Werdingite, a new borosilicate mineral from the granulite facies of the western Namaqualand metamorphic complex, South Africa

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ABSTRACT

A new borosilicate mineral, werdingite, is reported from the granulite facies of the Namaqualand metamorphic complex at Bok se Puts, Namaqualand, South Africa. The mineral occurs in association with kornerupine and grandidierite in a sillimanite-hercynite-rich band in a supracrustal gneissic sequence. It has the chemical composition MgO 4.46, FeO 5.06, Al_2O_3 59.49, TiO_2 0.05, SiO_2 19.83, B_2O_3 10.19, sum 99.08 wt%. This corresponds to the ideal formula $(Mg,Fe)_2Al_{14}Si_4B_4O_{37}$. The unit cell of werdingite is triclinic, space group $P\bar{1}$, with $a = 7.995(2)$, $b = 8.152(1)$, $c = 11.406(4)$ Å, $\alpha = 110.45(2)°$, $\beta = 110.85(2)°$, $\gamma = 84.66(2)°$, $V = 650.5(3)$ Å^3, and $Z = 1$. The X-ray powder-diffraction lines with the strongest intensities are [d(Å), I, hkl] 5.43(80)($1\bar{1}0$), 5.23(100)(110), 4.98(75)(002,$11\bar{2}$), 3.392(50)($2\bar{1}0$); 2.708(60)($2\bar{2}0$), 2.194(50)($2\bar{1}\bar{4}$,$03\bar{4}$), and 1.527(40)($2\bar{4}4$,$4\bar{2}\bar{4}$). Werdingite is brownish yellow and translucent with a vitreous luster, conchoidal fracture, and Mohs' hardness of 7. It has a measured density of 3.04 g/cm^3, and a calculated value of 3.07 g/cm^3, and it occurs as anhedral to subhedral xenoblasts up to 3 mm in diameter. The optical properties of werdingite include biaxial (−); $2V = 33(1)°$ (meas.), 42°(calc.); $\alpha = 1.614(2)$, $\beta = 1.646(2)$, $\gamma = 1.651(2)$; strong dispersion, $r > v$; $Z = c$; pleochroism, X, Z colorless and Y yellow. Werdingite is named in honor of Dr. Günter Werding, Institut für Mineralogie, Ruhr-Universität, Bochum, Germany.

INTRODUCTION

During a field examination of high-grade metamorphic rocks at the Vaalputs National Radioactive Waste Disposal Facility, Namaqualand District, South Africa, in 1986, rock samples containing the rare borosilicate minerals kornerupine and grandidierite were collected in asociation with lenses of a sillimanite-hercynite-rich rock. In addition, some of these samples contained a honey-colored mineral that did not conform either compositionally or optically to any known mineral. Further study revealed that the unknown species was a new magnesium-iron-aluminum borosilicate mineral that has been named *werdingite*.

Several poorly characterized borosilicate phases not reported in nature were found in high-temperature (±800 °C) synthesis experiments in the system MABSH [MgO-Al_2O_3-B_2O_3-SiO_2-H_2O] (Werding and Schreyer, 1984), and werdingite may represent one of these phases. The species has been approved by the Commission on New Minerals and Mineral Names of the International Mineralogical Association and is named after Dr. Günter Werding of the Institut für Mineralogie, Ruhr-Universität, Bochum,

Germany, in recognition of his pioneering experimental work in systems such as MABSH. Cotype material has been deposited at the South African Museum, Cape Town, under the catalogue numbers SAMG7140-7150. Additional material is held by the first author at the Department of Mineralogy and Geology, University of Cape Town.

OCCURRENCE

The sample site is situated in the northwest portion of the farm Bok se Puts, northwest Cape, South Africa, at approximately 30°7′S, 18°27′E. The locality falls within the boundaries of the Vaalputs National Radioactive Waste Facility, approximately 100 km southeast of the town of Springbok. The geology of the disposal site is described by Andreoli et al. (1987).

