h.c.p. ⟶ c.c.p.

Fig. 4. Mechanism of the h.c.p. → c.c.p. transformation giving rise to orientations of the second kind. First (left side) alternate layers slip half way; secondly all the formed vertical close-packed layers slip upwards giving rise to the (a) orientation, or slip downwards giving rise to the (b) orientation.

tations might be sought for in any internal stresses perpendicular to the prismatic faces. These would hamper the development of the normal mechanism of transformation, which involves expansion perpendicular to these faces. On the other hand, the anomalous mechanism would help to compensate for the internal stresses, because of the contraction of the structure along this direction.

The six anomalous orientations observed here might be called orientations *of the second kind*, as compared with the two normal orientations, which should be referred to as being *of the first kind*.

The corresponding anomalous orientations of h.c.p. which could be derived on the c.c.p. → h.c.p. transformation would produce prismatic faces of the h.c.p.

parallel to the (111) face of the c.c.p. However this does not seem physically probable because it would give rise to expansion in the same direction as the normal orientation, and would therefore be as unfavourable to the relief of any internal stresses as would the normal orientations.

References

BRINDLEY, G. W. (1963). *Crystallographic aspects of some decomposition and recrystallization reactions.* From *Progress in Ceramic Science*, Vol. 3, p. 7. London: Pergamon Press.
CHRISTIAN, J. W. (1951). *Proc. Roy. Soc.* A, **206**, 51.
ERVIN, G. (1952). *Acta Cryst.* **5**, 103.
FRANCOMBE, M. H. & ROOKSBY, H. P. (1959). *Clay Miner. Bull.* **4**, 1.
GLASSER, L. S. D., GLASSER, F. P. & TAYLOR, H. F. W. (1962). *Quart. Rev. Chem. Soc. Lond.* **16**, 343.
GOLDSZTAUB, S. (1935). *Bull. Soc. franç. Minér. Crist.* **58**, 6.
KEELING, R. O., JR. & WICK, D. A. (1963). *Science*, **141**, 1175.
LIMA-DE-FARIA, J. (1963). *Z. Kristallogr.* **119**, 176.
LIMA-DE-FARIA, J. & GAY, P. (1962). *Miner. Mag.* **33**, 37.
SLEESWYK, A. W. (1962). *Phil. Mag.* **7**, 1597.

High Pressure NaAlGeO4, a Calcium Ferrite Isotype and Model Structure for Silicates at Depth in the Earth's Mantle

BY A. F. REID AND A. D. WADSLEY

Division of Mineral Chemistry, C.S.I.R.O., Melbourne, Australia

AND A. E. RINGWOOD

Department of Geochemistry and Geophysics, Australian National University, Canberra, Australia

The high pressure phase $NaAlGeO_4$ formed at 120 kilobars and 900 °C has the calcium ferrite structure, space group *Pnma*, unit-cell dimensions $a = 8\cdot87$, $b = 2\cdot84$, $c = 10\cdot40$ Å and $D_x = 4\cdot73$ g.cm^{-3}. The isomorphous silicate $NaAlSiO_4$, $D_x = 3\cdot9 \pm 0\cdot1$ g.cm^{-3}, should exist in the earth's mantle, being transformed by pressure from nepheline or jadeite.

Introduction

The phases in the earth's mantle at depths between 400 and 900 kilobars are generally believed to be denser polymorphic varieties of common silicate minerals (Birch, 1952). Although it is still not practicable to achieve the experimental pressures and temperatures

which simulate conditions at depths below 600 km and to transform many silicates directly, a technique of particular value is to replace them with their germanium analogues, which undergo transitions at much lower pressures (Ringwood, 1966).

High pressure synthesis is expected to result in an increase in both the density of the phase and the co-

ordination number of the metals, but there is little guide to the structures which can be expected to form. Germanian pyroxenes and olivines are altered to high symmetry spinel, garnet, ilmenite and perovskite phases, but at present there is no indication of what happens in the mantle to the abundant silicate minerals containing the alkali metals.

