

Six-Coordinate Silicon: High Pressure Strontium and Barium Aluminosilicates with the Hollandite Structure

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Strontium and barium aluminosilicates have been converted at 100–120 kbars and 900C to new dense phases having the tetragonal hollandite structure, in which all aluminium and silicon are six-coordinated, and in which strontium and barium show partial occupancy of the available structural sites. The new phases have the compositions $\text{Sr}_x\text{Al}_{2x}\text{Si}_{4-2x}\text{O}_8$ and $\text{Ba}_x\text{Al}_{2x}\text{Si}_{4-2x}\text{O}_8$, with $x \approx 0.75$, and lattice parameters $a = 9.32$, $c = 2.72$ Å and $a = 9.415$, $c = 2.72$ Å, respectively. Hollandite phases with the ideal feldspar compositions $\text{SrAl}_2\text{Si}_2\text{O}_8$ and $\text{BaAl}_2\text{Si}_2\text{O}_8$ could not be formed, in contrast to the behavior of KAlSi_3O_8 , and sodium, calcium and rubidium aluminosilicates did not give rise to high pressure hollandite phases at any appropriate composition.

The members of the feldspar group of minerals are the most abundant constituents of the Earth's crust (1), and their behavior at high pressures is relevant to the physical and chemical state of the upper mantle of the Earth. It is particularly important to determine whether the common crustal minerals have high pressure counterparts, and are able to retain their chemical identity in the mantle. The behavior of the less common minerals needs also to be elucidated in order to determine both their probable genesis and the ability of their high pressure polymorphs or reaction products to form solid solutions with other high pressure phases. This behavior will determine the distribution in the mantle of the elements which they contain.

We have recently shown (2) that sanidine, KAlSi_3O_8 , can be transformed at 120 kbars and 900C to the high density hollandite (3) structure, with all silicon and aluminium six-coordinated to oxygen atoms, and with the large potassium ions contained in linear "tunnels" formed by the conjunction of the metal-oxygen octahedra. It was of interest to determine whether other feldspars, or initially, their germanate analogs, could follow suit. Germanium albite, $\text{NaAlGe}_3\text{O}_8$, and $\text{RbAlGe}_3\text{O}_8$ were transformed to hollandite form, as noted previously (4), and Kume *et al.* (5) have shown that KAlGe_3O_8 (feldspar-type) can be similarly transformed. On the other hand $\text{NaAlSi}_3\text{O}_8$ is known (6, 7) to disproportionate to jadeite, $\text{NaAlSi}_2\text{O}_6$,

which contains (8) aluminium six-coordinated and silicon four-coordinated, and is stable to pressures in excess of 200 kbars (9, 10).

We have therefore extended our investigation to the calcium, strontium, barium and, rubidium aluminosilicates with the feldspar composition. These compounds showed a wide variation in their high pressure behavior, and only in the strontium and barium systems could phases with the hollandite structure be obtained.

Experimental

Homogeneous crystalline compounds of established structure, or homogeneous glasses made by quenching melts of appropriate composition, were used as starting materials. The compositions examined were the silicates $\text{CaAl}_2\text{Si}_2\text{O}_8$ (anorthite), $\text{Ca}_{0.5}\text{AlSi}_3\text{O}_8$, $\text{SrAl}_2\text{Si}_2\text{O}_8$, $\text{Sr}_{0.5}\text{AlSi}_3\text{O}_8$, $\text{BaAl}_2\text{Si}_2\text{O}_8$ (celsian), $\text{Ba}_{0.5}\text{AlSi}_3\text{O}_8$, $\text{RbAlSi}_3\text{O}_8$, $\text{CsAlSi}_2\text{O}_6$ (pollucite) and $\text{CsFeSi}_2\text{O}_6$; and the germanates $\text{NaAlGe}_3\text{O}_8$ and $\text{RbAlGe}_3\text{O}_8$. In each case a few milligrams of the finely ground material, moistened with a trace of water, was allowed to react at 100 and 120 kbars and 900C for several minutes (11), and the specimen was cooled to room temperature while still under pressure.