The host rocks form part of the granulite-facies terrane of the mid-Proterozoic Namaqualand metamorphic complex (Waters, 1986) and occur within a supracrustal sequence of metasedimentary and metavolcanic gneisses (Moore, 1986) from the Garies Subgroup of the Okiep Group (SACS, 1980). The supracrustal rocks were intruded by semi-concordant tongues and sheets of granitic gneiss during the 1100 Ma Namaqua tectono-metamorphic event. Peak metamorphic conditions in the granulite-facies zone are estimated to be 800 to 850 °C at

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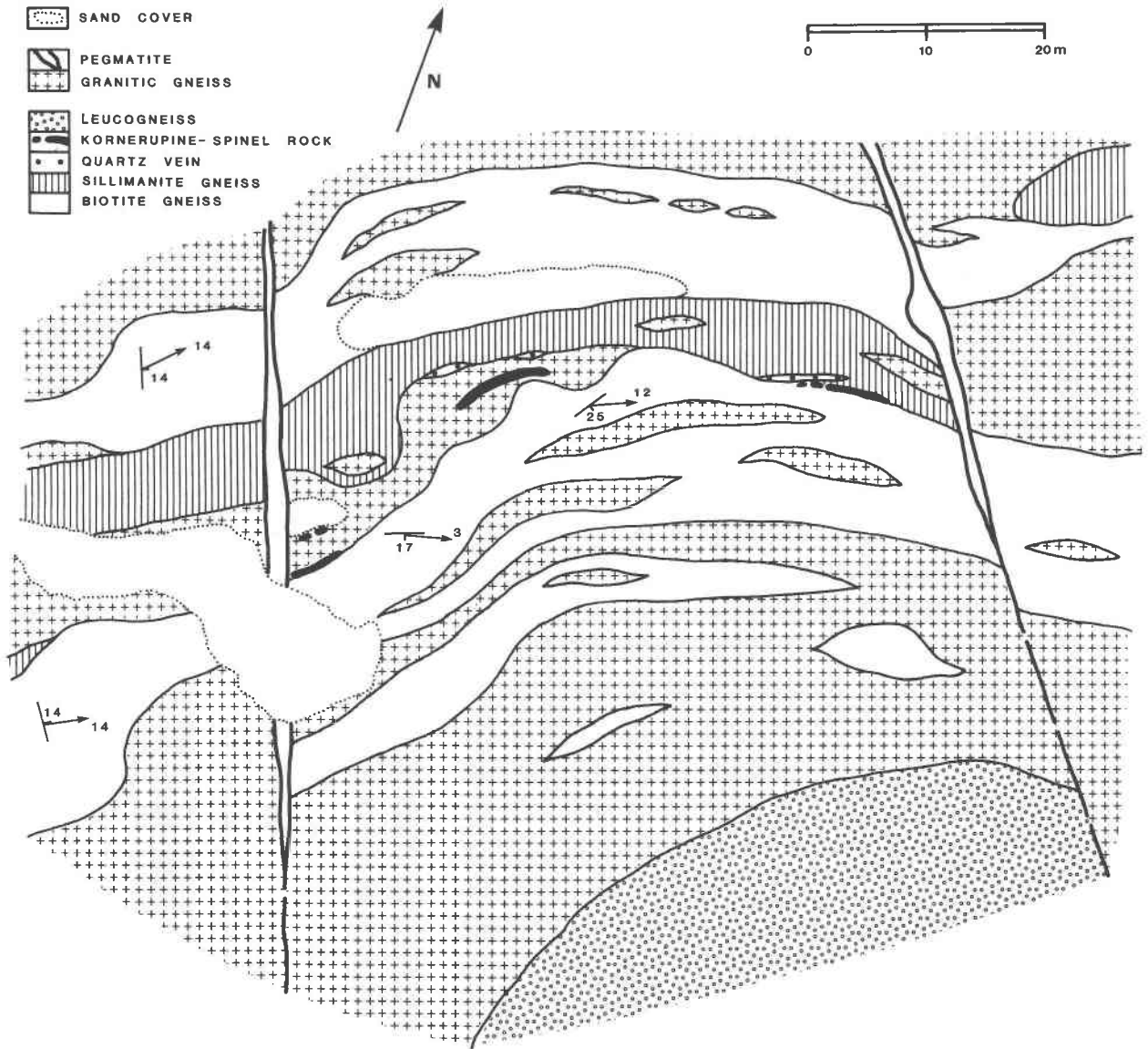
Fig. 1.   Detailed geological map of the Bok se Puts locality.

5-kbar pressure (Waters, 1989), and *P-T* conditions at the sample site are assumed to have been close to this peak.

