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Co-ordination of boron in sillimanite

ION-MICROPROBE analyses of six sillimanites associated with kornerupine show that the sillimanite can incorporate from 0.035 to 0.43 wt. % B_2O_3 (Grew and Hinthorne, 1983). Boron appears to substitute for silicon concomitantly with Mg substitution for Al such that the atomic Mg/B ratio is close to 0.5. This substitution results in a deficiency of cationic charge, which Grew and Hinthorne (1983) attributed to a submicroscopic rearrangement of the sillimanite structure involving loss of oxygen. A possible substitution scheme is $2(B + xMg) \rightarrow 2(Si + xAl) + (1 + x)O$, where $x \simeq 0.5$. In the present study, we have addressed the question of co-ordination of boron in sillimanite. As boron can occur in trigonal or tetrahedral co-ordination with oxygen, there is no compelling reason that B substitution for Si implies tetrahedral co-ordination for B.

Two of the boron-bearing sillimanites analysed by Grew and Hinthorne (1983), samples E 2724 and 3083D from South India (these authors' samples no. 2 and 4), and a sillimanite from a pegmatite lacking borosilicate minerals from Antarctica, sample 556 (no. 8, see also Grew, 1980; Rossman *et al.,* 1982), are in fragments suitable for single crystal infra-red studies. Spectra were obtained on (010) cleavage fragments $// c$ and $// a$ with a Perkin Elmer 180 spectrometer (fig. 1). Prominent absorption bands in the B-rich sillimanite E 2724 (0.42 % B_2O_3) are centred at 1372, 1327, 1281, 1244, and 1128

cm^{-1} in the $E // c$ polarization and 1317 cm^{-1} in $E // a$. These bands, which are less conspicuous in the boron-poor sillimanite 3083D (0.035 % B_2O_3) and are weak or absent in the Antarctic sillimanite, lie in the range 1100 to 1450 cm^{-1} in which BO_3 groups absorb (Moenke, 1974; Weir and Schroeder, 1964; Weir, 1966). Absorption due to BO_4 groups lies in the 1180 to 800 cm^{-1} region. Unfortunately, this region is largely inaccessible under our experimental conditions due to the opacity of the samples at wave numbers below 1050 cm^{-1}. We suggest that the observed spectral features between 1372 and 1128 cm^{-1} in the two boron-bearing sillimanites are due to B in threefold co-ordination. The B–O polyhedron could be either a triangle in which the B is coplanar with the three oxygens, or a highly distorted tetrahedron, in which the B lies slightly out of the plane of the three closest oxygens and is weakly bonded to a fourth oxygen extended from the boron: BO_3–O.

The absorption features appear not to be caused by submicroscopic inclusions in sillimanite of borosilicates with BO_3 groups such as grandidierite (which is present as a constituent in E 2724), tourmaline (present in 3083D), or dumortierite. M. A. Carpenter (written communication, 1983) has examined a small sample of sillimanite E 2724 with the transmitting electron microscope (TEM) and did not observe any submicroscopic features that could represent incipient exsolution of a B-rich
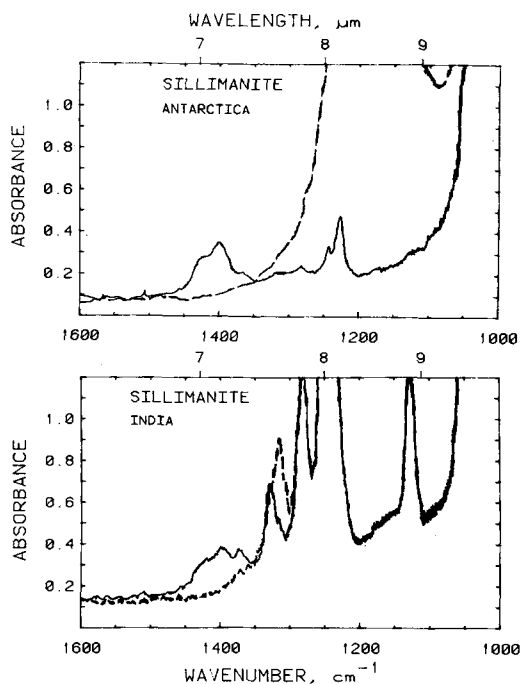
WAVELENGTH, μm

FIG. 1. Single crystal infra-red spectra of sillimanite (sample No. 556) from Reinbolt Hills, Antarctica (top) and of sillimanite (sample no. E 2724) from Paderu, India (bottom). Crystals about 34 μm thick. Polarizations: solid line E ∥ c; dashed line E ∥ a.

phase from sillimanite. However, Carpenter cautions that isolated, widely dispersed inclusions of a B-rich phase would probably escape detection by the TEM. A further indication that the spectral features are caused by B in the sillimanite is the correlation of their intensities with B_2O_3 contents analysed with the ion microprobe (Table I).

