up of alternate layers of rocksalt AX and perovskite ABX_3.

Each A ion has one relatively short A–X bond directed along the c axis, four equal, approximately equatorial, A–X bonds of length close to $a/\sqrt{2}$, and four bonds of similar length oblique to the c axis. The B ion has four equatorial bonds of length $a/2$, and two directed parallel to the c axis of length cz_0. In Ca_2GeO_4, the four equatorial Ge–O distances are fixed at 1.85 Å while the other two are 1.94 Å. The average nine-coordinate Ca–O distance is 2.56 Å.

As all atoms are situated on fourfold symmetry axes, the relationships of bond lengths to unit cell dimensions are well defined, and the possible combinations of A and B ions is limited by ionic radii ratios. From the viewpoint of touching spheres, the tolerance factor (*21*), (*22*) for the K_2NiF_4 structure types, $t = (r_A + r_0)/\sqrt{2}.(r_B + r_0)$, is ideally unity. Actual values of t lie mainly in the range 0.90–0.96, although a value of 0.855 has been observed for La_2NiO_4 (*22*). The tolerance factors for a number of compounds of geochemical interest or which can be considered as geochemical analogues are as follows:

Ca_2SiO_4, 0.961; Ca_2GeO_4, 0.904;
Ca_2MnO_4, 0.901; Mn_2SiO_4, 0.888;
Fe_2SiO_4, 0.864; Mg_2SiO_4, 0.841;
and Mn_2GeO_4, 0.835.

The present work has shown that Ca_2GeO_4, $t = 0.904$, adopts the K_2NiF_4 structure at high pressures, while Ca_2MnO_4, $t = 0.901$, is of K_2NiF_4-type at zero pressure (*21*). However, Mn_2GeO_4, $t = 0.835$, transforms at high pressure from olivine type to an entirely different dense structure (*23*), that of strontium plumbate (*24*). In this form, which is 18% more dense than the corresponding olivine, the Mn^{2+} ions are in prismatic six-coordination and the Ge^{4+} ion is in octahedral six-coordination. It appears on ionic radii criteria that Ca_2SiO_4, $t = 0.961$, will ultimately transform to K_2NiF_4 type at high pressures. However, Mg_2SiO_4 in a form more dense than the distorted spinel structure (2), (3), (4), and (5) appears more likely to be of strontium plumbate type, since its tolerance factor is very close to that of Mn_2GeO_4.

Many K_2NiF_4 and all Sr_2PbO_4 isotypes are comprised of rocksalt (AX) plus rutile (BX_2) constituents, and a plot of the formula volumes of the former versus those of the latter, Fig. 2, shows the occurrence fields of these two dense structure types. This presentation is equivalent to plotting r_A vs r_B (*25*), (*26*), and (*27*), or $r_A{}^3$ vs $r_B{}^3$, since the formula volumes in Å^3, of molar volumes in cm^3, of simple oxides are smooth functions of ionic radii (*28*) or of metal–oxygen bond lengths (*29*), but it also demonstrates the ranges of constituent oxide or fluoride volumes which the K_2NiF_4 and Sr_2PbO_4 structures can accommodate. It is clear that high pressure Ca_2SiO_4 will lie well within the K_2NiF_4 field, while Mg_2SiO_4, when finally transformed beyond its high pressure spinel-like form (2), (3), (4), and (5) will much more probably be of Sr_2PbO_4 type.

The determination of the relative volumes of different structural types, and of the actual volumes of particular compositions in presumed structural forms, is also of great importance. Such volumes, or the corresponding densities, are for example required for comparison with shock wave data, and with estimated densities of the earth's mantle obtained by seismic means. The unit cell volume of a given structure is directly related to the sum of the volumes of the coordination polyhedra comprising the structure, and such polyhedral volumes