At pressures below 25 kilobars (kb) and temperatures up to 1200 °C the reaction

$$\text{albite} + \text{nepheline} \rightarrow 2 \text{ jadeite}$$
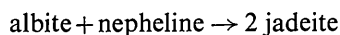
which can be represented by an ideal equation

$$NaAlSi_3O_8 + NaAlSiO_4 \rightarrow 2NaAlSi_2O_6$$

was reported by Robertson, Birch & MacDonald (1957). Dachille & Roy (1962) demonstrated that the same reactions occurred with the germanian analogues, but at 10 kb and up to 600 °C.

Ringwood & Major (1967) recently showed that germanian jadeite glass decomposed at 120 kb and 900 °C to GeO_2 and a new unidentified phase according to the equation

$$NaAlGe_2O_6 \rightarrow NaAlGeO_4 + GeO_2 \text{ (rutile)}$$

and confirmed the formula by making $NaAlGeO_4$ at the same temperature and pressure directly from a glass of the same composition. They suggested that the siliceous systems would follow suit, giving from jadeite the dense variety of $NaAlSiO_4$ together with the rutile form of SiO_2 (stishovite), or dense $NaAlSiO_4$ directly from nepheline. We now wish to report that the new germanium phase is a member of an isomorphous family of compounds $NaA^{3+}B^{4+}O_4$ crystallizing with the $CaFe_2O_4$ structure, of which $NaScTiO_4$ is a typical member (Reid, Wadsley & Sienko, 1967).

Experimental

The high pressure, high temperature apparatus, consisting of a pair of Bridgman anvils with a heater placed between them, has been described elsewhere (Ringwood & Major, 1966). The length of a run was between three and five minutes, and the sample was quenched while still under pressure. The specimen, a few milligrams of moistened $NaAlGeO_4$ glass, was completely converted at 120 kb and 900 °C into a highly birefringent, finely crystalline single phase with a mean refractive index of 1·815.

Its powder pattern, obtained with an 11·4 cm Debye–Scherrer camera using filtered copper radiation, was very similar to that of $NaScTiO_4$ separately recorded under identical conditions. This provided a means of calibration, as the lattice parameters of $NaScTiO_4$, together with its structure, had been accurately determined (Reid, Wadsley & Sienko, 1967). Corrections of less than 0.05° out to 80° in 2θ were required, and the resulting $\sin^2 \theta_{obs} - \sin^2 \theta_{calc}$ values had a normal distribution with no systematic trends, the standard deviations in $\sin^2 \theta$ being of the order of

20×10^{-5}. The pattern of $NaScTiO_4$ initially was also useful for assigning indices to the lines of $NaAlGeO_4$, and iterative index selection and least-squares refinement procedures led to the unit-cell dimensions listed in Table 1. The completely indexed pattern is given in Table 2, confirming that the preparation consists of a single phase.

Table 1. *High pressure* $NaAlGeO_4$, *crystallographic data*
Orthorhombic symmetry, space group $Pnma$ (no. 62).

	$NaAlGeO_4$	$NaScTiO_4$
a (Å)	8·871 ± 0·006	9·277
b (Å)	2·840 ± 0·003	3·048
c (Å)	10·402 ± 0·007	10·917
V (Å^3)	262·1 ± 0·5	308·7
Z	4	4
Formula wt.	186·57	179·85
D_x (g.cm^{-3})	4·73 ± 0·01	3·87

Table 2. *High pressure* $NaAlGeO_4$ *diffraction data*
Cu $K\alpha$, $\lambda = 1·5418$ Å

