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## Weringite from the Urungwe District, Zimbabwe

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### Introduction

WERDINGITE,  $(\text{Mg,Fe})_2\text{Al}_{12}(\text{Al,Fe})_2\text{Si}_4\text{B}_2(\text{B,Al})_2\text{O}_{37}$ , was originally described from a silica-undersaturated, prismatic-rich granulite-facies rock in the Namaqualand complex, Bok se Puts, South Africa, where it is inferred to have formed at 800–850°C, 4.5–6 kbar (Moore *et al.*, 1990; Waters and Moore, in prep.). Grew (1996) subsequently found werdingite in two granitic pegmatites cutting granulite-facies rocks (see also Grew *et al.*, in press) and in a specimen of silica-undersaturated grandierite-rich rock from a boron-rich zone in the Proterozoic Magondi belt in the Urungwe District, 60 km west-north-west of Karoi, northern Zimbabwe. The geologic situation and mineralogy of this zone has many features in common with those at the type locality. Grandierite, kornerupine and tourmaline were originally described from this zone by Anderson (1975) and are currently under study by Treloar (1995 and in prep.). Conditions of its crystallization were estimated to be 700–750°C, 5–6 kbar (Treloar and Kramers, 1989; Munyanyiwa *et al.*, 1993; Treloar, 1995 and in prep.). In the

present paper we report the details on the werdingite occurrence in the Urungwe District.

### Geologic situation and mineralogy of the werdingite-bearing rocks

The rocks containing grandierite (55–75%) and subordinate kornerupine and tourmaline constitute a 'boron zone' in a sequence of enderbite and cordierite-garnet-biotite-sillimanite-bearing paragneisses; a spinel-rich contact zone lies between the paragneiss and the boron zone (Anderson, 1975; Treloar, 1995). The 'boron zone' is intruded concordantly by a pegmatite, but no boron minerals were reported from the pegmatite.

Specimen #144869, which the US National Museum of Natural History received from S. Anderson of the Geological Survey of Rhodesia in 1979, undoubtedly originated from Anderson's (1975) boron zone, although the locality is only given as 'Kariba area'. It is a dark-coloured rock consisting largely of randomly oriented grandierite prisms, and subordinate tourmaline, prismatic, hercynite, and ilmenite. Monazite, zircon, corundum,

sillimanite, biotite, and werdingite are present in traces. Magnetite, apatite and anorthite, which were reported by Anderson (1975) and Treloar (1995), were not found in #144869. Grandidierite grains are subequant to elongate, mostly 0.3–0.7 mm across and up to 4 mm long, and are randomly oriented. Individual prismatic grains are up to 2 mm across and extinguish simultaneously; these appear to be lobes of a single prism roughly 1 cm long and 2 mm across. Tourmaline is dark brown in thin section, and typically occurs interstitial to grandidierite grains or between grandidierite and prismatic. It is commonly riddled with vermicules of hercynite, constituting a hercynite–tourmaline symplectite. A few tourmaline patches contain clusters of fine corundum platelets, which are texturally distinct from medium-grained corundum associated with medium-grained hercynite and ilmenite. Sillimanite is found interstitial to or enclosed in grandidierite grains, near the center of some tourmaline patches, and enclosed in prismatic. Sillimanite habit ranges from tight clusters of fine prisms (0.01–0.02 mm across) in grandidierite to individual grains 0.1–0.6 mm across. Hercynite in highly irregular grains commonly 1 to 2 mm across is more abundant than ilmenite. Biotite occurs with tourmaline or interstitially to grandidierite.

Three grains of werdingite were found; all are enclosed in grandidierite, and they measure 0.15–0.3 mm across (Fig. 1). They are characteristically surrounded by ‘necklaces’ of fine-grained hercynite in the host grandidierite. Sillimanite occurs adjacent to one, possibly two, of these grains. Werdingite is recognized by its pale yellow pleochroism, twinning and birefringence exceeding that of sillimanite. Isolated clusters of hercynite in grandidierite elsewhere in the thin section surround what could be werdingite not exposed on the surface of the thin section (Fig. 1B); clusters without any evident werdingite could mark the position of former werdingite grains.

