

Raman spectroscopic identification of B-free and B-rich kornerupine (prismatine)

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ABSTRACT

This is the first application of Raman spectroscopy to the characterization of the kornerupine group of borosilicate minerals. Raman microprobe spectra were collected from ~100 to ~4000 cm⁻¹ from 13 samples of kornerupines (from different localities) containing a wide range of boron content (0.02 to 0.84 boron atoms per formula unit of 21.5 O atoms). The Raman spectra of the kornerupines are consistent with the structure of the mineral as determined by X-ray diffraction (XRD) analysis, which locates the boron in a tetrahedron at the center of a trimer of corner-sharing tetrahedra and with the presence of only hydroxyl ions (OH) but no molecular water (H₂O). Two of the Raman vibrational modes of kornerupines (at ~803 Δcm⁻¹ and at ~884 Δcm⁻¹) are sensitive to the presence of boron, and their relative intensities can be used to discriminate between kornerupine and prismatine. Based on the intensities of those boron-sensitive bands, the Raman spectroscopic technique could potentially provide a semi-quantitative measure of the boron content of kornerupine.

INTRODUCTION

The borosilicate kornerupine is an interesting mineral for several reasons. It is one of the few minerals that contains a wide range of boron and thus can provide insights into the effect of the B = Si,Al substitution. It is difficult to analyze by wet chemical methods as well as by electron microprobe analysis; and more than 10 new localities have been discovered in the last five years. Kornerupine is a mineral that might turn out to be less exotic and more petrologically relevant once investigators learn to recognize it and search for it (Grew and Anovitz 1996).

Minerals of the kornerupine group (kornerupine *sensu lato* or simply kornerupine) are ideal samples to test the feasibility of applying Raman spectroscopy to obtain information on both the amount of boron present and its coordination symmetry. These ferromagnesian B-bearing aluminosilicates have been reported from nearly 70 localities worldwide in upper amphibolite- and granulite-facies metamorphic rocks (Grew 1996). The simplified formula (□,Fe,Mg)(Mg,Fe,Al)₉(Si,Al,B)₅O₂₁(OH,F) includes the minerals kornerupine *sensu stricto* (B < 0.5 atoms per formula unit, apfu) and prismatine (B > 0.5 apfu; Grew et al. 1996). Boron content in natural and synthetic kornerupine ranges continuously from 0 to 1.0 B pfu (roughly 0 to 4.7 wt% B₂O₃), with 1.0 B pfu being the theoretical maximum (e.g., Werding and Schreyer 1978, 1996; Schreyer and Abraham 1976; Grew et al. 1990; Hawthorne et al. 1995; Grew 1996; Cooper 1997). Boron is not an essential constituent of kornerupine, but to date only three localities for natural B-free kornerupine (i.e., B ≤ 0.02 apfu) have been reported. Determination of the boron content in kornerupine group minerals is difficult with most analytical techniques. It can be measured by electron microprobe analysis (EMPA) but only with special accessories and if

great care is taken (Hawthorne et al. 1995; McGee and Anovitz 1996). Other techniques for measuring boron content are wet chemistry, ion microprobe analysis (SIMS), and single-crystal refinement (SREF) X-ray analysis, which involve either large samples or equipment and expertise not readily available to most investigators. Cooper (1997) has developed a procedure for the quantitative analysis of boron using EMPA and powder X-ray diffraction (XRD) but the latter requires bulk samples. This paper presents the first Raman spectra of kornerupine and prismatine, and shows that Raman microprobe spectroscopy can be used to distinguish between B-rich, B-poor, and B-free kornerupine-group minerals at the micrometer scale.