Line	hkl	$\sin^2 \theta_{obs}$	$\sin^2 \theta_{calc}$	I_{obs}	I_{calc}
1	002	0·02185	0·02197	65	65
2 (br)	102	0·02977	0·02952	vs	195
	200		0·03021		303
3	202	0·05207	0·05218	50	39
4	103	0·05666	0·05698	20	5
5	301	0·07313	0·07345	35	11
6	011	0·07910	0·07916	25	12
	203		0·07964		5
7	004	0·08754	0·08787	s	276
8	302	0·08987	0·08993	vs	447
9 (br)	112	0·10316	0·10319	vs	379
	210		0·10388		186
10	211	0·10924	0·10937	10	5
11	204	0·11754	0·11808	20	9
	303		0·11739		14
12	013	0·12293	0·12310	40	40
13	212	0·12616	0·12585	40	14
	401		0·12631		19
14	113	0·13077	0·13065	130	132
15	402	0·14276	0·14279	60	54
16	311	0·14700	0·14713	65	91
17	213	0·15330	0·15330	10	17
18	312	0·16356	0·16360	20	18
19	114	0·16908	0·16910	90	69
20	214	0·19176	0·19175	200	233
21	410	0·19458	0·19449	130	169
22	411	0·19972	0·19999	40	39
23	106	0·20505	0·20527	25	19
	305		0·20526		4
24	015	0·21072	0·21097	40	9
	502		0·21075		35
25	412	0·21629	0·21646	20	19
26	206	0·22812	0·22792	80	59
27	413	0·24390	0·24392	20	6
28	306	0·26611	0·26567	45	68
29	600	0·27161	0·27185	45	58
30	116	0·27870	0·27894	50	99
31	414	0·28317	0·28236	165	155
32	020	0·29480	0·29468	80	97
33	216	0·30159	0·30159	70	62
34	220	0·32571	0·32489	25	14
35	316	0·34002	0·33934	20	13
36	108	0·36000	0·35904	50	10
	604		0·35972		47
37	322	0·38455	0·38461	100	76
38	416	0·39246	0·39221	35	30

Table 2 (cont.)

Line	hkl	$\sin^2 \theta_{obs}$	$\sin^2 \theta_{calc}$	I_{obs}	I_{calc}
39	317	0·41163	0·41074	10	5 }
	323		0·41207		1 }
40	421	0·42075	0·42099	10	2
41	118	0·43301	0·43271	20	15 }
	614		0·43339		4 }

Intensities were at first placed in relative order by visual examination, and then measured approximately by comparison with a calibrated film strip. The four strongest lines were too strong for evaluation by this simple expedient, and were omitted in normalizing I_{obs} with I_{calc}.

Structure calculation

A set of intensities was calculated for $NaAlGeO_4$ assuming exact isomorphism with $NaScTiO_4$. All atoms were in the 4(c) point positions of the space group Pnma (Table 3), and it was also assumed that Al and Ge occupied the two available octahedral sites at random. This is certainly true for all members of the family comprising $NaFeTiO_4$, $NaFeSnO_4$, $NaScTiO_4$, $NaScSnO_4$, $NaScZrO_4$ and $NaScHfO_4$ (Reid, Wadsley & Sienko, 1967), and consequently seems justifiable for the present new member.

Table 3. *Positional parameters for* $NaAlGeO_4$*

Space group Pnma (no. 62).
All atoms in point positions 4(c), $\pm(x,\frac{1}{4},z)$, $\pm(\frac{1}{2}-x,\frac{3}{4},\frac{1}{2}-z)$.

|	x	y	z	U_{iso}
Na	0·244	0·250	0·348	0·024
Al or Ge(1)	0·067	0·250	0·111	0·015
Al or Ge(2)	0·080	0·250	0·606	0·009
O(1)	0·290	0·250	0·651	0·021
O(2)	0·386	0·250	−0·016	0·016
O(3)	0·479	0·250	0·216	0·016
O(4)	0·074	0·250	−0·073	0·016

* Based on those for $NaScTiO_4$.

These results are included in Table 2, and show good agreement throughout. $R_{Io} = 100 \Sigma (I_o - I_c)/\Sigma I_o$ is 22·5%, a satisfactorily low value in view of the crude method we used to provide numerical values for the line intensities. It furnishes convincing proof that high pressure $NaAlGeO_4$ is indeed isomorphous with $NaScTiO_4$ and has the calcium ferrite structure. This places some confidence in the theoretical density of $NaAlGeO_4$, 4·73 ± 0·01 g.cm^{-3}.

