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# THE CRYSTAL STRUCTURE OF STRONALSITE AND A REDETERMINATION OF THE STRUCTURE OF BANALSITE

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## ABSTRACT

The structures of stronalsite, $SrNa_2Al_4Si_4O_{16}$, and banalsite, $BaNa_2Al_4Si_4O_{16}$, have been determined by direct methods using single-crystal X-ray diffractometry with a CCD area detector. The structures are topologically identical and adopt the non-centrosymmetric space-group *Iba*2 rather than the centrosymmetric space-group *Ibam* previously ascribed to banalsite. Unit-cell parameters are: $a$ 8.4080(9), $b$ 9.8699(11), $c$ 16.7083(18) Å, $V$ 1386.6(3) Å$^3$, $Z = 4$, $D_{calc.}$ 2.92 g/cm$^3$ for stronalsite (Khibina massif, Kola, Russia); $a$ 8.5400(7), $b$ 10.0127(9), $c$ 16.7897(14) Å, $V$ 1435.7(2) Å$^3$, $D_{calc.}$ 3.05 g/cm$^3$ for banalsite from Wales (Benallt mine, UK), and $a$ 8.5068(16), $b$ 9.9811(18), $c$ 16.7485(31) Å, $V$ 1422.1(5) Å$^3$, $D_{calc.}$ 3.08 g/cm$^3$ for banalsite from Långban (Sweden). The structures are built on an infinite framework of corner-sharing tetrahedra, with Si and Al being completely ordered at four independent sites. Alternately pointing up (U) and down (D) Si(1)–Al(1) and Si(2)–Al(2) tetrahedra form four- and eight-fold rings parallel to the (001) plane, resulting in a –UDUD– framework, which differs from the –UUDD– framework of feldspars. The stacking results in six-fold rings parallel to the (100) plane. The interstices of the framework are occupied by large Sr or Ba atoms ($^{X}A^{2+}$), and smaller $^{VI}Na^+$, ordered at alternate levels parallel to (001), and separated by ¼ $\mathbf{c}$. The isostructural character of banalsite and stronalsite accords well with the complete solid-solution $Ba_{1-x}Sr_xNa_2Al_4Si_4O_{16}$ occurring in nature.

*Keywords*: tectosilicate, stronalsite, banalsite, crystal structure, lisetite, solid solution, feldspar.

## SOMMAIRE

Nous avons déterminé la structure de la stronalsite, $SrNa_2Al_4Si_4O_{16}$, et celle de la banalsite, $BaNa_2Al_4Si_4O_{16}$, par méthodes directes au moyen de données en diffraction X prélevées sur monocristaux et d'un détecteur à aire CCD. Les structures sont topologiquement identiques; elles adoptent le groupe d'espace non centrosymétrique *Iba*2 plutôt que le groupe centrosymétrique *Ibam* attribué antérieurement à la banalsite. Les paramètres réticulaires sont: $a$ 8.4080(9), $b$ 9.8699(11), $c$ 16.7083(18) Å, $V$ 1386.6(3) Å$^3$, $Z = 4$, $D_{calc}$ 2.92 g/cm$^3$ pour la stronalsite (complexe de Khibina, péninsule de Kola, Russie); $a$ 8.5400(7), $b$ 10.0127(9), $c$ 16.7897(14) Å, $V$ 1435.7(2) Å$^3$, $D_{calc}$ 3.05 g/cm$^3$ pour la banalsite provenant du Pays de Galles (mine Benallt, UK), et $a$ 8.5068(16), $b$ 9.9811(18), $c$ 16.7485(31) Å, $V$ 1422.1(5) Å$^3$, $D_{calc}$ 3.08 g/cm$^3$ pour la banalsite de Långban (Suède). Les structures contiennent une trame infinie de tétraèdres partageant leurs coins, avec Si et Al complètement ordonnés sur quatre sites indépendants. Les tétraèdres Si(1)–Al(1) et Si(2)–Al(2) pointent en alternance vers le haut (U) et vers le bas (D) pour former des anneaux à quatre et huit membres parallèles à (001), ce qui mène à une trame –UDUD–, distincte de la trame –UUDD– des feldspaths. L'empilement mène à des anneaux à six membres parallèles au plan (100). Les interstices de cette trame contiennent les gros atomes Sr ou Ba ($^{X}A^{2+}$) et les atomes plus petits de $^{VI}Na^+$, ordonnés à des niveaux alternants parallèles à (001), avec une séparation de ¼ $\mathbf{c}$. Le caractère isostructural de la banalsite et de la stronalsite explique la solution solide complète $Ba_{1-x}Sr_xNa_2Al_4Si_4O_{16}$ observée dans la nature.

(Traduit par la Rédaction)

*Mots-clés*: tectosilicate, stronalsite, banalsite, structure cristalline, lisetite, solution solide, feldspath.

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## INTRODUCTION

Tectosilicates with the stoichiometry $ANa_2Al_4Si_4O_{16}$ include banalsite, stronalsite, and lisetite, where $A$ = Ba, Sr, and Ca, respectively (Deer *et al.* 2001). Only limited crystallochemical data for these rare minerals are available. In common with feldspars, their structures are built on an infinite framework of four- and eightfold irregular rings of corner-shared tetrahedra. Apical atoms of oxygen of the rings point alternately up (U) and down (D) with respect to the (001) plane in banalsite, [the (100) plane in lisetite, nonstandard space-group $Pbc2_1$], giving rise to a –UDUD– framework, which is one of the four possible ways to built up rings of tetrahedra (Smith & Rinaldi 1962). This arrangement differs from the –UUDD– framework of feldspars (Haga 1973, Rossi *et al.* 1986), and is similar to the framework in nepheline, which consists of regular and irregular six-membered –UDUD– rings (Tait *et al.* 2003).

In this paper, we present the results of the crystal-structure study of single crystals of stronalsite and banalsite. Discussion of the crystal chemistry, genesis and parageneses of stronalsite, banalsite and their naturally occurring complete solid-solution series are presented in Liferovich *et al.* (2006).

## BACKGROUND INFORMATION

In the structure model presented for lisetite in space group $Pbc2_1$ (nonstandard setting of $Pca2_1$) and nonstandard origin, offset by [¼, ¼, 0], Si and Al are fully ordered at the tetrahedral positions of the framework, and the intraframework $^{VII}$Ca and $^{VI}$Na cations are distributed throughout common $Ca + 2Na$ layers (Rossi *et al.* 1986). This structural model is in accord with the composition of lisetite and the aluminum-avoidance principle (Loewenstein 1954) for tectosilicates with a Si-to-Al ratio of unity (Smith *et al.* 1986). In contrast, the structure of banalsite was originally described as a framework of tetrahedra with a disordered distribution of Si and Al but with ordering of $^{X}$Ba and $^{VI}$Na cations into alternate layers owing to "the large difference in their ionic radii" (Rossi *et al.* 1986). The structure was considered in the centrosymmetric space-group *Ibam* by Haga (1973). This structural model does not seem to be reasonable given that the same Si-to-Al ratio occurs in both banalsite and lisetite.

Stronalsite has an X-ray powder-diffraction pattern very similar to that of banalsite (Matsubara 1985). In the absence of a structure refinement, stronalsite has been assumed to be isostructural with *Ibam* banalsite, although the possibility of complete ordering of Si and Al, resulting in an *Iba*2 polymorph, was also considered by Matsubara (1985) and Hori *et al.* (1987).

The small grain-size and compositional heterogeneity of stronalsite from previously known occurrences (*e.g.* Fig. 1a) have precluded a determination of the structure. Stronalsite occurs as crystals measuring up to 4 mm in size in drill-core material collected from the Khibina peralkaline complex, Kola alkaline province, Russia. The remarkable compositional homogeneity of these crystals (Fig. 1b) permitted us to undertake the first single-crystal determination of the structure of stronalsite.

As expected on the basis of the aluminum-avoidance rule (Loewenstein 1954), the results of the refinement of the structure of stronalsite is consistent with an ordered distribution of Si and Al in independent tetrahedral sites (see below). We considered that ordering of Si and Al, similar to that found in stronalsite and lisetite on the basis of the 1:1 Si to Al ratio, should also occur in banalsite. The extensive banalsite–stronalsite solid solution that is known to exist in nature (Matsubara 1985, Koneva 1996, Liferovich *et al.* 2006) also suggests their close structural similarity. In this context, we have used single-crystal X-ray methods for the determination of the structure of stronalsite from Khibina and a redetermination of the structure of banalsite from two localities; the type locality in Wales (Benallt mine, Rhiw, Lleyn Peninsula, UK) and from Långban, (Värmland, Filipstadt, Sweden) (Figs. 1c and 1d, respectively) and have confirmed that these sodic tectosilicates of Sr and Ba are isostructural.