STRUCTURE OF KORNERUPINE

Kornerupine-group minerals are complex, hydrous B-containing Mg-Al-silicates, whose structure contains corner-sharing SiO₄, AlO₄, and BO₄ tetrahedra. A formula unit of either kornerupine or prismatine has 15 distinct cation sites including three tetrahedral, five octahedral, and one highly distorted largely vacant cubic site (e.g., Moore and Bennett 1968; Moore and Araki 1979; Klaska and Grew 1991; Cooper 1997). The structure is built of two sheets parallel to *b* {010}, one of which contains walls parallel to *c* [001] of edge- and corner-sharing octahedra linked by the distorted cubes. The other sheet consists of edge- and corner-sharing octahedral chains parallel to *a* [100], tetrahedral (T1; nomenclature of Moore and Araki 1979) Si₂O₇ dimers, and tetrahedral (Si,Al)₂(Si,B)O₁₀ trimers (T2, T3). B substitutes for Si in the central (T3) tetrahedron of the trimer, whereas Al substitutes for Si in the terminal tetrahedra (T2) of the trimer. Therefore, kornerupine has Al-O and Si-O terminal bonds, Al-O-Si, Si-O-Si, and B-O-Si, and, possibly, some B-O-Al linkages between AlO₄, SiO₄, and BO₄ tetrahedra. Cooper (1997) reported the following compositional ranges for the tetrahedral cations on the basis of EMPA and SREF X-ray analy-

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ses in 52 natural kornerupine crystals: B = 0.016–0.880 apfu, Al = 0.288–1.438 apfu, and Si = 3.546–3.884 apfu, with the B content being inversely proportional to the Al content (Grew et al. 1996).

SAMPLES

Thirteen samples ranging in boron content from 0.02 to 0.86 B apfu (Table 1) were selected from Cooper's (1997) set of 52 samples. Full details on the compositions and sources of the samples were given by Cooper; many of these samples were originally studied by Grew et al. (1990, 1996). Samples required minimal or no preparation for laser Raman microprobe (LRM) analysis. Individual needles were either studied in situ on the intact mineral hand specimen or individual microcrystals were broken out from the hand specimen and laid on a glass slide.

RAMAN SPECTROSCOPY

The Raman spectroscopic measurements were done with a Jobin Yvon S-3000 triple-monochromator laser Raman microprobe with multi-channel detection. The instrument consists of a 320 mm double-monochromator with two 600 grooves/mm gratings in subtractive mode, and a 1 m third stage with interchangeable gratings (600 grooves/mm were used). A research grade optical microscope (ISA-modified Olympus BH2) equipped with an Olympus MS-Plan 80× ultralong-work-distance objective (N.A. = 0.75, ~8 mm working distance) was used to optically image the sample (with a video camera and a TV monitor), focus the laser beam (514.5 nm line from a Coherent Innova-70 5W argon ion laser). The theoretical diffraction-limited focal spot diameter at the sample surface was about 1 μm for this objective. The 180° backscattered light was detected with a 1 in, 1024-element, proximity-focused, intensified, optical diode array detector.

Spectral windows of about 1000 cm⁻¹ width were collected with a spectral resolution of about 1.4 cm⁻¹/diode element of the detector. To cover the total Raman spectral range (~100 to ~4000 Δcm⁻¹), data were acquired in four different, overlapping spectral windows centered at 830, 1600, 2600, and 3500 Δcm⁻¹. No attempt was made to either depolarize the incident laser radiation or to scramble the polarization of the scattered Raman radiation. Count-

ing times for kornerupine samples were between 0.5 and 4 s for each the spectral acquisition and the background measurement. Typically there were 64 or 128 individual acquisitions for each spectral window, and they are coadded together to improve the signal-to-noise ratio. The total analysis time for all four spectral windows ranged from about 9 min to as long as 1 h. The spectra were obtained with a resolution of about 7 cm⁻¹, and a wavelength accuracy of ±1 cm⁻¹. Two orientations of each sample relative to the polarization direction of the exciting laser beam were recorded to determine to polarization susceptibility of the band intensities. One orientation was with the obvious long striations in the crystal face aligned parallel to the polarization direction of the laser beam (called the 0° orientation), and the other orientation with the crystal turned 90° to the first orientation (called the 90° orientation).