The resulting materials, of which approximately 1 mg was usually recoverable, were examined optically as well as by X-ray powder photography, using $\text{CuK}\alpha$ radiation and a Debye-Scherrer

TABLE I
HIGH PRESSURE ALUMINOSILICATES AND ALUMINOGERMANATES WITH THE
TETRAGONAL HOLLANDITE STRUCTURE

	Lattice parameters, Å		Ref.
	$a, \pm .01$	$c, \pm .01$	
$Ba_xAl_{2x}Si_{4-2x}O_8^a$	9.41 ₅	2.72	This work
$Sr_xAl_{2x}Si_{4-2x}O_8^b$	9.32	2.72	This work
$KAlSi_3O_8$	9.38	2.74	Ringwood, Reid, and Wadsley (2)
$RbAlGe_3O_8$	9.78	2.86	This work
$KAlGe_3O_8$	9.72	2.86	Kume, Matsumoto, and Koizumi (5)
$NaAlGe_3O_8^c$	$9.648 \pm .005$	$2.856 \pm .005$	This work

^a $x \approx 0.75$.

^b x assumed to be approximately 0.75 by analogy with the Ba compounds.

^c Data obtained with a Guinier camera, with an internal KCl standard included with the sample.

camera of 114-mm radius. Careful attention was paid to back angle measurements in order to obtain accurate lattice parameters. Where appropriate, intensities were measured visually with a calibrated film strip. Unit cell parameters, Table I, were obtained in each case by a least squares fit of the powder data.

Preliminary experiments showed that anorthite, $CaAl_2Si_2O_8$, completely disproportionated at 100 kbars and 900C into a complex mixture of the garnet grossular, $Ca_3Al_2Si_3O_{12}$; kyanite, Al_2SiO_5 ; and the rutile form of SiO_2 (stishovite (12)). This parallels the work of Hays (13), who observed that anorthite was decomposed to grossular, kyanite, and quartz at pressures up to 35 kbars.

$SrAl_2Si_2O_8$ was converted almost entirely into a very well crystallized cubic or pseudocubic phase (14), but a few lines ascribable to a hollandite phase could also be identified. A sample of celsian, $BaAl_2Si_2O_8$, gave a strong hollandite pattern after transformation, but a considerable amount of a second phase was also present. Rubidium feldspar, $RbAlSi_3O_8$, gave an entirely new phase, which was found (4) to be isomorphous with the products of transformation of $RbAlSi_2O_6$, $CsAlSi_2O_6$ (pollucite) and $CsFeSi_2O_6$. It has not yet been determined whether the stoichiometry of this phase corresponds to the feldspar or the pollucite composition. In any case, the transformation of $RbAlGe_3O_8$ was not paralleled by that of the silicate.

The behavior of the Sr and Ba feldspars indicated

the formation of nonstoichiometric hollandite phases characterized by a partial occupancy of the "tunnel" sites available to the alkaline earth metals. Such a nonstoichiometric hollandite structure is typical of a number of manganese minerals (3), the titanium mineral priderite (15), and many synthetic titanium-based compounds (16-18), for all of which the general formula $A_xM_4O_8$ can be written, where A is the "tunnel" ion, M the metal or metals in octahedral sites, and x lies in range 0.5-1.00. We accordingly examined the compositions $Ca_{0.5}AlSi_3O_8$, $Sr_{0.5}AlSi_3O_8$ and $Ba_{0.5}AlSi_3O_8$ using glasses as starting materials. Disproportionation to complex mixtures still occurred in the calcium case, but the products of transformation of the strontium and barium systems gave well defined hollandite powder patterns together with a few additional lines.

On the basis of a random 50% occupancy of tunnel sites, the X-ray scattering power of $\frac{1}{2}Sr$ (atomic number 38) would be extremely close to that of K (atomic number 19), and the relative intensities of the powder diffraction lines of high pressure " $Sr_{0.5}AlSi_3O_8$ " were similar to those of the hollandite form of $KAlSi_3O_8$. The powder pattern intensities of high pressure " $Ba_{0.5}AlSi_3O_8$ " were rather different from those of $KAlSi_3O_8$, with the $hh0$ reflections being particularly affected. This may be expected from the very different scattering power of Ba and K, which occupy identical special positions in the structure. A set of intensities for $Ba_{0.5}AlSi_3O_8$ was

TABLE II
 VARIATION IN DIFFRACTION INTENSITY^a WITH Ba CONTENT OF
 $Ba_xAl_{2x}Si_{4-2x}O_8$

<i>hkl</i>	Ba occupancy, <i>x</i> (I_{calc}^b)				I_{obs}
	0.50	0.60	0.70	0.75	
100	0	2.4	7	10	9
200	0.7	0.1	1.4	2.4	2
220	24	26	25	23	27
411 ^c	35	32	27	25	22

^a For the two most sensitive reflections, (110) and (200), and two easily measured reflections of relatively constant calculated intensity.