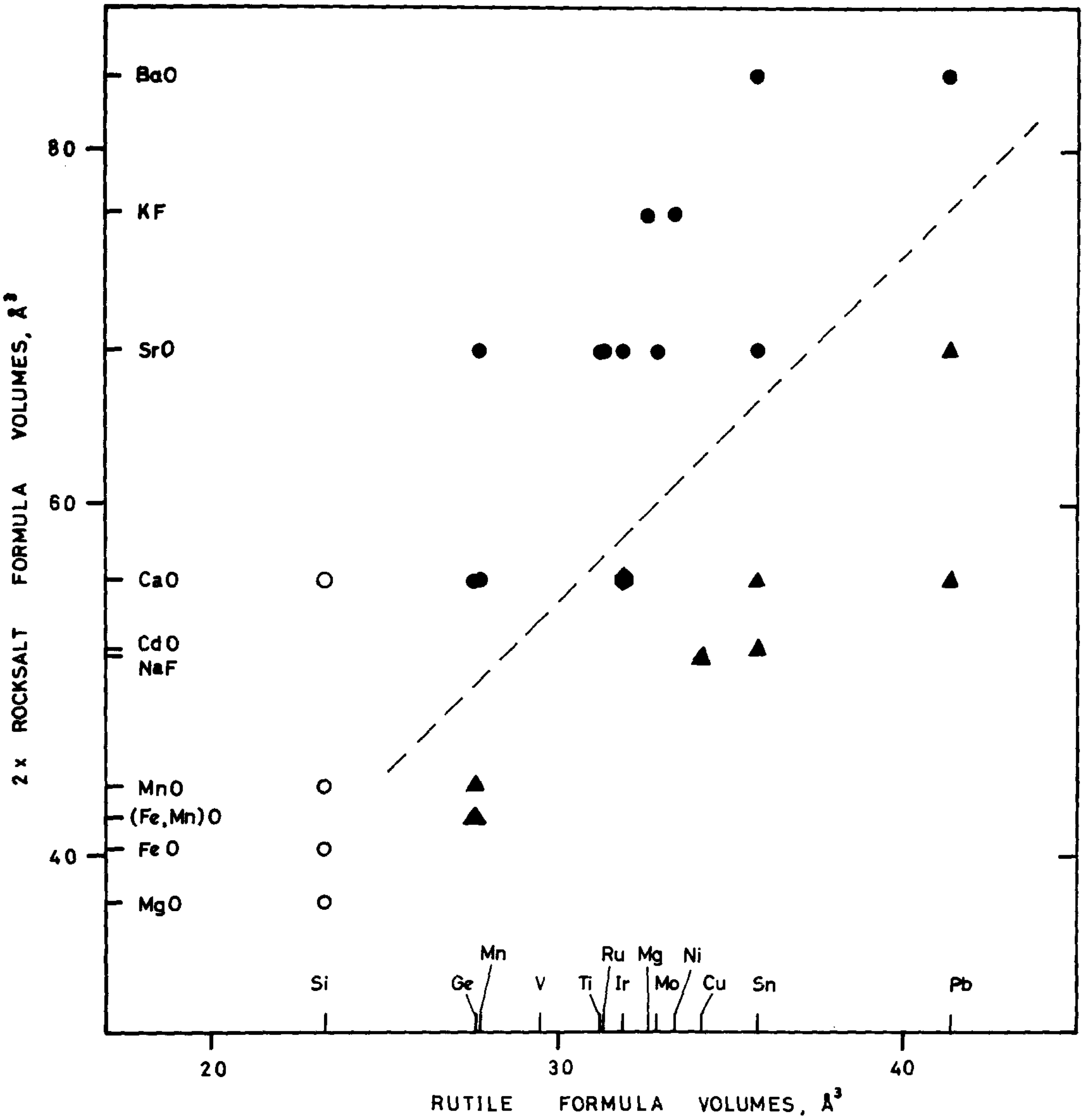

FIG. 2. Occurrence fields for dense A_2BX_4 polymorphs as a function of the formula volumes of their rocksalt and rutile-type constituents. Black circles K_2NiF_4 type, triangles Sr_2PbO_4 type, hexagon Ca_2IrO_4 type. Open circles show the positions which A_2SiO_4 polymorphs would occupy. On the rutile axis, "Mg," "Ni," and "Cu" refer to the difluorides.

