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Edward S. Grew

University of Maine - Main, esgrew@maine.edu

A. T. Rao

K.K. V.S. Raju

C. Hejny

J. M. Moore

See next page for additional authors

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Authors

Edward S. Grew, A. T. Rao, K.K. V.S. Raju, C. Hejny, J. M. Moore, D. J. Waters, Martin G. Yates, and C. K. Shearer

Prismatine and ferrohögbomite-2N2S in granulite-facies Fe-oxide lenses in the Eastern Ghats Belt at Venugopalapuram, Vizianagaram district, Andhra Pradesh, India: do such lenses have a tourmaline-enriched lateritic precursor?

E. S. GREW^{1,*}, A. T. RAO², K. K. V. S. RAJU², C. HEJNY³, J. M. MOORE⁴, D. J. WATERS⁵, M. G. YATES¹ AND C. K. SHEARER⁶

¹ Department of Earth Sciences, University of Maine, 5790 Bryand Center, Orono, Maine 04469, USA

² Department of Geology, Andhra University, Visakhapatnam 530 003, India

³ School of Physics, University of Edinburgh, The King's Buildings, Edinburgh EH9 3JZ, UK

⁴ Department of Exploration Geology, Rhodes University, P O Box 94, Grahamstown, 6140 South Africa

⁵ Department of Earth Sciences, Oxford University, Parks Road, Oxford OX1 3PR, UK

⁶ Institute of Meteoritics, University of New Mexico, Albuquerque, New Mexico 87131, USA

ABSTRACT

Fluorine-rich prismatine, $(\square, \text{Fe, Mg})(\text{Mg, Al, Fe})_5\text{Al}_4(\text{Si, B, Al})_5\text{O}_{21}(\text{OH, F})$, with $F/(\text{OH}+\text{F}) = 0.36\text{--}0.40$ and hercynite are major constituents of a Fe-Al-B-rich lens in ultrahigh-temperature granulite-facies quartz-sillimanite-hypersthene-cordierite gneisses of the Eastern Ghats belt, Andhra Pradesh, India. Hemo-ilmenite, sapphirine, magnetite, biotite and sillimanite are subordinate. Lithium, Be and B are concentrated in prismatine (140 ppm Li, 170 ppm Be, and 2.8–3.0 wt.% B_2O_3). Another Fe-rich lens is dominantly magnetite, which encloses fine-grained zincian ferrohögbomite-2N2S, $(\text{Fe}^{2+}, \text{Mg, Zn, Al})_6(\text{Al, Fe}^{3+}, \text{Ti})_{16}\text{O}_{30}(\text{OH})_2$, containing minor Ga_2O_3 (0.30–0.92 wt.%). Fe-Al-B-rich lenses with prismatine (or kornepurine) constitute a distinctive type of B-enrichment in granulite-facies rocks and have been reported from four other localities worldwide. A scenario involving a tourmaline-enriched lateritic precursor affected by dehydration melting is our preferred explanation for the origin of the Fe-Al-B-rich lenses at the five localities. Whole-rock analyses and field relationships at another of these localities, Bok se Puts, Namaqualand, South Africa, are consistent with this scenario. Under granulite-facies conditions, tourmaline would have broken down to give kornepurine-prismatine (\pm other borosilicates) plus a sodic melt containing H_2O and B. Removal of this melt depleted the rock in Na and B, but the formation of ferromagnesian borosilicate phases in the restite prevented total loss of B.

KEYWORDS: prismatine, ferrohögbomite, Eastern Ghats Belt, India, Namaqualand, South Africa.

Introduction

ELEVATED concentrations of the light lithophile trace elements Li, Be and B are not common in granulite-facies rocks. For this reason the report by Ramesh Kumar *et al.* (1995) of relatively abundant B- and Ga-bearing surinamite, $(\text{Mg, Fe})_3(\text{Al, Fe})_3\text{O}[\text{AlBeSi}_3\text{O}_{15}]$, in cordierite-sillimanite gneisses from several localities in the

Vizianagaram (Vijayanagaram) district, an area in the Eastern Ghats Belt, attracted our interest. However, our study of samples from this area, including several examined by Ramesh Kumar *et al.* (1995), did not turn up surinamite, but abundant hypersthene instead, and thus the B-Be-Ga enrichment reported by Ramesh Kumar *et al.* (1995) could not be confirmed (Grew *et al.*, 2001). Associated with the quartz-sillimanite-hypersthene-cordierite gneisses are lenses rich in oxide, one of which contained abundant prismatine, the B-dominant member of the kornepurine

* E-mail: esgrew@maine.edu

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series (Grew *et al.*, 1996), while another contained a hōgbomite-group mineral in minor amounts. This particular prismatine contains minor Be, and hōgbomite, minor Ga, so that the trace elements reported by Ramesh Kumar *et al.* (1995) are found in the Eastern Ghats Belt, although not in the proportions and concentrations reported by those authors.

Prismatine is the B-dominant member of the kornerupine-prismatine series, $(\square, \text{Fe}, \text{Mg})(\text{Mg}, \text{Al}, \text{Fe})_5\text{Al}_4(\text{Si}, \text{B}, \text{Al})_5\text{O}_{21}(\text{OH}, \text{F})$, which has been reported from about 70 localities worldwide, with rare exceptions in Precambrian upper amphibolite- and granulite-facies metamorphic complexes (Grew, 2002a), including Paderu and Kondapalli in the Eastern Ghats belt (e.g. Higgins *et al.*, 1979; Grew, 1982; Nanda *et al.*, 1983; Grew *et al.*, 1990a). Prismatine and kornerupine have commonly formed from the prograde breakdown of tourmaline or in anatectic melts, but B metasomatism has played a role in some cases (Grew, 2002a). This series is most commonly found in silica-undersaturated, relatively aluminous and magnesian rocks, but members richer in B can occur in a greater diversity of chemical environments, including the iron oxide-rich rocks described in the present paper.

Ferrohōgbomite-2N2S, $(\text{Fe}^{2+}, \text{Mg}, \text{Zn}, \text{Al})_6(\text{Al}, \text{Fe}^{3+}, \text{Ti})_{16}\text{O}_{30}(\text{OH})_2$, is an Fe-dominant polysome of the polysomatic hōgbomite group (Armbruster, 2002; Hejny *et al.* 2002). Hōgbomite-group minerals are found rather widely, though sparsely, in a variety of environments, notably iron deposits, sulphide deposits and in medium- to high-grade metamorphic rocks (e.g. Petersen *et al.*, 1989; Grew *et al.*, 1990b), including Kantakapalli in the Eastern Ghats (Rao *et al.*, 1997). In many cases, hōgbomite-group minerals did not crystallize at high temperature, but instead formed by breakdown or reaction of Fe-Mg-Al-Ti oxides during retrogression under hydrating or oxidizing conditions.

In the present paper, we describe in detail the newly found prismatine and ferrohōgbomite-2N2S and outline a scenario for prismatine formation from granulite-facies metamorphism of a tourmaline-enriched lateritic precursor.

Samples

The two samples are from Venugopalapuram (18° 09' 30" N, 83° 26' 40" E), a few kilometres north of Vizianagaram town. One sample (#15) is a prismatine-oxide lens in quartz-sillimanite-

hypersthene-cordierite gneiss. In hand specimen the rock is black and appears to be opaque, but in thin section it has a cellular structure consisting of subparallel prisms up to several mm long of prismatine partly enclosed in oxides (Fig. 1). Prismatine is transparent and is pleochroic from very pale yellow to pale grey-blue. Abundant hercynite is riddled with blebs and lamellae of exsolved magnetite except in narrow margins around larger grains of magnetite (Fig. 2) and hematite-ilmenite intergrowths, both of which are subordinate to hercynite. Sapphirine, sillimanite, biotite and zircon are present in trace amounts. Sapphirine occurs with hercynite and magnetite (Fig. 2), whereas sillimanite and biotite are enclosed in prismatine (Fig. 3). The second sample (#14) is a mass of magnetite collected along the contact between pegmatite and quartz-sillimanite-hypersthene-cordierite gneiss. A hōgbomite-group mineral forms subhedral to euhedral platelets 0.1–0.4 mm dispersed in magnetite (Fig. 4); small amounts of rutile and corundum are also enclosed, whereas muscovite occurs around the margins.

