

## Wilkinsonite, $\text{Na}_2\text{Fe}_4^{2+}\text{Fe}_3^{3+}\text{Si}_6\text{O}_{20}$ , a new member of the aenigmatite group from the Warrumbungle Volcano, New South Wales, Australia

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### ABSTRACT

Wilkinsonite, ideally  $\text{Na}_2\text{Fe}_4^{2+}\text{Fe}_3^{3+}\text{Si}_6\text{O}_{20}$ , is a new member of the aenigmatite group. Its principal known occurrence is as anhedral groundmass grains associated with anorthoclase, clinopyroxene (aegirine-hedenbergite solid solution), sodalite, analcime, and traces of eudialyte and arfvedsonite in a fine-grained silica-undersaturated trachyte from the Warrumbungle Volcano, central New South Wales, Australia. A complete solid-solution series exists between the Ti-free end-member wilkinsonite through intermediate compositions to Ti-deficient aenigmatite, via the coupled substitution  $2\text{Fe}^{3+} = \text{Fe}^{2+}\text{Ti}$ . Al, Mn, Ca, Zr, and Nb occur in minor amounts, although the last may reach almost 4 wt%  $\text{Nb}_2\text{O}_5$ .

Ti-free wilkinsonite is biaxial positive with a low  $2V$  (ca.  $10^\circ$ ),  $\alpha = 1.79(1)$ ,  $\beta = 1.79(1)$  and  $\gamma = 1.90(1)$ . The pleochroism is strong from olive green through gray-brown to very dark brown with  $Z > Y > X$ , but the mineral begins to acquire the reddish brown tints typical of aenigmatite when  $\text{TiO}_2$  exceeds about 3 wt%. Wilkinsonite, black with a brown streak and a vitreous luster, is triclinic and structurally similar to aenigmatite. Unit cell parameters, determined by X-ray powder diffraction, are  $a = 10.355(2)$  Å,  $b = 10.812(2)$  Å,  $c = 8.906(2)$  Å,  $\alpha = 105.05(1)^\circ$ ,  $\beta = 96.63(1)^\circ$ ,  $\gamma = 125.20(1)^\circ$ ,  $V = 741.07(2)$  Å<sup>3</sup> and  $Z = 2$ . The calculated density is 3.89 g/cm<sup>3</sup>.

Stability of the aenigmatite structure appears to be enhanced by the presence of Ti. However, wilkinsonite is apparently restricted to silica-undersaturated, mildly peralkaline hosts with very low  $\text{TiO}_2$  concentrations, crystallizing under a limited range of  $T/f\text{O}_2$ . Oxygen fugacity probably is restricted to a range below that defined by the fayalite-magnetite-quartz (FMQ) buffer curve.

### INTRODUCTION

Aenigmatite is a relatively common constituent of peralkaline volcanic and plutonic rocks and, through the advent of the electron microprobe, much compositional data are now available on the mineral (Deer et al., 1978).

The empirical formula of aenigmatite was determined by Kelsey and McKie (1964) to be  $\text{Na}_2\text{Fe}_3^{2+}\text{TiSi}_6\text{O}_{20}$ , and most published analyses show only limited departure from this composition. However, several substitutions occur to a minor degree, including  $\text{Mn}^{2+} = \text{Fe}^{2+}$ ,  $\text{Mg} = \text{Fe}^{2+}$ ,  $\text{Zr}^{4+} = \text{Ti}^{4+}$ , and the coupled substitutions  $\text{CaAl} = \text{NaSi}$ ,  $\text{Fe}^{3+}\text{Al} = \text{Fe}^{2+}\text{Si}$ ,  $\text{Fe}^{3+}\text{Al} = \text{Fe}^{2+}\text{Ti}$ , and  $2\text{Fe}^{3+} = \text{Fe}^{2+}\text{Ti}$ , which can be considered in terms of respective end-member components  $\text{Ca}_2\text{Fe}_5^{2+}\text{TiAl}_2\text{Si}_4\text{O}_{20}$  (Mg-free rhönite),  $\text{Na}_2\text{Fe}_4^{2+}\text{TiFe}^{3+}\text{AlSi}_5\text{O}_{20}$ ,  $\text{Na}_2\text{Fe}_4^{2+}\text{Fe}^{3+}\text{AlSi}_6\text{O}_{20}$ , and  $\text{Na}_2\text{Fe}_4^{2+}\text{Fe}_3^{3+}\text{Si}_6\text{O}_{20}$ . In most natural aenigmatite, the last of these is the most important end-member component but is still limited to no more than a few mole percent. Most natural aenigmatite has Ti content in the range 0.75 to 1.05 atoms per formula unit (equivalent to 6.8–10.0 wt%  $\text{TiO}_2$ ), representing only limited solid solution between aenigmatite  $\text{Na}_2\text{Fe}_3^{2+}\text{TiSi}_6\text{O}_{20}$  and a Ti-free end-member,  $\text{Na}_2\text{Fe}_4^{2+}\text{Fe}_3^{3+}\text{Si}_6\text{O}_{20}$ . In very rare instances, however, more extensive solid solution of this type has been recorded.