#### Chemical composition of the minerals

Constituents with  $Z \geq 9$  were analysed with an ARL SEMQ electron microprobe (EMP) at the University of Maine (15 kV accelerating voltage and 10 nA beam current). Li, Be and B were analysed using a Cameca IMS 4f ion microprobe (secondary ion mass spectrometry or SIMS) operated on the University of New Mexico (UNM) campus by a UNM-Sandia National Laboratories consortium. Details of the electron and ion microprobe analytical methods are given in Grew *et al.* (in press). In the case of Li, standards were matched as closely as possible with the unknowns in order to minimize matrix effects, that is, lithian schorl was used as a standard for tourmaline, and prismatic (sample BM1940,39) as a

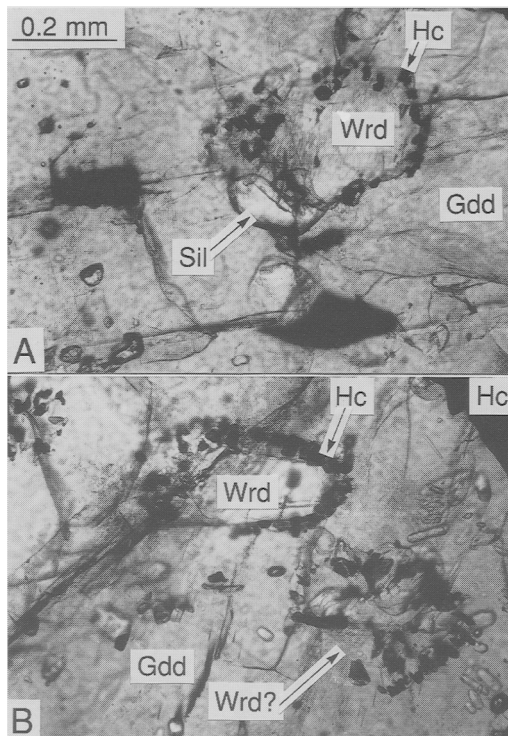


FIG. 1. Photomicrographs of werdingite grains (Wrd) surrounded by a ‘necklace’ of hercynite (Hc) in grandidierite (Gdd) matrix. (A) Werdingite grain analysed by SIMS. Sil - sillimanite. (B) A second werdingite grain near a large hercynite. Wrd? is an aggregate of fine hercynite surrounding a grain that might be relict werdingite. Scale applies to both photos. Sample #144869, plane light.

standard for prismatic. For the other minerals, an average of the two standards was used.

The brown tourmaline, which was analysed at one spot only, is calcic ( $Ca/(Ca+Na) = 0.71$ ) and deficient in large cations ( $Ca+Na+K = 0.56$ ). The kornerupine-group mineral, also analysed at one spot only, is prismatic ( $B > 0.5$  p.f.u., Grew *et al.*, 1996). In recalculating werdingite compositions to 37 O and assuming that the two grains not analysed by SIMS have the same B, Be and Li contents as the one grain analysed by SIMS (Table 1), cation totals ranged from 23.975 to 23.996, suggesting that all the Fe in werdingite is ferrous (Niven *et al.*, 1991). Hercynite in the ‘necklaces’ (3 analyses) around werdingite differ only slightly in composition from medium-grained hercynite (one analysis); it contains less  $Cr_2O_3$  (0.05–0.09 wt.%) and  $Fe_2O_3$  (2.9–3.1 wt.%, e.g. Table 2) and is more ferroan ( $Fe^{2+}/(Fe^{2+} + Mg) =$

TABLE 1. Analyses of silicate minerals in #144869

	Werdingite 1	Grandidierite 1	Prismatine	Tourmaline	Sillimanite <sup>1</sup> Ave. of 2 SIMS
EMPA, wt. %					
SiO <sub>2</sub>	20.16	19.84	28.27	33.82	35.54
TiO <sub>2</sub>	b.d.	b.d.	0.11	1.17	b.d.
Al <sub>2</sub> O <sub>3</sub>	60.87	50.48	42.07	34.68	62.45
Fe <sub>2</sub> O <sub>3</sub>	—	—	—	—	0.92 <sup>2</sup>
FeO	5.19 <sup>3</sup>	9.03 <sup>3</sup>	13.38 <sup>3</sup>	7.11 <sup>3</sup>	—
MnO	b.d.	0.10	0.27	b.d.	b.d.
MgO	3.83	8.98	9.99	6.35	0.20
CaO	b.d.	b.d.	b.d.	2.09	b.d.
Na <sub>2</sub> O	b.d.	b.d.	b.d.	0.47	b.d.
K <sub>2</sub> O	b.d.	b.d.	b.d.	0.19	b.d.
F	—	—	0.39	0.66	—
Cl	—	—	b.d.	0.01	—
SIMS, wt %					
Li <sub>2</sub> O	0.008	<0.0001	0.14	0.0028	≤0.001
BeO	0.011	<0.0001	0.013	<0.0001	0.003
B <sub>2</sub> O <sub>3</sub>	10.18	11.71	3.75	10.59	0.45
Calculated, wt %					
H <sub>2</sub> O	—	—	0.98	3.33	—
O=F,Cl	—	—	-0.16	-0.28	—
Total	100.25	100.14	99.20	100.19	99.56
Formulae					
O	37	9	21.5	29	4.977
Si	4.046	0.991	3.631	5.561	0.961
Be	0.005	0	0.004	0	0
B	3.526	1.009	0.831	3.006	0.021
Ti	0	0	0.011	0.145	0
Al	14.396	2.970	6.368	6.721	1.991
Fe <sup>3+</sup>	—	—	—	—	0.019
Fe <sup>2+</sup>	0.871	0.377	1.437	0.978	—
Mn	0	0.004	0.029	0	0
Mg	1.146	0.668	1.913	1.557	0.008
Li	0.006	0	0.072	0.002	0
Ca	0	0	0	0.368	0
Na	0	0	0	0.150	0
K	0	0	0	0.040	0
Total	23.996	6.019	14.296	18.528	3.0 <sup>4</sup>
F	—	—	0.158	0.343	—
Cl	—	—	0	0.003	—
OH <sub>calc</sub>	—	—	0.842	3.654	—
X <sub>Fe<sup>2+</sup></sub>	0.43	0.36	0.43	0.39	—