The only other borosilicate found in this area is tourmaline in pegmatites.

X-ray diffraction

Single crystal X-ray diffraction (XRD) on a Siemens SMART CCD system gave the following lattice parameters for the hōgbomite-group mineral, $a = 5.71 \text{ \AA}$, $c = 18.36 \text{ \AA}$, which indicates the predominance of the 8H polysome, i.e. the mineral is identified as ferrohōgbomite-2N2S (Armbruster, 2002; Hejny *et al.*, 2002).

Chemical composition

Method

Concentrations of elements with $Z \geq 9$ were determined by M.G. Yates with a wavelength dispersive ARL SEMQ electron microprobe at the University of Maine and by C. Hejny with a wavelength dispersive Cameca SX-50 with the assistance of Edwin Gnos at the University of Bern. Analytical conditions on the ARL were 15 kV, accelerating voltage, 10 nA beam current, and a 3 μm spot size. Natural silicates and oxides were used as standards and data were processed with a $\phi(\rho z)$ scheme in which the effect of constituents not analysed with the electron microprobe (H_2O , B_2O_3) were included. F and Cl were analysed during separate sessions on the ARL

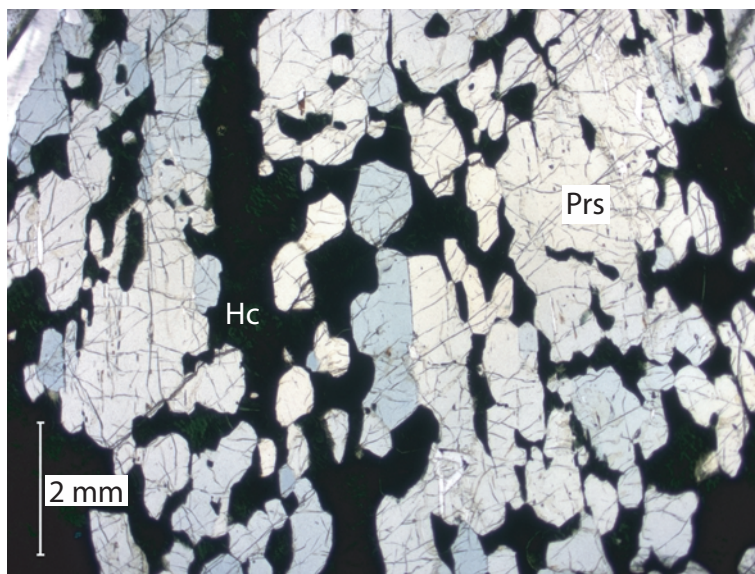


FIG. 1. Photomicrograph of prismatic (Prs)-bearing rock #15. The differing orientation of the prismatic prisms is evident from variations in colour. The dominant oxide is dark-green hercynite (Hc) riddled with magnetite exsolution. Plain light.

SEMQ, also at 15 kV and 10 nA, with an Ovonics 60 Å crystal, using polythionite (9.6 wt.% F) and scapolite as standards (Grew *et al.*, 1998a). Fluorine counts were fully corrected for peak

overlaps, and backgrounds for F were determined from mean atomic number rather than offsets.

The conditions in the Cameca SX-50 were 15 kV and 14 nA. The following minerals and

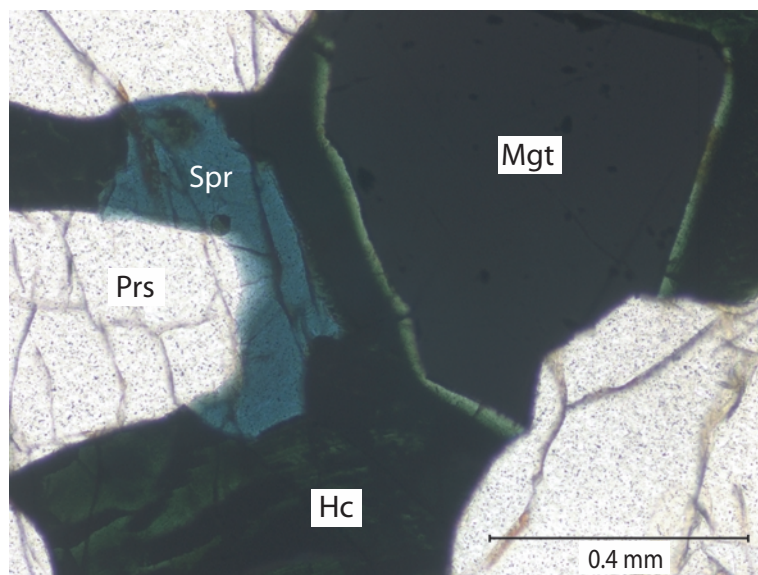


FIG. 2. Photomicrograph of prismatic (Prs), sapphirine (Spr, analysis in Table 1), hercynite (Hc) riddled with magnetite exsolution except in a narrow margin adjacent to magnetite (Mgt). Sample #15. Plain light.

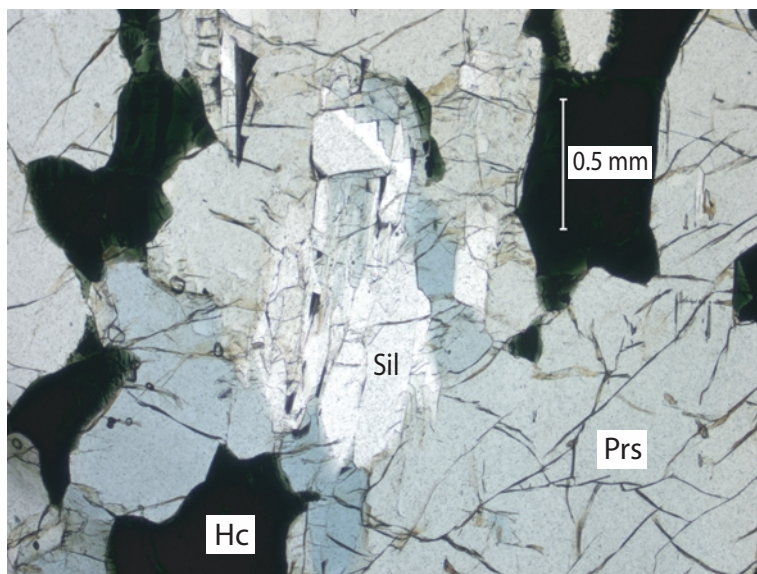


FIG. 3. Photomicrograph of a sillimanite aggregate (Sil, cf. col. 2, Table 2) enclosed in prismaticine (Prs). Hc – hercynite. Sample #15. Plain light.

synthetic materials were used as standards: corundum Al- $K\alpha$ (TAP), spinel Mg- $K\alpha$ (TAP), ilmenite Ti- $K\alpha$ (PET), almandine Fe- $K\alpha$ (LiF), gahnite Zn- $K\alpha$ (LiF), V_2O_5 V- $K\alpha$, eskolaite Cr- $K\alpha$ (LiF), tephroite Mn- $K\alpha$ (LiF), SnS_2

Sn- $K\alpha$ (LiF), NiO Ni- $K\alpha$ (LiF), $HgGa_2S_4$ Ga- $K\alpha$ (LiF), anorthite Ca- $K\alpha$ (PET), phlogopite F- $K\alpha$ (TAP), scapolite Cl- $K\alpha$ (PET). The overlap of V- $K\alpha$ with Ti- $K\alpha$ on LiF could not be corrected.