The entire spectral range for kornerupine is shown in Figure 1 for the most B-rich and the most B-poor samples. The effects of orientation of the prismatic crystal relative to the direction of polarization of the laser beam (0° and 90°) are shown for the spectra region containing lattice and internal mode (100 to 1200 Δcm⁻¹) in Figure 2. The Raman spectra of six samples with different boron content (0.02 ≤ B ≤ 0.84 apfu) aligned for 0° orientation are compared in Figure 3. All kornerupine group samples studied exhibited several strong, sharp, characteristic Raman peaks. The spectra of kornerupine group minerals (Figs. 1, 2, and 3) were characterized by a series of intense bands in the 100 to 1200 Δcm⁻¹ region that arose from excitations of the fundamental modes of coupled (Al,Si,B)O₄ tetrahedra and one or more strong bands between 3400 and 3800 Δcm⁻¹ that represented the O-H stretching mode(s) of the hydroxyl ion, which was consistent with SREF results and infrared evidence for O-H bonds (Klaska and Grew 1991; Cooper 1997). There was no evidence of a Raman band near 1620 Δcm⁻¹, which was associated with the bending vibrational mode of water. Thus, the Raman spectra of kornerupines were consistent with the presence of a hydroxyl ion (OH) in the structure as opposed to molecular water (H₂O). In particular, the Raman spectrum of boron-free sample no. 9365 provided no evidence for H₂O molecules that Klaska and Grew (1991) proposed to explain by excess H₂O in the chemical analysis of this sample

TABLE 1. Frequencies of Raman active fundamental modes of kornerupine group minerals

Sample no.*	Origin	Boron [†] (pfu)	FeO [‡] (wt%)	Orientation§ (degrees)	Raman peak positions (Δcm ⁻¹)						
					A	B	C	D	E	F	
BM1940,39 (K11)	South Africa	0.86	12.1	90	708	764	805	881	981	1025	–
141255 (K9)	Madagascar	0.84	4.8	0	708	760	803	884	976	–	1028
141255 (K9)	Madagascar	0.84	4.8	90	707	759	803	884	971	1021	–
24752 (K17)	Australia	0.77	10.4	90	707	746	801	878	983	1013	–
1892.1438 (K34)	Germany	0.76	4.9	mixed	708	760	801	882	982	1014	1026
171.350 (K7)	Madagascar	0.75	3.3	0	703	760	798	883	967	–	1028
MALLEY (K5)	Sri Lanka	0.75	4.1	0	708	756	801	879	967	–	1029
BM1978,467 (K23)	Kenya	0.73	0.0	90	708	761	801	883	972	1012	–
PHN984 (K26)	Uganda	0.51	7.3	90	696	742	–	875	956	1003	–
8497 (K22)	Zimbabwe	0.42	1.3	90	701	752	–	876	965	1000	–
3083D (K1)	India	0.40	4.5	90	699	748	–	878	963	1000	–
DC707H (K30)	Tajikistan	0.11	0.2	0	704	750	–	878	963	–	1002
XF-4 (K36)	Australia	0.04	4.5	0	701	742	–	–	956	–	1000
9365 (K35)	Zimbabwe	0.02	3.2	0	698	745	–	–	959	–	1001
9365 (K35)Zimbabwe 0.02		3.2	90	698	745	–	959	991	–	–	–

*Sample numbers starting with the letter K are Cooper's (1997) nomenclature.

†Compositional data taken from Cooper (1997).

‡Samples assumed to have Fe²⁺.

§Orientation of crystal relative to laser beam.

||Peak labels A through F correspond to those shown in Figure 3.

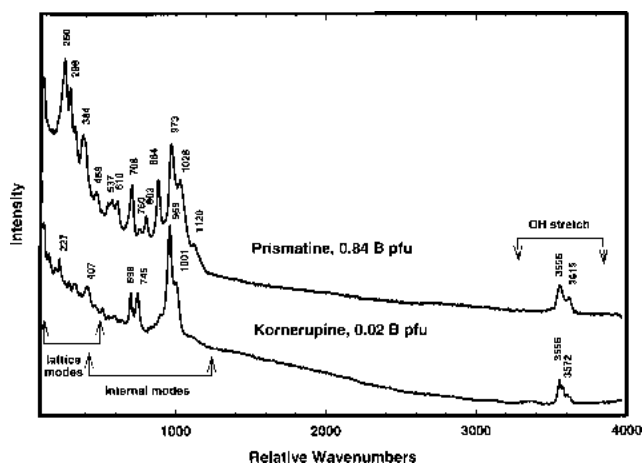


FIGURE 1. Raman spectra of prismatic (sample no. 141255 with 0.84 B pfu) and boron-free kornerupine (sample no. 9365 with 0.02 B pfu).

and confirmed Cooper's (1997) conclusion that H_2O molecules are unlikely in kornerupine due to the absence of suitable H-bond acceptors.