## EXPERIMENTAL

The sample containing stronalsite was collected from a drill core derived from a depth of 182 m in the tectonomagmatic contact zone between a semicircular ijolite–urtite body and nepheline syenite in the north-eastern segment of the Khibina peralkaline complex, Kola alkaline province, Russia. The sample represents an altered xenolith of cuspidine–melilitolite rock, which is unusual for this sodic peralkaline complex. A detailed description of this rock and of its metasomatic alteration is given by Khomyakov *et al.* (1990). On the basis of textural relationships, stronalsite is interpreted as a late phase formed by alteration of nepheline or an unusual Sr-rich melilite (or both). In turn, stronalsite is commonly subjected to low-temperature alteration. Slightly altered stronalsite shows anomalous interference-colors and cloudy extinction in transmitted light, as a result of changes in composition and significant deviations from the theoretical stoichiometry due to leaching of Na. Further alteration results in replacement of stronalsite by a fine-grained mixture of strontianite and unidentified zeolites. Unaltered stronalsite is preserved only where mantled by andradite or clinopyroxene (Fig. 1b). The paragenesis of the Khibina stronalsite is similar to that described in melilitolite from the Turiy Mys peralkaline complex, Kola alkaline province, Russia (Dunworth & Bell 2003).

Descriptions of the banalsite occurrences in Mn-rich ores from the Benallt mine (Wales, UK) and

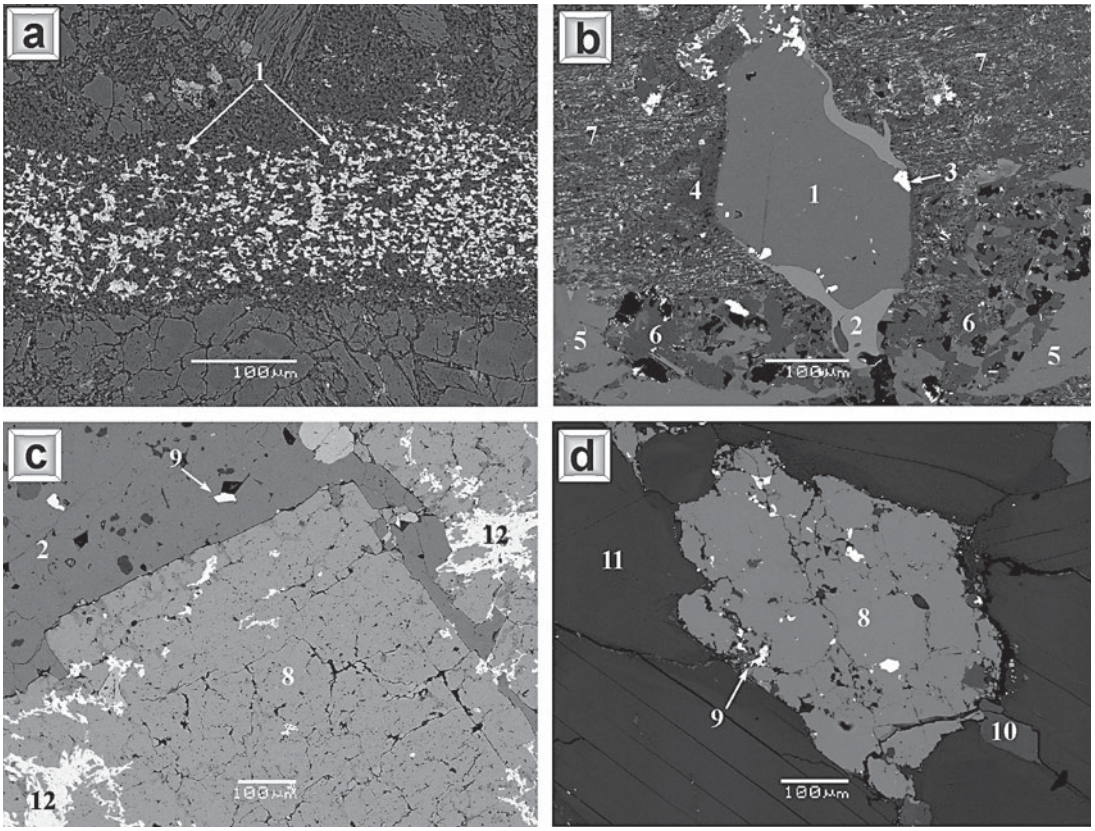

FIG. 1. Back-scattered electron images of (a) stronalsite in an altered ultramafic xenolith from a jadeitic rock (Ohsa, Rendai, Japan), (b) stronalsite in an altered cuspidine–melilite xenolith from nepheline syenite (Khibina, Kola alkaline province, northwestern Russia), (c) banalsite in manganiferous metasediment (type-locality occurrence at Benallt mine, Wales, Rhiw, Lleyn Peninsula, UK), (d) banalsite in an alkaline metasomatic rock (Långban, Värmland, Filipstadt, Sweden). 1 Stronalsite, 2 andradite, 3 strontianite, 4 richterite, 5 burbankite, 6 pectolite, 7 complex fine-grained mixture composed predominantly of zeolites; 8 banalsite, 9 barite, 10 clinopyroxene, 11 phlogopite.

micaceous alkaline metasomatic assemblages from Långban, Sweden, are given by Campbell Smith (1945), Campbell Smith *et al*. (1944a, b), and Welin (1968), respectively.

### *Composition of stronalsite and banalsite*

The compositions of stronalsite and banalsite were determined by energy-dispersion X-ray spectrometry using a JEOL JSM–5900 scanning electron microscope equipped with a Link ISIS 300 analytical system incorporating a Super ATW Element Detector (133 eV FWHM Mn*K*). Raw EDS spectra were acquired for 130 s (live time) with an accelerating voltage of 20 kV, and beam current of 0.475 nA on a Ni standard. The spectra were processed with the LINK ISIS–SEMQUANT quantitative software package, with full ZAF corrections applied. The following well-characterized mineral and synthetic standards were used: jadeite (Na), wollastonite (Ca), orthoclase (K), corundum (Al), glass of pyroxene composition DJ35 (Si), barite (Ba), and $SrTiO_3$ (Sr). Other elements were sought, but not detected.

To reduce analytical errors due to the possible loss of Na resulting from electron-beam damage, we employed raster scanning and reduced the counting periods to 50 s (live time). Reproducibility of the compositions of stronalsite and banalsite within the analytical errors, and agreement of the atomic proportions of elements present for all samples with the theoretical stoichiometry of stronalsite and banalsite (Table 1), demonstrate that the compositions determined are accurate. The accuracy of our EDS method has been cross-checked numerous times by the analysis of diverse sodic silicate and oxide minerals by wavelength-dispersion electron-microprobe analysis (WDS–EMPA) using an automated CAMECA SX–50 microprobe (University of Manitoba) following methods described by Mitchell & Vladykin (1993) and Chakhmouradian & Mitchell (1999, 2002). In addition, the accuracy of analyses of stronalsite and banalsite was cross-checked by the analysis of nepheline, feldspar, analcime and natrolite associated with these minerals.

### *CCD single-crystal X-ray diffraction*

Compositionally homogeneous crystals of stronalsite and banalsite were located in polished thin sections using back-scattered-electron imagery (Figs. 1b, c, d) and then extracted under a binocular optical microscope. Optically homogeneous fragments were then selected using an immersion liquid. Fragments of stronalsite and banalsite crystals were mounted on a Bruker PLATFORM three-circle X-ray diffractometer, operating at 50 keV and 40 mA, equipped with a 4K APEX CCD detector and a crystal-to-detector distance of 4.7 cm. A sphere of three-dimensional data was collected using graphite-monochromatized Mo$K\alpha$ X-radiation ($\lambda$ = 0.71073 Å) and frame widths of 0.3° $\omega$, with count-times per frame of 20 s (stronalsite) or 15 s (banalsite). Comparison of the intensities of equivalent reflections measured at different times during data acquisition showed no significant decay for any of the datasets. The unit-cell parameters of stronalsite and banalsite and data-collection parameters are listed in Table 2. The three-dimensional intensity data were reduced and corrected for Lorentz, polarization, and background effects using the Bruker program Saint. A semi-empirical correction for absorption was applied with the program Xprep (Sheldrick 1998) to each dataset on the basis of intensities of equivalent reflections, and in each case the crystal shape was modeled as an ellipsoid.

