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High-Pressure $KAlSi_3O_8$, an Aluminosilicate with Sixfold Coordination

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Synthetic potassium feldspar $KAlSi_3O_8$ (sanidine) undergoes a polymorphic transition at 120 kilobars pressure and 900°C into the hollandite structure, space group $I4/m$ with $a = 9{\cdot}38$ and $c = 2{\cdot}74$ Å. Aluminum and silicon are randomized in octahedral positions, and the average bond length ($\frac{1}{4}$Al, $\frac{3}{4}$Si)–O is 1·80 Å. The density increased from 2·55 to 3·84 g.cm^{-3}. It is probable that feldspars are transformed to the high-density hollandite structure in the transition zone within the earth's mantle.

The predominant phases at depths between 200 and 900 kilometers in the earth's mantle are generally believed to be denser high-pressure polymorphs, or disproportionation products, of common silicate minerals (Birch, 1952). A number of temperature–pressure studies of the alkali-metal aluminosilicates, as well as the corresponding germanates which transform much more easily, have been reported. The relationships albite–nepheline–jadeite are well documented below 25 kilobars (kb) (Robertson, Birch & McDonald, 1957; Dachille & Roy, 1962), but above 100 kb a different series of transformations take place. Both germanian nepheline and jadeite are altered to a new $NaAlGeO_4$ phase (Ringwood & Major, 1967), which proves to have the orthorhombic calcium ferrite structure (Reid, Wadsley & Ringwood, 1967). $NaAlSiO_4$ could be expected to follow suit at even higher pressures.

Potassium is too large an ion to occupy sites in this particular structure (Reid, Wadsley & Sienko, 1968). Instead the closely packed hollandite arrangement (Byström & Byström, 1951) typified by the compound $KAlTi_3O_8$ (Bayer & Hoffmann, 1966) was considered to be likely for high-pressure potassium-bearing minerals, particularly for the feldspars orthoclase or sanidine having the same stoichiometry, $KAlSi_3O_8$ (Reid, Wadsley & Ringwood, 1967). The germanium analogue $KAlGe_3O_8$ was recently described (Kume, Matsumoto & Koizumi, 1966) and we are now able to report that sanidine itself transforms at 120 kb and 900°C to the hollandite structure. It is therefore the first aluminosilicate with Al and Si both octahedral, and indeed the first oxygen compound other than very high pressure SiO_2 (stishovite) and SiP_2O_7 (Levi & Peyronel, 1935) with silicon having a coordination number of six.

Crystalline synthetic sanidine, $KAlSi_3O_8$, moistened with a trace of water, was allowed to react at 120 kb and 900°C for several minutes in a device consisting

Table 1. *Compounds with the tetragonal hollandite structure containing aluminum*
Space group $I4/m$.

	Lattice parameters *a*	Lattice parameters *c*	Average octahedral bond length	Alkali metal–oxygen bond length	Reference
$KAlSi_3O_8$	9·38 Å	2·74 Å	1·80 Å	2·78 Å	This paper
$KAlGe_3O_8$	9·72	2·86	1·87	2·88	Kume, Matsumoto & Koizumi (1966)
$K_{0.80}Al_{0.80}Ti_{3.20}O_8$	10·07	2·94			Bayer & Hoffmann (1966)
$K_{0.89}Al_{0.89}Ti_{3.11}O_8$	10·06	2·94			
$KAlTi_3O_8$	10·04	2·94	1·93	2·97	
$RbAlTi_3O_8$	10·10	2·94	1·94	2·99	

of a pair of Bridgman anvils with a heater placed bebetween them, and quenched under pressure. The compressed material was a somewhat fibrous single phase with straight extinction and a mean refractive index of 1·745. Its Debye–Scherrer pattern, taken with Cu $K\alpha$ radiation on an 11·4 cm camera independently calibrated with finely powdered KCl, could be readily indexed on a body-centred tetragonal unit cell with the dimensions $a=9{\cdot}38$, $c=2{\cdot}74\pm0{\cdot}01$ Å. These lattice parameters are compared in Table 1 with those for a number of other compounds with the hollandite structure.