Specifically, Ti contents in the range 0.2–0.8 atoms per formula unit (1.7–6.8 wt%  $\text{TiO}_2$ ) have been reported for aenigmatite from the Sierra Prieta nepheline-analcime syenite and other intrusions of the Diablo Plateau, Texas (Hodges and Barker, 1973; Barker and Hodges, 1977).

The Ti-free phase  $\text{Na}_2\text{Fe}_4^{2+}\text{Fe}_3^{3+}\text{Si}_6\text{O}_{20}$  was synthesized by Ernst (1962) but its stability field appears to be restricted relative to Ti-bearing aenigmatite. No natural occurrences of the Ti-free phase have been reported and documentation of low Ti-contents is restricted to the one occurrence listed above.

This paper describes Ti-poor aenigmatite in silica-undersaturated trachytes from the Warrumbungle Volcano, central New South Wales, Australia. In particular, a mildly silica-undersaturated peralkaline trachyte from the southeast flank of the volcano contains an aenigmatite-group phase in which Ti content is below the limit of detection of the electron microprobe. This phase constitutes a new member of the aenigmatite group and is named wilkinsonite for John Frederick George Wilkinson, Emeritus Professor of Geology at the University of New England, New South Wales, Australia, in recognition of his noteworthy contributions to the mineralogy and petrology of alkaline volcanic rocks and especially those of

**TABLE 1.** Chemical analysis and CIPW norm of trachyte, Bingie Grumble Mountain

Analysis				CIPW Norm	
	Wt%		ppm		Wt%
SiO <sub>2</sub>	58.87	Ba	<2	Or	27.72
TiO <sub>2</sub>	0.04	Rb	595	Ab	54.34
Al <sub>2</sub> O <sub>3</sub>	16.39	Sr	107	Ne	2.08
Fe <sub>2</sub> O <sub>3</sub>	3.50	Pb	50	Ac	1.44
FeO	1.90	Th	84	Di	2.90
MnO	0.23	U	22	Ol	0.58
MgO	0.35	Zr	3660	Mt	4.35
CaO	1.06	Nb	575	Il	0.08
Na <sub>2</sub> O	7.07	La	389	Ap	0.02
K <sub>2</sub> O	4.69	Ce	775	Zc	0.74
P <sub>2</sub> O <sub>5</sub>	0.01	Y	271	Cc	0.64
H <sub>2</sub> O <sup>+</sup>	1.81	Ni	<1		
H <sub>2</sub> O <sup>-</sup>	1.42	Cr	2		
CO <sub>2</sub>	0.28	Zn	900		
Total	97.54	Ga	90		

Note: BMR specimen 83260100. Low total reflects unanalyzed Cl present in sodalite.

the Tertiary province of eastern Australia, which includes the Warrumbungle Volcano.

