A new 2c superstructure in beryllian sapphirine from Casey Bay, Enderby Land, Antarctica

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ABSTRACT

Transmission electron microscopy of a beryllian sapphirine from Enderby Land, Antarctica, has revealed a new structural variant with a doubled c-axis repeat. Otherwise, diffraction and imaging behaviors are similar to those of the usual $2M$ polytype of sapphirine. Such a modification may be described as sapphirine-$Ma2b2c$ in the currently accepted nomenclature for polytypes and modulated structures. Cell parameters are $a = 11.320$, $b = 14.367$, $c = 2 \times 9.897 = 19.794$ Å, $\beta = 125.49°$, Z = 8 for the twenty-oxygen formula unit.

This is the first reported instance of structural variation in sapphirine along a direction other than the monoclinic b axis. It is suggested that the superstructure is produced by BeSi-AlAl ordering, and possible controlling factors are discussed.

INTRODUCTION

Grew (1981) reported the occurrence of a beryllian sapphirine from "Zircon Point," Enderby Land, Antarctica, in a pegmatite with a suite of unusual beryllian minerals. He gave the composition of the sapphirine in his sample 2234L(3) as $(Mg_{2.74}Fe_{0.96}Al_{4.30})(Al_{2.85}Fe_{0.04}Be_{0.71}Si_{2.40})O_{20}$. This sapphirine has higher Si and Be than any other known, suggesting that the coupled substitution BeSi for AlAl is operative. Anomalous diffraction and imaging behaviors noted in this material during examination by high-resolution transmission electron microscopy (HRTEM) suggest the presence of a superstructure with doubled c-axis repeat, not previously seen in sapphirine. Cell parameters and the TEM observations are presented, with some crystal-chemical discussion of the new structure.

EXPERIMENTAL WORK

Sapphirine grains were hand-picked from the rock, crushed in an agate mortar, and deposited from alcohol suspension onto 2.3-mm-diameter C-coated Cu grids. Specimens thus prepared were examined in a JEOL JEM 100CX microscope, configured as described in Christy and Putnis (1988).

Diffraction patterns with the electron beam parallel to (a) [100] and (b) [010] are compared with corresponding patterns from other sapphirines in Figure 1. It may be seen that the Casey Bay material shows extra spots in rows that index as having half-integral l using the conventional cell for sapphirine-$2M$ (Moore, 1969). These extra reflections suggest a doubled c-axis repeat, which was also faintly discernible in high-resolution images. Attempts to image by dark-field electron microscopy any antiphase domain structure that might occur were unsuccessful, however. This failure is likely to be a consequence of the weakness of the superlattice reflections, and the difficulty of excluding contributions to the image by sublattice reflections since the angular separation of diffracted beams is very small (ca. 1 mrad) for a unit cell of this size.

It may be noted that periodicities are unaffected along the a and b axes. The new structure would be described as sapphirine-$Ma2b2c$ in the notation recommended by Guinier et al. (1984) for polytypes and modulated structures.

Suppression of the c lattice vector of conventional sapphirine-$2M$ does not require loss of either the [010] screw diads or (010) a-glides of that phase, so by analogy with normal sapphirine, the crystal symmetry is likely to be monoclinic, with space group $P2_1/a$. The cell parameters in fact failed to refine satisfactorily in the triclinic system. They were determined from 2θ measurements of indexed lines on a Guinier photograph, and are as follows: $a = 11.320(3)$, $b = 14.367(5)$, $c = 2 \times 9.897 = 19.794(8)$ Å, $\beta = 125.49(4)°$, Z = 8. Dimensions b and $c/2$, but not a, are smaller than the corresponding dimensions for the type sapphirine from Fiskenaesset, Greenland (Moore, 1969), as would be expected given the higher proportion of small cations in the Casey Bay material.

DISCUSSION

The characteristic intensity distribution in the [100] diffraction pattern of sapphirine-$2M$ (Fig. 1) is due to the existence of $a/2 + b/2 \pm c/4$ translational pseudorepeats relating successive (010) layers of the structure (Fleet, 1967; Dornberger-Schiff and Merlino, 1974). Corresponding stacking vectors evidently occur in Casey Bay sapphirine as well. In addition, Christy and Putnis (1988) have shown that the distribution of cations and vacant cation sites in the cubic close-packed anion array of sapphirine must remain invariant in the a-c plane if edge-sharing of coordination tetrahedra and face-sharing of tetrahedra with octahedra is to be avoided. It therefore seems likely that the 2c superstructure arises as a result of cation ordering, with no change in structural topology. Presumably, BeSi-rich and Al-rich subcells are alternating along c.