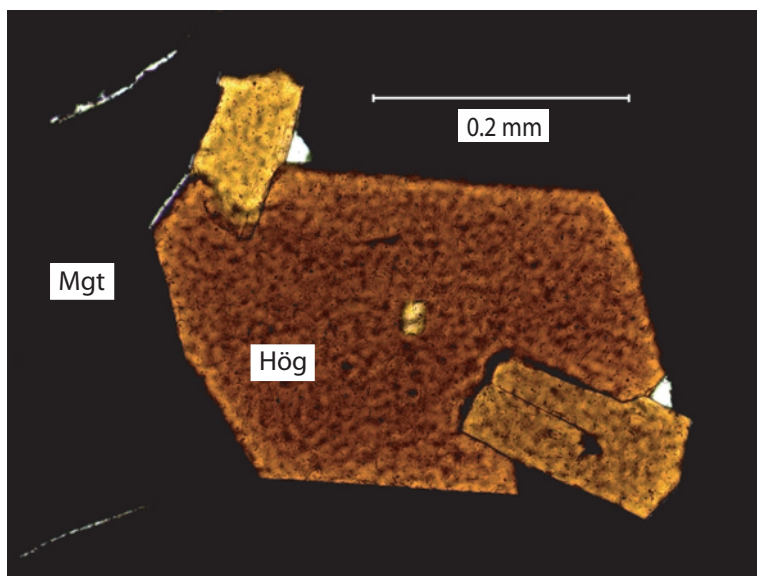


FIG. 4. Photomicrograph of euhedral ferrohögbomite-2N2S grains (Hög) in magnetite (Mgt). Sample #14. Plain light.

Lithium, Be and B were determined by secondary ion mass spectrometry (SIMS) with a Cameca ims 4f ion microprobe operated on the University of New Mexico campus by the Institute of Meteoritics. These elements were analysed under the following conditions: $^{16}\text{O}^-$ beam accelerated through 10 kV, a 15 nA primary beam current, 15 μm beam spot diameter, sample voltage offset of -105 ± 25 V and a 150 μm secondary ion image field with a 33 μm field aperture inserted. Prior to each analysis, the sample surface was cleaned using a rastered ion beam and imaged to better define the location of the analysis. Mass peaks for $^{6.5}\text{background}$ (2 s), $^7\text{Li}^+$ (3 s), $^9\text{Be}^+$ (5 s), $^{11}\text{B}^+$ (5 s) and $^{30}\text{Si}^+$ (3 s) were counted; and each spot analysis involved ten such counting cycles. These counting times resulted in internal precision of better than 5% for all elements. The calibration curves were produced using the relationship: [$^7\text{Li}^+$, $^9\text{Be}^+$ or $^{11}\text{B}^+ / ^{30}\text{Si}^+$] count ratio * SiO_2 wt.%] vs. element concentration in the following standards (all minerals): dravite, lithian schorl and elbaite for Li and B (Dyar *et al.*, 2001), type khmaralite (2.77 wt.% BeO) and surinamite no. 2292C for Be (Grew *et al.* 2000; Barbier *et al.*, 2002), and prismatic no. BM1940,39 for B (Cooper, 1997). The Li, Be and B contents (ppm element or wt.% oxide) were calculated from $^7\text{Li}^+ / ^{30}\text{Si}^+ * \text{SiO}_2$, $^9\text{Be}^+ / ^{30}\text{Si}^+ * \text{SiO}_2$ and $^{11}\text{B}^+ / ^{30}\text{Si}^+ * \text{SiO}_2$ (count ratio * wt.% by electron microprobe analyses) with the unknowns corrected using these calibration curves. Several standards, including the ones listed above, were run at various times during the day to monitor and correct for instrument drift. The analyses were performed at mass resolution of ~ 320 , which is sufficient for the $^{27}\text{Al}^{3+}$ signal not to interfere with the $^9\text{Be}^+$ signal in prismatic and sapphirine, and probably in sillimanite as well. The minimum Be content needed to avoid such interference in Al-rich minerals was estimated by Grew *et al.* (1998b) to be 0.001 wt.% BeO, which corresponds to 4 ppm Be (incorrectly given as 30 ppm Be by Grew *et al.*, 1998b).

Major and trace elements in the Bok se Puts rocks were determined with a Philips PW1400 and Siemens SRS-1 wavelength-dispersive sequential X-ray fluorescence spectrometers in the Department of Geological Sciences, University of Cape Town (Moore and Waters, 1990). Major elements were analysed by the Norrish fusion method (Norrish and Hutton, 1969); Na and trace elements by using 5-g

pressed briquettes. The data were calibrated with USGS and South African NIMROC standards.

Prismatic

Compared to prismatic from other localities, the sample from Venugopalapuram has a modest B content and relatively high Fe content; analyses at three different spots indicate minor chemical heterogeneity in terms of Fe/Mg ratio, B and F contents (Table 1). Although we are not able to measure the $\text{Fe}^{3+}/\text{Fe}^{2+}$ ratio directly, we suspect that substantial Fe^{3+} is present. The relatively elevated Fe^{3+} content and $\text{Fe}^{3+}/\text{Fe}^{2+}$ ratio, respectively, of associated sillimanite (Table 2) and sapphirine (Table 1) suggest that the prismatic $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratio could be at least 0.20, a relatively high value for the kornerupine-prismatic series (Grew *et al.*, 1999). The Venugopalapuram prismatic is one of the two most F-rich reported, cf. 0.94 wt.% F/0.374 F per 21.5 O from Paderu (Cooper, 1997; Hawthorne *et al.*, in prep.; this paper, Fig. 5).

Fe-Ti oxides

Overall, 23 individual grains of the h ogbomite-group mineral were analysed (Table 3). In all but one grain, the main variation is Zn substitution for other divalent cations, mainly Fe^{2+} and Mg, whereas Ti content is constant (Fig. 6a,b). The calculated $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratio and (Al + Ga) content are more scattered, but appear to be, like Ti, independent of variations among the divalent cations (Figs 6c, 7). Similar relationships were reported in ferroh ogbomite-2N2S from Sinnan Rocks, Antarctica (Grew *et al.*, 1990b; Hejny *et al.*, 2002). The compositions of grains 2-21, 2 & 4 are consistent with identification as ferroh ogbomite-2N2S using XRD on another grain from the same sample. One grain (#1) has a markedly higher Ti and lower Al + Ga content; the equation $0.5\text{Ti} + 0.5(\text{Fe}^{2+} + \text{Mg} + \text{Zn}) \approx 1(\text{Al} + \text{Ga} + \text{Fe}^{3+})$ on a 32 (O,OH) basis relates its composition to those of the others. This grain could be another polysome, but identification is not possible on the basis of composition alone.

The TiO_2 and Fe_2O_3 contents of the Venugopalapuram ferroh ogbomite-2N2S are typical for ferroh ogbomite-2N2S (Hejny *et al.*, 2002). It contains more Ga than most other h ogbomite-group minerals in which Ga had been sought, but its Ga content is not the highest reported; up to 1.79 wt.% Ga_2O_3 has been

TABLE 1. Analyses of prismatic (Prs) and sapphirine (Spr) in sample #15.