are smooth functions of the cubes of the average metal–oxygen bond lengths (*29*) or metal ion radii (*28*). For rutile types BX_2 for example, the plot of r_B^3 versus formula volume is a straight line (*30*); for AX rocksalt types, the plot of bond length cubed versus formula volume is necessarily linear. The volumes of compounds formed from rocksalt plus rutile type should be close to proportional to $ar_A^3 + br_B^3$, where a and b are constants, and in fact a similar relationship should hold for any A and B, as for example in La_2NiO_4. Rather than extract these parameters, we have chosen the much simpler alternative of comparing the volume per formula unit, V, with the sum of the formula volumes of the constituent oxides, V_0, Fig. 3 and Table II. The volumes for rutile types have been collected by Rogers et al. (*30*); those for rocksalt types were taken from the compilation of Wyckoff (*31*). Volumes for K_2NiF_4 and Sr_2PbO_4 structure types have previously been listed (*16*), and those for olivines and spinels were largely obtained from the unit cell parameters listed by Wyckoff (*19*).

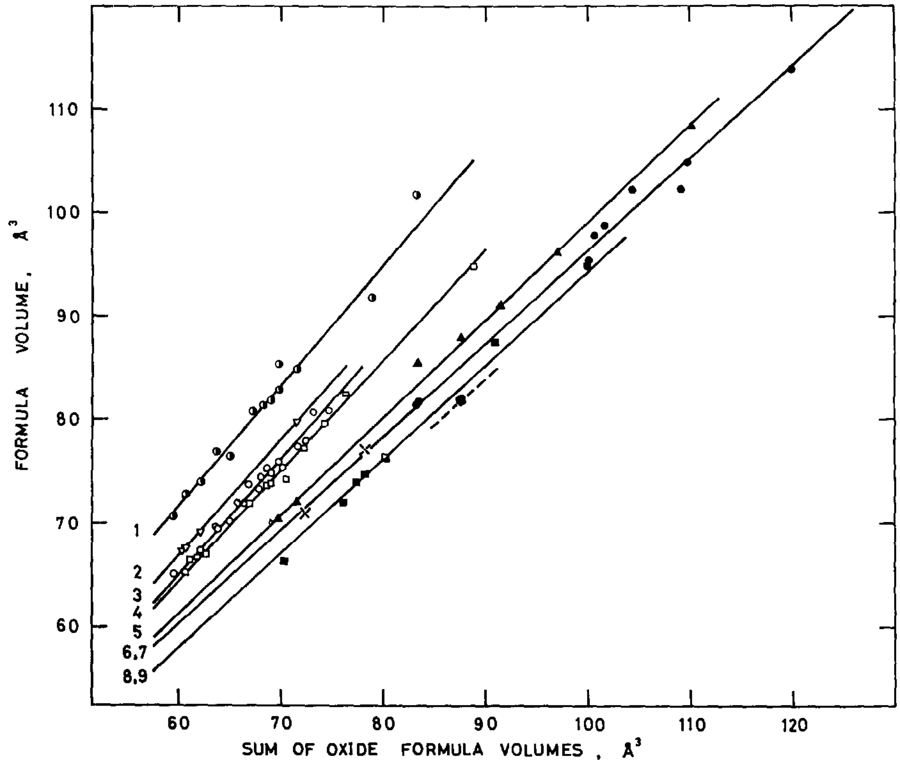

FIG. 3. The formula volumes of A_2BO_4 and AB_2O_4 polymorphs versus the volumes of their isochemical mixtures of 2(AX) rocksalt plus BX_2 (rutile) or AO rocksalt plus B_2O_3 (corundum). The structure types shown are: 1. Olivine (19), vertically shaded circles; 2. Orthorhombic variant of spinel (3, 4, 5), inverted triangles; 3. A_2BO_4 spinel (19), open circles; 4. AB_2O_4 spinel (19), open squares; 5. Sr_2PbO_4 (16), shaded triangles; 6. $CaMn_2O_4$ (47), crosses; 7. K_2NiF_4 (16, 19), black circles; 8. $CaFe_2O_4$ (26, 47), shaded squares; 9. Ca_2IrO_4 (41), shaded hexagon.