Table 1 lists the positions of the major Raman bands observed for the 13 different samples studied. The common and very characteristic Raman feature of all kornerupine and prismatic samples studied (regardless of their orientation with respect to the laser polarization) is the presence of a very strong pair of two overlapping bands near 965 and 1010 cm^{-1} plus a second strong pair of bands near 700 and 750 cm^{-1} (Figs. 1 and 2). A comparison of the spectra of boron-free and boron-rich kornerupine shows that regardless of crystal orientation, boron-rich kornerupine had two bands at $\sim 800 \text{ cm}^{-1}$ and $\sim 880 \text{ cm}^{-1}$, which are not found in the Raman spectrum of the boron-free kornerupine (Fig. 3). The intensities of those two bands depend upon both the boron content and the orientation of the crystal relative to the polarization direction of the laser beam. The band at $\sim 880 \text{ cm}^{-1}$ is the stronger of the two, and it is present in all the kornerupines with $B > 0.11$ pfu. The other band typical for B-containing samples at $\sim 800 \text{ cm}^{-1}$ is weaker and only showed up for kornerupines with $B > 0.50$ pfu. Thus, the presence of the $\sim 800 \text{ cm}^{-1}$ and $\sim 880 \text{ cm}^{-1}$ bands in the kornerupine Raman spectrum indicates the presence of boron in the crystal lattice, and the intensities of these bands give additional information about the amount of boron present.

DISCUSSION

An evaluation of the Raman spectra of kornerupines requires consideration of the Raman bands arising from tightly coupled, corner-sharing Si_2O_7 pairs and the coupled trimer of tetrahedra $(\text{Al,Si})_2(\text{Si,B})\text{O}_{10}$. The Raman bands of kornerupines are expected to occupy similar frequency regions as those observed for chain silicates, even though only dimers and linear trimers occur in the structure of kornerupine-group minerals. The bands below 600 cm^{-1} in the Raman spectra of kornerupines are associated with either lattice modes of the crystal or with internal bending modes of coupled tetrahedra. Raman lines clearly associated with the presence of boron in the structure could not be readily differentiated in the lattice-mode region of the spectrum, based on the data

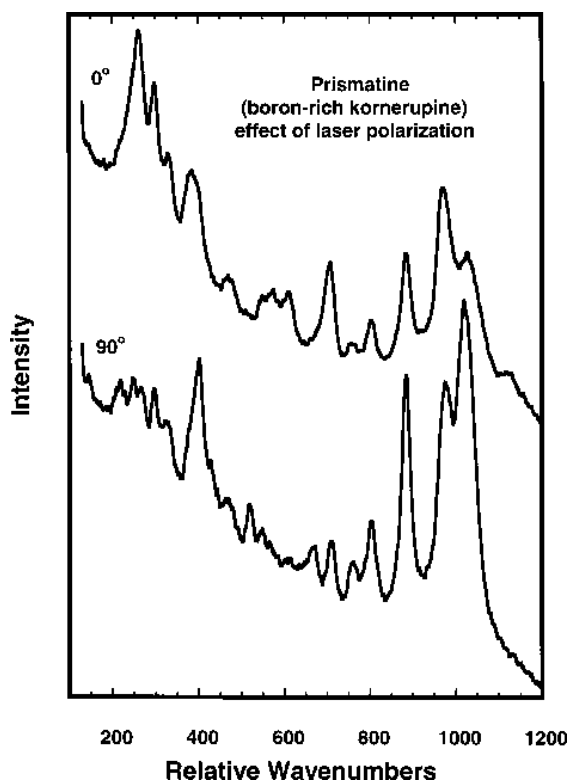


FIGURE 2. The effect of crystal orientation relative to the polarization direction of the exciting laser light on the Raman spectrum of a kornerupine-group mineral (sample is prismatic no. 141255 with 0.84 B pfu).