The nongeneric name wilkinsonite has been chosen in preference to ferri-aenigmatite as previously applied to the equivalent hypothetical end-member component (Larsen, 1977; Grapes et al., 1979) because the nature of the available material does not permit quantitative determination of the concentration of Fe<sup>3+</sup>, although charge balance and other considerations imply its presence. The name cossyrite has sometimes been applied to Fe<sup>3+</sup>-bearing aenigmatite. However, it has also been used as a synonym for aenigmatite and resurrection of the name is inappropriate for the phase under discussion.

The mineral and the name have been approved by the Commission on New Minerals and Mineral Names of the International Mineralogical Association. Type material for wilkinsonite is housed in the Petrological Museum, Bureau of Mineral Resources, Canberra (catalogue number R29655; field number 83260100).

### OCCURRENCE

Located 350 km northwest of Sydney in central New South Wales, the Warrumbungle Volcano (Fig. 1) is a deeply dissected Miocene shield complex approximately 55 km in diameter. The volcano erupted lavas that form alkaline rock types ranging from alkali basalt and hawaiite to peralkaline nepheline- and quartz-bearing trachyte and minor rhyolite. A detailed account of the mineralogy and petrology of the Warrumbungle Volcano will be published elsewhere (Duggan and Knutson, in preparation).

Except in the most Ti-poor hosts, aenigmatites in quartz-bearing trachytes and alkali rhyolites of the Warrumbungles display no unusual features, and their compositions compare closely with those of aenigmatite samples elsewhere. However, aenigmatite in the groundmass

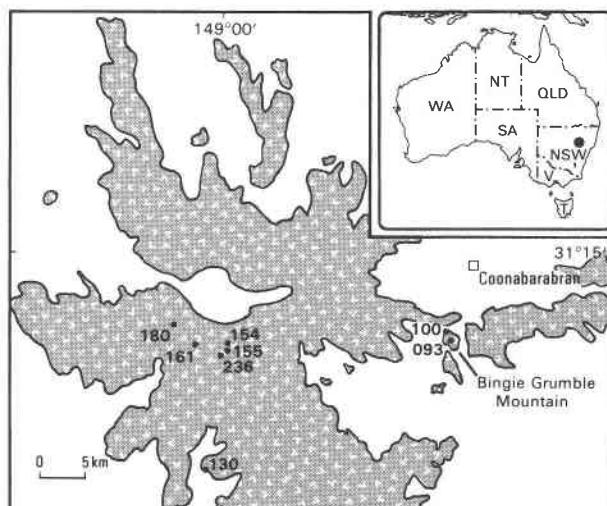


Fig. 1. Simplified geological map of the Warrumbungle Volcano showing specimen localities. Specimen numbers refer to final three digits of BMR Collection number (Table 4).

of some silica-undersaturated trachytes has variably low Ti content. The lowest Ti content occurs in an aenigmatite-like mineral from fine-grained trachytes on the northern margin of a lava dome forming Bingie Grumble Mountain, a dome-shaped hill some 2 km in diameter and about 250 m high; the mountain is located 10 km southwest of the township of Coonabarabran (lat. 31°18.9'S; long. 149°11.1'E) and lies some 18 km southeast of the deeply eroded center of the volcano. The sodalite-bearing trachyte has a highly evolved composition (Table 1) with strong enrichment in Rb, Nb, Zr, Y, and REE, and depletion in Mg, Ba, Sr, and Ti. It consists of phenocrysts of anorthoclase (ave. Ab<sub>72</sub>Or<sub>28</sub> mol%) approximately 2 mm in length in a groundmass of anorthoclase (ave. Ab<sub>66</sub>Or<sub>34</sub> mol%), clinopyroxene (an aegirine-hedenbergite solid solution, Hd<sub>71</sub>Ac<sub>29</sub> to Hd<sub>24</sub>Ac<sub>76</sub> mol%), nepheline, sodalite, wilkinsonite, traces of arfvedsonite and eudialyte, and rare minute grains of other unidentified Ca-Zr and REE-bearing phases. Other wilkinsonite-