| Mineral Grain | Prs 1 | Prs 2 | Prs 3 | Spr 1 |
|--------------------------------|--------|--------|--------|--------|
| Wt. % | | | | |
| SiO ₂ | 29.72 | 29.92 | 29.00 | 13.44 |
| TiO ₂ | 0.31 | 0.32 | 0.33 | 0.08 |
| Al ₂ O ₃ | 41.21 | 40.71 | 41.84 | 56.48 |
| Fe ₂ O ₃ | — | — | — | 4.98 |
| FeO | 9.00 | 8.94 | 8.68 | 9.07 |
| MnO | 0.11 | 0.11 | 0.14 | 0.12 |
| MgO | 14.72 | 14.85 | 15.08 | 14.76 |
| CaO | 0.03 | 0.04 | 0.03 | 0.00 |
| K ₂ O | 0.00 | 0.00 | 0.00 | 0.00 |
| Na ₂ O | 0.06 | 0.06 | 0.05 | 0.00 |
| Li ₂ O | 0.03 | 0.03 | 0.03 | 0.01 |
| BeO | 0.05 | 0.05 | 0.05 | 0.04 |
| B ₂ O ₃ | 2.84 | 3.03 | 2.91 | 0.35 |
| F | 1.01 | 0.91 | 0.97 | — |
| Cl | 0.00 | 0.00 | 0.00 | — |
| H ₂ O | 0.72 | 0.76 | 0.74 | — |
| F=O | -0.43 | -0.39 | -0.41 | — |
| Sum | 99.38 | 99.36 | 99.44 | 99.33 |
| ppm | | | | |
| Li | 140 | 146 | 143 | 26 |
| Be | 175 | 171 | 166 | 137 |
| B | — | — | — | 1100 |
| Formulae | | | | |
| O | 21.5 | 21.5 | 21.5 | 20 |
| Si | 3.725 | 3.750 | 3.632 | 1.647 |
| Ti | 0.029 | 0.030 | 0.031 | 0.008 |
| Al | 6.087 | 6.013 | 6.177 | 8.159 |
| Fe ³⁺ | — | — | — | 0.459 |
| Fe ²⁺ | 0.943 | 0.937 | 0.910 | 0.929 |
| Mn | 0.012 | 0.012 | 0.015 | 0.013 |
| Mg | 2.749 | 2.774 | 2.816 | 2.696 |
| Ca | 0.004 | 0.005 | 0.004 | 0.000 |
| Na | 0.014 | 0.014 | 0.011 | 0.000 |
| Li | 0.015 | 0.016 | 0.015 | 0.003 |
| Be | 0.015 | 0.014 | 0.014 | 0.011 |
| B | 0.615 | 0.655 | 0.629 | 0.075 |
| Sum | 14.209 | 14.220 | 14.255 | 14.000 |
| F | 0.402 | 0.362 | 0.384 | — |
| OH | 0.598 | 0.638 | 0.616 | — |

Note: All Fe analysed as FeO. Li, Be and B determined by ion microprobe (SIMS). Ferric/ferrous ratio calculated in sapphirine assuming 14 cations/20 oxygens. H₂O calculated in prismatic

reported (Grew *et al.*, 2000; Hejny *et al.*, 2002; Hejny and Armbruster, 2002). The amounts of V,

TABLE 2. Composition of sillimanite in sample #15.

| Grain | 1 | 2 |
|--------------------------------|-------|-------|
| Wt. % | | |
| SiO ₂ | 36.68 | 36.24 |
| B ₂ O ₃ | 0.26 | 0.19 |
| TiO ₂ | 0.04 | 0.04 |
| Al ₂ O ₃ | 61.13 | 61.36 |
| Fe ₂ O ₃ | 1.75 | 1.60 |
| MnO | 0.00 | 0.00 |
| MgO | 0.13 | 0.12 |
| ppm | | |
| Li | <0.1 | <0.1 |
| Be | 13 | 10 |
| B | 800 | 594 |
| Sum | 99.99 | 99.55 |
| Formulae per 5 O | | |
| Si | 0.995 | 0.987 |
| B | 0.012 | 0.009 |
| Ti | 0.001 | 0.001 |
| Al | 1.954 | 1.971 |
| Fe ³⁺ | 0.036 | 0.033 |
| Mg | 0.005 | 0.005 |
| Sum | 3.003 | 3.005 |

Note: All Fe calculated as Fe₂O₃. Li, Be, B determined by ion microprobe (SIMS)

Cr, Ni and Sn are close to the limits of detection or below it.

The host magnetite contains negligible Ti; the most abundant impurities are Al₂O₃ and MnO (0.2–0.3 wt.% each). Much subordinate hematite contains 4% TiO₂; rutile, 0.8 wt.% FeO; corundum contains 0.5 wt.% Fe₂O₃ and 0.09 wt.% Ga₂O₃.

Gallium and Zn are below detection and Cr is negligible in hercynite in sample #15 (Table 3).

Distribution of the light elements in the silicates

Boron

Sillimanite and sapphirine incorporate B (Tables 1, 2). In general, the B contents of these two minerals increase modestly with increasing B content of associated kornerupine-prismatic until the latter mineral's B content reaches 0.65–0.9 B per formula unit, at which point their B contents increase more markedly (Fig. 8). The kink in the trend appears to be related to the maximum B

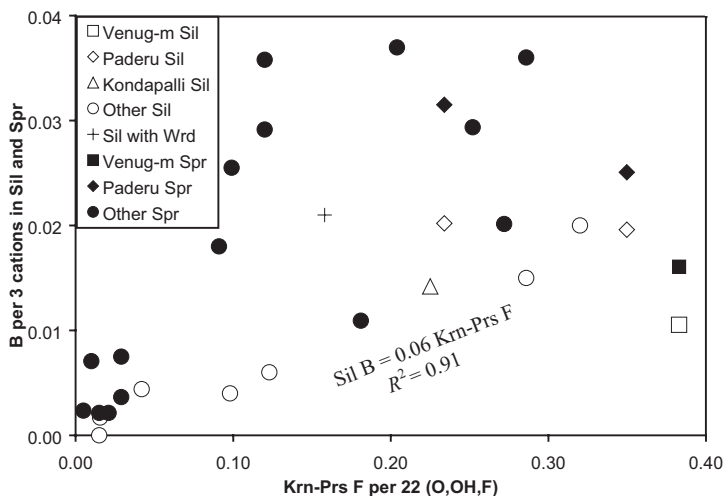


FIG. 5. Boron contents of sillimanite (Sil) sapphirine (Spr) as a function of kornepine-prismatine (Krn-Prs) F content. Sources: Grew *et al.* (1990a, 1992, 1998a) and references cited therein for other sillimanite and sapphirine; Grew *et al.* (1997) for sillimanite associated with werdingite (Wrd); this study for Venugopalapuram (Venug-m). The line is a least-squares fit to the data excluding sillimanite from Venugopalapuram and sillimanite associated with werdingite.

permissible in prismatine – 1 B/21.5 O (e.g. Grew, 2002a); the B content of the Venugopalapuram prismatine is below this limit. A linear increase of sillimanite B content with kornepine-prismatine F was noted by Grew *et al.* (1990a) and Grew (2002a) (reproduced here in Fig. 5); sapphirine B/ Σ cations ratio exceeds that of sillimanite, but otherwise shows no relationship to F. Exceptions to the linear trend are the newest data on sillimanite, i.e. sillimanite associated with werdingite and the Venugopalapuram sillimanite. The deviation of the werdingite-bearing sample is not surprising because B-bearing sillimanite is interpreted to contain werdingite-like domains (Niven *et al.*, 1991; Werding and Schreyer, 1992), and thus more B might be expected in sillimanite associated with werdingite. However, the relatively low values of the Venugopalapuram sillimanite and sapphirine calls into question the generality of the linear relationship. Grew *et al.* (1990a) attributed the relationship between sillimanite B and kornepine-prismatine F to temperature and water activity: as temperature increases and $a_{\text{H}_2\text{O}}$ decreases, the OH-F phases kornepine and prismatine become increasingly F rich and solid solution of werdingite increases in sillimanite. Moreover, the rocks in the Venugopalapuram area were subjected to ultra-high-temperature granulite-facies conditions,

which resulted in hypersthene + sillimanite + quartz and sapphirine + quartz assemblages (Kamineni and Rao, 1988; Grew *et al.*, 2001), conditions comparable to those experienced by rocks in nearby Paderu (e.g. Pal and Bose, 1997; Bhattacharya and Kar 2002). The discrepancy suggests that the linear relationship could be a coincidence resulting from the few samples studied, and that further examples will show that there is no simple relationship between sillimanite B and kornepine-prismatine F contents.