TABLE 1. COMPOSITION OF STRONALSITE AND BANALSITE

| | Stronalsite | | Banalsite | | |
|---|---|---|---|---|---|
| | Khibina | Ideal comp. | Benallt mine, Wales | Långban | Ideal comp. |
| $SiO_2$ wt.% | 39.6 | 39.41 | 36.4 | 36.2 | 36.44 |
| $Al_2O_3$ | 33.5 | 33.44 | 31.0 | 31.4 | 30.92 |
| BaO | - | - | 22.9 | 23.4 | 23.25 |
| SrO | 16.0 | 16.99 | - | - | - |
| CaO | 0.2 | - | 0.2 | - | - |
| $Na_2O$ | 10.4 | 10.16 | 9.4 | 9.5 | 9.40 |
| Total | 99.7 | 100.0 | 99.9 | 100.5 | 100.0 |
| Si *apfu* | 4.01 | 4 | 3.99 | 3.96 | 4 |
| Al | 3.99 | 4 | 4.01 | 4.04 | 4 |
| Ba | - | - | 0.98 | 1.00 | 1 |
| Sr | 0.94 | 1 | - | - | - |
| Na | 2.04 | 2 | 2.00 | 2.00 | 2 |
| Ca | 0.02 | - | 0.02 | - | - |

-: below detection limit. The number of cations is based on 16 atoms of oxygen per formula unit (*apfu*).

The Atoms 6.0 software package (Dowty 1999) was used to determine angles describing the distortion of coordination polyhedra and selected bond-lengths. The Ivton 2.0 program (Balić-Žunić & Vicković 1996) was employed to characterize the coordination spheres of the cations, volumes of coordination polyhedra, and displacements (shifts) of cations from the centroids of coordination polyhedra.

## Structure Refinement

Scattering curves for neutral atoms, together with corrections for anomalous dispersion, were taken from International Tables for X-ray Crystallography (Wilson 1992). The Shelxtl Version 5 series of programs was used for the solution and refinement of the crystal structures (Sheldrick 1998). The structures of stronalsite and banalsite were solved by direct methods and were refined on the basis of $F^2$ for all unique data.

### *Stronalsite: structure solution*

Systematic absences of reflections for stronalsite are consistent with space groups *Ibam* and *Iba*2. We found it possible to refine the structure of stronalsite to an agreement factor ($R_1$ value) of approximately 4 to 5% in both the centrosymmetric *Ibam* and noncentrosymmetric *Iba*2 space-groups. All atoms can be refined with anisotropic displacement parameters. As a result of averaging, the uncertainties in bond lengths are lower in the centrosymmetric model.

Using the atom coordinates of Haga (1973) as a starting model, the crystal structure of stronalsite was refined in the *Ibam* centrosymmetric space-group to $R_1$ = 5.1% with GooF value of 1.13, $R_{\text{int}}$ = 12.3%, and $wR_2$ = 12.2% for 1515 independent reflections.

As the Si-to-Al ratio in stronalsite is unity (Table 1), we then attempted to model the structure with complete order of Si and Al. Direct methods were used to solve the stronalsite structure in space group *Iba*2. This noncentrosymmetric model resulted in a refinement of the structure to $R_1$ = 4.3%, GooF = 0.89, $R_{\text{int}}$ = 11.5%, and $wR_2$ = 9.2% for 2914 independent reflections (Table 2), *i.e.*, a better fit than for the centrosymmetric *Ibam* model. Assigning phases to a set of normalized structure-factors gave mean values of $|E^2 - 1|$ of 0.746 and 0.800 [generated from the intensity data by the software WinGx (Ferrugia 1999) and by Bruker XPREP (Sheldrick 1998), respectively], consistent with a noncentrosymmetric structure.

There is some correlation and anti-correlation (absolute maximum 0.81) in the *Iba*2 model among the refined parameters, because the structure can be viewed as being close to centrosymmetric. However, the degree of correlation is lower than would be expected if the structure was truly centrosymmetric and misdescribed in a non-centrosymmetric space-group, in which case the expected degree of correlation would be very close to unity (Massa 2004).

The structure solution in the *Iba*2 space group was assessed for the presence of higher symmetry using the ADDSYM SHELX routine in the program PLATON (Spek 2003). No higher symmetry was found, probably because of the non-equivalence of the Al and

TABLE 2. CELL DIMENSIONS AND MISCELLANEOUS DATA ABOUT THE REFINEMENT OF STRONALSITE AND BANALSITE

| | Stronalsite | | Banalsite | | |
|---|---|---|---|---|---|
| | Khibina, Russia* | Rendai, Japan[†] | Benallt mine, Wales* | Långban, Sweden* | Benallt mine, Wales[‡] |
| $a$ (Å) | 8.4080(9) | *8.407(2)* | 8.5400(7) | 8.5068(16) | *8.496(2)* |
| $b$ (Å) | 9.8699(11) | *9.886(2)* | 10.0127(9) | 9.9811(18) | *9.983(2)* |
| $c$ (Å) | 16.7083(18) | *16.691(5)* | 16.7897(14) | 16.7485(31) | *16.755(3)* |
| $V$ (Å$^3$) | 1386.6(3) | *1387.2* | 1435.7(2) | 1422.1(5) | *1421.1* |
| Space group | *Iba*2 | - | *Iba*2 | *Iba*2 | *Ibam* |
| $Z$ | 4 | - | 4 | 4 | 4 |
| Absorption coeff., $\mu$ (mm$^{-1}$) | 4.65 | - | 3.50 | 3.53 | - |
| $F$(000) | 1184.0 | - | 1256.0 | 1256.0 | - |
| $D_{\text{calc.}}$ (g/cm$^3$) | 2.922 | 2.943 | 3.052 | 3.081 | *3.045* |
| Crystal size (mm) | 0.15 ×<br>0.12 ×<br>0.02 | - | 0.12 ×<br>0.08 ×<br>0.03 | 0.08 ×<br>0.08 ×<br>0.06 | *0.10 ×*<br>*0.10 ×*<br>*0.06* |
| Count time /frame (s) | 20/0.3° | - | 15/0.3° | 15/0.3° | - |
| Radiation<br>filter | Mo*K*α<br>graphite | - | Mo*K*α<br>graphite | Mo*K*α<br>graphite | Mo*K*α |
| $2\theta$ range (°) | 4.88-69.06 | - | 4.86-68.86 | 4.86-69.22 | - |
| $R$(int) (%) | 11.5 | - | 6.11 | 5.52 | - |
| Reflections collected | 13570 | - | 13682 | 13859 | - |
| Independent reflections | 2914 | - | 2970 | 2979 | *1074* |
| $\lvert F_o \rvert \geq 4\sigma_F$ | 2077 | - | 2582 | 2615 | - |
| Goodness of fit on $F^2$ | 0.890 | - | 0.966 | 0.914 | - |
| Final $R_{1(\text{obs})}$ (%)<br>[$F_o > 4\sigma_F$] | 4.3<br>(5.1)[§] | - | 2.6<br>(3.4)[§] | 2.3<br>(3.0)[§] | - |
| $R_1$ (all data) (%) | 6.3 | - | 3.1 | 2.7 | *3.7* |
| $wR_2$ | 9.2 | - | 5.6 | 4.8 | - |
| Chemical formula | $SrNa_2Al_4Si_4O_{16}$ | - | $BaNa_2Al_4Si_4O_{16}$ | | |
| Formula weight | 609.858 | - | 659.565 | 659.565 | *659.565* |
| Parameters refined | 124 | - | 124 | 124 | - |
| Weighting $a$ | 0.01678 | - | 0.0178 | 0.0123 | - |
| Mean shift/*e.s.d.* | 0.000 | - | 0.000 | 0.000 | - |
| Peaks ($e$/Å$^3$) | 1.5-1.1 | - | 1.2-1.1 | 1.0-0.4 | - |

* Data from X-ray diffractometer. Data given *in italics* : [†] from Matsubara (1985; structure not refined), and [‡] from Haga (1973); - no data available.

$R1 = [\Sigma \lvert\lvert F_o \rvert - \lvert F_c \rvert\rvert] / \Sigma \lvert F_o \rvert \times 100$. $wR_2 = [\Sigma[w(F_o^2 - F_c^2)^2] / \Sigma[w(F_o^2)^2]]^{0.5} \times 100$, $w = 1/(\sigma^2(F_o^2) + (a \bullet P)^2 + b \bullet P)$, and $P = 1/3 \max(0, F_o^2) + 2/3 F_c^2$.

[§] for *Ibam* model

Si positions in the model. The inversion twin-law $[\bar{1}00/0\bar{1}0/00\bar{1}]$ was applied to the *Iba*2 refinement of the stronalsite structure to account for the possible presence of two enantiomorphic components. This resulted in a statistically zero twin-scale factor within the limits of analytical error, consistent with the presence of only one enantiomorph in the stronalsite crystal investigated.