**TABLE 2.** Composition of wilkinsonite

	Wt%	Range	STD
SiO <sub>2</sub>	40.44	39.15–41.50	0.54
TiO <sub>2</sub>	0.63	<0.02–1.94	0.66
ZrO <sub>2</sub>	0.20	<0.04–0.50	0.20
Al <sub>2</sub> O <sub>3</sub>	0.66	0.03–0.85	0.13
FeO*	45.98	43.97–47.86	1.27
MnO	1.25	1.04–1.37	0.09
MgO	0.02	<0.02–0.18	0.04
CaO	0.16	0.08–0.24	0.05
Na <sub>2</sub> O	7.23	7.06–7.35	0.09
K <sub>2</sub> O	0.05	0.02–0.09	0.02
Nb <sub>2</sub> O <sub>5</sub>	1.64	<0.04–3.72	1.04
Total	98.26		

Note: Average of 22 microprobe analyses of nine grains in type specimen. STD is standard deviation.

\* Total Fe expressed as FeO.

TABLE 3. Analyses of wilkinsonite and aenigmatite

	1	2	3	4	5	6	7	8	9	10	11
	0100	0100	0100	0093	0130	0154	0161	0155	0236	0180	30423
SiO <sub>2</sub>	40.95	40.58	39.15	38.97	40.07	40.63	38.85	39.81	40.01	40.87	41.30
TiO <sub>2</sub>	<0.02	<0.02	1.68	1.26	1.50	1.73	4.01	3.38	6.40	6.75	1.68
ZrO <sub>2</sub>	<0.04	0.52	0.17	0.57	0.34	0.49	0.17	0.11	0.24	0.12	0.42
Al <sub>2</sub> O <sub>3</sub>	0.42	0.76	0.81	1.49	0.91	0.69	0.98	0.30	0.58	0.28	0.57
FeO*	47.80	46.42	44.20	45.40	45.98	45.35	45.57	44.10	43.08	41.53	43.24
MnO	1.04	1.26	1.32	1.20	1.20	1.18	0.84	1.64	1.00	1.56	1.35
MgO	0.02	<0.02	<0.02	<0.02	0.03	0.08	0.08	0.08	<0.02	0.05	0.18
CaO	0.08	0.21	0.16	0.40	0.40	0.29	0.42	0.25	0.75	0.08	0.18
Na <sub>2</sub> O	7.30	7.27	7.13	6.95	7.15	7.12	7.14	7.08	6.82	7.26	7.22
K <sub>2</sub> O	0.05	0.09	0.06	<0.02	0.07	<0.02	0.02	0.02	0.06	<0.02	0.08
Nb <sub>2</sub> O <sub>5</sub>	0.06	1.11	3.72	1.81	0.75	0.71	0.28	0.42	0.49	0.26	1.32
Total	97.22	98.24	98.40	98.05	98.40	98.27	98.33	97.19	99.43	98.76	97.54
Fe <sub>2</sub> O <sub>3</sub> **	19.40	17.15	11.41	14.44	15.94	13.79	14.85	12.98	6.73	5.72	11.04
FeO**	30.35	30.99	33.93	32.40	31.63	32.94	32.21	32.42	37.02	36.38	33.31
Total	99.67	99.94	99.54	99.49	99.99	99.65	99.82	98.49	100.10	99.33	98.65
<b>Cation proportions based on 20 oxygen atoms</b>											
Si	5.931	5.884	5.752	5.703	5.803	5.847	5.637	5.844	5.785	5.914	6.029
Al	0.072	0.130	0.140	0.257	0.155	0.118	0.168	0.053	0.099	0.048	0.098
Ti	—	—	0.186	0.139	0.163	0.189	0.438	0.373	0.696	0.735	0.184
Zr	—	0.037	0.012	0.041	0.024	0.035	0.012	0.008	0.017	0.008	0.030
Fe <sup>3+</sup>	2.114	1.871	1.261	1.591	1.738	1.506	1.622	1.433	0.732	0.623	1.213
Fe <sup>2+</sup>	3.676	3.758	4.170	3.966	3.831	3.999	3.909	3.980	4.477	4.403	4.066
Mn	0.128	0.155	0.164	0.149	0.147	0.145	0.103	0.205	0.122	0.191	0.167
Mg	0.004	—	—	—	0.006	0.017	0.017	0.019	—	0.011	0.039
Ca	0.012	0.033	0.025	0.063	0.062	0.045	0.065	0.040	0.116	0.012	0.028
Na	2.050	2.044	2.031	1.972	2.008	2.004	2.009	2.014	1.912	2.037	2.044
K	0.009	0.017	0.011	—	0.013	—	0.004	0.004	0.011	—	0.015
Nb	0.004	0.073	0.247	0.120	0.049	0.047	0.016	0.028	0.032	0.017	0.087