Beryllium

The Venugopalapuram sapphirine-prismatine pair is the second richest in Be reported and the two richest pairs suggest a preference of Be for kornepine-prismatine over sapphirine (Fig. 9), itself a Be sink in high-grade metamorphic rocks (e.g. Grew, 2002b). In contrast, distribution in Be-poor pairs suggest the reverse preference, but interpretation of this preference is complicated by the difficulty of measuring small amounts of Be in Al-rich minerals at low mass resolution with the ion microprobe (e.g. Grew *et al.*, 1990a). Analysis of coexisting kornepine-prismatine – sapphirine pairs at higher mass resolution is needed to clarify Be distribution between these two minerals.

TABLE 3. Compositions of hercynite (Hc) and högbomite-group minerals (Hög).

| Mineral | Hc | Hc | Hög | Hög | Hög | Hög |
|--------------------------------|--------|--------|--------|--------|--------|--------|
| Sample # | 15 | 15 | 14 | 14 | 14 | 14 |
| Section | — | — | 1 | 2 | 2 | 2 |
| Grain | 1 | 2 | 2 & 4 | 1 | 5 | 19 |
| Wt. % | | | | | | |
| TiO ₂ | 0.00 | 0.00 | 4.57 | 7.38 | 4.59 | 4.51 |
| SnO ₂ | — | — | 0.00 | 0.02 | 0.01 | 0.08 |
| Al ₂ O ₃ | 61.11 | 59.32 | 58.83 | 56.87 | 59.60 | 60.52 |
| V ₂ O ₃ | — | — | — | 0.14 | 0.17 | 0.01 |
| Cr ₂ O ₃ | 0.11 | 0.00 | 0.00 | 0.00 | 0.01 | 0.00 |
| Ga ₂ O ₃ | 0.00 | 0.00 | 0.56 | 0.92 | 0.42 | 0.54 |
| Fe ₂ O ₃ | 2.97 | 4.78 | 9.67 | 5.75 | 8.93 | 8.46 |
| FeO | 24.91 | 26.19 | 12.60 | 12.59 | 11.52 | 11.12 |
| MnO | 0.10 | 0.10 | 0.60 | 1.08 | 0.92 | 1.13 |
| MgO | 10.90 | 9.91 | 3.82 | 4.56 | 3.98 | 4.85 |
| ZnO | 0.00 | 0.00 | 7.22 | 7.79 | 7.90 | 6.51 |
| NiO | — | — | — | 0.06 | 0.01 | 0.01 |
| H ₂ O | — | — | 1.40 | 1.39 | 1.40 | 1.41 |
| Sum | 100.10 | 100.29 | 99.27 | 98.54 | 99.45 | 99.16 |
| Formulae | | | | | | |
| O | 4 | 4 | 31 | 31 | 31 | 31 |
| Ti | 0.000 | 0.000 | 0.738 | 1.201 | 0.737 | 0.719 |
| Sn | — | — | 0.000 | 0.002 | 0.001 | 0.007 |
| Al | 1.938 | 1.902 | 14.885 | 14.506 | 15.003 | 15.122 |
| V | — | — | — | 0.023 | 0.028 | 0.002 |
| Cr | 0.002 | 0.000 | 0.000 | 0.000 | 0.002 | 0.000 |
| Ga | 0.000 | 0.000 | 0.077 | 0.128 | 0.057 | 0.073 |
| Fe ³⁺ | 0.060 | 0.098 | 1.562 | 0.936 | 1.435 | 1.350 |
| Fe ²⁺ | 0.561 | 0.596 | 2.263 | 2.278 | 2.057 | 1.971 |
| Mn | 0.002 | 0.002 | 0.109 | 0.197 | 0.167 | 0.202 |
| Mg | 0.437 | 0.402 | 1.222 | 1.472 | 1.266 | 1.532 |
| Zn | 0.000 | 0.000 | 1.144 | 1.245 | 1.246 | 1.019 |
| Ni | — | — | — | 0.011 | 0.002 | 0.002 |
| Sum | 3.000 | 3.000 | 22.000 | 22.000 | 22.000 | 22.000 |
| H | — | — | 2.000 | 2.000 | 2.000 | 2.000 |
| X _{Mg} | 0.438 | 0.403 | 0.351 | 0.393 | 0.381 | 0.437 |

Note: All Fe analysed as FeO. F, Cl and Ca are below detection in ferrohögbomite-2N2S. Ferric/ferrous ratio calculated in hercynite assuming 2 cations/3 oxygens, and in ferrohögbomite-2N2S assuming 22 cations/31 oxygens. H₂O calculated in högbomite-group minerals assuming OH = 2/31 oxygens. $X_{Mg} = Mg/(Mg + Fe^{2+})$. Analyst: Col. 1–3 – M.G. Yates; Col. 4–6 – C. Hejny

Lithium

In general, this alkali is preferentially incorporated in kornrupine-prismatine relative to sapphirine (Grew *et al.*, 1990a), and this preference is evident in the Venugopalapuram assemblage (Table 1).

Origin of the boron enrichment

The Venugopalapuram prismatine-rich lens is one of the few examples of rocks enriched in Al, Fe and B in relatively high-temperature granulite-facies rocks (Table 4). These Al-Fe-B-rich rocks appear to be restricted to lenses a few tens of

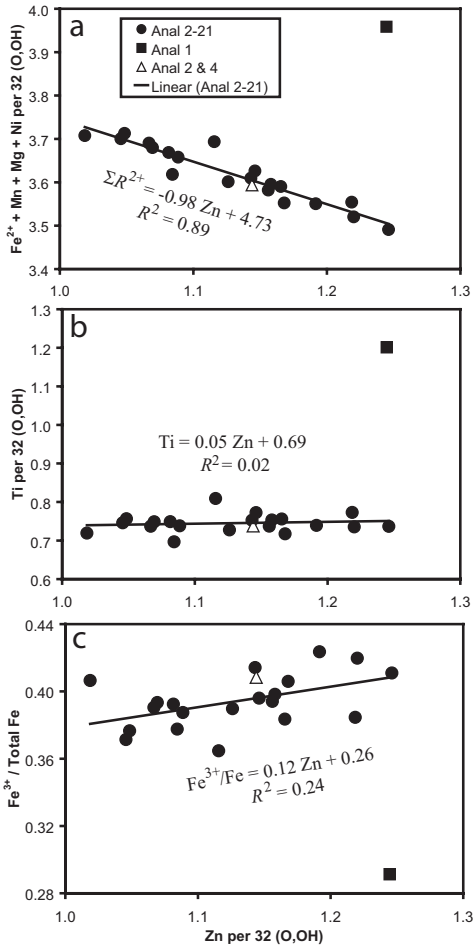


FIG. 6. Variations of total divalent cations (ΣR^{2+}), Ti and Fe^{3+}/Fe ratio with Zn in ferrohögbonite-2N2S from Venugopalapuram calculated in terms of 30 O and 2OH. Grains 1–21 were analysed by C. Hejny; grains 2 (3 points) and 4 were analysed by M.G. Yates in another section. The lines are least-squares fits.

centimetres thick where found *in situ*, and are typically associated with similar rocks lacking borosilicate: rocks enriched in sillimanite, hercynite, and ilmenite rock at Bok se Puts (Fig. 10) and the ferrohögbonite-2S2N-bearing magnetite lens at Venugopalapuram. The B-rich rocks are silica-undersaturated, whereas associated Al-Fe rocks lacking borosilicate are quartz-bearing in some cases. Relatively high f_{O_2} in the Al-Fe-B-rich rocks is indicated by the presence of hematite or hematite lamellae in ilmenite and relatively high sillimanite Fe_2O_3 contents.

Only the Bok se Puts rocks have been analysed (Table 5). Like other upper amphibolite and granulite-facies aluminous rocks containing borosilicates (e.g. Grew, 2002a), the Bok se Puts borosilicate rock is depleted in Ca and Na and enriched in Mg and Fe; additionally it is depleted in K; the small quantities of biotite and absence of feldspar (except anorthite at Urungwe and possible K-feldspar at Labwor) suggest depletion in Na, K and Ca in the other rocks as well. However, kornepurine-prismatine has incorporated considerable Li (Table 4), suggesting little depletion of this alkali. Despite the high Fe content, the ferromagnesian silicates are Mg dominant (e.g. Table 1); much Fe^{2+} is combined with Ti, Fe^{3+} and Al in the oxide phases.