At the Bok se Puts locality, an Al-Fe–rich horizon, consisting mainly of sillimanite + hercynite + ilmenite, lies at the upper contact of a metapelitic cordierite-sillimanite gneiss unit enclosed by biotite gneisses (Fig. 1). The Al-Fe horizon occurs as three discrete lenses, each less than 8 m in length and 50 cm in thickness. Enclosed within the sillimanite-oxide rocks is a B-rich layer, 2–20 cm thick, consisting predominantly of large poikiloblastic crystals of kornerupine. Werdingite occurs in association with grandidierite in small lenticular pockets, a few centimeters across, within the kornerupine layer. Werdingite forms millimeter-sized rounded grains and small clusters of grains in kornerupine, and itself contains inclusions of sillimanite, tiny rounded zircons, and slender, parallel-oriented needles of a dark-colored phase (rutile?). Contacts between werdingite and kornerupine are commonly marked by rims of grandidierite (Fig. 2), and those between werdingite and oxide-hercynite clusters by broad lobes of grandidierite-hercynite symplectite (Fig. 3). The symplectite progressively replaces werdingite and forms embayments in adjacent oxide-hercynite clusters.

Borosilicate-rich rocks are a widespread, if uncommon, component of the metamorphosed supracrustal sequences in the western Namaqualand metamorphic complex. Tourmaline-rich quartzitic and metapelitic rocks are present in the amphibolite-facies terrane, together with rare dumortierite in sillimanite-topaz–rich rocks (Willner et al., 1990), and in the lower-*T* region of the granulite-

Fig. 2. Kornerupine (K) enclosing werdingite (W) that contains sillimanite inclusions. Replacement of werdingite by grandidierite (G) (±hercynite) occurs at kornerupine-werdingite boundaries. In the bottom left corner, grandidierite-hercynite symplectite replaces werdingite from a hercynite-werdingite boundary. Photo length is 2 mm.
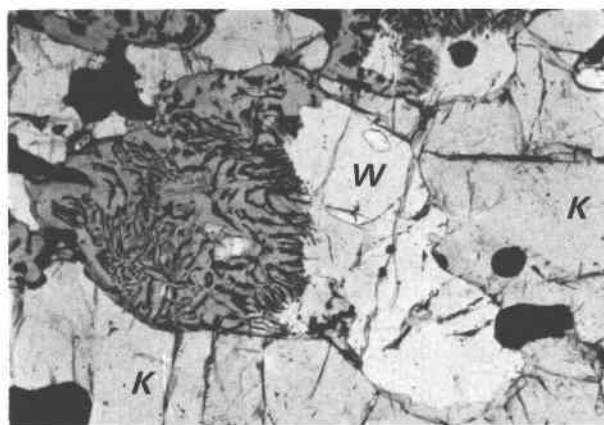

Fig. 3. Grandidierite-hercynite symplectite replacing werdingite (W), whereas adjacent kornerupine (K) appears unaffected. Photo length is 3 mm.

facies terrane (Moore, 1986). Kornerupine (±tourmaline) occurs at several localities on the farms Dabeeb and Hytkoras in the granulite-facies zone (Waters and Moore, 1985). Here kornerupine coexists with sillimanite, hercynite, and ilmenite in cordierite + phlogopite ± orthoamphibole ± orthopyroxene Mg-Al–rich gneisses (Moore and Waters, 1990). Texturally older tourmaline is also present. The Bok se Puts locality is the only site in the western Namaqualand metamorphic complex from which grandidierite has been reported. Grandidierite, together with kornerupine and tourmaline, has been described from the eastern Natal portion of the Namaqua-Natal metamorphic belt (de Villiers, 1940).

PHYSICAL AND OPTICAL PROPERTIES

Separated grains of werdingite are a translucent, honey-colored brownish yellow with a vitreous luster and a conchoidal fracture. A poor prismatic cleavage or parting is suggested by planar surfaces on some fractured grains, but no cleavage is visible in thin section. The streak is buff white and the maximum grain size, determined in thin section, is about 3 mm. The Mohs' hardness is 7, very slightly softer than kornerupine. The magnetic susceptibilities of werdingite and coexisting minerals increase in the order: sillimanite < werdingite < grandidierite < kornerupine < oxides (hercynite + ilmenite). Werdingite does not fluoresce in ultraviolet radiation. The density of werdingite, determined by suspension in di-iodomethane diluted with acetone, is 3.04(2) g/cm³, compared with the calculated value of 3.07 g/cm³.