Note: Specimen numbers represent the final four digits of BMR Collection numbers (Table 4) except for 30423 (Otago University specimen from Logan Point Quarry, Dunedin, New Zealand; analysis of host rock given in Price and Coombs, 1975).

\* Total Fe expressed as FeO.

\*\* Ferric and ferrous iron calculated assuming stoichiometry (14 cations and 20 oxygen atoms).

bearing trachytes lack sodalite and eudialyte but are otherwise petrographically and chemically similar to the Bingie Grumble rocks.

The wilkinsonite forms very small anhedral grains less than 50 μm in diameter, closely associated with sodic pyroxene and enclosing abundant groundmass anorthoclase laths. Inclusion-free volumes of the mineral rarely if ever exceed 20 μm in diameter. Although some alteration of rock is pervasive, the wilkinsonite is always unaltered.

### CHEMISTRY

The composition of wilkinsonite, as determined from 22 electron microprobe analyses of grains in the type specimen, is given in Table 2. This composition

yields the formula  $(\text{Na}_{2.04}\text{Ca}_{0.02}\text{K}_{0.01})_{\Sigma 2.07}(\text{Fe}_{3.90}^{2+}\text{Mn}_{0.15})_{\Sigma 4.05}(\text{Fe}_{1.69}^{3+}\text{Nb}_{0.11}\text{Ti}_{0.07}\text{Zr}_{0.01})_{\Sigma 1.88}(\text{Si}_{5.88}\text{Al}_{0.11})_{\Sigma 5.99}\text{O}_{20}$ , with the ratio of Fe<sup>2+</sup> to Fe<sup>3+</sup> calculated assuming stoichiometry (14 cations and 20 oxygen atoms anhydrous). Some representative microprobe analyses of wilkinsonite and aenigmatite from Bingie Grumble Mountain and other localities in the Warrumbungle Mountains and in a phonolite from the Dunedin Volcano, New Zealand, are in Table 3. Details of host rocks and localities of analyzed aenigmatite and wilkinsonite are given in Table 4.

Analyses were obtained by wavelength-dispersive analysis on a Cameca Camebax Microbeam electron probe microanalyzer using an accelerating voltage of 15 kV, a beam current of about 30 nA, a take-off angle of 40° and ZAF corrections. Pure metals (Fe, Nb), synthetic phases

TABLE 4. Host rock and locality data for wilkinsonite and aenigmatite, Warrumbungle Volcano

Spec. no.	Rock type	Locality	Grid reference*
83260093	Analcime trachyte	Bingie Grumble Mountain	8735-083324
83260100	Sodalite trachyte	Bingie Grumble Mountain	8735-079333
83260130	Nepheline trachyte	Black Mountain	8635-886202
84260154	Trachyte	The Breadknife	8635-898320
84260155	Quartz trachyte	Grand High Tops	8635-896316
84260161	Trachyte	Bluff Mountain	8635-881319
84260180	Comendite	Danu Saddle	8635-864335
86260236	Quartz trachyte	Crater Bluff	8635-897312

\* Grid references refer to Australian Map Grid, Zone 55, sheets 8635 (Tenandra) and 8735 (Coonabarabran).