For each of the A_2BO_4 structure types olivine, spinel, strontium plumbate and K_2NiF_4-type, a close scatter of V/V_0 values about a mean value was obtained, Table II, regardless of whether the individual isotypes were high or low pressure phases. Thus in all known cases of olivine-spinel polymorphism, the formula volumes for the two polymorphs fall as expected on the lines defining the structural classes. Similarly the formula volumes of Ca_2GeO_4 of olivine and K_2NiF_4-types, and of Mn_2GeO_4 of olivine and strontium plumbate types fall on the lines appropriate to their isotypes. In a study to be reported elsewhere, we have, at a series of pressures, converted $FeMnGeO_4$ from olivine to each of spinel and strontium plumbate forms, again with three formula volumes closely in agreement with the values appropriate to their structure types, Fig. 3.

Relative volumes for a number of structure types are given in Table III. Since the same V/V_0 values apply for both high and low pressure isotypes of a particular structural class, Table II, we can use these values, or the plots shown in Fig. 3, to predict with considerable confidence the formula volume of any A_2BO_4 composition in any of the appropriate structures.

In transformations involving increases in the coordination numbers of the metal ions, the anion coordination numbers (*32*) must necessarily also increase. Since in any structure the total number of bonds from metal to oxygen atoms must be equal to the number of bonds from oxygen to metal atoms, the sum of the products (number of metal atoms of given coordination number) × (coordination number) must be equal to the sum of the products (number of oxygen atoms of given coordination number) × (coordination number), as is seen to be the case, Table III. This requirement leads, in phases as dense as or denser than the corresponding mixtures of simple oxides, to oxygen coordination numbers as high as 5 and 6.