The Al-Fe±B-rich lenses are commonly found in pelitic gneisses, for example, gneisses containing orthopyroxene + sillimanite + cordierite (Venugopalapuram), or cordierite, garnet and/or sillimanite (Urungwe) or along the contacts between cordierite-sillimanite gneiss and biotite gneiss (Bok se Puts, Fig. 10), whereas at Labwor, the lenses occur in mafic granulite. The host rocks for the Paderu borosilicates are not known; by analogy with other sapphirine-bearing rocks from Paderu, the borosilicate-rich rocks could have originated as lenses in khondalite (sillimanite-garnet metapelite) or along the contacts between khondalite and mafic granulite (Lal *et al.*, 1987), or as lenses in quartzofeldspathic gneisses such as leptynite, granite and charnockite (Pal and Bose, 1997; Bhattacharya and Kar, 2002).

In general, granulite-facies rocks are depleted in B so that any enrichment raises the question of what mechanism can counter the effects of devolatilization and anatexis (e.g. Leeman and Sisson, 2002). In other words, what mechanism would explain the mineralogical and chemical features of the rocks listed in Table 4? One explanation is that metamorphism was not isochemical and the present composition resulted not only from the precursor composition, but also from various processes associated with granulite-facies metamorphism. One possibility is that B was introduced metasomatically during metamorphism, e.g. by an anatectic process (Anderson, 1975) or from an intrusion. The Al-Fe±B and associated rocks are intruded by pegmatite at Urungwe and Labwor, but tourmaline is found in pegmatite only at Bok se Puts and Venugopalapuram. The tourmaline-bearing pegmatites were emplaced after the major metamorphic events during which

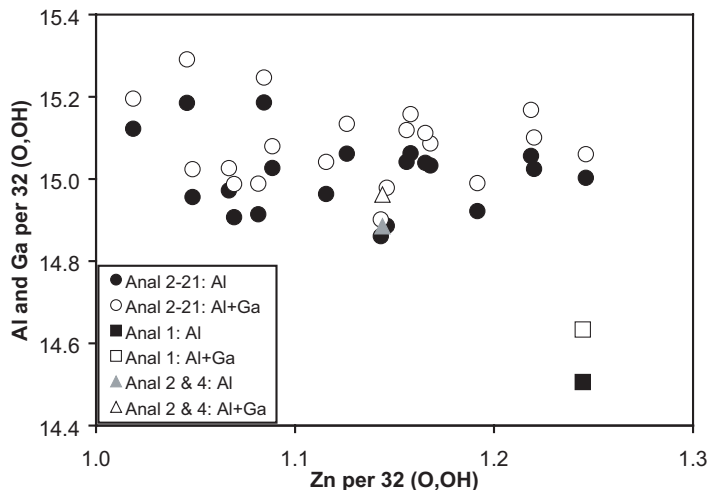


FIG. 7. Variations of Al and Ga with Zn in ferrohögbonite-2N2S from Venugopalapuram calculated in terms of 30 O and 2OH. For grain reference, see Fig. 6.

the other borosilicates crystallized at Bok se Puts, and it is possible that the pegmatites at Venugopalapuram are also post-metamorphic and would not have contributed B to the prismatic-rich lens.

Treloar (1995) proposed that the Urungwe B-rich rock was an extremely refractory restite into which B was partitioned relative to the melt; Bhattacharya and Kar (2002) inferred a role for melting in the metamorphism of sapphirine-

bearing rocks at Paderu. The absence of evidence for melting in the B-rich layer at Bok se Puts could be the result of complete removal of melt. But such melting would also be expected to deplete a rock in B given the ready solubility of this element in granitic melts (e.g. Dingwell *et al.*, 2002), so that a melting process in the areas listed in Table 4 should have left a restite depleted in B.

Alternatively, the Al-Fe±B-rich rocks resulted from a roughly isochemical metamorphism of a

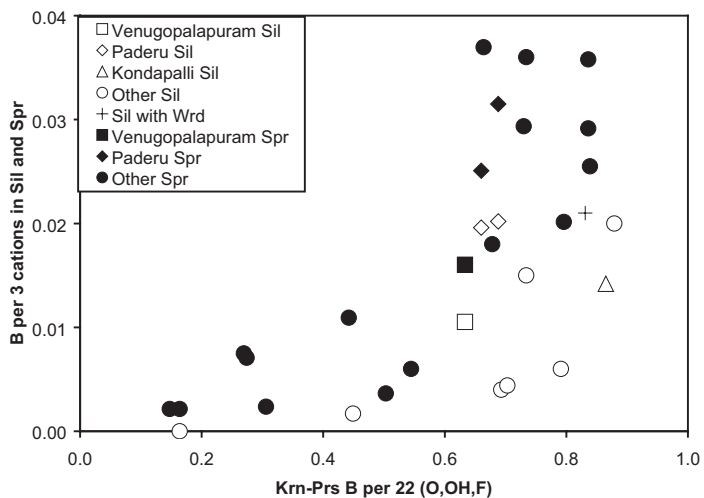


FIG. 8. Boron contents of associated sillimanite (Sil), sapphirine (Spr) and korerupine-prismatine. Sources: same as Fig. 5. Wrd – werdingite.

TABLE 4. Examples of Al-Fe-rich rocks containing abundant borosilicate minerals.

| Locality | Constituents | Peak <i>T-P</i> conditions | Sil Fe ₂ O ₃ wt.% | Km/Prs Be ppm | Wrd Be ppm | Km/Prs Li ppm | Primary sources |
|--|--|----------------------------|---|---------------|------------|---------------|---|
| Venugopalapuram, India (Eastern Ghats Belt) | Prs, Spr, Bt, Sil, Zrn, Hc, Hem-Ilm, Mgt | ~1000°C, ~7 kbar | 1.60–1.75 | 166–175 | – | 140–146 | Grew <i>et al.</i> (2001), this paper |
| Paderu, India (Eastern Ghats belt) | Prs, Gdd, Spr, Bt, Sil, Hem-Ilm, Hc, Crn | ~1000°C, ~10 kbar | 1.29–1.30 | 0–14 | – | 230–290 | Grew and Hinthorne (1983); Grew <i>et al.</i> (1990a); Pal and Bose (1997); Bhattacharya and Kar (2002) |
| Labwor Hills, Uganda (probably Archaean) | Krn, Spr, Sil, Bt, Kfs(?), Zrn, Hc, Mgt, Hem-Ilm | ~1000°C, 7–9 kbar | 1.58 | 14–18 | – | 90–120 | Nixon <i>et al.</i> (1973, 1984); Sandiford <i>et al.</i> (1987) |
| 'Boron zone', Urungwe, Zimbabwe (Magondi belt) | Gdd, Prs, Sil, Wrd, Tur, Bt, An, Zrn, Crn, Hc, Mgt, Ilm, Ap, Mnz | 700–800°C, 5–6 kbar | 0.92 | 47 | 40 | 650 | Anderson (1975); Treloar and Kramers (1989); Treloar (1995); Munyanyiwa <i>et al.</i> (1993); Grew <i>et al.</i> (1997); Munyanyiwa and Maaskant (1998) |
| Bok se Puts, South Africa (Namaqualand) | Prs, Wrd, Sil, Gdd, Hc, Ilm, Zrn | 800–850°C, 5 kbar | 1.57 | – | 54 | – | Moore <i>et al.</i> (1990); Grew <i>et al.</i> (1998b); Waters and Moore (unpublished) |

Note: An – anorthite; Ap – apatite; Bt – biotite; Crn – corundum; Gdd – granddiertite; Hc – hercynite; Hem – hematite; Ilm – ilmenite; Kfs – K-feldspar; Km – kornepine; Mgt – magnetite; Mnz – monazite; Prs – prismatic; Spr – sillimanite; Tur – sapphirine; Wrd – tourmaline; Zrn – zircon