It is interesting at this point to compare the cation-ordering pattern found in the tetrahedral chains of normal sapphirines (Moore, 1969; Higgins and Ribbe, 1979;
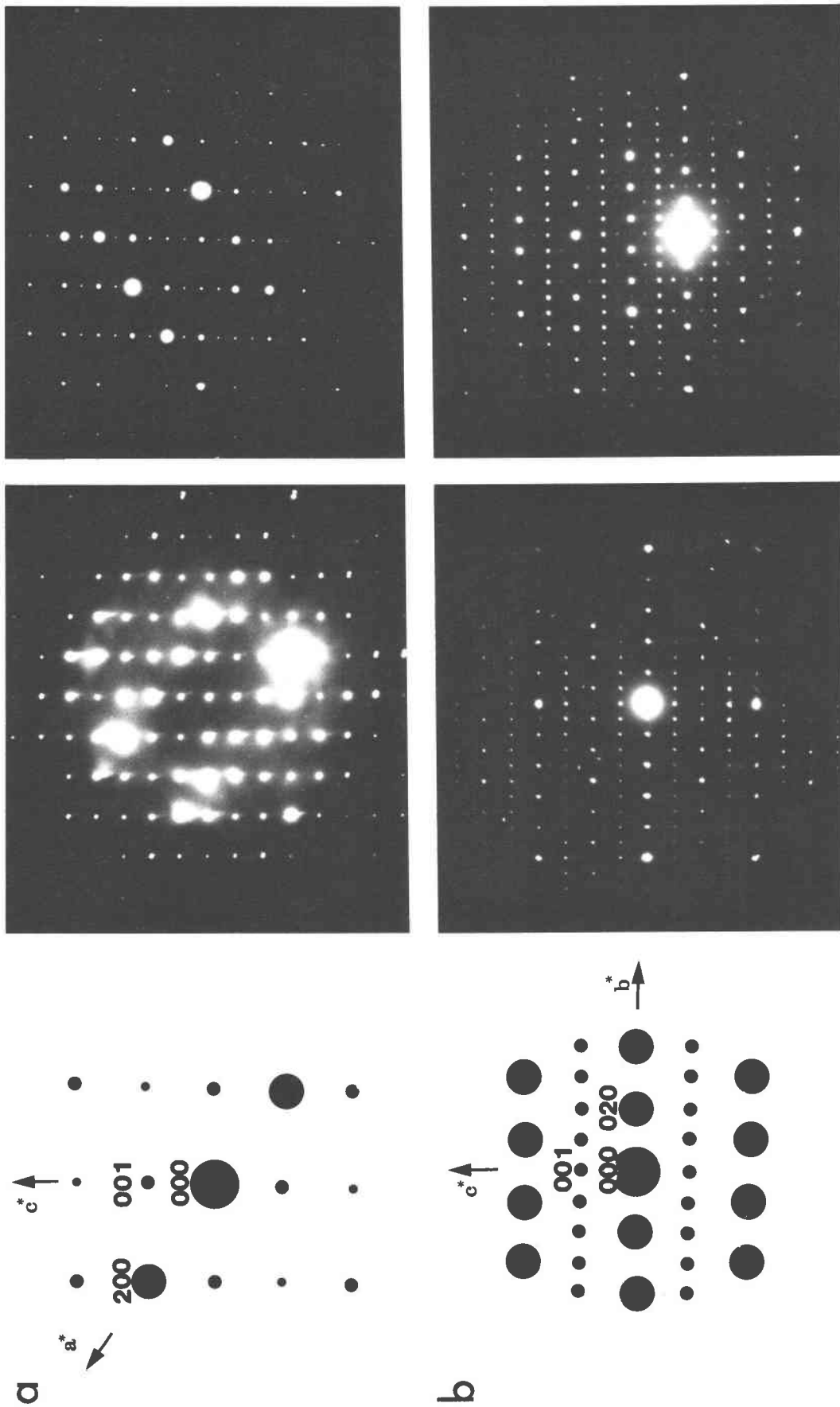
Fig. 1. Electron-diffraction patterns from conventional sapphirine-2M compared with Casey Bay material. (a) Incident beam parallel to b axis; (left) double-scale schematic, sapphirine from (center) Strangways Range, Australia, and (right) Casey Bay sapphirine. (b) Beam parallel to a axis; sapphirine-2M from (center) Chantel, Haute-Loire, France, and (right) Casey Bay.
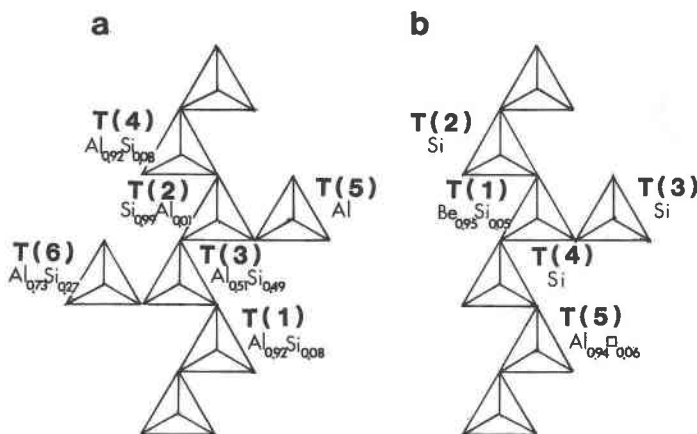
Fig. 2.   Tetrahedral site occupancies for (a) sapphirine (Higgins and Ribbe, 1979) and (b) surinamite (Moore and Araki, 1983).