^b Normalized to I_{obs} in the Table.

^c Intensities are summed for 411 and 141.

calculated using the fractional atomic coordinates found for the isomorphous phase $Ba_{0.5}Mg_{0.5}Ti_{3.5}O_8$ (16). Except for (110) and (200) these showed fairly satisfactory agreement with the relatively

TABLE III
 POWDER DIFFRACTION PATTERN OF TETRAGONAL
 $Ba_xAl_{2x}Si_{4-2x}O_8$ $CuK\alpha$ RADIATION

<i>hkl</i>	$\sin^2 \theta_{obs}$	$\sin^2 \theta_{calc}$	I_{obs}	I_{calc}^a $x = 0.75$
110	.0134	.0134	9	8
200	.0270	.0268	2	2
220	.0536	.0536	27	19
310	.0672	.0670	100	99
101	.0869	.0871	9	11
400	.1078	.1073	3	<1
211	.1139	.1139	12	35
330	.1210	.1208	3	3
420	.1334	.1341	24	22
301	.1409	.1407	39	28
321	.1675	.1675	6	17
510	.1740	.1743	9	13
411	.1941	.1944	22	20
440	.2134	.2145	4	2
530	.2277	.2279	4	7
600	.2408	.2413	12	8
521	.2748	.2749	24	23
002	.3220	.3215	3	4
611	.3286	.3284	3	9
541	.3553	.3552	21	19
631	.3821	.3840	3	7
312	.3882	.3886	15	10

^a $I_{hkl} \neq I_{khl}$. Calculated intensities have been summed for *hkl*, *khl*. Intensity units arbitrary.

crude observed intensities, with $R = 100\sum(I_o - I_c)/\sum I_o$ being 30%. However, a series of calculations for different occupancies in the general composition $Ba_xAl_{2x}Si_{4-2x}O_8$ showed that the agreement for the (110) and (200) reflections was greatly improved at $x = 0.70$ to $x = 0.75$, Table II, and that the overall *R* factor was reduced to 26% for this range of compositions. The value of 0.75, which is probably an upper limit, was chosen for the calculation of the intensities shown in Table III. The lattice parameters for the new high pressure hollandite phases, together with those for the other high pressure hollandites so far known, are listed in Table I.

Discussion

The partial occupancy found for Sr^{2+} and Ba^{2+} is probably due to a combination of several effects. The diameter of the Ba^{2+} ion is virtually the same as the dimension of the *c* axis, and overcrowding of the sites would result if they were all filled. Ba^{2+} is also more highly charged than K^+ , although almost the same size, and repulsion between ions on contiguous sites is therefore greater. There is no ready explanation for the apparent lower stability of the Sr^{2+} aluminosilicate hollandite, nor for the nonoccurrence of the calcium phase, except that alternative phases may be more stable. Similar behavior is found in titanate based hollandites, where K^+ (17) and Ba^{2+} (16) can enter the structure, but Ca^{2+} cannot be made to do so. $CaTiO_3$ for example forms as a separate phase from $CaO-Fe_2O_3-TiO_2$ compositions appropriate to the hollandite structure (21).

The feldspar-forming alkali and alkaline earth metals Na, K, Rb, Ca, Sr, and Ba are seen to enter a variety of different and more dense aluminosilicate

structures at high pressure. For Na, the stable high-pressure phase is jadeite, $\text{NaAlSi}_2\text{O}_6$, (6, 7, 9, 10) which would be expected (19) ultimately to disproportionate into stishovite and NaAlSiO_4 with the calcium ferrite structure and with all Al and Si six-coordinated. For K, Sr, and Ba, the hollandite structure, in which all Al and Si are six-coordinated, is readily formed. For Rb (and Cs) yet another new dense structure occurs (4, 20), although moderate quantities of rubidium can probably substitute for potassium in a high pressure hollandite phase. The calcium system appears to favour the garnet structure at intermediate pressures, as found in this work and that of Hays (13), but at pressures in excess of 150 kbars, the calcium garnet may further disproportionate into even more dense species such as CaSiO_3 (perovskite) plus Al_2O_3 (corundum).

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