It is interesting to note that the three zero-

TABLE II

DENSE M_3O_4 COMPOUNDS[a], FORMULA VOLUMES, Å³

Compound	V,Å³	V/V_0[b]
1. Olivine type		
Ni_2SiO_4 (60)	70.58	1.186
Mg_2SiO_4 (61)	72.68	1.199
Co_2SiO_4 (4)	73.96	1.191
Mg_2GeO_4 (35)	76.34	1.175
Fe_2SiO_4 (61)	76.81	1.206
Mn_2SiO_4 (19)	80.70	1.201
$MgMnSeO_4$ (62)	81.29	1.191
$CoMnGeO_4$ (62)	81.72	1.185
$FeMnGeO_4$ (62)	82.76	1.186
Mn_2GeO_4 (19)	84.84	1.186
$CaMgSiO_4$ (19)	85.27	1.222
γ-Ca_2SiO_4 (19)	96.75	1.226
Ca_2GeO_4 (19)	102.1	1.226
2. Spinel (II) type[c]		
*$(Mg_{0.85}Ni_{0.15})_2SiO_4$ (5)	67.21	1.112
*Mg_2SiO_4 (2, 4)	67.41	1.112
*Co_2SiO_4 (4)	69.08	1.112
*Mn_2GeO_4 (3)	79.72	1.115
3. A_2BO_4 Spinel		
*Ni_2SiO_4 (63)	65.04	1.093
*Co_2SiO_4 (III) (4, 63)	67.37	1.085
Ni_2GeO_4 (19, 64)	69.45	1.088
*Fe_2SiO_4 (61)	69.78	1.096
Mg_2GeO_4 (35)	70.09	1.079
Li_2NiF_4 (19)	71.81	1.092
Co_2GeO_4 (19, 64)	71.94	1.083
*$NiMnGeO_4$ (62)	73.03	1.079
Mg_2VO_4 (19)	73.71	1.103
Fe_2GeO_4 (19)	74.38	1.094
*$CoMnGeO_4$ (62)	74.78	1.084
Co_2TiO_4 (19)	75.13	1.073
Mg_2TiO_4 (19)	75.15	1.096
*$FeMnGeO_4$ (62)	75.90	1.088
Fe_2TiO_4 (19)	77.74	1.085
Mg_2SnO_4 (19)	80.59	1.103
Co_2SnO_4 (19)	80.73	1.082
4. AB_2O_4 Spinel (19)		
$NiAl_2O_4$	65.16	1.075
$MgAl_2O_4$	66.48	1.087
$CoAl_2O_4$	66.60	1.076
$FeAl_2O_4$	66.90	1.067
$MgCr_2O_4$	71.79	1.072
$FeCr_2O_4$	73.46	1.073
$MgFe_2O_4$	73.64	1.068
Fe_3O_4	73.98	1.049
$MnCr_2O_4$	75.04	1.068
$MnFe_2O_4$	77.06	1.067
Mn_3O_4[d]	78.00	1.076
$CdCr_2O_4$	79.39	1.070
$CdFe_2O_4$	82.45	1.082
$CdIn_2O_4$	94.66	1.064
5. Sr_2PbO_4 type (24)		
*$FeMnGeO_4$ (62)	70.21	1.006
*Mn_2GeO_4 (23)	71.90	1.005
*Mn_2SnO_4 (67)	80.63	1.012
Na_2CuF_4[e] (34)	85.28	1.022
Cd_2SnO_4 (65)	87.85	1.004
Ca_2SnO_4 (65)	90.95	0.995
Ca_2PbO_4 (24)	96.00	0.990
Sr_2PbO_4 (24)	108.30	0.984
6. $CaMn_2O_4$ type (46)		
*Mn_3O_4 (47)	70.93	0.979
$CaMn_2O_4$ (46)	77.00	0.984
7. K_2NiF_4 type (18, 19)		
*Ca_2GeO_4	81.30	0.976
Ca_2MnO_4	81.35	0.975
Sr_2TiO_4	94.85	0.949
Sr_2RuO_4	95.38	0.951
Sr_2IrO_4	97.74	0.972
Sr_2MoO_4	98.64	0.970
Sr_2SnO_4	102.10	0.978
K_2NiF_4	104.92	0.956
K_2MgF_4	107.20	0.982
Ba_2SnO_4	113.95	0.950
Ba_2PbO_4	123.0	0.980
8. $CaFe_2O_4$ type (42, 43, 44)		
*$CaAl_2O_4$ (47)	66.03	0.939
β-$CaCr_2O_4$ (43)	71.90	0.944
CaV_2O_4 (43)	73.80	0.953
$CaFe_2O_4$ (38, 66)	74.55	0.954
$CaIn_2O_4$ (66)	87.45	0.962
9. $CaTi_2O_4$ (45)	76.08	0.951
10. Ca_2IrO_4 (41)	81.90	0.935

[a] References are to lattice parameter sources, or to the compilation of Wyckoff (*19*). Compounds preceded by an asterisk are high pressure phases.

[b] V is the volume per formula unit, V_0 the sum of the formula volumes of the constituent oxides of rocksalt, rutile or corundum type. Rocksalt volumes (*31*); rutile volumes (*30*), (*31*); corundum volumes (*19*), (*29*). The volume of hypothetical corundum-type Mn_2O_3 was calculated from the data of (*29*).

[c] Orthorhombic variant of spinel type. [d] Tetragonal distortion of spinel type. [e] Monoclinic distortion of Sr_2PbO_4 type.