Optically, werdingite is biaxial negative, with $2V = 33(1)°$ (meas.), $42°$ (calc.), and $\alpha = 1.614(2)$, $\beta = 1.646(2)$, and $\gamma = 1.651(2)$, measured in white light. Dispersion is moderately strong with $r > v$. Horizontal dispersion is also present. The pleochroic scheme is X and Z colorless, Y yellow, and the orientation is $Z = c$. Prism elongation

and the composition planes of simple twins are both parallel to c, as are thin rod-like inclusions (rutile?) in many grains. Simple twins are very common and lamellar twins with three or four individuals also occur.

X-RAY CRYSTALLOGRAPHY

The unit cell of werdingite was established as triclinic, $P1$ or $P\bar{1}$, by oscillation and Weissenberg methods, using single-crystal fragments. Subsequent determination of the crystal structure (Niven et al., in preparation) revealed the presence of parameter correlations and centers of symmetry, indicating that $P\bar{1}$ is the correct space group. Precise lattice parameters were determined by least-squares analysis of the setting angles of 24 reflections ($16 < \theta < 17°$), which were automatically located and centered on an Enraf-Nonius CAD4 diffractometer with graphite-monochromated MoKα radiation ($\lambda = 0.7107\text{Å}$). The resulting parameters are $a = 7.995(2)$, $b = 8.152(1)$, $c = 11.406(4)$ Å, $\alpha = 110.45(2)°$, $\beta = 110.85(2)°$, and $\gamma = 84.66(2)°$, with $V = 650.5$ Å³ and $Z = 1$.

The X-ray powder-diffraction data were measured with a semiautomated Philips powder diffractometer using CuKα radiation (Table 1). The X-ray diffraction pattern of werdingite shows a superficial resemblance to that of grandidierite and sillimanite in that single peaks in the sillimanite pattern are represented by groups of peaks in werdingite. There are also similarities, although not exact matches, with the borosilicate phases B-mullite 1 and 2 (W. Schreyer, personal communication), produced in synthesis experiments in the Al-rich part of the system MABSH by Werding and Schreyer (1984). The arrangement of AlO_6 octahedral chains in the werdingite crystal structure (Niven et al., in preparation) is similar to that in grandidierite (Stephenson and Moore, 1968) and sillimanite, and the principal differences among these minerals occur in the bridging cation sites. This structural relationship accounts for the superficial similarity in their diffraction patterns.

TABLE 1. Complete X-ray powder-diffraction data for werdingite

I_{obs}	d_{obs}	d_{calc}	hkl	I_{obs}	d_{obs}	d_{calc}	hkl
80	5.433	5.436	1$\bar{1}$0				
100	5.226	5.245	110				
75	4.979	5.012	002	10	1.863	1.867	400
		5.009	11$\bar{2}$			1.865	1$\bar{4}$0
20	3.690	3.704	11$\bar{2}$			1.864	132
		3.703	022			1.863	24$\bar{2}$
15	3.652	3.667	11$\bar{2}$			1.861	231
		3.664	20$\bar{2}$	10	1.826	1.833	22$\bar{4}$
30	3.437	3.449	1$\bar{2}$0			1.832	40$\bar{4}$
50	3.392	3.402	2$\bar{1}$0			1.831	1$\bar{4}$3
10	3.342	3.350	120			1.829	024
30	3.299	3.307	210			1.828	4$\bar{1}$0
		2.852	11$\bar{4}$	10	1.806	1.811	204
30	2.846	2.860	11$\bar{3}$			1.809	42$\bar{4}$
		2.898	221			1.799	410
60	2.708	2.718	2$\bar{2}$0			1.766	10$\bar{6}$
30	2.612	2.622	220	8	1.760	1.766	42$\bar{1}$
		2.622	2$\bar{1}$2			1.765	236
30	2.520	2.525	02$\bar{4}$			1.765	31$\bar{3}$
		2.525	20$\bar{4}$			1.762	01$\bar{6}$
10	2.427	2.435	130			1.761	145
		2.383	1$\bar{3}$0			1.761	32$\bar{6}$
8	2.372	2.379	2$\bar{2}$2	20	1.708	1.710	24$\bar{2}$
		2.378	31$\bar{2}$	20	1.652	1.710	33$\bar{2}$
8	2.333	2.338	122	20	1.584	1.654	420
		2.337	23$\bar{2}$			1.586	13$\bar{4}$
15	2.257	2.267	11$\bar{4}$			1.562	31$\bar{4}$
		2.265	31$\bar{4}$	8	1.559	1.562	24$\bar{2}$
		2.259	131			1.561	15$\bar{2}$
50	2.194	2.198	21$\bar{4}$			1.561	51$\bar{4}$
		2.198	034			1.561	23$\bar{4}$
20	2.164	2.172	014			1.561	05$\bar{4}$
		2.171	23$\bar{4}$	40	1.527	1.530	24$\bar{4}$
30	2.135	2.138	230			1.529	42$\bar{4}$
20	2.065	2.068	2$\bar{3}$0	10	1.489	1.491	224
		1.970	222			1.490	44$\bar{4}$
		1.968	33$\bar{2}$	30	1.424	1.426	22$\bar{8}$
10	1.963	1.968	134			1.318	044
		1.967	31$\bar{4}$	15	1.317	1.318	308
		1.967	32$\bar{5}$			1.318	14$\bar{8}$
						1.317	26$\bar{4}$