Intensity data, obtained from multiple films simultaneously exposed in the powder camera and measured visually with a calibrated film strip, are given in Table 2. Crystallographic data are listed in Table 3, including atomic position parameters taken as equal to those found for tetragonal $\mathrm{Ba}_x\mathrm{Mg}_x\mathrm{Ti}_{4-x}\mathrm{O}_8$ (Dryden & Wadsley, 1958). Calculated intensities using these data showed good agreement (Table 2), $R=100\,\Sigma\,(I_o-I_c)/\Sigma I_o$ being 19%. It should be noted that the space group $I4/m$, containing only the one reflexion plane, makes it impossible directly to use the powder diffraction data for refinement, since $F(hkl)\neq F(\bar{h}kl)$ and these two groups of reflexions coincide.

Hollandite is essentially a rearranged rutile structure affording open tunnels in which the alkali-metal (or alkaline earth) ions are situated (Wadsley, 1964). The size of the metal–oxygen octahedron determines the a and c axis lengths, the latter being the dimension of the octahedral edge (Table 1). The fractional atomic coordinates should therefore be almost identical whatever the composition. In any case the *average* metal–oxygen distance will be largely independent of small variations, and its relation to the cell volume is shown in Fig. 1. Just as in the tetrahedral aluminosilicates, the average octahedral metal–oxygen distance varies with the silicon to aluminium ratio. The present value of 1·80 Å for $(\frac{1}{4}\mathrm{Al},\frac{3}{4}\mathrm{Si})$–O may be compared with the mean of 1·77 Å for Si–O in stishovite and 1·88 Å (predicted) for $(\frac{1}{2}\mathrm{Al},\frac{1}{2}\mathrm{Si})$–O in $\mathrm{NaAlSiO_4}$. This latter distance was predicted (Reid, Wadsley & Ringwood, 1967) by smooth extrapolation of a graph like that in Fig. 1, using measured data from a number of $\mathrm{Na}A^{3+}B^{4+}\mathrm{O}_4$ phases with the calcium ferrite structure.

Table 2. *Powder diffraction pattern of tetragonal* $\mathrm{KAlSi_3O_8}$

hkl	$\sin^2\theta_{\rm obs}$	$\sin^2\theta_{\rm calc}$	I_o	I_c
110	0·0135	0·0135	15	12
200	0·0271	0·0270	15	11
220	0·0541	0·0541	18	17
*310	0·0676	0·0676	81	70
101	0·0859	0·0861	4	4
400	0·1085	0·1082	4	4
*211	0·1132	0·1132	22	19
330	0·1212	0·1217	1	1
*420	0·1352	0·1352	12	13
301	0·1403	0·1402	54	58
*321	0·1674	0·1672	6	5
*510	0·1757	0·1758	10	13
*411	0·1944	0·1943	22	24
440	0·2157	0·2163	1	1
*530	0·2305	0·2298	2	2
600	0·2434	0·2434	12	19
501	0·2492	0·2484	2	0
521	0·2755	0·2754	21	30
002	0·3172	0·3174	6	11
*611	0·3284	0·3295	4	5
550	0·3382	0·3380	1	1
*541	0·3567	0·3565	17	28
*312 *631	0·3850	0·3850 0·3836	6	12
*730	0·3914	0·3921	3	4

* $I_{hkl}\neq I_{khl}$. These are summed for I_c.

Table 3. *Crystallographic data for high-pressure* $\mathrm{KAlSi_3O_8}$

Symmetry: Tetragonal
Lattice parameters: $a=9{\cdot}38$, $c=2{\cdot}74\pm0{\cdot}01$ Å
$D_x=3{\cdot}84$ g.cm^{-3}
$Z=2$
Systematic absent reflexions: hkl with $h+k+l\neq2n$
Space group: $I4/m$

Atomic positions*:	x	y	z
K in 2(b)	0	0	$\frac{1}{2}$
($\frac{1}{4}$ Al, $\frac{3}{4}$ Si) in 8(h)	0·167	0·384	0
O(1) in 8(h)	0·208	0·152	0
O(2) in 8(h)	0·152	0·542	0

* From the isomorphous phase $\mathrm{Ba}_x\mathrm{Mg}_x\mathrm{Ti}_{4-x}\mathrm{O}_8$ (Dryden & Wadsley, 1958).