TABLE III

RELATIVE VOLUMES OF A_2BO_4 AND AB_2O_4 POLYMORPHS

Structure Type	Example, with Coordination Numbers of Metals and Anions	V/V_0[a]	Relative Structural Volumes[b]
Olivine (19)	$^{(6)}\mathrm{Mg}_2{}^{(4)}\mathrm{Si}^{(4)}\mathrm{O}_4$	1.20	1.20
Spinel II (4, 5)	$^{(6)}\mathrm{Co}_4{}^{(4)}\mathrm{Si}_2{}^{(4)}\mathrm{O}_6{}^{(5)}\mathrm{O}_1{}^{(3)}\mathrm{O}_1{}^{c}$	1.11_5	1.11_5
Spinel A_2BO_4 (2, 19)	$^{(6)}\mathrm{Fe}_2{}^{(4)}\mathrm{Si}^{(4)}\mathrm{O}_4{}^{c}$	1.09	1.09
Spinel AB_2O_4 (19)	$^{(4)}\mathrm{Mg}^{(6)}\mathrm{Al}_2{}^{(4)}\mathrm{O}_4$	1.07_5	1.09
$2AO + BO_2$	$2^{(6)}\mathrm{Mg}^{(6)}\mathrm{O} + {}^{(6)}\mathrm{Ti}^{(3)}\mathrm{O}_2$	1.00	1.00
$AO + B_2O_3$	$^{(6)}\mathrm{Mg}^{(6)}\mathrm{O} + {}^{(6)}\mathrm{Al}_2{}^{(4)}\mathrm{O}_3$	1.00	(1.01_4)
Sr_2PbO_4 (23, 24)	$^{(6)}\mathrm{Mn}_2{}^{(6)}\mathrm{Ge}^{(5)}\mathrm{O}_2{}^{(4)}\mathrm{O}_2{}^{c}$	1.00	1.00
$CaMn_2O_4$ (46, 47)	$^{(8)}\mathrm{Mn}^{(6)}\mathrm{Mn}_2{}^{(5)}\mathrm{O}_2{}^{(6)}\mathrm{O}_1{}^{(4)}\mathrm{O}_1{}^{c}$	0.98	0.99
Defect NiAs (50, 59)	$^{(6)}\mathrm{Fe}^{(6)}\mathrm{Cr}_2{}^{(5)}\mathrm{S}_2{}^{(4)}\mathrm{S}_2{}^{c,d}$	0.98	0.99
K_2NiF_4 (18, 19)	$^{(9)}\mathrm{Ca}_2{}^{(6)}\mathrm{Ge}^{(6)}\mathrm{O}_4{}^{c}$	0.96_5	0.96_5
$CaFe_2O_4$ (42, 47)	$^{(8)}\mathrm{Ca}^{(6)}\mathrm{Al}_2{}^{(5)}\mathrm{O}_4{}^{c}$	0.94_5	0.96
$CaTi_2O_4$ (45)	$^{(8)}\mathrm{Ca}^{(6)}\mathrm{Ti}_2{}^{(5)}\mathrm{O}_2{}^{(6)}\mathrm{O}_1{}^{(4)}\mathrm{O}_1$	0.94_5	0.96
Ca_2IrO_4 (41)	$^{(9)}\mathrm{Ca}_2{}^{(7)}\mathrm{Ca}_3{}^{(6)}\mathrm{Ca}_1{}^{(6)}\mathrm{Ir}_3{}^{(6)}\mathrm{O}_3{}^{(5)}\mathrm{O}_9$	0.93_5	0.93_5

[a] Structure volumes relative to sum of constituent oxide volumes, averaged from Fig. 3.

[b] Normalized to A_2BO_4 spinel.

[c] High pressure phase.

[d] M_3X_4 type not as yet obtained for oxides.

pressure fluorides Li_2NiF_4 [spinel type (*33*)], Na_2CuF_4 [a monoclinic distortion of the strontium plumbate type (*34*)] and K_2NiF_4 (*18*) conform to increasingly dense structures as the A ions increase in size. This behaviour, and the observed transformations of the olivines Mg_2GeO_4 (*35*), Mn_2GeO_4 (*23*) and Ca_2GeO_4 to these three structure types respectively, is in accord with the general observation (*29*), (*36*) that high pressure transformations do not usually lead to new structures, but instead extend the fields of occurrence of known dense structural types so as to include compounds in which the cation-anion radius ratios are lower than those normally found. However, at least in oxides, the metal-oxygen bond distances for a given metal in a high-pressure phase retained to zero pressure are not significantly different from those characterizing zero-pressure phases. Recent examples are α-Ga_2O_3 (*37*), α-$LiGaO_2$ (*38*), garnet-type $CdGeO_3$ (*39*), α-$NaAlO_2$ (*40*) and the present case of Ca_2GeO_4.