Given the unambiguous *E*-statistics, excellent solution of the structure, the order of Al and Si, and the absence of twinning, we infer that a center of symmetry is absent, and consider that stronalsite crystallizes in the non-centrosymmetric space-group *Iba*2.

TABLE 3. FINAL POSITIONS AND DISPLACEMENT PARAMETERS OF ATOM IN STRONALSITE

| | $x$ | $y$ | $z$ | $U_{eq}$* |
|---|---|---|---|---|
| Sr(1) | 0 | ½ | 0.1541(1) | 0.0169(1) |
| Na(1) | -0.0430(2) | 0.3244(1) | -0.0955(3) | 0.0215(3) |
| Al(1) | 0.0693(3) | 0.1912(2) | 0.0635(1) | 0.0115(4) |
| Al(2) | -0.2771(2) | 0.4507(2) | 0.3106(1) | 0.0105(4) |
| Si(1) | -0.2631(2) | 0.5546(2) | -0.0017(1) | 0.0108(4) |
| Si(2) | 0.0770(2) | 0.8009(2) | 0.2457(1) | 0.0101(4) |
| O(1) | -0.2154(3) | 0.4911(3) | 0.4079(4) | 0.0161(6) |
| O(2) | -0.0023(9) | 0.2154(3) | 0.1593(4) | 0.0183(6) |
| O(3) | -0.0776(5) | 0.1427(5) | -0.0040(3) | 0.0139(9) |
| O(4) | 0.2248(6) | 0.9064(5) | 0.2488(3) | 0.0142(10) |
| O(5) | 0.2278(6) | 0.0760(6) | 0.0571(4) | 0.0156(10) |
| O(6) | -0.4485(5) | 0.3534(5) | 0.3100(4) | 0.0150(10) |
| O(7) | 0.1218(7) | 0.6472(4) | 0.2720(4) | 0.0164(11) |
| O(8) | -0.1155(6) | 0.6439(4) | 0.0327(3) | 0.0134(10) |

* $U_{eq}$ is defined as one third of the trace of the orthogonalized $U_{ij}$ tensor.

## *Banalsite: redetermination of the structure*

The structure of both banalsite samples was solved in space groups *Ibam* and *Iba*2 on the basis of the models presented for stronalsite discussed above. In common with stronalsite, all atoms can be refined with anisotropic displacement parameters in both the centrosymmetric and non-centrosymmetric models. As a result of averaging, the bond-length uncertainties are lower in the centrosymmetric model.

The crystal structure of banalsite from the type locality in Wales was refined in the centrosymmetric space-group *Ibam* to $R_1$ = 3.4% and a GooF value of 1.27, $R_{\text{int}}$ = 6.49%, $wR_2$ = 7.7% for 1544 independent reflections (Table 2). The non-centrosymmetric *Iba*2 model resulted in a refinement with $R_1$ = 2.6%, GooF = 0.97, $R_{\text{int}}$ = 6.11%, $wR_2$ = 5.6% for 2970 independent reflections (Table 2), *i.e.*, a better fit than for the centrosymmetric *Ibam* model previously reported by Haga (1973) for banalsite from this locality. The inversion twin-scale factor refined to zero within the limits of analytical error, indicating that the crystal investigated is composed entirely of a single enantiomorph.

The crystal structure of banalsite from Långban can also be refined in both centrosymmetric and non-centrosymmetric models, with the latter having the better agreement-factors: *Ibam* $R_1$ = 3.0%, GooF = 1.30, $R_{\text{int}}$ = 5.81%, $wR_2$ = 6.4% for 1548 independent reflections; *Iba*2 $R_1$ = 2.3%, GooF = 0.91, $R_{\text{int}}$ = 5.52%, $wR_2$ = 4.8% for 2979 independent reflections. The scale factor of the inversion twin-law, $[\bar{1}00/0\bar{1}0/00\bar{1}]$,

TABLE 4. FINAL POSITIONS AND DISPLACEMENT PARAMETERS OF ATOMS IN BANALSITE

| | Benallt mine, Wales* | | | | Långban, Sweden* | | | |
|---|---|---|---|---|---|---|---|---|
| | $x$ | $y$ | $z$ | $U_{eq*}$ | $x$ | $y$ | $z$ | $U_{eq}$* |
| Ba(1) | 0 | ½ | 0.1545(1) | 0.0112(1) | 0 | ½ | 0.1544(1) | 0.0107(0) |
| Na(1) | -0.0421(1) | 0.3258(1) | -0.0954(3) | 0.0185(2) | -0.0422(1) | 0.3256(1) | -0.0958(3) | 0.0187(2) |
| Al(1) | 0.0706(2) | 0.1862(2) | 0.0635(1) | 0.0086(4) | 0.0709(2) | 0.1865(2) | 0.0632(1) | 0.0091(4) |
| Al(2) | -0.2793(2) | 0.4453(2) | 0.3111(1) | 0.0096(4) | -0.2787(2) | 0.4452(2) | 0.3113(1) | 0.0087(3) |
| Si(1) | -0.2652(2) | 0.5596(2) | -0.0025(1) | 0.0076(3) | -0.2655(2) | 0.5595(2) | -0.0024(1) | 0.0082(3) |
| Si(2) | 0.0789(2) | 0.8062(2) | 0.2462(1) | 0.0084(3) | 0.0787(2) | 0.8065(2) | 0.2459(1) | 0.0081(3) |
| O(1) | -0.2141(2) | 0.4846(2) | 0.4076(5) | 0.0129(4) | -0.2142(2) | 0.4851(2) | 0.4073(5) | 0.0127(4) |
| O(2) | -0.0056(6) | 0.2077(2) | 0.1582(5) | 0.0147(5) | -0.0052(5) | 0.2076(2) | 0.1580(5) | 0.0143(5) |
| O(3) | -0.0752(4) | 0.1448(4) | -0.0051(3) | 0.0119(8) | -0.0757(4) | 0.1439(4) | -0.0049(3) | 0.0124(7) |
| O(4) | 0.2223(5) | 0.9130(5) | 0.2492(3) | 0.0109(8) | 0.2223(4) | 0.9139(5) | 0.2499(3) | 0.0112(8) |
| O(5) | 0.2258(5) | 0.0714(5) | 0.0548(3) | 0.0133(9) | 0.2262(5) | 0.0719(5) | 0.0553(3) | 0.0140(9) |
| O(6) | -0.4499(4) | 0.3538(4) | 0.3112(3) | 0.0108(7) | -0.4499(4) | 0.3532(4) | 0.3114(3) | 0.0110(7) |
| O(7) | 0.1288(5) | 0.6553(4) | 0.2722(3) | 0.0119(8) | 0.1285(4) | 0.6548(4) | 0.2722(3) | 0.0124(8) |
| O(8) | -0.12181(5) | 0.6522(4) | 0.0317(3) | 0.0113(8) | -0.1222(5) | 0.6523(4) | 0.0312(3) | 0.0115(8) |

* $U_{eq}$ is defined as one third of the trace of the orthogonalized $U_{ij}$tensor.