The present result shows that the reaction

$$\mathrm{KAlSi_3O_8}\ \xrightarrow[900\,^{\circ}\mathrm{C}]{120\ \mathrm{kb}}\ \mathrm{KAlSi_3O_8} \qquad (1)$$

orthoclase or sanidine — hollandite

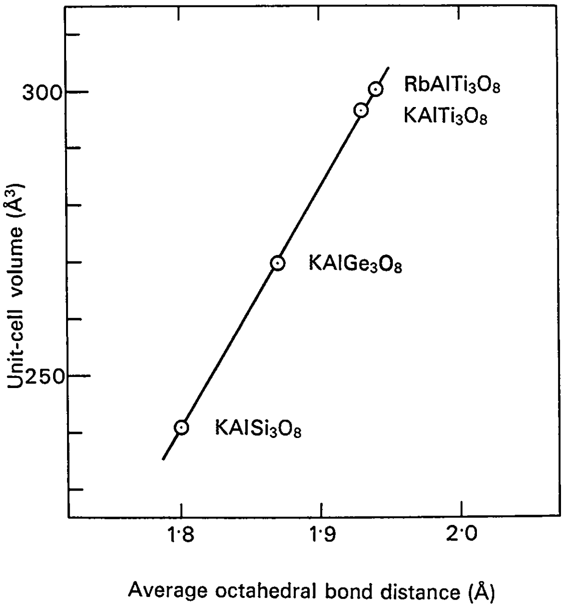

Fig. 1. Volume of unit cell *versus* octahedral bond distance in isomorphous structures.

is accompanied by a change of density from 2·55 to 3·84 g.cm^{-3}, an increase of 50%.

Under similar conditions natural leucite, whose composition is more appropriate to the mantle, disproportionated into hollandite together with a second phase we believe to be high-pressure $KAlO_2$

$$\underset{\text{leucite}}{3KAlSi_2O_6} \rightarrow \underset{\text{hollandite}}{2KAlSi_3O_8} + KAlO_2 \qquad (2)$$

but $KAlSiO_4$ remained unchanged. The germanium analogue $KAlGe_2O_6$ as well as $KAlGeO_4$ were both transformed at 90 kb and 900 °C according to the equations

$$3KAlGe_2O_6 \rightarrow 2KAlGe_3O_8 + KAlO_2 \qquad (3)$$

and

$$3KAlGeO_4 \rightarrow KAlGe_3O_8 + 2KAlO_2 . \qquad (4)$$

The unit-cell dimensions of tetragonal $KAlGe_3O_8$ in both cases were close to those reported by Kume, Matsumoto & Koizumi (1966). Only in reaction (4) was there sufficient $KAlO_2$ to record a good diffraction pattern, which could be indexed on the basis of a primitive tetragonal unit cell with $a = 9{\cdot}27$, $c = 2{\cdot}84$ Å. Although these dimensions resemble those of a hollandite-like phase the symmetry group is lower; we will report the structure in due course.

There are a number of reported studies on the pressure-temperature relationships of potassium feldspars. Lindsley (1966) showed that $KAlSi_3O_8$ transformed to leucite below 20 kb and temperatures above 1150°, and melted congruently to a liquid at temperatures and pressures above a triple point. The dry feldspar is stable up to 60 kb and 1000 °C (Seki & Kennedy, 1964). The present work shows that at higher pressures still the transition to the hollandite form becomes possible.

Feldspars are among the most abundant primordial minerals in the continental crust and pressures of 120 kb are not very high, geologically considered. Hence this study indicates strongly that the hollandite form, with octahedral silicon, may be present at no great depth in the transition zone in the mantle. It may even occur among surface minerals of igneous origin or, in the same way as naturally occurring stishovite (Chao, Fahey, Littler & Milton, 1962), be produced by meteoric impact.

The relationship between $KAlTi_3O_8$, $KAlGe_3O_8$ and $KAlSi_3O_8$, as well as that between $NaScTiO_4$, $NaAlGeO_4$ and (predicted) $NaAlSiO_4$ (Reid, Wadsley & Ringwood, 1967) indicates that not only is the transformation of germanate analogues a useful means of predicting the structure of silicates, but also that the crystal chemistry of titanates already existing should be equally useful as a guide to the structures of high pressure silicates containing six-coordinated silicon.

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