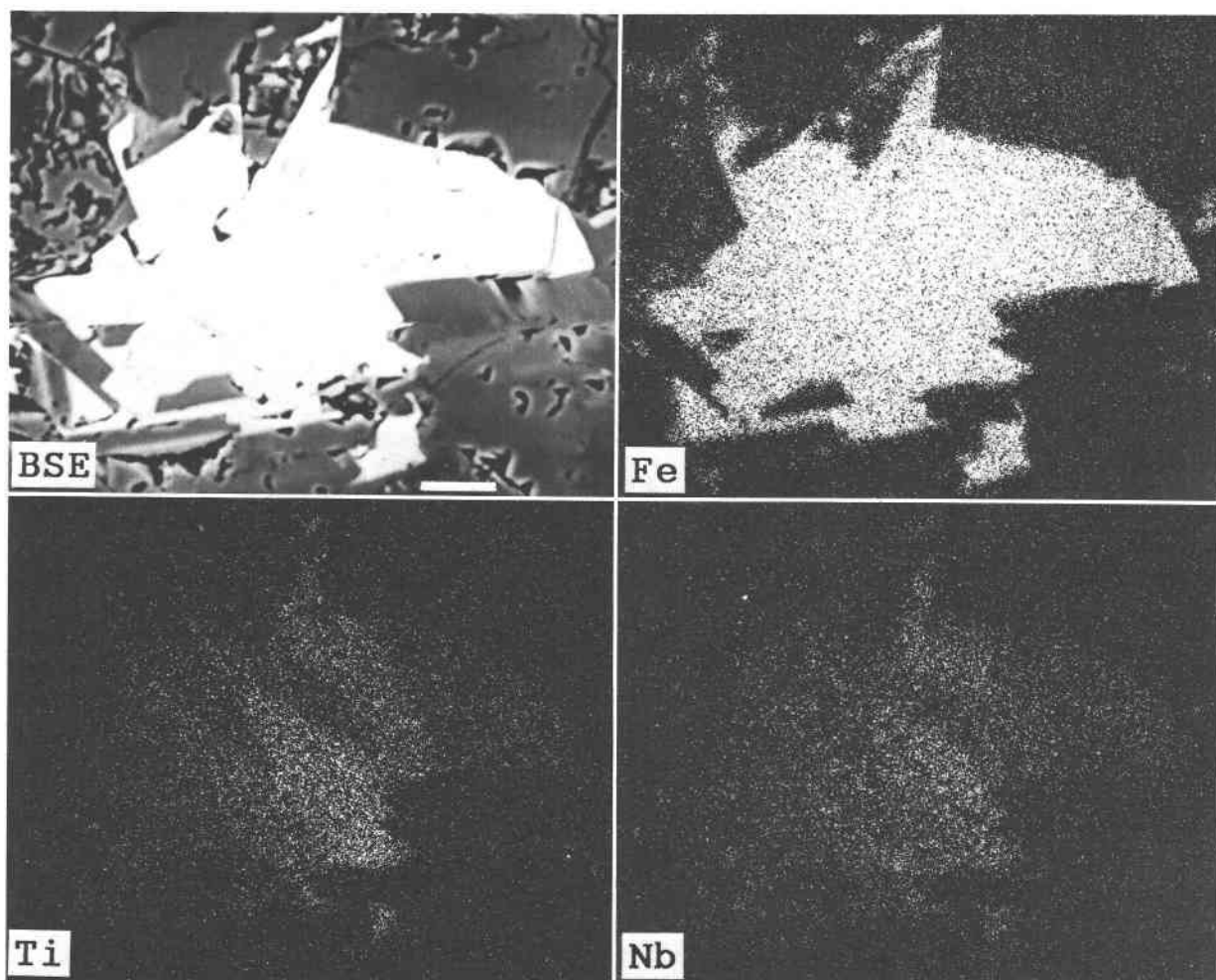


Fig. 2. Backscattered electron (BSE) and X-ray element distribution images (Fe, Ti, Nb) of a wilkinsonite crystal in sodalite trachyte 83260100. Scale bar is 10  $\mu\text{m}$ .

