Crystal–chemical characterization of NaAlSiO$_4$ with the CaFe$_2$O$_4$ structure

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ABSTRACT. A high-pressure modification of NaAlSiO$_4$ with the calcium ferrite structure was synthesized at pressures higher than 24 GPa using a double-stage split-sphere type high-pressure apparatus. The unit cell dimensions are: $a = 10.1546(8)$, $b = 8.6642(8)$, $c = 2.7385(4)$ Å, and $V = 240.93(3)$ Å^3 with the space group Pbnm. Calculated density is 3.916(1) g/cm^3. The crystal structure was determined by the ordinary powder X-ray method. Both $M1O_6$ and $M2O_6$ octahedra run parallel to the c-axis, forming edge-shared double chains. The shared edges exhibit remarkable shortening (2.25–2.39 Å). Sodium atoms are located in the 'tunnel' formed by the linked double chains, being in eightfold co-ordination. The structure is very similar to that predicted by Dempsey and Strens (1976) with the aid of the DLS method. The possible instability of the calcium ferrite type of Mg$_2$SiO$_4$ is discussed.

SINCE the germanate nepheline (NaAlGeO$_4$) was found to transform into the CaFe$_2$O$_4$ (calcium ferrite) type structure by Ringwood and his co-workers (Ringwood and Major, 1967; Reid et al., 1967), this structure has been regarded as the most probable high-pressure modification of NaAlSiO$_4$ (nepheline). Dempsey and Strens (1976) estimated the structure of this hypothetical high-pressure phase of NaAlSiO$_4$ by the distance least squares (DLS) method. Recently the view was confirmed by Liu (1977) who obtained NaAlSiO$_4$ with the calcium ferrite structure at pressures higher than 18 GPa. It was further demonstrated that the assemblages NaAlSiO$_4$ (CaFe$_2$O$_4$ type) plus SiO$_2$ (stishovite) and/or NaAlO$_2$ (α-NaFeO$_2$ type) are stabilized at pressures higher than 24 GPa over the whole range in the system NaAlO$_2$–SiO$_2$ including NaAlSi$_2$O$_6$ (jadeite) and NaAlSi$_3$O$_8$ (albite) (Liu, 1978). It follows that NaAlSiO$_4$ with the calcium ferrite structure might actually be the most dominant Na-bearing phase in the middle and lower mantle.

In the present study the structural determination has been carried out for NaAlSiO$_4$ with the calcium

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ferrite structure and a consideration of its crystal–chemical implications has been made, special attention being paid to the possibility of the existence of Mg$_2$SiO$_4$ with the calcium ferrite structure (Reid and Ringwood, 1969).

Experimental procedures. The high-pressure synthesis was carried out using a double-stage split-sphere type apparatus (Kawai and Endo, 1970). Experimental details were similar to those described elsewhere (Ito and Matsui, 1978). The temperature was monitored using a Pt/Pt13%Rh thermocouple without any correction for the pressure effect on e.m.f.

The starting materials were put directly into a cylindrical nichrome heater embedded in the centre of pyrophyllite octahedron baked at 700 °C for 30 minutes. The mixture of Na$_2$CO$_3$, Al$_2$O$_3$ and SiO$_2$ in the stoichiometric nepheline composition was heated at 1580 °C for 30 minutes and quenched to room temperature. The resultant glass was pulverized and used as starting material. After each sample was subjected to the desired P–T conditions, which were varied in the pressure range 24 to 30 GPa and temperature range 1000 to 1200 °C, for 30–45 minutes, it was quenched to room temperature. The quenched sample was examined by the powder X-ray diffraction method.

All the run products were found to be single phase NaAlSiO$_4$ with the calcium ferrite structure, with a trace of a high-pressure phase of pyrophyllite, Al$_5$Si$_5$O$_{17}$(OH) plus stishovite (Eggleton et al., 1978). Comparison of the half-widths of the diffraction peaks showed that those of NaAlSiO$_4$ with the CaFe$_2$O$_4$ structure were about 1.3 times broader than those other silicates synthesized at high pressures in our laboratory (e.g. Ito and Matsui, 1974; Ito, 1977; Ito and Matsui, 1978).

Powder X-ray diffraction data were obtained at ambient conditions employing a Rigaku Denki diffractometer equipped with a single channel pulse-height analyser and a graphite crystal monochromator. The goniometer was calibrated using an external standard of high-purity silicon powder whose unit cell length was taken to be 5.4301 Å.