TABLE 2. Mean compositions of werdingite and coexisting borosilicate minerals (sample VP-4)

	Werdingite $n = 14$	Grandidierite $n = 19$	Kornerupine $n = 8$
SiO_2	19.83(0.22)	20.05	28.82
TiO_2	0.05(0.02)	0.01	0.20
Al_2O_3	59.49(0.33)	51.35	42.34
FeO^*	5.06(0.13)	6.80	10.34
MnO	bd	0.17	0.50
MgO	4.46(0.08)	9.92	11.88
Na_2O	bd	bd	0.09
B_2O_3	10.19	11.70†	3.82
Total	99.08	100.00	98.00
Si	4.017(0.038)	3.964	3.654
Ti	0.008(0.003)	0.002	0.019
Al	14.208(0.061)	11.968	6.328
Fe	0.857(0.022)	1.125	1.096
Mn	0.001	0.028	0.054
Mg	1.347(0.028)	2.924	2.245
Na	0.000	0.000	0.022
B	3.562	3.990	0.836
Sum	24.000	24.000	14.255
Oxygens	36.910	35.945	21.5
Mg/(Mg + Fe)	0.611	0.722	0.672

Note: n = number of spots analyzed; bd = below detection limit. Standard deviations in parentheses.
* Total Fe as FeO.
† B_2O_3 by difference.

CHEMICAL COMPOSITION

Werdingite was chemically analyzed on a Cameca wavelength dispersive electron microprobe in the Department of Geochemistry, University of Cape Town. A wavelength scan through the range for all elements of atomic number >9 showed only Si, Al, Fe, Mg, and Ti in amounts above the detection limit. Quantitative analysis employed natural and synthetic mineral standards, namely, natural pyrope from Kakanui for Si, Fe, and Mg; rutile for Ti; and a synthetic glass of composition Mg-Al_2O_4 for Al. Mean compositions for werdingite and coexisting minerals are listed in Table 2. Bence-Albee ZAF correction procedures were attempted for the borosilicates. Both are subject to uncertainty because of the presence of >10% unanalysed constituents in both werdingite and grandidierite. The stoichiometry of grandidierite analyses, however, is good (Table 2), and the analyses of compositionally similar werdingite are thus unlikely to be greatly in error.

Boron was determined for werdingite and coexisting kornerupine using an IL PLASMA-200 ICP spectrometer in the Department of Analytical Sciences, University of Cape Town. Boron dissolution was achieved by pressure-bomb acid digestion using mixtures of nitric and hydrofluoric acid, a technique similar to that employed by Waters and Moore (1985). The sample size was 0.02 g for werdingite and 0.2 g for kornerupine. Glass standards containing 0.7 and 12.7 wt% B_2O_3 were employed as reference samples during the analytical run.

The unit cells of mullite, sillimanite, and grandidierite contain 6, 12, and 24 cations respectively, although their cation:oxygen ratios differ. If the composition of werdingite is expressed on the basis of 24 cations, assuming a structural relationship between the three above-mentioned minerals and werdingite, an oxygen total very close to 37 is obtained (Table 2). The empirical formula for werdingite, based on O = 37, is $(Mg_{1.35}Fe_{0.86})_{\Sigma2.21}Al_{14.24}Ti_{0.01}Si_{4.03}B_{3.57}O_{37.00}$.