In addition to the A_2BX_4 structure types so far discussed, Ca_2IrO_4 with a dense hexagonal structure has also been reported (*41*). Compared with its constituent oxides, it is 2–3% more dense than the K_2NiF_4 isotypes, Fig. 3. Its position in the occurrence fields shown in Fig. 2 is intermediate between those of K_2NiF_4 and strontium plumbate types, and it is possible that high pressure A_2BX_4 phases with this structure will yet be discovered.

While we wish to discuss AB_2X_4 and $ABCO_4$ polymorphs more fully in a separate paper, it should be noted that for those compounds formed from AO (rocksalt) plus B_2O_3 (corundum) constituents, plots of formula volume versus the sum of the constituent oxide volumes are linear for a number of structure types and thus V/V_0 is a constant for each structure type, Fig. 3 and Table II. The AB_2O_4 spinels are 8% less dense than their isochemical mixtures, and the three closely related structure types characterized by the compounds $CaFe_2O_4$ (*42*), (*43*), and (*44*), $CaTi_2O_4$ (*45*) and $CaMn_2O_4$ (*46*) are 2–5% more dense than their isochemical mixtures. Several high pressure examples of these structure types have been found, including Mn_3O_4 (*47*) of $CaMn_2O_4$ type, and $CaAl_2O_4$ (*47*) and $NaAlGeO_4$ (*48*) of calcium ferrite type. In addition several thiospinels AB_2S_4 (*49*), (*50*) and the selenide $CdCr_2Se_4$ (*51*) have been transformed to metal-deficient nickel arsenide type (*58*), (*59*) with typical density increases of 10%. An AB_2O_4 oxide with such a structure (*52*) would, therefore, be some few percent denser than its rocksalt plus corundum-type isochemical mixture.

Although shockwave data (*53*) tend to show that the very high pressure form of Mg_2SiO_4 is somewhat more dense than the isochemical mixture $2MgO + SiO_2$ (rutile form), Fig. 2 strongly indicates that a form containing six-coordinate silicon is likely to be of strontium plumbate rather than K_2NiF_4 type, and consequently almost identical in density with the oxide mixture, Tables II and III. However, the dense form of Ca_2SiO_4 containing six-coordinate silicon is most likely to be of K_2NiF_4 type; from the V/V_0 ratios shown in Tables II and III we would predict for it a zero-pressure formula volume of 77.0 Å^3, corresponding to a density of 3.71 g cm^{-3}.

Previous work has indicated that $CaSiO_3$ will adopt the perovskite structure at very high pressures (*13*) and the behaviour of systems having K_2NiF_4 and perovskite type end members is accordingly of geochemical interest. The existence of the phases $Ca_3Mn_2O_7$ and $Ca_4Mn_3O_{10}$ (*54*) intermediate between Ca_2MnO_4 (K_2NiF_4 type) and $CaMnO_3$ (perovskite type), suggests that under suitable conditions of temperature and pressure corresponding calcium silicates will occur. These $A_3B_2X_7$ and $A_4B_3X_{10}$ structures are derived from that of K_2NiF_4, Fig. 1, by the interleaving of either one or two additional perovskite layers between each rocksalt layer, and have been also observed in the CaO-TiO_2 (*55*), SrO–TiO_2 (*56*), and $CsCl$–$CdCl_2$ (*57*) systems. It is possible that members of these $AX.nABX_3$ series with values of n greater than three can exist, especially at high temperatures and pressures, and indeed it is also possible that the numbers of perovskite layers interleaved with rocksalt layers could either be randomized or show long range order when n is nonintegral. In any case, such intergrowth structures would provide high density assemblages for those systems in which K_2NiF_4 or perovskite end members are possible.

The dense M_3O_4 structure types discussed in the present paper, and to which in several cases olivines and spinels have been observed to transform, provide a number of alternatives for geochemical assemblages as dense as, or denser than, mixtures of the appropriate simple oxides. An unambiguous prediction of the high pressure structure for a given M_3O_4 composition is still not possible in all cases, but the examination of the crystal chemistry and existence fields of given structure types does provide criteria which appear to have been satisfied in the transformations so far observed. However, refinement of these criteria, and a continued search for observable high pressure transformations are still required before the structures of shockwave phases and those existing deep within the earth can be assigned with certainty.

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