The diffraction peaks of NaAlSiO$_4$ with the CaFe$_2$O$_4$ structure were indexed by comparing the observed 2θ values with those calculated for all the possible reflections for the space group Pbnm according to the unit cell dimensions reported by Liu (1977). The unit cell dimensions were then refined by the least squares method in

TABLE I. Comparison of cell parameters and density

a/Å	b/Å	c/Å	V/Å³	ρ_{calc}/g·cm⁻³	
10.1546(8)	8.6642(8)	2.7385(4)	240.93(3)	3.916(1)	Present study
10.206(8)	8.740(7)	2.746(2)			Liu (1977)
10.1	8.7	2.75	242	3.9(1)	Reid et al. (1967)
10.161	8.641	2.734	240.1		Dempsey & Strens (1976)

Standard errors are in parentheses and refer to the last decimal place.

which the quantity $\Sigma(Q_{obs} - Q_{calc})^2$, where $Q = 1/d^2$, was to be minimized. Re-indexing of diffraction lines were carried out based on the newly obtained unit cell dimensions. The final values are given in Table I, along with those reported by Liu (1977) and predicted by Reid et al. (1967) and Dempsey and Strens (1976). The obtained values are in excellent agreement with those predicted by Dempsey and Strens (1976). The calculated density shows reasonable agreement with the value by Reid et al. (1967). Present values are slightly smaller than those by Liu (1977). By reason of the accuracy of indexing of diffraction peaks and the higher resolving power of the goniometer used in this study (e.g. (020) → (020) + (210)), present values are superior to those by Liu (1977).

The powder X-ray intensities were measured planimetrically and normalized to that of the most intense peak (230). The intensities for overlapping peaks were estimated separately according to the calculated intensities. The influence of coexistent stishovite plus Al_5Si_5

$O_{17}(OH)$ on the intensities of $NaAlSiO_4$ with the $CaFe_2O_4$ structure were eliminated by the previously reported intensity data (Chao et al., 1962; Eggleton et al., 1978). The final intensities were obtained by averaging the data of three independent measurements of five run products. Powder X-ray data for $NaAlSiO_4$ of the $CaFe_2O_4$ type are given in Table II.

Results. In the structure of $NaAlSiO_4$ with the $CaFe_2O_4$ structure, all of the atomic sites (Na, $M1$, $M2$, O1, O2, O3, and O4) are in the same symmetric positions $4c$ of the space group $Pbnm$. Refinement was performed on fourteen positional parameters, a scale factor and an effective mass absorption coefficient using 75 intensity data obtained above with the aid of the least squares method. Starting co-ordinates were those of $NaAlGeO_4$ reported by Reid et al. (1967). We assumed furthermore that