Merlino, 1980) with that found in the related silicate surinamite, $(Mg_3Al_3)(AlBeSi_3)O_{16}$, which contains essential Be (Moore and Araki, 1983). The chains of both minerals are compared in Figure 2. It can be seen that both contain tetrahedra with one, two, and three bridging oxygens. In sapphirine, Si is found preferentially in the most highly polymerized sites, whereas the corresponding position in surinamite is occupied by Be. Si in surinamite occupies the positions adjacent to Be, as might be expected since this minimizes underbonding of the bridging oxygens in the BeO_4 tetrahedron.

The difference between the sapphirine and surinamite ordering schemes suggests that ordering may be driven by competition between Si and Be for the most polymerized sites in the sapphirine tetrahedral chains [the T(2) and T(3) tetrahedra], leading to a regular alternation along the chains of ordering patterns resembling those of normal sapphirine in one subcell and surinamite in the next.

Another factor that may have some bearing on the Si content of this sapphirine was suggested by Higgins et al. (1979), who pointed out that the Si content of most sapphirines (1.4–2.0 per 20 oxygens) is such that the mean edge lengths of octahedral and tetrahedral coordination polyhedra are similar, thus minimizing distortion of the anion array. Mean edge lengths were calculated by linear interpolation from the cation-oxygen distances of Baur (1981), and assuming regularity of coordination, for stoichiometries corresponding to (1) Be-free sapphirine, (2) a hypothetical sapphirine containing 1 Be per 20 oxygens, and (3) surinamite. The variation of mean polyhedral edge lengths with Si content for these stoichiometries may be seen in Figure 3. It may be seen that in all cases, the crossover point is near 1.5 Si, so this strain argument cannot explain the much higher Si contents in either Casey Bay sapphirine or in surinamite. The preservation of local charge balance appears to be a much more important factor.
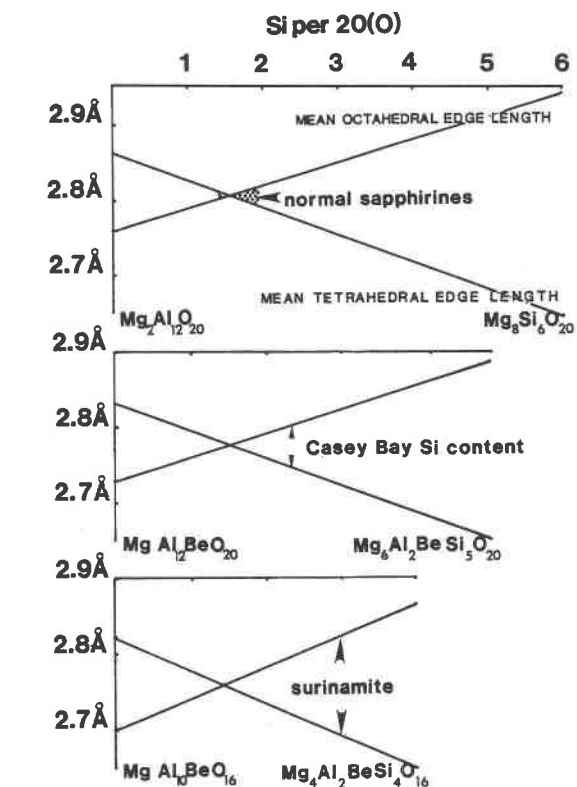

Fig. 3.   Mean tetrahedral and octahedral edge lengths plotted against Si content for coordination polyhedra of Be-free sapphirine, sapphirine with 1 Be per formula unit, and for surinamite.

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