EMPA = electron microprobe analysis, SIMS = secondary ion mass spectroscopy (ion probe), Calc = calculated  
 b.d. = below detection, dash = not sought. In Tur, Prs: BaO are b.d.

<sup>1</sup>Surrounded by tourmaline aggregate.

<sup>2</sup>All Fe presumed to be ferric.

<sup>3</sup>All Fe presumed to be ferrous.

<sup>4</sup>Sillimanite formula was normalized to 3 cations.

Table 2. Electron microprobe analyses of oxide minerals in #144869

	Hercynite coarse	Hercynite 'necklace'	Ilmenite
wt. %			
TiO <sub>2</sub>	b.d.	b.d.	50.75
Al <sub>2</sub> O <sub>3</sub>	55.94	56.78	b.d.
V <sub>2</sub> O <sub>3</sub>	0.08	0.08	0.08
Cr <sub>2</sub> O <sub>3</sub>	0.24	0.09	b.d.
FeO <sub>meas.</sub>	37.68	36.75	46.67
Fe <sub>2</sub> O <sub>3</sub>	5.67*	3.13*	3.06*
FeO	32.58*	33.93*	43.92*
MnO	0.20	0.20	0.51
MgO	5.19	4.06	0.68
ZnO	0.09	0.16	b.d.
Total	99.99	98.43	99.00
Formulae			
O	4	4	3
Ti	0	0	0.970
Al	1.872	1.928	0
V	0.002	0.002	0.002
Cr	0.005	0.002	0
Fe <sup>3+</sup>	0.121*	0.068*	0.059*
Fe <sup>2+</sup>	0.774*	0.818*	0.933*
Mn	0.005	0.005	0.011
Mg	0.220	0.174	0.026
Zn	0.002	0.003	0
Total	3.001	3.000	2.001
X <sub>Fe<sup>2+</sup></sub>	0.78	0.82	0.97

b.d. = below detection.

\*Ferric/ferrous ratio was calculated assuming O = 4,

Sum cations = 3 (hercynite) and O = 3,

Sum cations = 2 (ilmenite).

NiO b.d.

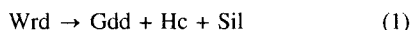
X<sub>Fe<sup>2+</sup></sub> = 0.79–0.82 vs. 0.78). Ilmenite (2 analyses) is calculated to contain 3.0–4.2 mole% hematite (e.g. Table 2).

Given the presence of significant Fe<sup>3+</sup> in sillimanite (0.64–0.92 wt.% Fe<sub>2</sub>O<sub>3</sub>, e.g. Table 1) and oxides, it is possible that some Fe<sup>3+</sup> is present in the other ferromagnesian borosilicates. However, there is no satisfactory method to estimate ferric/ferrous ratio in either prismatic or grandierite (Grew, 1996), or, for that matter, tourmaline, and thus Fe is assumed to be ferrous in these minerals. X<sub>Fe<sup>2+</sup></sub> increases (abbreviations in Fig. 2) Gdd (0.35–0.36) < Tur (0.39) < Wrd (0.40–0.43) < Prs (0.43) ≪ Hc (0.78–0.82) < ilmenite (0.97–0.98), that is, slightly richer in iron (except Hc) than the similar sequence reported by Treloar (1995 and in prep.).