TABLE II. Powder X-ray data for NaAlSiO₄ with the CaFe₂O₄ structure

h k l	d_{obs}/Å	d_{calc}/Å	I_{obs}	I_{calc}	h k l	d_{obs}/Å	d_{calc}/Å	I_{obs}	I_{calc}
1 1 0	——	6.591	——	0.5	2 4 1	1.6108	1.6111	13.7	13.8
2 0 0	5.081	5.077	22.2	23.8	5 1 1	1.6027	1.6031	1.0	1.2
2 1 0	4.381	4.381	24.0	22.4	6 2 0	1.5766	1.5764	33.7	23.9
0 2 0	4.334	4.332	73.3	72.7	3 4 1	1.5177	1.5183	7.8	2.5
1 2 0	3.978	3.985	0.5	1.4	5 4 0	1.4823	1.4815	7.4	1.9
2 2 0	3.298	3.296	25.9	26.9	6 3 0	1.4604	1.4602	16.3	10.5
3 1 0	3.151	3.153	10.9	1.8	1 5 1	1.4440	1.4493 }	19.9	0.7
1 3 0	2.779	2.778	10.5	8.1	0 6 0	1.4440	1.4440		14.1
1 0 1	2.645	2.644	14.6	7.7	4 5 0	1.4315	1.4312 }	3.3	1.7
4 0 0	2.537	2.539 }	72.7	69.9	7 1 0	1.4315	1.4307		1.3
1 1 1	2.537	2.529		4.5	5 3 1	1.4201	1.4204 }	25.1	3.3
2 3 0	2.509	2.510	100.0	99.7	6 1 1	1.4201	1.4202		22.3
4 1 0	2.436	2.436	4.2	3.7	4 4 1	1.4119	1.4119	43.7	44.9
2 1 1	2.321	2.322 }	46.7	31.9	2 5 1	1.4077	1.4070	23.7	24.9
0 2 1	2.321	2.315		14.4	0 0 2	1.3663	1.3692 }	58.5	39.8
3 3 0	2.196	2.197	13.3	9.3	6 2 1	1.3663	1.3662		18.4
0 4 0	2.163	2.166	3.0	2.5	5 5 0	1.3168	1.3182	1.3	1.0
3 0 1	2.121	2.129 ⎤		25.1	6 3 1	1.2886	1.2885	11.0	10.5
1 4 0	2.121	2.118 ⎥	51.1	29.0	7 0 1	1.2808	1.2919	2.0	1.2
2 2 1	2.121	2.106 ⎦		1.8	0 6 1	1.2766	1.2773	5.4	5.2
3 1 1	2.067	2.067	80.8	85.9	7 1 1	1.2689	1.2681	3.7	7.0
2 4 0	1.9923	1.9923	20.2	17.6	2 2 2	1.2646	1.2644	1.2	2.3
5 1 0	1.9775	1.9773	27.8	25.4	8 1 0	1.2555	1.2559 }	10.4	5.3
1 3 1	1.9506	1.9502	64.7	63.7	4 6 0	1.2555	1.2552		5.7
3 2 1	1.9101	1.9107 }	10.4	2.3	2 6 1	1.2382	1.2387	4.2	5.7
4 3 0	1.9101	1.9067		7.1	7 2 1	1.2288	1.2292 }	1.7	2.5
2 3 1	1.8503	1.8505	13.8	13.2	1 3 2	1.2288	1.2281		0.7
5 2 0	1.8391	1.8389	0.5	0.6	6 5 0	1.2104	1.2108	1.0	1.2
3 4 0	1.8204	1.8245 }	25.8	1.6	4 0 2	1.2059	1.2051	10.8	11.0
4 1 1	1.8204	1.8202		25.1	2 7 0	1.2024	1.2025 }	22.2	4.4
3 3 1	1.7104	1.7137 ⎤		5.8	2 3 2	1.2024	1.2021		18.3
4 2 1	1.7104	1.7105 ⎥	56.8	47.3	6 4 1	1.1997	1.1990	16.0	16.3
1 5 0	1.7104	1.7081 ⎦		5.5	3 6 1	1.1951	1.1951 }	2.3	1.0
0 4 1	1.6990	1.6989	31.4	33.2	4 1 2	1.1951	1.1936		1.0
1 4 1	1.6756	1.6756	24.7	23.7	5 5 1	1.1870	1.1878	1.0	1.4
5 3 0	1.6610	1.6613 }	8.1	1.2					
6 1 0	1.6610	1.6610		8.2					
4 4 0	1.6478	1.6478	4.6	4.6					
2 5 0	1.6404	1.6400	5.6	4.5					
5 0 1	1.6317	1.6313	3.6	3.7					

the distribution of Si and Al is random in $M1$ and $M2$ site. Isotropic temperature factors (in Å²) were varied from 0.4 to 0.7 for Na, Si, and Al, and from 0.5 to 0.7 for O1, O2, O3, and O4. The atomic scattering factors were taken from those by MacGillavry and Reik (1968), and Tokonami (1965). The best refinement was obtained by using neutral atomic scattering factors and isotropic temperature factors of 0.5 for $M1$ and $M2$, and 0.6 for the other atoms. The final R and weighted R factors were 0.067 and 0.039, respectively, with respect to the intensities.

TABLE III. Structural parameters for CaFe₂O₄-type NaAlSiO₄

Atom	X-structure*			D-structure**		
	x	y	z	x	y	z
Na	0.661(3)	0.764(3)	0.75	0.657	0.753	0.75
M1	0.890(3)	0.577(4)	0.25	0.898	0.576	0.25
M2	0.398(3)	0.556(3)	0.25	0.386	0.573	0.25
O1	0.365(5)	0.697(5)	0.75	0.356	0.723	0.75
O2	0.018(5)	0.612(5)	0.75	0.014	0.609	0.75
O3	0.201(5)	0.461(5)	0.25	0.206	0.482	0.25
O4	0.430(4)	0.438(6)	0.25	0.423	0.424	0.25

*X-ray derived structure; present study. Standard errors are in parentheses and refer to the last decimal place.
**DLS-derived structure; Dempsey and Strens (1976).