TABLE 5. Analyses of rocks from Bok se Puts, Namaqualand, South Africa.

| Sample | Prismatic rock | Spinel- magnetite rock | Cordierite- sillimanite gneiss |
|--------------------------------|-------------------|------------------------------|--------------------------------------|
| | VP-49 | VP-48 | VP-50 |
| Wt. % | | | |
| SiO ₂ | 21.23 | 0.82 | 73.16 |
| TiO ₂ | 2.48 | 2.48 | 0.61 |
| Al ₂ O ₃ | 46.38 | 47.44 | 13.83 |
| FeO | 19.94 | 44.84 | 4.76 |
| MnO | 0.41 | 0.60 | 0.09 |
| MgO | 7.43 | 5.22 | 1.56 |
| CaO | 0.08 | 0.02 | 0.79 |
| Na ₂ O | 0.03 | 0.03 | 0.60 |
| K ₂ O | 0.04 | 0.04 | 2.70 |
| P ₂ O ₅ | 0.13 | 0.02 | 0.12 |
| LOI | 0.07 | 2.45 | 1.12 |
| H ₂ O ⁻ | 0.1 | 0.05 | 0.12 |
| Total | 98.28 | 100.01 | 99.63 |
| ppm | | | |
| Sc | 79 | 29 | 15 |
| V | 221 | 477 | 59 |
| Cr | 282 | 508 | 73 |
| Co | 52 | 124 | 17 |
| Ni | 91 | 301 | 21 |
| Cu | 41 | <2 | 7 |
| Zn | 506 | 2217 | 78 |
| Rb | 5 | 2 | 168 |
| Sr | 27 | <2 | 58 |
| Y | 56 | 19 | 44 |
| Zr | 1117 | 1626 | 316 |
| Nb | 32 | 37 | 14 |
| Ba | 76 | 30 | 692 |
| La | 187 | 69 | 53 |
| Ce | 390 | 135 | 113 |
| Nd | 191 | 71 | 57 |
| Pb | 12 | 6 | 16 |
| Th | 77 | 27 | 18 |
| U | 2 | <3 | 2 |

Note: Analyst – J.M. Moore. Analysis for VP-49 was also reported in Grew (2002a). LOI – loss on ignition

distinctive B-rich sedimentary precursor. Although anatexis undoubtedly affected the bulk composition of the rocks, the presently observed composition still has many features attributable to the original composition. A notable characteristic of the sequence of rock types at Bok se Puts is asymmetry (Fig. 10), which, together with the unusual composition of the oxide and borosilicate rocks, suggests derivation from metamorphism of

a duricrust that capped a lateritic profile. Boron enrichments are possible in lateritic profiles (Moore and Waters, 1990); e.g. Angélica *et al.* (1996) reported 17% residual tourmaline, largely dravite, in latosol derived from weathering of lateritic iron crust in the Águas Claras deposit, Amazon region, Brazil. The latosol is mainly composed of kaolinite, goethite, gibbsite, hematite and quartz. A similar situation might pertain to the Loulo gold deposit, Mali, where 1500 ppm B were reported in a truncated weathering profile over tourmaline-bearing sandstone (Zeegers and Lecomte, 1992).

The sillimanite-cordierite gneiss could represent the base of the lateritic profile on the rhyodacitic precursor to the biotite gneisses that host the borosilicate occurrence at Bok se Puts (Fig. 10). Its spidergram (Fig. 11) is not unlike that of typical granitic rocks, with low Sr, P, and Ti, relative to *LREE* and Y; however Na is relatively low and its aluminium saturation index, $ASI = Al/(2Ca + K + Na) = 2.6$, is much higher than the ASI of fresh granitic rocks.

Figure 12 compares compositions of the Bok se Puts borosilicate and oxide rocks with an average for all bauxites (Bronevoy *et al.*, 1984, 1985); this average gives an overall orientation for lateritic bauxites as these constitute 88% of all bauxites in terms of weight (Bárdossy and Aleva, 1990). For a sizable number of constituents, notably, Al, Ti, Fe, Sc, V, Cr, Y, Nb, Ba and Th, there is a remarkable correspondence between the compositions of the Bok se Puts borosilicate and oxide rocks on the one hand and average bauxite on the other. The most marked discrepancies that are not obviously related to metamorphic or anatectic processes (see below) are the high contents of Mg, Mn, Co, Ni, Zn, Zr and La relative to their average content in bauxite. However, anomalously high contents of these elements may not be unique to Bok se Puts. Co, Ni, Zn, Zr and La are among the elements that Bol *et al.* (1989) found enriched in Fe – Al granofels consisting largely of plagioclase, spinel *sensu lato*, opaque oxide, cordierite and sillimanite from Rogaland, Norway, enrichments they attributed to pre-metamorphic lateritization of a basaltic protolith. In the case of Bok se Puts, the elevated contents of Zr and La could be due to resistant minerals (zircon, monazite) inherited from the parent rock, a phenomenon observed in bauxite (Bárdossy and Aleva, 1990; Moore and Waters, 1990). Enrichments of Mn and Ni have been reported in a few lateritic bauxite deposits, e.g. lithiophorite, $(Al, Li)(Mn^{4+}, Mn^{3+})O_2(OH)_2$

LATERITIC PRECURSORS OF GRANULITE-FACIES Fe-OXIDE LENSES?

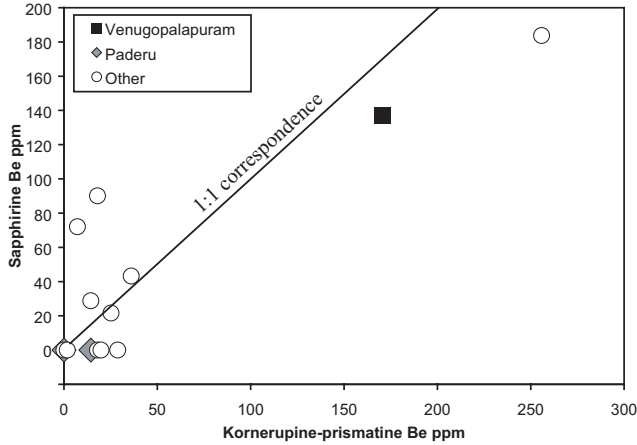


FIG. 9. Beryllium contents of associated sapphirine and kornerupine-prismaticine. Sources: Grew *et al.* (1990a, 1998a) and references cited therein for other and Paderu data; this study for Venugopalapuram data.

(Bárdossy and Aleva, 1990). If the precursors to the borosilicate and oxide rocks contained admixed kaolinite (as does the Amazon region latosol cited above) or montmorillonite, enrich-

ment in Li, Co, Ni and Zn is possible (Zeeegers and Lecomte, 1992).