TABLE 5. SELECTED CRYSTALLOCHEMICAL PARAMETERS FOR TETRAHEDRALLY COORDINATED ATOMS IN STRONALSITE AND BANALSITE

| | Stronalsite | Banalsite | | | Stronalsite | Banalsite | |
|---|---|---|---|---|---|---|---|
| | Khibina | Benallt mine, Wales | Långban | | Khibina | Benallt mine, Wales | Långban |
| | $Al(1)O_4$ tetrahedron | | | | $Si(1)O_4$ tetrahedron | | |
| Al(1)-(O2) | 1.727(7) | 1.732(8) | 1.727(8) | Si(1)-(O3) | 1.598(5) | 1.608(4) | 1.592(4) |
| Al(1)-(O3) | 1.740(5) | 1.746(5) | 1.743(5) | Si(1)-(O5) | 1.622(5) | 1.628(5) | 1.630(5) |
| Al(1)-(O8) | 1.751(5) | 1.759(4) | 1.752(4) | Si(1)-(O1) | 1.627(7) | 1.632(8) | 1.636(8) |
| Al(1)-(O5) | 1.755(5) | 1.761(5) | 1.752(5) | Si(1)-(O8) | 1.627(5) | 1.640(5) | 1.631(4) |
| <Al(1)-O> | 1.743(11) | 1.750(11) | 1.744(11) | <Si(1)-O> | 1.619(11) | 1.627(11) | 1.622(11) |
| $V_{\mathrm{Al(1)O4}}$ | 2.686(5) | 2.717(24) | 2.693(2) | $V_{\mathrm{Si(1)O4}}$ | 2.167(4) | 2.205(22) | 2.186(25) |
| $\mathrm{Shift}_{\mathrm{Al(1)}}{}^{*}$ | 0.078 | 0.096 | 0.091 | $\mathrm{Shift}_{\mathrm{Si(1)}}{}^{*}$ | 0.057 | 0.056 | 0.059 |
| $\mathrm{BVS}_{\mathrm{Al(1)}}{}^{\dagger}$ | 3.12 | 3.07 | 3.12 | $\mathrm{BVS}_{\mathrm{Si(1)}}{}^{\dagger}$ | 4.06 | 3.97 | 4.02 |
| $\Delta_{\mathrm{Al(1)O4}}{}^{\ddagger}$ | 0.04 | 0.04 | 0.03 | $\Delta_{\mathrm{Si(1)O4}}{}^{\ddagger}$ | 0.06 | 0.05 | 0.12 |
| $\delta_{\mathrm{Al(1)O4}}{}^{\S}$ | 29.9 | 29.5 | 26.6 | $\delta_{\mathrm{Si(1)O4}}{}^{\S}$ | 11.0 | 8.0 | 8.5 |
| | $Al(2)O_4$ tetrahedron | | | | $Si(2)O_4$ tetrahedron | | |
| Al(2)-(O6) | 1.732(5) | 1.722(4) | 1.722(4) | Si(2)-(O2) | 1.582(7) | 1.610(8) | 1.606(8) |
| Al(2)-(O4) | 1.748(5) | 1.759(5) | 1.742(5) | Si(2)-(O6) | 1.610(5) | 1.626(5) | 1.619(4) |
| Al(2)-(O7) | 1.748(6) | 1.758(4) | 1.749(4) | Si(2)-(O4) | 1.622(5) | 1.626(5) | 1.626(5) |
| Al(2)-(O1) | 1.752(7) | 1.758(8) | 1.745(9) | Si(2)-(O7) | 1.623(5) | 1.630(4) | 1.633(5) |
| <Al(2)-O> | 1.745(12) | 1.749(11) | 1.740(12) | <Si(2)-O> | 1.609(11) | 1.622(11) | 1.621(11) |
| $\mathrm{V}_{\mathrm{Al(2)O4}}$ | 2.699(5) | 2.721(28) | 2.678(31) | $\mathrm{V}_{\mathrm{Si(2)O4}}$ | 2.123(4) | 2.179(22) | 2.173(28) |
| $\mathrm{Shift}_{\mathrm{Al(2)}}{}^{*}$ | 0.105 | 0.105 | 0.100 | $\mathrm{Shift}_{\mathrm{Si(2)}}{}^{*}$ | 0.048 | 0.004 | 0.048 |
| $\mathrm{BVS}_{\mathrm{Al(2)}}{}^{\dagger}$ | 3.10 | 3.07 | 3.15 | $\mathrm{BVS}_{\mathrm{Si(2)}}{}^{\dagger}$ | 4.17 | 4.02 | 4.03 |
| $\Delta_{\mathrm{Al(2)O4}}{}^{\ddagger}$ | 0.02 | 0.08 | 0.04 | $\Delta_{\mathrm{Si(2)O4}}{}^{\ddagger}$ | 0.11 | 0.02 | 0.04 |
| $\delta_{\mathrm{Al(2)O4}}{}^{\S}$ | 27.67 | 24.3 | 23.1 | $\delta_{\mathrm{Si(2)O4}}{}^{\S}$ | 19.2 | 13.8 | 16.4 |

* $\mathrm{Shift}_n$: the distance to the centroid of the tetrahedra (Å); † $\mathrm{BVS}_n$: bond-valence sum (Brown & Altermatt 1985, Brese & O'Keeffe 1991), ‡ $\Delta_n$: bond-length distortion index (see text for explanations), § $\delta_n$ bond- angle variance for the regular polyhedra (see text for explanations).

obtained for the Långban banalsite is 64(2)%, consistent with an asymmetrical distribution of the enantiomorphic twin-components.

Atom coordinates and displacement parameters for stronalsite are summarized in Table 3, and for banalsite from Wales and from Långban in Table 4. Bond lengths within the framework tetrahedra, polyhedron volumes, displacements (shifts) of the atoms from the centroids of coordination polyhedra, and distortion indices for bond angles of Si and Al tetrahedra are listed in Table 5. Analogous parameters for large intra-framework Na, Sr and Ba atoms are listed in Table 6. Anisotropic displacement-parameters, and observed and calculated structure-factors are available from the Depository of Unpublished Data, CISTI, National Research Council, Ottawa, Ontario K1A 0S2, Canada.

## Discussion of the Structures of Stronalsite and Banalsite

### *Geometry of the structure*

In common with the structures of the feldspars, that of the $ANa_2Al_4Si_4O_{16}$ ($A$ = Ba, Sr or Ca) sodic aluminosilicates is built of an infinite framework of corner-sharing tetrahedra. Complete order of Al and Si in stronalsite and banalsite results in the presence of four different tetrahedrally coordinated sites, Al(1), Al(2), Si(1), and Si(2) (Fig. 2a), and eight different tetrahedral sites in lisetite [Rossi *et al.* 1986 (not distinguished individually on Fig. 2b)].

The tetrahedra in pairs, Si(1)–Al(1) and Si(2)–Al(2), point alternately up (U) and down (D), forming four-

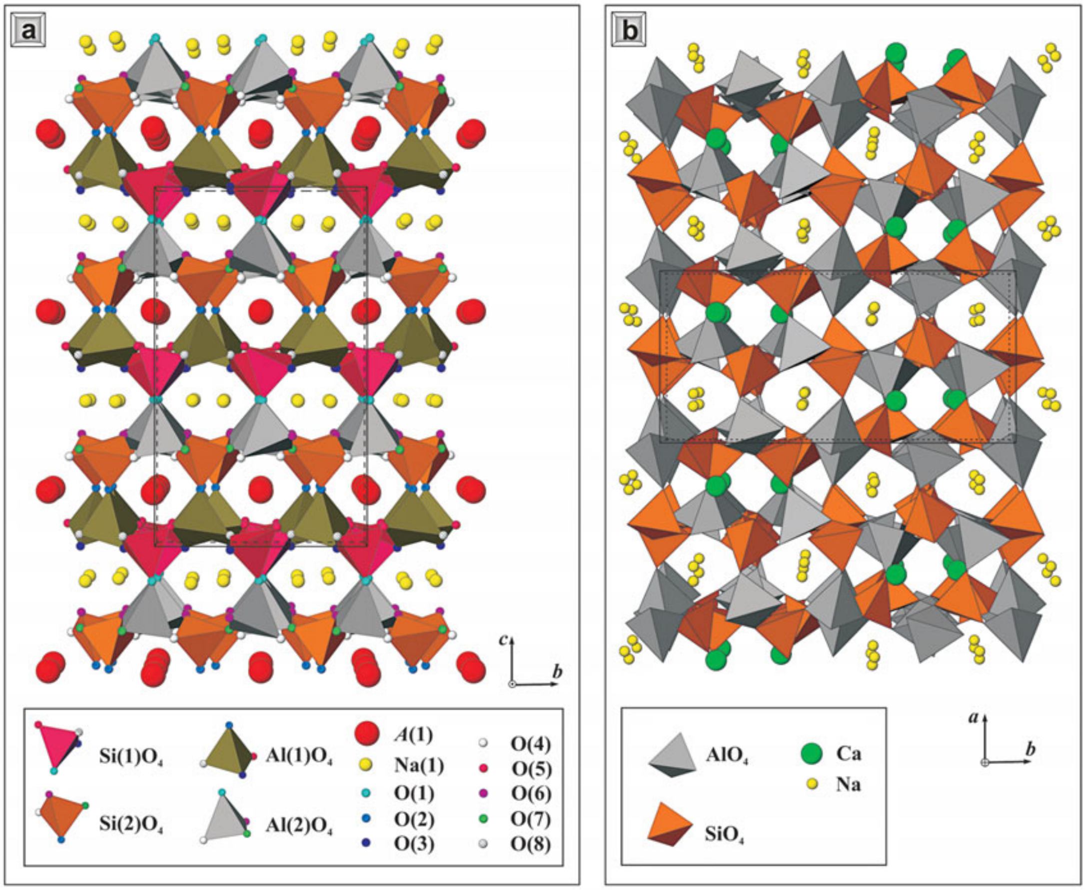

FIG. 2. Structures of $ANa_2Al_4Si_4O_{16}$ tectosilicates: (a) a perspective view of the *Iba*2 structure of stronalsite and banalsite along the *a* axis; (b) a perspective view of the $Pbc2_1$ structure of lisetite along the *c* axis (after Rossi *et al.* 1986). The volumes of unit cells are outlined.

and eight-fold –UDUD– rings parallel to the (001) plane (Figs. 3a, b). The rings are similar to those found in the structure of lisetite (Rossi *et al.* 1986) and nepheline (Tait *et al.* 2003), but differ from the –UUDD– rings of tetrahedra in the feldspars (Haga 1973, Rossi *et al.* 1986, Deer *et al.* 2001). The lateral connection in the (001) plane by means of vertex sharing of the tetrahedra results in layers of tetrahedra (Figs. 2a, b, 3).