TABLE IV. Interatomic distances and angles in NaAlSiO₄ of the CaFe₂O₄-type

NaO₈ polyhedron

Na-O1c (×2)	2.51(4) Å	O3d-O1c (×2)	2.97(6) Å	O3d-Na-O1c	74(2)°
-O2d (×2)	2.27(4)	O3d-O2d (×2)	2.65(5)	O3d- -O2d	69(1)
-O4c (×2)	2.41(4)	O3b-O1c (×2)	2.76(5)	O3b- -O1c	68(2)
-O3d	2.41(6)	O3b-O4c (×2)	2.70(6)	O3b- -O4c	68(1)
-O3b	2.41(6)	O1c-O2d (×2)	3.60(7)	O1c- -O2d	98(1)
		O1c-O4c (×2)	3.65(6)	O1c- -O4c	96(1)
Average	2.40 Å	O2d-O4c (×2)	2.87(6)	O2d- -O4c	76(2)
(Na-O1a	3.05(6) Å)	Average	3.03 Å		

M1O₆ octahedron

M1-O1c	1.98(5) Å	O1c-O2a (×2)	2.65(6) Å	O1c-M1-O2a	86(2)°
-O2c	1.89(5)	O1c-O3b (×2)	2.76(5)	O1c- -O3b	97(2)
-O3b (×2)	1.69(4)	O2c-O3b (×2)	2.65(5)	O2c- -O3b	96(2)
-O2a (×2)	1.92(4)	O2a-O2b	2.74(=c)	O2a- -O2b	91(3)
		O3b-O3c	2.74(=c)	O3b- -O3c	109(3)
Average	1.85 Å	O2a-O2c (×2)	2.40(7)*	O2a- -O2c	78(2)
		O2a-O3b (×2)	2.32(7)*	O2a- -O3b	80(2)

M2O₆ octahedron

M2-O1a (×2)	1.86(4)	O1a-O3a (×2)	2.97(6)	O1a-M2-O3a	95(2)°
-O3a	2.16(5)	O3a-O4a (×2)	2.70(6)	O3a- -O4a	87(2)
-O4a (×2)	1.74(4)	O1a-O4c (×2)	2.75(6)	O1a- -O4c	99(2)
-O4c	1.75(5)	O1a-O1b	2.74(=c)	O1a- -O1b	95(2)
		O4a-O4b	2.74(=c)	O4a- -O4b	104(3)
Average	1.85 Å	O1a-O4a (×2)	2.34(6)*	O1a- -O4a	81(1)
		O4a-O4c (×2)	2.26(7)*	O4a- -O4c	81(2)

M1 - M1	2.95(3) Å	M1-M1-M1	55(1)°
M2 - M2	2.66(2)	M2-M2-M2	62(1)

Selected comparison of interatomic distances

Na-O	2.469 Å	(NaAlSi₂O₆ jadeite	[Prewitt and Burnham, 1966])
Si-O	1.778	(SiO₂ stishovite	[Baur and Khan, 1971])
	1.79	(MgSiO₃ perovskite	[Ito and Matsui, 1978])
Al-O	1.928	(NaAlSi₂O₆ jadeite	[Prewitt and Burnham, 1966])
	1.886	(Mg₃Al₂Si₃O₁₂ pyrope	[Gibbs and Smith, 1965])

* Shared edges.
Standard errors are in parentheses and refer to the last decimal place.

The X-ray derived structural parameters are given in Table III, along with DLS-derived parameters by Dempsey and Strens (1976). Their predicted values are remarkably realistic in comparison with those obtained here. The resultant interatomic distances and angles are given in Table IV. The
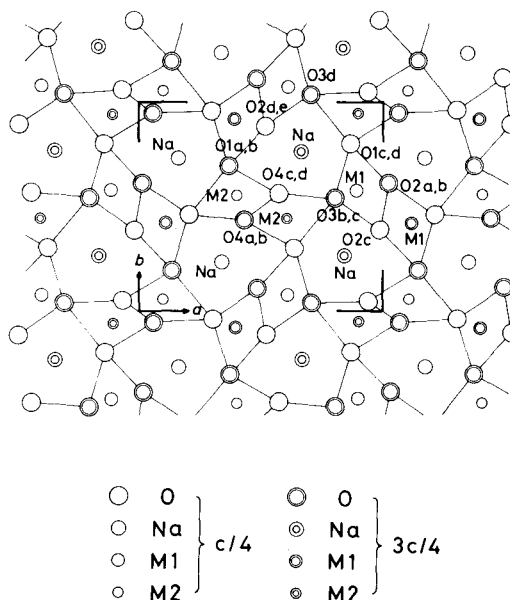

FIG. 1. Crystal structure of NaAlSiO₄ with the CaFe₂O₄ structure projected on (001), showing triangular 'tunnels' occupied by Na ions, which are formed by four double chains.

structure is illustrated in fig. 1 as the projection on to the (001) plane.