The relatively high MgO content is harder to explain. Bol *et al.* (1989) suggested that the

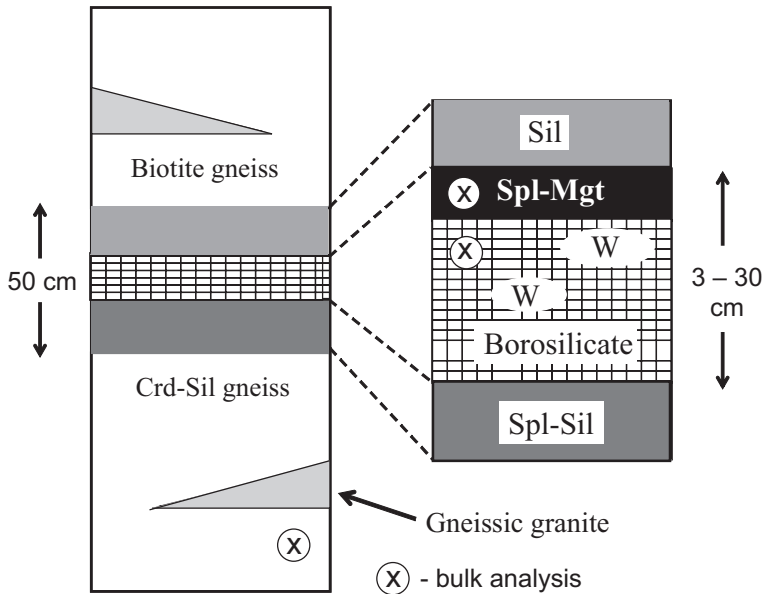


FIG. 10. Schematic cross sections of the borosilicate and associated oxide- and sillimanite-rich rocks at Bok se Puts, Namaqualand Metamorphic Complex, South Africa. The Spl-Mgt rock is hercynite-ilmenite-magnetite-sillimanite with minor amounts of biotite/phlogopite and zircon. The Sil and Sil-Spl rocks have the same constituents, but sillimanite and sillimanite + hercynite are dominant, respectively. The Crd-Sil gneiss is quartz-micropertthite-cordierite-plagioclase-biotite-sillimanite-hercynite with lesser ilmenite-magnetite, apatite, zircon and possibly monazite. The ovals labelled W indicate werdingite-bearing lenticular pockets in the borosilicate rock. Mineral abbreviations: Crd – cordierite, Mgt – magnetite, Sil – sillimanite, Spl – spinel *sensu lato*.

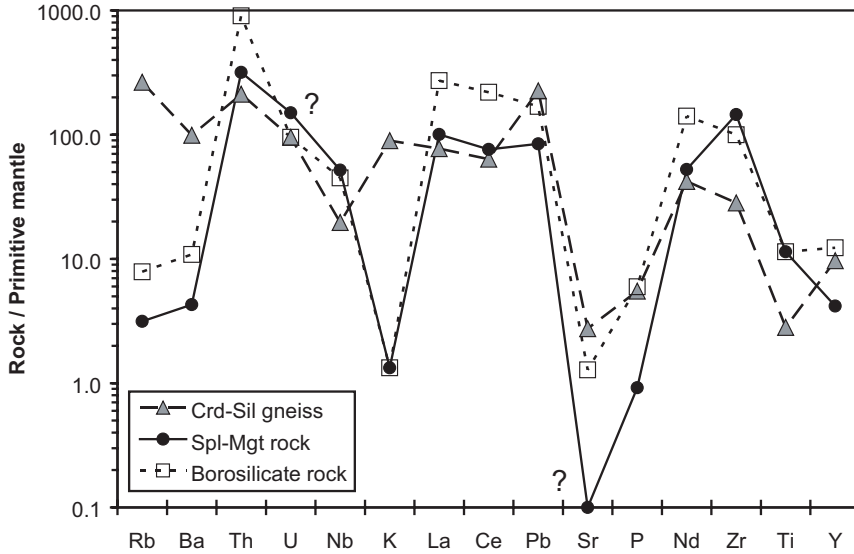


FIG. 11. Spidergram for three rocks from Bok se Puts, Namaqualand Metamorphic Complex, South Africa (Table 5) normalized to primitive mantle (Sun and McDonough 1989). The question mark (?) indicates that the plotted ratio is the maximum possible because the element is below detection (Sr and U in Spl-Mgt rock).

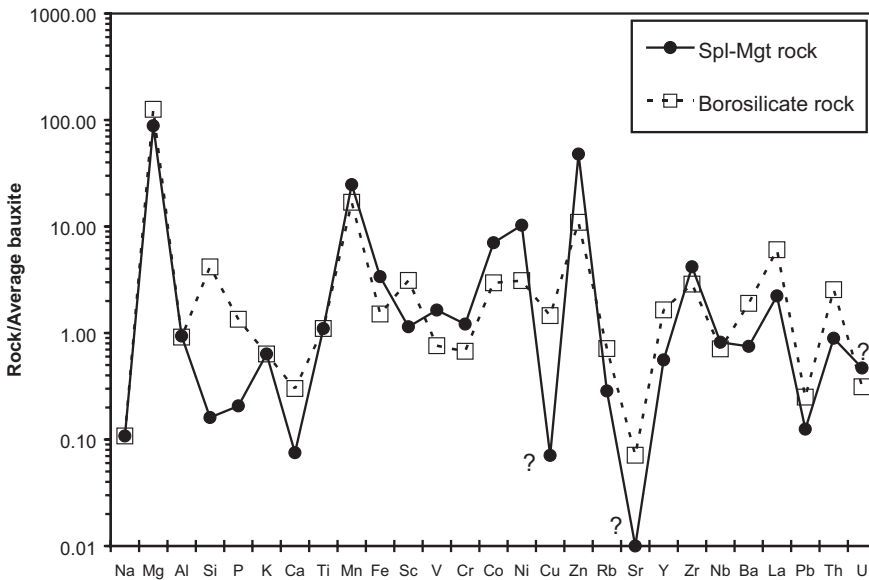


FIG. 12. Spidergram for two rocks from Bok se Puts, Namaqualand Metamorphic Complex, South Africa (Table 5) normalized to average bauxite (Bronevoy *et al.* 1984, 1985). The question mark (?) indicates that the plotted ratio is the maximum possible because the element is below detection (Cu, Sr, U in Spl-Mgt rock).

relatively high but variable MgO content in the Rogaland Fe-Al granofels resulted from metasomatic contamination from nearby dolomite marble. In the absence of marble at Bok se Puts, dravite might have contributed some of the Mg to the precursors of the borosilicate and spinel-magnetite rocks, but in the latter case, B was entirely lost during metamorphism. Clays are conceivably an Mg source, e.g. chlorite is a very rare constituent of bauxite (Bárdossy and Aleva, 1990). We cannot exclude the possibility that the laterite had a mafic component that was not preserved in its unweathered form. This could also account for the high V, Cr, Co, Zn and Ni contents.

Gallium, like Al, Cr and V, is generally present in elevated amounts in bauxite (Bárdossy and Aleva, 1990). The presence of significant Ga in ferrohöbomite-2N2S in the Venugopalapuram magnetite-rich rock suggests some bulk Ga enrichment, which lends support to its having a lateritic bauxite precursor.

Metamorphism and anatexis also had an effect, albeit subordinate, on the resulting compositions of the Al-Fe±B rocks, most likely, through dehydration melting of a tourmaline-bearing assemblage. In general, tourmaline dominated by the dravite component is stable up through the upper amphibolite facies of metamorphism, but has been found in granulite-facies rocks (e.g. Henry and Dutrow, 2002). Tourmaline did not survive the temperatures of $\geq 800^\circ\text{C}$ estimated for the localities listed in Table 4 except Urungwe, where secondary tourmaline developed as temperature dropped below $700\text{--}750^\circ\text{C}$ (Grew *et al.*, 1997). Experimental studies of the stability of dravitic tourmaline, reviewed in Werding and Schreyer (2002), indicate that at high temperature it undergoes incongruent melting reactions, leaving aluminous and B-bearing phases in the residue, notably prismaticine from 900 to 1000°C and from 5 to 25 kbar. Crucially, it appears that the entire Na content of tourmaline enters the melt and vapour phases. Therefore, the following reaction relationship is a possible explanation for tourmaline breakdown at localities listed in Table 4:

Dravitic tourmaline ± biotite → prismaticine ± grandidierite ± werdingite ± sapphirine + melt dominated by Na-plagioclase and containing B_2O_3 and H_2O

A melt of this composition might be sufficiently mobile not to leave typical leucosomes in the source rock, although it would have had

potential to interact with neighbouring rocks or form pegmatitic segregations. Removal of this melt could explain depletion of Na, Ca and Sr (also Pb and U?) in the Bok se Puts borosilicate and oxide rocks relative to average bauxite, whereas K, Rb and Ba were not greatly depleted (Fig. 12). The Mg-enriched lateritic precursor created an environment conducive to the formation of prismaticine and other borosilicates and thereby allowed significant retention of B in the restitic assemblage; prismaticine would also be a suitable host for retaining Li.

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