we collected. Typically, the Si-O-Si and Si-O-Al stretching modes are observed between 700 and 800 cm^{-1} in Si_2O_7 dimers and between 600 and 700 cm^{-1} in chain silicates (Farmer 1974; McMillan and Hofmeister 1988). Thus, in kornerupine, the bands in the 600 to 760 cm^{-1} region are associated with stretching modes in the Si-O-Si and Si-O-Al bridges, whereas the strong bands between 950 and 1050 cm^{-1} are associated with the terminal MO_3 ($M = \text{Si, Al}$) stretching modes of both the Si_2O_7 dimer and the $(\text{Al,Si})_2(\text{Si,B})\text{O}_{10}$ trimer of the crystal. The major differences that we observed between the B-rich and B-poor kornerupines are the presence of two Raman bands at $\sim 803 \text{ cm}^{-1}$ and $\sim 884 \text{ cm}^{-1}$ that correlated with the high boron content of the prismatic structure (Fig. 1). The intensity of these boron-sensitive bands in prismatic relative to the other fundamental modes in the spectrum is also quite dependent upon the orientation of the polarized laser beam with respect to the crystal orientation (Fig. 2). Based on our findings, samples showing both boron-sensitive Raman bands at $\sim 803 \text{ cm}^{-1}$ and $\sim 884 \text{ cm}^{-1}$ could be identified as "boron-rich," i.e., prismatic ($B > 0.5$ apfu) by Raman spectroscopy. In "boron-poor" kornerupines ($0.5 > B > 0.1$ apfu), i.e., kornerupine sensu stricto, only the stronger of the two boron-sensitive bands (the one at $\sim 884 \text{ cm}^{-1}$) is detected in the Raman spectrum. For samples with $B < 0.1$ apfu, neither one of the two boron-sensitive Raman bands is detected, and such a boron-poor kornerupine cannot be distinguished from boron-free kornerupine using Raman spectroscopy.