Probable density of 'high pressure $NaAlSiO_4$'

It now remains to estimate the density of the predicted isomorphous siliceous phase $NaAlSiO_4$. This can be done empirically by plotting the unit-cell volumes of the sodium-containing $CaFe_2O_4$ isotypes against the average octahedral metal–oxygen distance for each, and extrapolating to the most probable estimate of the distance in $NaAlSiO_4$ (Fig. 1). Similar extrapolations can also be made for unit-cell axes.

The A and B ions in the phases $NaA^{3+}B^{4+}O_4$ randomly occupy six-coordinated sites. These octahedra show some distortion, and it is necessary to average the metal–oxygen bond lengths. We note that the mean 'hybrid' metal–oxygen distance is midway between the average for the individual metals in related compounds. For example, the mean Sc–O bond length in $CaSc_2O_4$ with the $CaFe_2O_4$ structure is 2·12 Å (Reid, 1967; Müller-Buschbaum & von Schnering, 1965) while Ti–O distances for a wide range of compounds centre around 1·96 Å. The average of these two is 2·04 Å, which is identical with the value for (Sc,Ti)–O distances in $NaScTiO_4$ (Reid, Wadsley & Sienko, 1967).

The octahedral Si–O bond distance in stishovite is 1·77 Å if we assume a normal rutile structure and adopt the unit-cell dimensions of Chao, Fahey, Littler & Milton (1962). The Ge–O distance in the rutile form of GeO_2 is 1·88 Å, and the average (Si,Al)–O distance in $NaAlSiO_4$ should thus be $\frac{1}{2}(1·88 − 1·77)$ Å less than the (Ge,Al)–O distance in $NaAlGeO_4$, which gives us a value of 1·88 Å. This corresponds to a unit-cell volume of 242 Å^3, unit cell axes $a = 8·7$, $b = 2·75$, $c = 10·1$ Å, and to a density of $3·9 ± 0·1$ g.cm^{-3} for high pressure $NaAlSiO_4$. Nepheline of this composition has a calculated density 2·66, jadeite 3·35 and stishovite 4·35 g.cm^{-3}, so the reactions

$NaAlSiO_4 \rightarrow NaAlSiO_4$
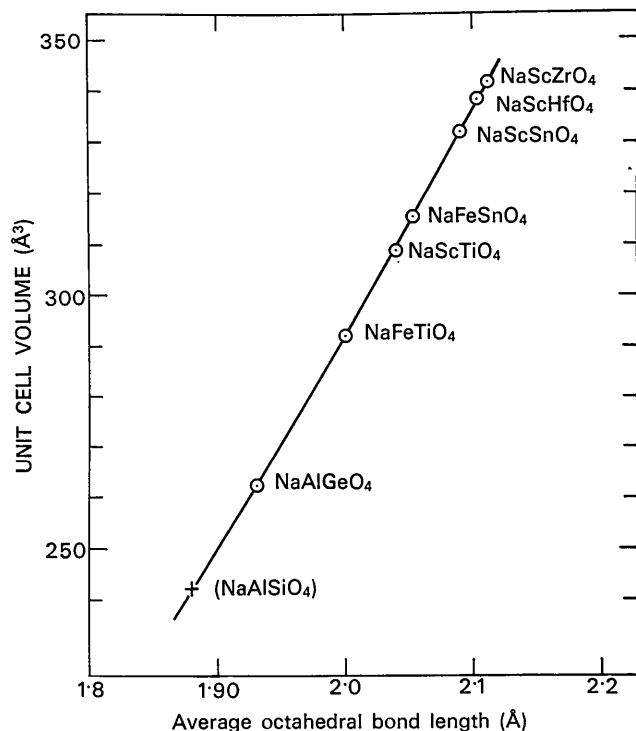(nepheline)   (calcium ferrite)
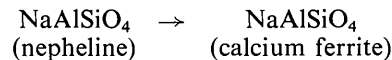
and

Fig. 1. Unit-cell volume *versus* average metal–oxygen octahedral bond length for $NaScTiO_4$ isomorphs. A similar plot can be made for unit-cell axes.

$$\text{NaAlSi}_2\text{O}_6 \rightarrow \text{NaAlSiO}_4 + \text{SiO}_2$$
$$\text{(jadeite)} \quad \text{(calcium ferrite)} \quad \text{(stishovite)}$$

represent density increases of 46·6% and 20·0% respectively.