The simplified formula of werdingite is $(Mg,Fe)_2Al_{14}Si_4B_4O_{37}$, which requires 11.62 wt% B_2O_3 instead of the 10.19 wt% B_2O_3 obtained in the analytical determination. There is a degree of uncertainty concerning the accuracy of the B analyses due to the unavoidably small sample size and the presence of fine inclusions of sillimanite and the B-free phases, zircon and rutile, in werdingite. The structural study (Niven et al., in preparation) confirms the oxygen total and, in addition, indicates that some Al substitutes for B, and some Fe for Al. The crystallographic result is $(Mg_{1.68}Fe_{0.32})_{\Sigma2.00}Al_{12}(Al_{1.58}Fe_{0.42})_{\Sigma2.00}Ti_{0.01}Si_{4.03}B_2(B_{1.54}Al_{0.46})_{\Sigma2.00}O_{37.00}$. The compatibility among chemical composition, density, and refractive indices has been checked by the Gladstone-Dale rule and

was found to be superior $[1 - (K_P/K_C) = -0.014]$ according to the scale of Mandarino (1976, 1979).

DISCUSSION

There remains a great deal of uncertainty regarding the role and fate of B in high-grade metamorphic terranes. Tourmaline is a common minor-to-trace constituent of a variety of metasedimentary lithologies in amphibolite-facies terranes, but it is either absent or rare in higher-grade rocks. Tourmaline is also a common constituent of granites, pegmatites, and veins, indicating that B preferentially enters the fluid phase or melt with the onset of partial melting (Manning and Pichavant, 1983). In contrast, kornerupine and grandidierite typically occur in high-grade rocks (granulite facies), where they may be found in association with tourmaline. Grandidierite commonly occurs in low-pressure environments such as contact metamorphic aureoles (van Bergen, 1980), whereas kornerupine is generally restricted to Al-rich rock types at pressures greater than 4 kbar (Grew, 1983).

Although in many rocks the relationship of kornerupine and grandidierite to co-existing tourmaline is not obvious from petrographic examination (Waters and Moore, 1985; Grew, 1983, 1988; Lonker, 1988), experimental studies using alkali-free tourmaline (Werding and Schreyer, 1984) and dravite (Robbins and Yoder, 1962) suggest that kornerupine and grandidierite represent breakdown products of tourmaline in prograde metamorphic reactions at temperatures in the region 750–900 °C. In these experiments, kornerupine generally formed at higher pressures than grandidierite. Tourmaline has been reported as a breakdown product of kornerupine in retrograde reactions (Ackermand et al., 1984) and as a replacement of grandidierite (Huijsmans et al., 1982; Vrána, 1979).

In addition to kornerupine and grandidierite, unidentified solid phases formed in minor amounts as breakdown products of tourmaline in both of the above-mentioned sets of experiments. Werdingite and kornerupine appear to coexist in textural equilibrium at Bok se Puts, and werdingite may well represent one of these unidentified phases. Subsequent to the discovery of the natural phase, the pure end-member equivalent of werdingite ($Mg_2Al_{14}Si_4B_4O_{37}$) was successfully synthesized at 830 °C and 4 kbar (G. Werding, personal communication) and further stability studies are in progress.

Werdingite is replaced by a grandidierite-hercynite symplectite at Bok se Puts, whereas kornerupine remains relatively unaffected, suggesting that werdingite is not only a high-temperature mineral phase but may also be pressure-sensitive. Examination of the interrelationships of the borosilicate minerals at this locality is beyond the scope of the present publication. It is apparent, however, that werdingite will play a significant role in studies of the fate of B in high-grade metamorphic processes.

ACKNOWLEDGMENTS

REFERENCES CITED

Ackermand, D., Herd, R.K., and Windley, B.F. (1984) Kornerupine replacement reactions involving tourmaline, Fiskenaesset region, W. Greenland. Neues Jahrbuch für Mineralogie Monatshefte, 490–500.