The interstices of the framework are occupied by large Sr or Ba cations (*A*), and smaller Na, ordered in alternating layers parallel to (001), and separated by ¼ ***c***. This arrangement of intra-framework cations differs from that occurring in lisetite, $CaNa_2Al_4Si_4O_{16}$, in which topologically identical layers of –UDUD– rings of tetrahedra contain both Ca and Na in the interstices (Fig. 2b). In stronalsite and banalsite, the Sr or Ba atoms, respectively, occupy ten-fold cages consisting of Al(2)–Si(2)–Al–(1)–Si(1)–Al(1)–Si(2) rings, and Na occupies six-fold cages within the Al(1)–Si(1)–Al(2)–Si(2)–Al(2)–Si(1) rings (Fig. 2a).

### *Geometry of the tetrahedra and Al–Si order in the framework of tetrahedra*

We employ the distortion index introduced by Shannon (1976) to illustrate bond-length distortion in polyhedra, *i.e.*, $\Delta_n = [\Sigma\ (r_i - \bar{r})/\bar{r}]^2 \bullet 10^3$, where $r_i$ and $\bar{r}$ are individual and average bond-lengths in the polyhedron, respectively. The bond-length distortion index is a measure of the distortion of polyhedra induced by stretching, compression or extension of <cation–oxygen> bonds, which violate the ideal symmetry of an undistorted polyhedron.

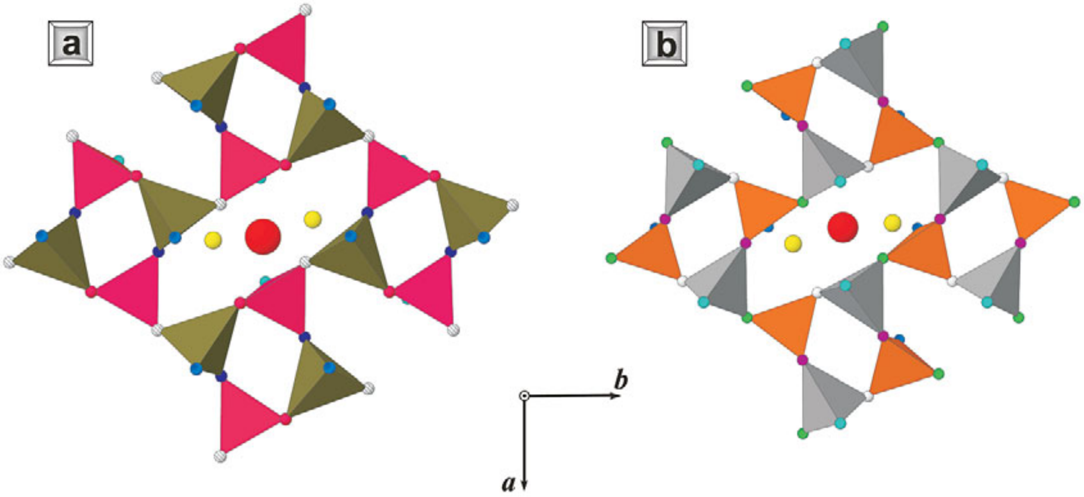

FIG. 3. Unit layers parallel to (001) in the *Iba*2 structure of stronalsite and banalsite, consisting of the four- and eight-member rings of tetrahedra. The rings consist of tetrahedra alternately pointing up and down. (a) An Al(1)–Si(1) layer; (b) an Al(2)–Si(2) layer. For legend, see Figure 2.

TABLE 6. SELECTED INTERATOMIC DISTANCES (Å), VOLUMES (Å$^3$), AND CRYSTALLOCHEMICAL PARAMETERS FOR COORDINATION POLYHEDRA OF INTRAFRAMEWORK ATOMS IN STRONALSITE AND BANALSITE

| Stronalsite | Khibina | Banalsite* | Benallt mine, Wales | Långban |
|---|---|---|---|---|
| 2× Sr(1)-O(7) | 2.652(6) | 2× Ba(1)-O(7) | 2.745(4) | 2.734(4) |
| 2× Sr(1)-O(8) | 2.660(5) | 2× Ba(1)-O(8) | 2.766(5) | 2.765(4) |
| 2× Sr(1)-O(2) | 2.810(3) | 2× Ba(1)-O(2) | 2.927(2) | 2.919(2) |
| 2× Sr(1)-O(5) | 2.903(5) | 2× Ba(1)-O(5) | 2.965(4) | 2.949(4) |
| 2× Sr(1)-O(4) | 2.951(5) | 2× Ba(1)-O(4) | 2.985(4) | 2.979(4) |
| <Sr(1)-O> | 2.795(16) | <Ba(1)-O> | 2.878(13) | 2.869(12) |
| $V_{SrO10}$ | 46.424(11) | $V_{BaO10}$ | *50.35(7)* | 49.90(7) |
| $\Delta_{SrO10}$[†] | 1.92 | $\Delta_{BaO10}$[†] | 1.25 | 1.22 |
| $Shift_{Sr(1)}$[‡] | 0.003 | $Shift_{Ba(1)}$[‡] | 0.021 | 0.018 |
| $BVS_{Sr(1)}$[§] | 1.69 | $BVS_{Ba(1)}$[§] | 2.12 | 2.17 |
| Na(1)-O(1) | 2.328(3) | Na(1)-O(1) | 2.401(2) | 2.390(2) |
| Na(1)-O(6) | 2.362(6) | Na(1)-O(6) | 2.387(5) | 2.367(5) |
| Na(1)-O(3) | 2.374(6) | Na(1)-O(3) | 2.380(5) | 2.384(5) |
| Na(1)-O(8) | 2.542(7) | Na(1)-O(8) | 2.562(6) | 2.556(6) |
| Na(1)-O(7) | 2.628(8) | Na(1)-O(7) | 2.665(6) | 2.653(6) |
| Na(1)-O(1) | 2.726(3) | Na(1)-O(1) | 2.706(2) | 2.701(2) |
| <Na(1)-O> | 2.493(14) | <Na(1)-O> | 2.517(11) | 2.509(11) |
| $V_{NaO6}$ | 13.901(8) | $V_{NaO6}$ | 14.54(5) | 14.39(5) |
| $\Delta_{NaO6}$[†] | 3.07 | $\Delta_{NaO6}$[†] | 2.46 | 2.49 |
| $Shift_{Na(1)}$[‡] | 0.520 | $Shift_{Na(1)}$[‡] | 0.540 | 0.539 |
| $BVS_{Na(1)}$[§] | 0.99 | $BVS_{Na(1)}$[§] | 0.92 | 0.94 |

* Haga (1973); [†] $\Delta_n$: Polyhedron bond-length-variation parameter, [‡] $Shift_n$: the distance to the centroid of the coordination polyhedron (Å), [§] $BVS_n$: bond-valence sum (Brown & Altermatt 1985, Brese & O'Keeffe 1991).

To characterize deviations from the ideal bond-angles in regular polyhedra, we calculate the bond-angle variance index, $\delta_n$, where $\delta_n = [\Sigma(\theta_i - \theta_n)^2]/(n-1)$ and $\theta_i$ are the observed bond-angles at the central atom of a polyhedron, and $\theta_n$ is the ideal O–*M*–O or O–*T*–O angle in an undistorted polyhedron (Robinson *et al.* 1971). The bond-angle variance index reflects twisting or tilting deformation of coordination polyhedra whose <cation–oxygen> distances may remain equal in length (Robinson *et al.* 1971) and thus, are similar in terms of bond-length variations. Both the $\Delta_n$ and $\delta_n$ distortion parameters provide specific insights into the complex geometrical distortions of given polyhedra.