High density model silicate systems

A number of dense alkali aluminosilicate high pressure structures can be postulated on the basis of the crystal chemistry of alkali oxycompounds of the tri- and quadrivalent metals. Li^+, too small an ion for the $CaFe_2O_4$ structure, forms instead a wide range of spinels of the same stoichiometry, $LiA^{3+}B^{4+}O_4$ (Blasse, 1963). $LiAlGeO_4$ is an exception (Strunz & Jacob, 1960) but is nevertheless transformed from phenacite-type to spinel above 8 kb and 700 °C (Gaines, Perrotta & Stephenson, 1966). K^+ is too large, and potassium feldspars could be expected to form the high pressure phase $KAlSi_3O_8$ with the hollandite structure, which has a wide range of isomorphs with the ideal composition $KA^{3+}B_3^{4+}O_8$ (Bayer & Hoffmann, 1966). $KAlGe_3O_8$ with this structure has recently been prepared under pressure (Kume, Matsumoto & Koizumi, 1966).

We have previously attempted unsuccessfully to synthesize compounds $NaA^{3+}B_2^{4+}O_6$, $A = Al$, Fe or Sc and $B = Ti$, and stable octahedral structures with this stoichiometry appear not to exist; the decomposition of germanian jadeite supports this view. Where $A = Sc$ or Fe this composition on heating gives calcium ferrite and $NaA^{3+}B_3^{4+}O_8$ phases, the latter having the structure of sodium titanium bronze $NaTi_4O_8$ (Andersson & Wadsley, 1962) which also has a wide range of isomorphs (Bayer & Hoffmann, 1965). The possibility that sodium feldspars could adopt this structure, or mixed sodium–potassium feldspars that of hollandite, should be investigated. Both are extremely stable and their formation would lead to density increases which can be estimated to be at least 25%.

In any case at least some of the sodium in the mantle is most probably present in a calcium ferrite-type structure containing octahedrally coordinated silicon.

References

ANDERSSON, S. & WADSLEY, A. D. (1962). *Acta Cryst.* **15**, 201.

BAYER, G. & HOFFMANN (1965). *Z. Kristallogr.* **121**, 9.

BAYER, G. & HOFFMANN (1966). *Amer. Min.* **51**, 511.

BIRCH, F. (1952). *J. Geophys. Res.* **57**, 227.

BLASSE, G. (1963). *J. Inorg. Nuclear Chem.* **25**, 230.

CHAO, A. A., FAHEY, A. A., LITTLER, A. A. & MILTON, A. (1962). *J. Geophys. Res.* **67**, 419.

DACHILLE, F. & ROY, R. (1962). Chapter 9 in *Modern Very High Pressure Techniques*, Ed. R. H. Wentorf. London: Butterworth.

GAINES, A. M., PERROTTA, A. J. & STEPHENSON, D. A. (1966). *J. Amer. Ceram. Soc.* **49**, 516.

KUME, S., MATSUMOTO, T. & KOIZUMI, M. (1966). *J. Geophys. Res.* **71**, 4999.

MÜLLER-BUSCHBAUM, H. & VON SCHNERING, H. G. (1965). *Z. anorg. Chem.* **336**, 295.

REID, A. F. (1967). *Inorg. Chem.* **7**, 631.

REID, A. F., WADSLEY, A. D. & SIENKO, M. J. (1967). *Inorg. Chem.* In the press.

RINGWOOD, A. E. (1966). In *Advances in Earth Science.* p. 357. Ed. P. M. Hurley. M.I.T. Press.

RINGWOOD, A. E. & MAJOR, A. (1966). *Earth and Planetary Science Letters*, **1**, 241.

RINGWOOD, A. E. & MAJOR, A. (1967). *Earth and Planetary Science Letters*, **2**, March 1967.

ROBERTSON, E. C., BIRCH, F. & MACDONALD, G. J. F. (1967). *Amer. J. Sci.* **255**, 115.

STRUNZ, H. & JACOB, P. (1960). *Neues Jb. Mineral Monatsh.* p. 78.