Discussion. The small cations (M atoms), Al and Si, are octahedrally co-ordinated by oxygen atoms. The mean M-O distance is 1.85 Å. This value is smaller than the Al-O distance in octahedral co-ordination and longer than Si-O as given in Table IV. Both $M1O_6$ and $M2O_6$ octahedra run parallel to the c-axis with shared edges of O2-O3 for the $M1O_6$ octahedron and O1-O4 for $M2O_6$. The MO_6 octahedra share two further edges (O2-O2 or O4-O4) with an adjacent equivalent MO_6 octahedron, forming a 'double chain' extending along the c-axis. The double chains are further linked with each other by sharing O1 and O3. Sodium atoms are located within 'tunnels' which run parallel to the c-axis, surrounded by four double chains. The Na atom is regarded as being in eightfold co-ordination, six of eight oxygen atoms ($O1c$, $O1d$, $O2d$, $O2e$, $O4c$, and $O4d$) forming a prism and the other two ($O3b$ and $O3d$) being on the top of two pyramids added on the prism. The Na-O1a distance is too great (3.05(6) Å) for O1a to be a member of an NaO$_x$ polyhedron (fig. 1).

Very short M-O distance, 1.69(4) and 1.74(4) Å, appear in the $M1O_6$ and $M2O_6$ octahedra, respectively. This difference is, however, statistically

insignificant, and therefore the possible site preference of Si and Al cannot be determined only by the interatomic distances.

As a result of the rather long $M1$-$M1$ distance (2.95(3) Å) across the O2-O2 edge, the $M1$-$M1$-$M1$ angle has smaller value (55(1)°) than the corresponding $M2$-$M2$-$M2$ angle (62(1)°). Therefore $M1$ atoms are located separate to each other in a double chain. The very short O-O distance (2.26(7) Å) appears in the $M2O_6$ octahedron with no elongation in the $M2$-$M2$ distance.

In the MO_6 octahedron four edges out of twelve are shared; these exhibit the strong shortening in edge lengths (2.26-2.40 Å) and can be compared with the shared edge in stishovite (2.29 Å) (Baur and Khan, 1971). The other O-O distances of the MO_6 octahedra are noticeably long, ranging from 2.65 to 2.76 Å in the $M1O_6$ octahedron and from 2.74 to 2.97 in $M2O_6$; they are considered to be very large for edges of SiO_6 and AlO_6 octahedra. The situation might well be favourable for the incorporation of the Na ion, having a suitably large size and a small charge. In this context it is noted that the shared edges of MO_6 octahedra and NaO_8 polyhedra show virtually no shortening, which may be consistent with the small charge of Na^+.

The broad diffraction peaks may imply the following possibilities, provided the synthesis (crystal growth) is perfect: a vacancy plus Si might be contained in the structure as $Al^{3+} + Na^+ \rightarrow Si^{4+} + \square$; furthermore the structure might have a lower symmetry than that of *Pbnm* and the unit cell discussed above might constitute a subcell of a superstructure. More detailed study, especially the refinement using single crystal, is desired to solve the problems.

Reid and Ringwood (1969) proposed that Mg_2SiO_4 might assume at very high pressures the calcium ferrite structure in which a half of Mg^{2+} could be placed in the eightfold co-ordinated site and the rest of Mg^{2+} and Si^{4+} in the octahedral

TABLE V.   Input data on DLS simulation for Mg_2SiO_4 with the $CaFe_2O_4$ structure

Mg - O (8-coordinated)		2.2222 Å
Mg - O (6-coordinated)		2.0980
Si - O		1.7780
O - O		
in SiO_6 octahedron	(unshared)	2.5592
	(shared)	2.4243
in MgO_6 octahedron	(unshared)	3.0162
	(shared)	2.8677
in MgO_8 polyhedron	O2d-O4c	
	O1c-O4c }	2.5000
	O1c-O2d	