Among the silicates analysed by SIMS (Table 1), F increases Prs < Tur (one F maximum p.f.u. in Tur), Li increases Gdd, Sil < Tur < Wrd < Prs and Be increases Gdd, Tur < Sil < Wrd < Prs, trends also reported by Grew *et al.* (1990) for kornerupine *sensu lato*, grandierite and tourmaline. That is, these light elements are preferentially incorporated in prismatic, and secondarily, in werdingite.

### Interpretation of the assemblage

Treloar (1995 and in prep.) suggested that prismatic and grandierite formed early during metamorphism of the Urungwe District boron-rich zone, and subsequently reacted to form tourmaline + hercynite (cf. Anderson, 1975). The assemblage formed at peak pressure-temperature conditions in sample #144869 is Gdd+Prs+Hc+Crn; Treloar (1995 and in prep.) reported this assemblage in other rocks from the boron-rich zone. Sillimanite is present throughout sample #144869, but mostly as inclusions. It appears to have formed early in the metamorphic evolution, and again later, but it does not appear to be part of the peak assemblage. Textural relations suggest that werdingite crystallized prior to grandierite and subsequently broke down to grandierite + hercynite. This reaction considered in isolation requires substantial metasomatism. Waters and Moore (in prep.) calculated from the proportion of grandierite and hercynite in symplectites at the type locality that the breakdown of werdingite to Gdd + Hc symplectite resulted from influx of Mg and Fe with little change in SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub> and B<sub>2</sub>O<sub>3</sub>. Figure 2 suggests that the local assemblage Wrd+Sil+Hc+Gdd (Fig. 1A) in #144869 could have formed by one of two scenarios. In both, the textures are assumed to result from decreasing pressure during decompression in the early stages of retrogression (cordierite formation in associated metapelites, Treloar, 1995 and in prep.). In one, Wrd broke down according to a continuous reaction in the FeO-MgO-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> (FMAS) system open to B<sub>2</sub>O<sub>3</sub>:



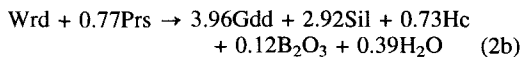
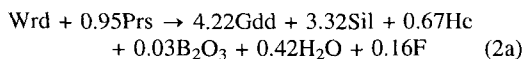
that is, the Gdd+Hc+Sil association became increasingly magnesian and replaced werdingite. Alternatively, werdingite could have been a major constituent that coexisted with prismatic in a precursor assemblage such as Prs+Wrd+Gdd+Hc±Crn±Sil (the presence of Sil is suggested by the Sil inclusion in Prs; additional phases are possible if Fe<sub>2</sub>O<sub>3</sub>, F and/or B<sub>2</sub>O<sub>3</sub> behaved as inert components). Subsequently, werdingite reacted with prismatic (Grew, 1996):



which proceeded almost to completion, leaving mere relics of werdingite. This reaction is discontinuous in

FMAS if the system had been open to F,  $\text{Fe}_2\text{O}_3$ ,  $\text{B}_2\text{O}_3$  and  $\text{H}_2\text{O}$ . The bulk composition was such that the amounts of grandierite and hercynite greatly exceeded that of sillimanite, which ended up as inclusions in grandierite.

The Urungwe assemblage bears close similarity to that at the type locality for werdingite at Bok se Puts, South Africa (Fig. 2). However, primary grandierite is absent at Bok se Puts and there is no evidence for a stable Gdd + Sil join (Moore *et al.*, 1990; Waters and Moore, in preparation). Grew (1996) suggested that the Bok se Puts and Urungwe assemblages could be related by reaction 2. Calculating reaction 2 from formulae of the ferromagnesian minerals simplified from Moore *et al.* (1990), Waters and Moore (in prep. and Tables 1-2: ferric and ferrous iron are combined;  $\text{Al}_2\text{SiO}_5$  used for sillimanite), we get, respectively, for Urungwe (2a) and Boks se Puts (2b):



Waters and Moore (in prep.) calculated that in the model  $\text{MgO-Al}_2\text{O}_3\text{-B}_2\text{O}_3\text{-SiO}_2$  system open to  $\text{H}_2\text{O}$ , reactions of  $\text{Wrd} + \text{Prs} + \text{Spl}$  or  $\text{Crn}$  breakdown to  $\text{Gdd} + \text{Sil}$  would have positive slopes with  $\text{Wrd} + \text{Prs}$  on the high-pressure side. However, Waters and Moore (in prep.) noted that the sequence of reactions at Bok se Puts is consistent with the anticlockwise  $P$ - $T$  trajectory inferred for this area only if the  $\text{Wrd} + \text{Prs}$  breakdown reactions had negative slopes with  $\text{Wrd} + \text{Prs}$  on the high-pressure side. The difference in the metamorphic temperatures at roughly equal pressures inferred for Bok se Puts (800–850°C) and Urungwe District (700–750°C) is also consistent with a negative slope, as is the absence of prismatic and presence of  $\text{Gdd} + \text{Sil} + \text{Qtz}$  in two pegmatites containing werdingite, which crystallized at 600–700°C, 3–4 kbar (Grew *et al.*, in press). If reaction 2 does have a negative slope, then  $\text{Prs} + \text{Wrd}$  dehydrates with decreasing temperature, an