In principle, the boron content of kornerupine could be esti-

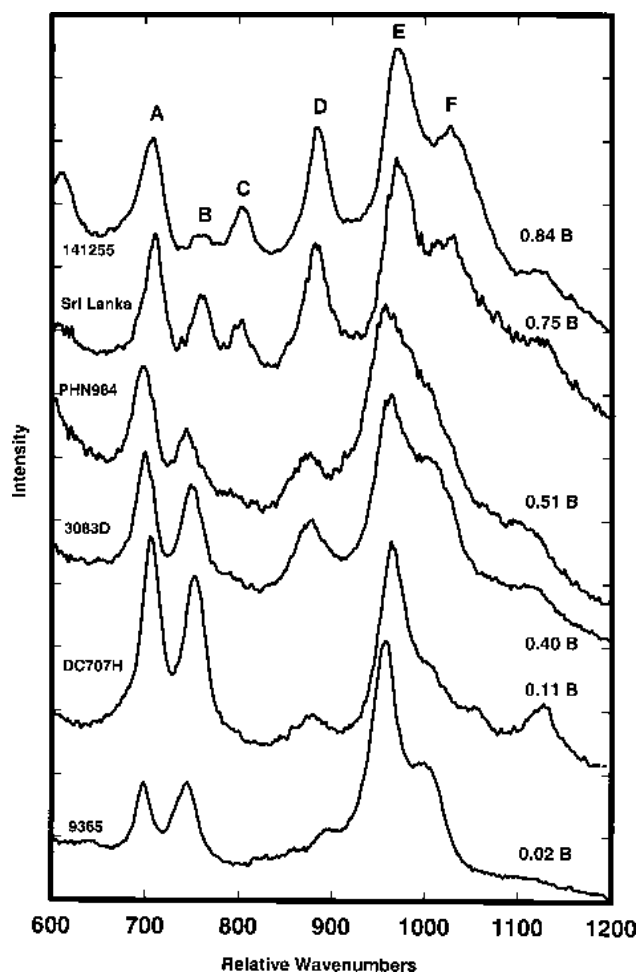


FIGURE 3. Comparison of the fundamental Raman bands of boron-free, boron-poor, and boron-rich kornerupine-group minerals with 0° crystal orientation with respect to the polarization orientation of the exciting laser beam. Bands C ($\sim 803 \Delta\text{cm}^{-1}$) and D ($\sim 884 \Delta\text{cm}^{-1}$) are sensitive to the presence and the concentration of boron in the mineral. Boron content of samples varied between 0.02 B pfu and 0.84 B pfu; see Table 1 for sample identification and peak positions.

mated by correlating the ratio of the intensity of the boron-sensitive Raman peak at $\sim 880 \Delta\text{cm}^{-1}$ (peak D in Table 1) to the intensity of the peak at $\sim 970 \Delta\text{cm}^{-1}$, which is due to the terminal $[\text{Al},\text{Si}]\text{O}_3$ group (peak E in Table 1). A graph (not shown) of these peak intensity ratios vs. the boron concentration of the 13 samples studied is nonlinear, and at boron concentrations $> \sim 0.5$ B apfu the graph shows two separate branches, one for each orientation of the kornerupine crystal with respect to the polarization orientation of the exciting laser beam. For such a correlation curve to be of practical value, the calibration would need to be established with single crystals (whose axes can be reproducibly oriented with respect to the laser) of a series of kornerupines.

In addition, we found that the peak frequencies of the MO_3 and M-O-M internal modes depended upon boron content (Fig. 1). The seven fundamental modes lying between 700 and $1050 \Delta\text{cm}^{-1}$ show an increase of 10 to 30 cm^{-1} as the boron content rises from near 0 to 0.85 apfu. (When alignment of the crystal relative to the laser beam polarization direction is taken into account, the broad peak at $\sim 1010 \text{ cm}^{-1}$ actually consists of at least two unresolved bands separated by $\sim 10 \text{ cm}^{-1}$; both of these bands showed a frequency dependence upon the boron content of the kornerupine-group mineral; band F in Table 1). The observed peak shifts as a function of boron content are due to changes in the bonding strengths of the coupled tetrahedra arising from insertion of boron into the central T_3 tetrahedron of the $(\text{Al},\text{Si})_2(\text{B},\text{Si})\text{O}_{10}$ trimer. To use such correlations of boron content vs. peak shift as a means to quantify the boron content of a kornerupine-group mineral, calibration curves based on investigations with increased spectral resolution would be required.

Based upon XRD studies (Moore and Araki 1979), the coordination of the boron site in kornerupine is tetrahedral. Vibrational spectroscopy can be used to distinguish between the planar trigonal and tetrahedral coordination sites of isolated BO_x anions (Ross 1974; Table 2), and infrared spectroscopy has been able to detect the presence of the planar BO_3 group in borosilicate minerals (Moenke 1974; Grew and Rossman 1985). However, the positive detection of the BO_4 group in IR spectra (theoretically expected bands in the region of 600 and 1100 cm^{-1} ; Table 2) is hampered in practice by the fact that absorptions in this spectral region are masked by the IR absorptions of the aluminosilicate tetrahedra. It should be possible to verify the tetrahedral symmetry of the boron site in kornerupine through Raman spectroscopy, because the tetrahedral BO_4 Raman

TABLE 2. Effect of environment on vibrational band positions (cm^{-1}) of boron oxyanions in minerals

Oxyanion	Normal mode	Isolated oxyanions		Coupled oxyanions		
		Range for six minerals*	Sinhalite†	Tourmaline‡	Danburite§	Kornerupine group
BO_3	$\nu_1(\text{R})$	910–960		731–780		
	$\nu_3(\text{IR})$	1210–1290		1412–1442		
	$\nu_2(\text{IR},\text{R})$	705–760		741–765		
	$\nu_4(\text{IR},\text{R})$	600–660				
BO_4	$\nu_1(\text{R})$		800		880–1087	875–884
	$\nu_3(\text{IR})$		980, 1170, 1175		880–1087	875–884
	$\nu_2(\text{R})$		450, 500		556–684	798–805
	$\nu_4(\text{IR})$		509, 728		556–684	798–805

*Ross (1974). Range for IR data obtained on fluorborite, nocerin, kotoite, ludwigite, vonsenite, and pinakioilite.