In framework aluminosilicates (tectosilicates *sensu lato*), differences between the mean bond-lengths in coordination tetrahedra can be used to indicate the degree of the order of Al ($^{IV}R^{3+} = 0.39$ Å) and Si ($^{IV}R^{4+} = 0.26$ Å; values from Shannon 1976) over the tetrahedral sites. Bond lengths found in the ordered feldspars, lisetite and nepheline can be compared with those of stronalsite and banalsite. In the structure of completely ordered anorthite (Wainwright & Starkey 1971, Ghose *et al.* 1993), the <Al–O> distances are in the range 1.742–1.755 Å. The mean <Al(1)–O> and <Al(2)–O> distances in the structure of stronalsite are 1.743(11) and 1.745(12) Å (Table 5). The mean <Al(1)–O> and <Al(2)–O> distances in the banalsite from Wales are 1.750(11) and 1.749(11) Å; in banalsite from Långban, they are 1.744(11) and 1.740(12) Å, respectively (Table 5). These are statistically identical to the values of 1.736, 1.742, 1.747 and 1.748 Å obtained for the <Al–O> distances in the structure of lisetite (Rossi *et al.* 1986), and very close to the <Al–O> distances known for slawsonite and paracelsian, ordered aluminosilicates of Sr and Ba, which are 1.748 and 1.747 Å, respectively (Griffen *et al.* 1977, Chiari *et al.* 1985). The relatively short <Al–O> distances in nepheline, ranging from 1.723 to 1.736 Å, have been considered to result from the entry of limited amounts of $^{IV}Si^{4+}$ ($\leq$ 0.13 *apfu* Si) at the Al tetrahedral suite (Tait *et al.* 2003). Since the mean <Al–O> distances in stronalsite and banalsite are statistically identical to those in other ordered tectosilicates, including strontian and barian feldspars, we may infer with confidence that Si does not enter the Al site.

The mean <Si(1)–O> and <Si(2)–O> distances in the stronalsite structure are 1.619(11) and 1.609(11) Å (Table 5). The mean <Si(1)–O> and <Si(2)–O> distances in banalsite from Wales are 1.627(11) and 1.622(11) Å; in banalsite from Långban, they are 1.622(11) and 1.621(11) Å, respectively (Table 5). The <Si–O> distances in completely ordered anorthite are in the same range and vary from 1.608 to 1.617 Å (Wainwright & Starkey 1971, Ghose *et al.* 1993). These values are close to the <Si–O> distances in lisetite: 1.619, 1.620, 1.622 and 1.623 Å (Rossi *et al.* 1986). Similar bond-lengths are found in slawsonite (1.624 Å; Griffen *et al.* 1977), paracelsian (1.613 Å; Chiari *et al.* 1985), and in nepheline (1.603–1.616 Å; Tait *et al.* 2003). Thus the <Si–O> distances observed in stronalsite and banalsite also are in good agreement with complete Si:Al order in the frameworks of tetrahedra.

Bond-length variation, $\Delta_4$, in the tetrahedra of stronalsite and banalsite is low (Table 5) and similar to the distortions of tetrahedra found in feldspars (Deer *et al.* 2001), heterophyllosilicates of the astrophyllite group (Piilonen *et al.* 2003), and complex frameworks such as the one involving octahedra and tetrahedra in titanite (*e.g.*, Kunz *et al.* 2000, Liferovich & Mitchell 2005a, b, c). All bond-length variations are considerably greater than those calculated for all tetrahedra in the structure of nepheline ($\Delta_4 \leq 0.01$; Tait *et al.* 2003). There is no regular trend in bond-length distortion of Si and Al tetrahedra in stronalsite and banalsite, which range from 0.02 to 0.12 (Table 5). The distortion of the framework sites in stronalsite and banalsite differs from that in lisetite (Rossi *et al.* 1986), where variations in bond-length distortion in the smaller $SiO_4$ tetrahedra are significantly less than those in the larger $AlO_4$ tetrahedra (0.02–0.03 *versus* 0.06–0.16, respectively). This is a seemingly paradoxical structural response, as from a steric viewpoint, incorporation of the much larger $Ba^{2+}$ and $Sr^{2+}$ cations instead of the $Ca^{2+}$ in an identical Si–Al framework might be expected to result in much greater extent of deformation of that framework. Clearly, deformation of framework-forming polyhedra resulting from entry of cations larger than $Ca^{2+}$ results in a $Pbc2_1 \rightarrow Iba2$ transformation, owing to the order of the larger (Sr,Ba) cations into layers distinct from those occupied by Na cations.

In contrast to the small distortion of the bond lengths in the tetrahedra, the O–*T*–O bond angles show significant variation, as measured by the $\delta_4$ variance index (Table 5). The values of $\delta_4$ for the larger $AlO_4$ tetrahedra of stronalsite and banalsite are significantly greater than those of the smaller $SiO_4$ tetrahedra (Table 5), indicating that the $AlO_4$ tetrahedra experience a greater degree of tilting or twisting deformation within the infinite corner-shared framework as compared to the $SiO_4$ tetrahedra, which rotate almost rigidly. Similarly, the larger Al-dominated tetrahedra of other tectosilicates, *e.g.*, slawsonite and lisetite, experience larger bond-angle distortions in comparison with the smaller Si-dominated sites (Griffen *et al.* 1977, Rossi *et al.* 1986, respectively). The same phenomenon is known for low albite (Wainwright & Starkey 1971), partially disordered celsian (Griffen & Ribbe 1976), and paracelsian (Chiari *et al.* 1985). Rossi *et al.* (1986) assumed that in the framework of tectosilicates, oxygen anions bonded to Al might be more strongly influenced by the intra-framework cations than those bonded to Si, and that, among these, the higher-charge cations (Ca, Sr, Ba) exert more influence on oxygen than the lower-charge Na. In the case of stronalsite and banalsite, which have an ordered *A*:Na distribution, this might be the cause of the selectively high bond-angle distortion of the $AlO_4$ tetrahedra.

The Al cations have a greater displacement from the centroids of their coordination polyhedra than do the Si atoms in both stronalsite and banalsite (Table 5). The Al and Si cations are displaced regularly, as inferred from the regular variations of individual bond-lengths in the $Si(1)O_4$, $Si(2)O_4$, $Al(1)O_4$ and $Al(2)O_4$ tetrahedra. In pairs of tetrahedra, which connect the layers of tetrahedra by sharing the apical O(1) and O(2) anions (Fig. 2a), Si(2) and Al(1) cations are displaced toward the bridging O(2) anion, *i.e.*, toward each other, as indicated by the shortness of the <Al(1)–O(2)> and <Si(2)–O(2)> bonds in the $Al(1)O_4$ and $Si(2)O_4$ tetrahedra (Table 5). In the alternate pair of Si(1) and Al(2) atoms, bonds to the bridging O(1) atom do not differ from most other bonds in the $Al(2)O_4$ and $Si(1)O_4$ tetrahedra within the accuracy of determination (Table 5), thus implying that the Al(2) and Si(1) atoms are not displaced toward the bridging O(1) atom and each other. Nevertheless, the Al and Si cations in the latter pair exhibit even greater displacements from the centroids of coordination polyhedra compared to the Si(2) and Al(1) cations (Table 5). This difference is due to displacement of the Si(2) and Al(1) atoms at obtuse angles to [001], resulting in shortening of a basal <*T*–O> bond. As a result, the Si(1)–O(3) and Al(2)–O(6) bonds are the shortest in the $Si(1)O_4$ and $Al(2)O_4$ tetrahedra (Table 5, Fig. 2a), respectively. Clearly, the different occupancies of the interlayer cages at alternating levels in the structure of stronalsite and banalsite (Fig. 2a) induces different directions of displacement of the *T* cations in the couples of apex-sharing tetrahedra from adjacent layers. The cages within the Al(2)–Si(2)–Al(1)–Si(1)–Al(1)–Si(2) rings accommodate only one ${}^{X}A^{2+}$ cation (${}^{X}R_{Ba}{}^{2+}$= 1.52 Å, ${}^{X}R_{Sr}{}^{2+}$= 1.36 Å; Shannon 1976), whereas the cages within the Al(1)–Si(1)–Al–(2)–Si(2)–Al(2)–Si(1) rings host two ${}^{VI}Na^{+}$ cations (2 × ${}^{VI}R_{Na}{}^{+}$ = 2.04 Å). The Al(1) and Si(2) cations are thus displaced away from the intra-layer levels densely populated by ${}^{VI}Na$ (Fig. 2a) toward the intra-layer levels with a lower population density of ${}^{X}A$ cations and along [001] with period of ½ ***c***. Thus, the difference in displacive distortion of alternate pairs of apex-sharing tetrahedra is induced by the order of the large intra-framework cations into alternate levels parallel to (001) in stronalsite and banalsite.