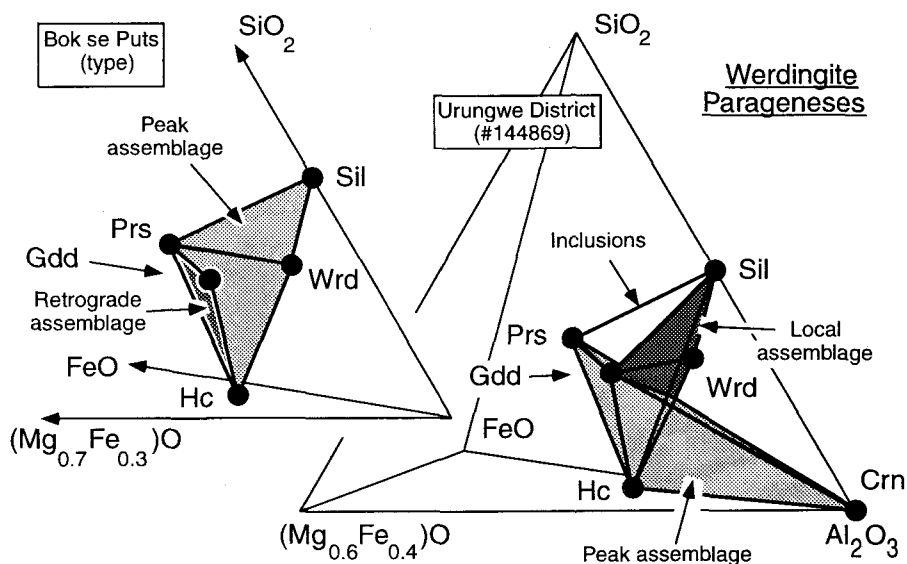
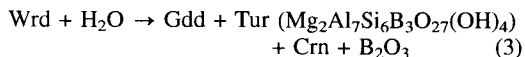


FIG. 2. Compatibilities among sillimanite (Sil), prismatic (Prs), werdingite (Wrd), corundum (Crn), hercynite (Hc) and grandierite (Gdd) in the  $\text{FeO-MgO-Al}_2\text{O}_3\text{-SiO}_2$  system at Bok se Puts, South Africa (Moore *et al.*, 1990; Waters and Moore, in prep.) and in sample #144869, Urungwe District, Zimbabwe. The front faces of the tetrahedra are sections at the approximate Fe/Mg ratio of the ferromagnesian borosilicates. The  $\text{B}_2\text{O}_3$  contents of the borosilicates are ignored in plotting, resulting in relationships for a system open to  $\text{B}_2\text{O}_3$ .

anomalous situation that has also been reported in experiments with a kornerupine-group mineral: B-free Krn  $\rightarrow$  enstatite + Crn + H<sub>2</sub>O (Wegge and Schreyer, 1994; Werding and Schreyer, 1996).

Werdning and Schreyer (1992, 1996) reported the breakdown of werdingite in the MgO-Al<sub>2</sub>O<sub>3</sub>-B<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub>-H<sub>2</sub>O system at  $P_{\text{H}_2\text{O}} = 3\text{--}4.5$  kbar,  $T = 650\text{--}750^\circ\text{C}$  as follows:



Despite the significant F, FeO and CaO contents of tourmaline and FeO contents of werdingite and grandidierite in #144869, as well as  $P_{\text{H}_2\text{O}} \ll P_{\text{tot}}$  during metamorphism (Treloar and Kramers, 1989; Munyanyiwa *et al.*, 1993; Treloar, 1995 and in prep.), it is remarkable that the final assemblage in this rock, Tur+Crn+Sil+Gdd+Hc, turns out to be so close to Werding and Schreyer's breakdown assemblage. Moreover, the  $P$ - $T$  conditions estimated for Wrd breakdown in the Urungwe District granulite,  $P \leq 6$  kbar,  $T \approx 700\text{--}750^\circ\text{C}$ , are comparable to the  $P$ - $T$  conditions Werding and Schreyer reported in their experiments.

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