†Data calculated by Ross (1974) except for ν_3 , which is quoted from IR reflection studies of sinhalite.

‡Gosharova et al. (1977).

§Best et al. (1994).

||This work.

bands ($\sim 800 \text{ cm}^{-1}$ for the isolated group; Table 2) should be distinctly resolved from the Raman bands of SiO_4 tetrahedra. In principle, this means that Raman spectroscopy should be better suited than IR spectroscopy to detect BO_4 groups in silicates.

When interpreting the Raman spectra of kornerupines in terms of the known vibrational bands for the isolated boron oxyanions, however, we encountered immediate difficulty. Not only is the frequency of the 884 cm^{-1} boron-sensitive band of kornerupine located at a frequency intermediate between those of isolated, planar BO_3 and isolated, tetrahedral BO_4 [see assignments given by Ross (1974) listed in Table 2], but this frequency matches exactly the 884 cm^{-1} Raman line of trigonal, planar BO_3 in crystalline boric acid [$\text{B}(\text{OH})_3$, Durig et al. 1968]. Thus, assignments based upon Raman frequencies of isolated BO_3 or BO_4 groups led to ambiguity and contradiction in assigning the coordination symmetry of the boron oxyanion in kornerupines and other B-containing minerals.

Any meaningful assignment of the boron-sensitive Raman peaks of kornerupine must take into account the symmetry of the boron tetrahedron coupled in the center of the $\text{O}_3\text{Si-O-BO}_2\text{-O-[Al,Si]O}_3$ trimer of tetrahedra found in kornerupine. Few reports exist in the current literature where a complete vibrational analysis was applied to borosilicates containing coupled BO_x oxyanions from which we might have drawn analogies for the BO_x symmetry in kornerupine. In the case of coupled, planar BO_3 groups, detailed studies on the polarized Raman spectra of the tourmalines were published by Gasharova et al. (1997, and references therein). The tourmaline Raman spectra have been interpreted in terms of stretching and bending modes of isolated BO_3 and of coupled SiO_4 groups. In the case of the infrared active bands, the presence of bands in the 1400 to 1500 cm^{-1} region of borosilicate minerals are clearly correlated with the presence of planar BO_3 oxyanions. The case of tetrahedral BO_4 coupled with tetrahedral SiO_4 is presented by Best et al. (1994) who conducted a detailed polarized Raman study of danburite. This mineral consists of linked Si_2O_7 and B_2O_7 dimers and contains no terminal MO_3 groups. A summary of the BO_x frequencies in these various symmetry environments is presented in Table 2. Data are insufficient to draw any useful correlations between the Raman frequencies of boron-sensitive modes and the symmetry of the coupled BO_x oxyanion.

Based on the assignments of Best et al. (1994), the 884 cm^{-1} boron sensitive mode in kornerupine is associated with the B-O stretching vibration of the coupled tetrahedron, whereas the 803 cm^{-1} boron-sensitive band is probably associated with the B-O-Si vibrations, although B-O-Al vibrations are also possible. The Al content in the terminal T2 tetrahedra of the $[\text{Al,B,Si}]_{10}$ trimer of tetrahedra is inversely proportional to the boron content of the internal T3 tetrahedron in this same trimer (Cooper 1997). This finding excludes the possibility that the boron-sensitive 803 cm^{-1} band arises from any B-O-M vibrational mode involving an Al atom. A complete assignment of the boron sensitive modes in the kornerupines would, however, require a detailed polarized Raman study of single crystals of all the kornerupine-group minerals. In conclusion, the major advantage of the laser Raman microprobe technique used in this study is that it permits recognition of "Raman

fingerprints" characteristic of the kornerupine mineral and provides a semi-quantitative determination of boron in micrometer-sized crystals of kornerupine in thin-section where textural relations and compositional zoning can be complex.

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