The pattern for the Antarctic sample indicates that traces of boron are present even in sillimanite from a rock lacking borosilicates. As Pearson and Shaw (1960) and Evers and Wevers (1984) report 20 to 180 ppm B (equivalent to 0.006 to 0.06 wt. % B_2O_3) in sillimanite from environments not enriched in boron, it appears that sillimanite may in general contain traces of boron at the $0.0X$% (B_2O_3) level.

The crystal-chemical mechanism by which B is incorporated in sillimanite remains an open question. The analytical data of Grew and Hinthorne (1983) suggest that B substitution is coupled with Mg, the atomic Mg/B ratio is close to 0.5, and that sillimanites richer in boron (0.30–0.43 wt. % B_2O_3) also contain significant Fe_2O_3 (1.29–1.39 wt. %).

TABLE I. *Intensity ratios of infra-red absorption features attributed to boron in sillimanite*

Sample no. locality	556 Antarctica	3083D India	E 2724 India
Absorption (cm^{-1})			
1244	0.239	1.0	off scale
1281	0.376	1.56	10
1128	too weak	1.49	10
1327	—	1.10	10
wt. % B_2O_3			
Infra-red*	0.01	0.063	0.42
Ion Microprobe†	—	0.035	0.42

* Estimated from most reliable features and scaled to the 0.42 % B_2O_3 analysed in E 2724.

† Estimated precision is ±0.04 for E 2724 (Grew and Hinthorne, 1983).

Dash: not measured.

However, a B-bearing sillimanite from the kornerupine rock of Waldheim, Saxony, has an atomic Mg/B ratio of 0.7 and contains only 0.33 wt. % Fe_2O_3 (Table II). Thus oxidizing environments, which result in sillimanite Fe_2O_3 contents above 1 wt. % (e.g. Grew, 1980), are not essential for B incorporation in sillimanite. Moreover, B incorporation in sillimanite appears not to involve hydroxyl, for none was detected in an infra-red trace from 3000 to 4000 cm^{-1} obtained on a slice of E 2724 100 μm thick (sensitivity, 0.01 % H_2O).

TABLE II. *Composition of sillimanite from Waldheim kornerupine rock (sample no. 5105c)*

	Weight %	Recalculated to three cations
SiO_2	35.96	0.978
Al_2O_3	62.02	1.988
Cr_2O_3	0.09	0.002
Fe_2O_3	0.33	0.007
MgO	0.27	0.011
B_2O_3	0.32	0.015
Total	98.99	3.0

Electron microprobe analysis, except boron, which was analysed with ion microprobe by method of Grew and Hinthorne (1983). TiO_2, MnO, Na_2O, K_2O, and CaO ≤ 0.03%.

Fluorine was not detected with the ion microprobe in any of the sillimanites analysed by Grew and Hinthorne (1983) or in the Waldheim sillimanite. One mechanism for B incorporation as BO_3 or BO_3-O groups is rearrangement of the sillimanite structure in the immediate vicinity of the boron–oxygen group to resemble the grandidierite stucture, $(Mg,Fe^{2+})^{V}Al^{V}Al_2^{VI}Si^{IV}B^{III}O_9$, which was refined by Stephenson and Moore (1968). McKie (1965) first noted that sillimanite and grandidierite have similar cell dimensions. However, Stephenson and Moore (1968) suggested that the grandidierite structure was more closely related to andalusite, a suggestion consistent with infra-red data (Povarennykh, 1970).

The structures of grandidierite and sillimanite contain chains of AlO_6 octahedra parallel to c and have a nearly identical c axis repeat (5.760 Å for grandidierite, McKie, 1965, $vs.$ 5.7774 Å for sillimanite and 5.5566 Å for andalusite, Winter and Ghose, 1979). Moreover, sillimanite and grandidierite have similar dimensions perpendicular to c, if structurally equivalent directions are compared, as suggested by McKie (1965) and Stephenson and Moore (1968). These are a and b of grandidierite, which are 10.335 Å and 10.978 Å, respectively $vs.$ the diagonals [110] and [1$\bar{1}$0] in Al_2SiO_5, which are 10.727 Å in sillimanite and 11.103 Å in andalusite. Consequently, the dimensions of half a grandidierite unit cell are closer to the unit cell dimensions of sillimanite than to those of andalusite. Despite the differences in crystal structure discussed by Stephenson and Moore (1968), a unit cell of grandidierite might fit with little adjustment into a space occupied by four contiguous half unit cells of sillimanite. This mechanism would explain the loss of oxygen noted by Grew and Hinthorne (1983). Grandidierite has only nine oxygens for six cations compared to ten for Al_2SiO_5, so that $B + Mg \rightarrow Si + Al + O$ and $x = 1$ (see above). As $x < 1$ for the seven B-bearing kornerupines analysed to date, we considered the possibility that Fe^{2+} might be involved in the substitution. No Fe^{2+} was detected spectroscopically in sample E 2724 in the 400 to 1200 nm region. If we assume a molar absorbtivity for Fe^{2+} of three, the sensitivity limit for Fe^{2+} content would be 0.07 wt. % (0.002 per formula unit of three cations), an upper limit, as the molar absorbtivity is undoubtedly higher. Consequently, we doubt that sufficient Fe^{2+} is present in sillimanite to bring the $(Mg + Fe^{2+})/B$ ratio to unity, the value in grandidierite. Possibly the rearranged part of sillimanite does not correspond to a full unit cell of grandidierite, resulting in Mg/B less than unity.