TABLE VI.   Crystallographic data for simulated Mg_2SiO_4 with the $CaFe_2O_4$ structure

Lattice parameters			
a/Å	b/Å	c/Å	
10.413	8.434	2.818	Present study
10.362	8.918	2.789	Dempsey & Strens (1976)

Atomic positions			
	x	y	z
Mg(VIII)	0.679	0.772	0.75
Mg(VI)	0.379	0.551	0.25
Si	0.919	0.581	0.25
O1	0.345	0.729	0.75
O2	0.030	0.619	0.75
O3	0.191	0.465	0.25
O4	0.428	0.378	0.75

sites. Dempsey and Strens (1976) estimated the unit cell dimensions of Mg_2SiO_4 with the $CaFe_2O_4$ structure by the DLS method, starting from the structural data of Reid *et al.* (1967). Following the study of Dempsey and Strens (1976), we examined the possible structure of Mg_2SiO_4 with the calcium ferrite structure by the DLS technique described by Ito and Matsui (1978). The obtained unit cell parameters and atomic co-ordinates for $NaAlSiO_4$ with the $CaFe_2O_4$ structure (Tables I and II) were used as starting values. It was further assumed that Si^{4+} and Mg^{2+} prefer $M1$ and $M2$ site, respectively. Prescribed interatomic distances are given in Table V. The DLS-simulated crystallographic data for Mg_2SiO_4 with the $CaFe_2O_4$ structure shown in Table VI along with those by Dempsey and Strens (1976). Although they assumed the different starting values and input data, their estimated values are in reasonable agreement with those of present study. The density of Mg_2SiO_4 with the $CaFe_2O_4$ structure (3.77 g/cm^3) is decidedly smaller than that (3.94 g/cm^3) of the assemblage $MgSiO_3$ (perovskite) plus MgO (periclase), which was recognized as the most likely post-spinel assemblage of Mg_2SiO_4 (Liu, 1976; Ito, 1977). Furthermore the DLS-derived structure violate the extended Pauling's third rule proposed by Baur (1972): the length of shared edges (O2a-O2c, O2a-O3b, O1a-O4a, and O4a-O4c) tend to be longer whereas the unshared length (O2d-O4c) shorter. Therefore it appears unlikely that Mg_2SiO_4 should assume the $CaFe_2O_4$ structure.

REFERENCES

Baur, W. H. (1972) *Am. Mineral.* **57**, 709–31.
——and Khan, A. A. (1971) *Acta Crystallogr.* **B27**, 2133–9.
Chao, E. C. T., Fahey, J. J., Littler, J., and Milton, D. J. (1962) *J. Geophys. Res.* **67**, 419–21.
Dempsey, M. J., and Strens, R. G. J. (1976) In *The Physics and Chemistry of Minerals and Rocks* (R. G. J. Strens, ed.), 443–58, John Wiley & Sons, London.

Eggleton, R. A., Boland, J. N., and Ringwood, A. E. (1978) *Geochem. J.* **12**, 191–4.

Gibbs, G. V., and Smith, J. V. (1965) *Am. Mineral.* **50**, 2023–38.

Ito, E. (1977) *Geophys. Res. Lett.* **4**, 72–4.

——and Matsui, Y. (1974) *Phys. Earth Planet. Inter.* **9**, 344–52.

————(1978) *Earth Planet. Sci. Lett.* **38**, 443–50.

Kawai, N., and Endo, S. (1970) *Rev. Sci. Instrum.* **46**, 1178–81.

Liu, L. (1976) *Nature*, **262**, 770–2.

——(1977) *Geophys. Res. Lett.* **4**, 183–6.

—— (1978) *Earth Planet. Sci. Lett.* **4**, 438–44.

MacGillavry, C. H., and Reik, G. D. (1968) *International Tables for X-ray Crystallography*, **3**, Kynoch Press, Birmingham.

Prewitt, C. T., and Burnham, C. W. (1966) *Am. Mineral.* **51**, 956–75.

Reid, A. F., and Ringwood, A. E. (1969) *Earth Planet. Sci. Lett.* **6**, 205–8.

——Wadsley, A. D., and Ringwood, A. E. (1967) *Acta Crystallogr.* **23**, 736–9.

Ringwood, A. E., and Major, A. (1967) *Earth Planet. Sci. Lett.* **2**, 106–10.

Tokonami, M. (1965) *Acta Crystallogr.* **19**, 486.