### *Environment of the Na and Sr atoms*

The Na and the *A* positions in stronalsite and banalsite are coordinated by six and ten oxygen anions, respectively. The $AO_{10}$ polyhedron can be described as a distorted bicapped square antiprism (Figs. 4, 5a). The $NaO_6$ coordination polyhedron is an irregular pentagonal pyramid (Figs. 4, 5b). In stronalsite, the large-cation coordination-polyhedra are linked in infinite chains of $SrO_{10}$ and a pair of edge-sharing $NaO_6$, which alternate along [001] in a 1:2 ratio (Fig. 4). These irregular polyhedra share alternating pairs of O(7) and O(8) oxygen atoms at their vertices. The pairs of $NaO_6$ polyhedra share two O(1) atoms, which form edges parallel to (001). The mean bond-lengths are 2.795(16) Å for <Sr–O> and 2.493(14) Å for <Na–O> in stronalsite (Table 6). In banalsite, the mean <Ba–O> distance is 2.878(13) and 2.869(12) Å for the samples from Wales and from Långban, respectively. The mean <Na–O> distance is similar to that of stronalsite for both the Långban material, 2.509(11) Å, and the material from Wales, 2.517(11) Å. The <Na–O> distances in stronalsite and banalsite are relatively small compared with those of other framework sodic aluminosilicates, albite, natrolite, and nepheline (Meier 1960, Ribbe *et al.* 1969, Tait *et al.* 2003). In lisetite, the <Na–O> distance is 2.483 Å (Rossi *et al.* 1986).

Indices of bond-length distortion show that the range of Na–O distances from the mean bond-length is much greater than those of Sr–O and Ba–O coordination spheres (Table 6). The Sr cation in stronalsite is located effectively at the geometrical center of the $SrO_{10}$ coordination polyhedron (Figs. 4, 5a). The Ba cation in banalsite is slightly shifted from the geometrical center of the $BaO_{10}$ coordination polyhedron (Table 6). The Na cation in both tectosilicates is significantly shifted from the geometrical centers of $NaO_6$ coordination polyhedra (Figs. 4, 5b).

### *Implications for solid solution*

In common with lisetite, the structures of stronalsite and banalsite are non-centrosymmetric, with complete order of the Al and Si at the tetrahedral sites. The body-centered structures of stronalsite and banalsite have intra-framework cations (Na and Sr,Ba) segregated into alternate levels along [001], separated by ¼ ***c***. In contrast, in lisetite the intra-framework cations Na and Ca are distributed at the same levels in the structure. The structural relationships between these three minerals are in accord with the degree of solid solution of the divalent cations observed in natural specimens. A complete $Ba_{1-x}Sr_xNa_2Al_4Si_4O_{16}$ solid solution is known to exist in various silica-undersaturated rocks (Matsubara 1985, Koneva 1996, Liferovich *et al.* 2006), whereas Ca substitution in these minerals is limited to 0.15 *apfu* $Ca^{2+}$, or ~1.4 wt.% CaO (Liferovich *et al.* 2006). The $Pbc2_1 \rightarrow Iba2$ phase transition in the $ANa_2Al_4Si_4O_{16}$ tectosilicates is induced by different mechanisms of ordering of the intra-framework cations for the smaller Ca *versus* Sr and Ba. As illustrated by the very limited miscibility between stronalsite–banalsite and lisetite, the $Pbc2_1 \rightarrow Iba2$ phase transition occurs with minor $(Sr,Ba)^{2+} \rightarrow Ca^{2+}$ substitutions. Unfortunately, lisetite is known only from the type locality in the Liset eclogite pod, Selje district, Norway. This holotype material does not contain detectable Sr and Ba (Smith *et al.* 1986) and thus does not permit empirical estimation of possible limit for entry of (Sr,Ba) into the structure.

In common with tetrahedra in the framework of other ordered and partially disordered aluminosilicates, the larger tetrahedra in stronalsite and banalsite ($AlO_4$) exhibit higher bond-angle distortions compared with those of the smaller tetrahedra ($SiO_4$) as a result of tilting and twisting, the deformation resulting from the fit of these larger polyhedra into the completely corner-shared framework. Segregation of Na and (Sr,Ba) atoms into alternate layers along [001] with period of 1/4 ***c*** (Fig. 2a) results in differing displacement of Si and Al atoms from pairs of adjacent layers of tetrahedra. These are displaced from the levels populated by Na, giving rise to shorter Si–O–Al distances repeated along [001] with a period of ½ ***c***.

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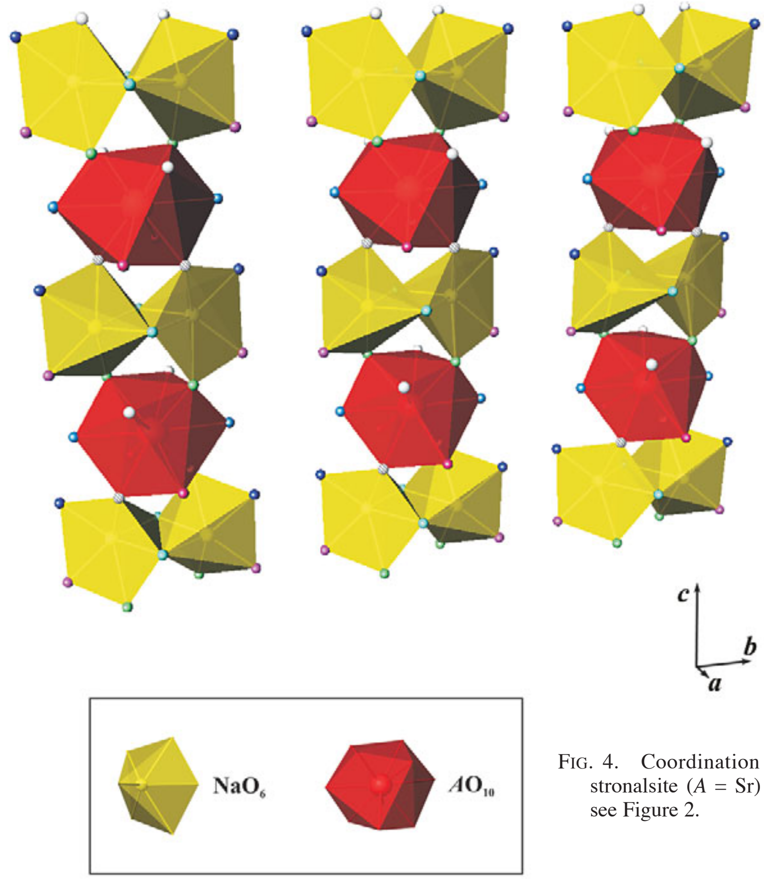

FIG. 4. Coordination polyhedra of ${}^{X}A$ and ${}^{VI}$Na sites in stronalsite ($A$ = Sr) and banalsite ($A$ = Ba). For legend, see Figure 2.

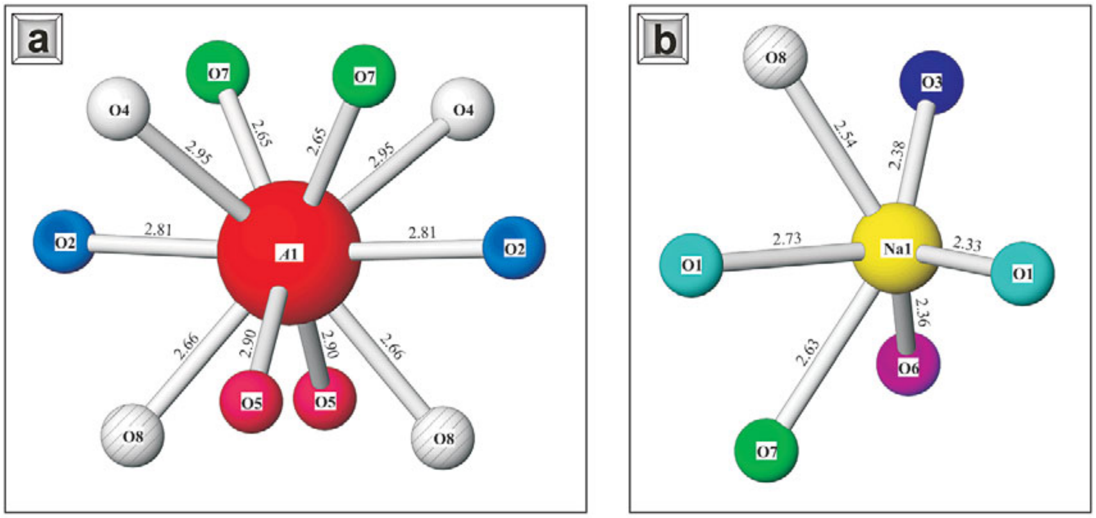

FIG. 5. Large intra-framework cation coordination in the structure of stronalsite and banalsite: (a) ${}^{X}A$ and (b) ${}^{VI}$Na. For legend, see Figure 2.

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