( $\text{CaAl}_2\text{O}_4$ ,  $\text{CaSiO}_3$ ,  $\text{TiO}_2$ ,  $\text{ZrO}_2$ ,  $\text{MgO}$ ,  $\text{MnO}$ ), and natural anorthoclase were used as primary standards, with analytical accuracy monitored using a variety of natural minerals including pyroxene, garnet, plagioclase, and ilmenite as secondary standards.

Wilkinsonite in the fine-grained marginal rocks of Bingie Grumble Mountain typically has a Ti-bearing core (with up to 2.0 wt%  $\text{TiO}_2$ ), with an anhedral rim that has very little, or is totally devoid of, Ti (Fig. 2). In other rocks from Bingie Grumble Mountain, wilkinsonite contains significantly more Ti (1.5–3.5 wt%  $\text{TiO}_2$ ) but is similarly zoned.

There is an obvious antithetic relationship between the Ti and (Fe + Mn + Mg + Nb) contents of aenigmatite and wilkinsonite from Bingie Grumble Mountain and elsewhere in the Warrumbungle Volcano (Fig. 3). This relationship supports an interpretation (Hodges and Barker, 1973; Grapes et al., 1979; Larsen, 1977) that a decrease in Ti results from a coupled substitution of the type  $\text{Fe}^{2+} + \text{Ti} = 2\text{Fe}^{3+}$ , which defines solid solution be-

tween aenigmatite ( $\text{Na}_2\text{Fe}_5^{2+}\text{TiSi}_6\text{O}_{20}$ ) and Ti-free wilkinsonite ( $\text{Na}_2\text{Fe}_4^{2+}\text{Fe}_2^{3+}\text{Si}_6\text{O}_{20}$ ). Departure from the join between these end-members reflects minor substitution of Ca, Al, Mn, and Mg combined with analytical uncertainties.

Most wilkinsonite analyses have  $(\text{Si} + \text{Al}) < 6.0$ . This suggests that a small amount of  $\text{Fe}^{3+}$  is present in tetrahedral coordination, a feature noted in much aenigmatite (Larsen, 1977; Deer et al., 1978). Most analyses also have  $(\text{Na} + \text{Ca}) > 2.0$ ; Larsen (1977) has suggested that this may reflect a small systematic error introduced by the large ZAF correction required for Na in the relatively heavy-element matrix of aenigmatite.

Irrespective of their Ti contents, the Warrumbungle aenigmatite and wilkinsonite contain minor Zr (up to 0.6 wt%  $\text{ZrO}_2$ ).  $\text{ZrO}_2$  abundances are significantly less than those of coexisting groundmass sodic pyroxene, which typically contains about 2 wt% and, in rare instances, up to 14 wt%  $\text{ZrO}_2$  (Duggan, 1988). These data are consistent with the respective Zr partition coefficients for heden-

TABLE 5. X-ray powder-diffraction data for wilkinsonite

$l_{\text{obs}}$	$d_{\text{obs}}$	$d_{\text{calc}}$	$hkl$	$l_{\text{obs}}$	$d_{\text{obs}}$	$d_{\text{calc}}$	$hkl$
100	8.10	8.10	001	70	2.115	2.117	333
		8.09	010			2.115	204
20	7.41	7.40	011			2.115	251
20	6.38	6.35	111	30	2.070	2.070	411
30	4.82	4.83	011	20	2.005	2.005	250
10	4.39	4.40	012			2.005	214
		4.39	021	20	1.965	1.966	152
30	4.18	4.18	221			1.966	520
		4.17	201	10	1.941	1.942	302
20	3.773	3.770	122	20	1.917	1.918	023
40	3.702	3.701	022			1.917	032
20	3.474	3.475	230	20	1.734	1.733	215
		3.473	212	10	1.683	1.683	354
10	3.221	3.221	121	10	1.635	1.636	414
100	3.149	3.150	012			1.635	543
		3.148	021	40	1.623	1.624	315
60	2.935	2.937	031			1.622	045
		2.935	120	10	1.613	1.614	235
10	2.844	2.845	331			1.613	315
20	2.808	2.808	122	20	1.589	1.590	163
30	2.750	2.749	311			1.589	402
		2.748	123			1.588	361
80	2.696	2.697	030	10	1.551	1.551	623
		2.696	241	20	1.511	1.512	643
		2.695	203			1.511	453
10	2.657	2.657	300	30	1.494		
10	2.577	2.577	213	50	1.481		
		2.577	240	30	1.465		
		2.575	340	10	1.374		
80	2.533	2.531	420	10	1.347		
<10	2.457	2.459	142	20	1.333		
		2.458	202	10	1.325		
		2.456	211	10	1.223		
10	2.418	2.417	022	10	1.210		
20	2.338	2.340	440				
		2.338	422				
20	3.304	2.305	301				
		2.303	421				
		2.302	410				