Andreoli, M.A.G., Andersen, N.J.B., Levin, M., and Niemand, N. (1987) Geology of the Vaalputs Radioactive Waste Disposal Site in the Republic of South Africa: Explanatory notes for the geological map of the site on the scale 1:25000. Atomic Energy Corporation of South Africa, PER-151, 40 p.

de Villiers, J.E. (1940) Iron-rich kornerupine from Port Shepstone, Natal. Mineralogical Magazine, 25, 550–556.

Grew, E.S. (1983) A grandidierite-sapphirine association from India. Mineralogical Magazine, 47, 401–403.

——— (1988) Kornerupine at the Sar-e-Sang, Afghanistan, whiteschist locality: Implications for tourmaline-kornerupine distribution in metamorphic rocks. American Mineralogist, 73, 345–357.

Huijsmans, J.P.P., Barton, M., and van Bergen, M.J. (1982) A pegmatite containing Fe-rich grandidierite, Ti-rich dumortiertie and tourmaline from the Precambrian, high-grade metamorphic complex of Rogaland, S.W. Norway. Neues Jahrbuch für Mineralogie Abhandlungen, 143, 249–261.

Lonker, S.W. (1988) An occurrence of grandidierite, kornerupine, and tourmaline in southeastern Ontario, Canada. Contributions to Mineralogy and Petrology, 98, 502–516.

Mandarino, J.A. (1976) The Gladstone-Dale relationship. Part I: Derivation of new constants. Canadian Mineralogist, 14, 498–502.

——— (1979) The Gladstone-Dale relationship. Part III: Some general applications. Canadian Mineralogist, 17, 71–76.

Manning, D.A.C., and Pichavant, M. (1983) The role of fluorine and boron in the generation of granitic melts. In M.P. Atherton and C.D. Gribble, Eds., Migmatites, melting and metamorphism, p. 94–109. Shiva, Nantwich, Cheshire, U.K.

Moore, J.M. (1986) A comparative study of metamorphosed supracrustal rocks from the western Namaqualand Metamorphic Complex, 370 p. Ph.D. thesis, University of Cape Town, Cape Town, South Africa.

Moore, J.M., and Waters, D.J. (1990) Geochemistry and origin of cordierite-orthoamphibole/orthopyroxene-phlogopite rocks from Namaqualand, South Africa. Chemical Geology, in press.

Robbins, C.R., and Yoder, H.S., Jr. (1962) Stability relations of dravite, a tourmaline. Carnegie Institution of Washington Year Book 61, 106–108.

South African Commission on Stratigraphy (SACS) (1980) Stratigraphy of South Africa. Compiled by L.E. Kent. Handbook of the Geological Society of South Africa, 8, 690 p.

Stephenson, D.A., and Moore, P.B. (1968) The crystal structure of grandidierite, $(Mg,Fe)Al_3SiBO_9$. Acta Crystallographica, B24, 1518–1522.

van Bergen, M.J. (1980) Grandidierite from aluminous metasedimentary xenoliths within acid volcanics, a first record in Italy. Mineralogical Magazine, 43, 651–658.

Vrána, S. (1979) A polymetamorphic assemblage of grandidierite, kornerupine, Ti-rich dumorticrite, tourmaline, sillimanite and garnet. Neues Jahrbuch für Mineralogie Monatshefte, 22–33.

Waters, D.J. (1986) Metamorphic zonation and thermal history of pelitic gneisses from western Namaqualand, South Africa. Transactions of the Geological Society of South Africa, 89, 97–102.

——— (1989) Metamorphic evidence for the heating and cooling path of Namaqualand granulites. In J.S. Daly, R.A. Cliff, and B.W.D. Yardley, Eds., Evolution of metamorphic belts. Geological Society Special Publication, 42, 357–363.

Waters, D.J., and Moore, J.M. (1985) Kornerupine in Mg-Al-rich gneisses from Namaqualand, South Africa: Mineralogy and evidence for late-metamorphic fluid activity. Contributions to Mineralogy and Petrology, 91, 369–382.

Werding, G., and Schreyer, W. (1984) Alkali-free tourmaline in the system MgO-Al$_2$O$_3$-B$_2$O$_3$-SiO$_2$-H$_2$O. Geochimica et Cosmochimica Acta, 48, 1331–1344.

Willner, A., Schreyer, W., and Moore, J.M. (1990) Peraluminous metamorphic rocks from the Namaqualand Metamorphic Complex: Evidence for an exhalation-related, sedimentary origin in a mid-Proterozoic rift system. Chemical Geology, in press.