Our infra-red data are consistent with the orientation of BO_3 groups in a grandidierite segment oriented such that the c axis of grandidierite is parallel to the c axis of sillimanite, and a or b of grandidierite parallel to [110] of sillimanite. Thus the BO_3 groups, which are oriented nearly parallel to (010) in grandidierite (Stephenson and Moore, 1968), would lie roughly parallel to (110) in sillimanite. In grandidierite two B–O bonds make a small angle to c, while the third is perpendicular. This orientation could result in the abundant absorption features in $E \parallel c$ and fewer features in $E \parallel a$ present in our patterns. However, of the four sharp bands von Knorring et al. (1969) and Povarennykh (1970) attributed to trigonal boron in spectrometer tracings of powdered grandidierite, namely 1465–1458 cm^{-1} (medium intensity), 1415–1407 cm^{-1} (strong), 1375–1370 cm^{-1} (medium), and 1315–1308 cm^{-1} (strong), only two are close to bands in the sillimanite pattern, namely 1372 cm^{-1} (weak) and 1327–1317 cm^{-1} (medium). The presence of bands below 1300 cm^{-1} and absence of bands above 1400 cm^{-1} in the sillimanite pattern indicates a somewhat different environment for boron in sillimanite, which might result if the BO_3 groups were not strictly planar and the boron were weakly co-ordinated to a fourth oxygen.

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Pekoite from Narechen, Bulgaria—a possible solution to the bonchevite problem

A NUMBER of Pb–Bi–S minerals, including bonchevite (Kostov, 1958), galenobismutite and lillianite (Kupcik *et al.*, 1969), have been recorded from scheelite-bearing quartz veins near the town of Narechen, in the Southern Rhodope Mountains, Bulgaria. The quartz veins are up to 0.5 m thick and cut muscovite–biotite schists of the Rhodopian Complex (Bonev, 1982). One of the authors (W.D.B.) collected several specimens of quartz from a vein north of Narechen during the International Mineralogical Association excursion in September 1982. The specimens contain thin bladed crystals, up to 1 mm wide and 2 cm long of a soft, steel-grey mineral which gave an X-ray powder diffraction pattern close to that of bismuthinite. However, long-exposure Weissenberg X-ray films taken of a small fragment of the mineral revealed weak superlattice spots characteristic of pekoite (Mumme and Watts, 1976*a*, *b*). Several small fragments from the same X-rayed crystal were mounted, polished, and examined under reflected light. The pekoite was very weakly pleochroic, cream in colour, and strongly anisotropic. The prismatic crystals were made up of a mosaic of grains elongated roughly parallel to a well-defined 010 cleavage. No inclusions were observed.

Electron microprobe analyses (Table I), obtained from the same fragments, show a range in composition within a single crystal, deviating from the standard formula for pekoite ($PbCuBi_{11}S_{18}$). The mole % of Bi_2S_3 ranges from 74 to 83, largely within the pekoite compositional field reported by Harris

TABLE I. *Electron microprobe analyses (in wt. %) of pekoite from Narechen, Bulgaria*

	1	2	3	4	5	6
Cu	2.41	1.71	1.75	1.59	1.52	1.59
Pb	8.31	5.98	5.68	5.26	5.25	5.20
Bi	70.44	73.56	74.04	74.55	74.81	74.36
S	17.32	17.35	17.63	17.48	17.64	17.69
Total	98.48	98.60	99.10	98.88	99.22	98.84
Formulae (S = 18.00)						
Cu	1.27	0.90	0.92	0.83	0.79	0.82
Pb	1.33	0.96	0.88	0.83	0.82	0.82
Bi	11.23	11.71	11.59	11.79	11.72	11.61
S	18.00	18.00	18.00	18.00	18.00	18.00

Notes. Analysis was by a JEOL microprobe with a beam voltage of 20 kV and a specimen current of 0.018 μA. Standards used were pure metals (Bi, Cu, Sb, Ag, Zn, Fe) troilite (S), and galena (Pb). Sb, Ag, Fe, and Zn were below detection limits at all points analysed. (Analyst: W. Birch.)

and Chen (1976). The increase in Bi is matched by a decrease in Cu and Pb, but with the Cu/Pb ratio remaining close to unity. These data are plotted in the Cu_2S–PbS–Bi_2S_3 system in fig. 1.

The physical and optical properties of the Narechen pekoite are similar to those of the incompletely characterized mineral bonchevite, as described from Narechen by Kostov (1958). On the basis of the X-ray powder diffraction data, Kostov suggested that the mineral was related to galenobismutite and bismuthinite. However, Fleischer