Note: Intensities visually estimated.

bergite-matrix (0.71) and aenigmatite-matrix (0.10) for phenocrysts in a pantellerite from the island of Pantelleria (Kovalenko et al., 1988).

A notable feature of the Warrumbungle aenigmatite and wilkinsonite is their relatively high Nb contents (Table 3). Almost all analyses show measurable Nb (>0.05 wt% Nb<sub>2</sub>O<sub>5</sub>), and in extreme cases up to nearly 4 wt% Nb<sub>2</sub>O<sub>5</sub> is present. The average Nb<sub>2</sub>O<sub>5</sub> content determined from 22 analyses of wilkinsonite from specimen 83260100 is 1.64 wt%, and that of 102 wilkinsonite and aenigmatite analyses from other samples is 0.47 wt%. There is no correlation between Nb and any gross chemical features of the host rocks such as, for example, the level of silica saturation. Rather, the high Nb contents appear to be a simple consequence of relatively high host-rock Nb concentrations (up to 600 ppm Nb), partitioning of Nb into wilkinsonite relative to coexisting silicate phases, and the absence of other potential Nb-bearing phases such as ilmenite or titanite. Concentration of Nb along with Ti in

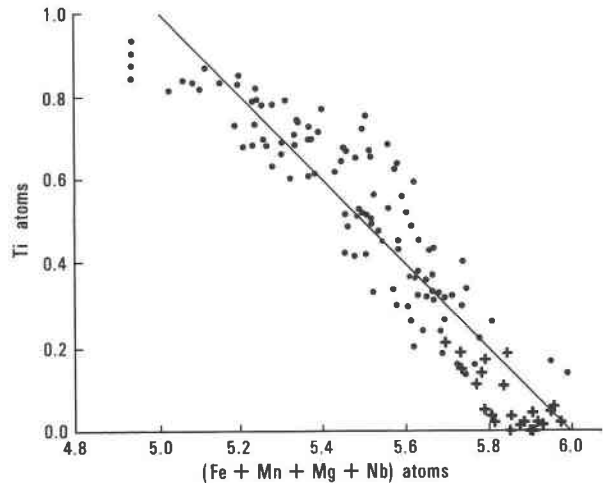


Fig. 3. Ti vs. (Fe + Mn + Mg + Nb) in aenigmatite and wilkinsonite from the Warrumbungle Volcano. The straight line represents ideal solid solution between Na<sub>2</sub>Fe<sub>3</sub><sup>+</sup>TiSi<sub>6</sub>O<sub>20</sub> and Na<sub>2</sub>Fe<sub>4</sub><sup>+</sup>Fe<sub>3</sub><sup>+</sup>Si<sub>6</sub>O<sub>20</sub>. Scatter from this line results from Fe<sup>3+</sup> in tetrahedral coordination, other ions in octahedral coordination, and analytical error. Crosses represent wilkinsonite from type specimen 83260100.

the earlier-formed cores of groundmass wilkinsonite (Fig. 2) suggests that the crystal-liquid partition coefficient ( $K_d$ ) for this wilkinsonite-matrix pair is greater than unity. By contrast, Kovalenko et al. (1988) obtained an aenigmatite-matrix  $K_d$  of 0.79 for a pantellerite glass from the island of Pantelleria. Unless vacancies develop in the wilkinsonite structure, substitution of Nb<sup>5+</sup> is probably facilitated by a substitution relation of the type Fe<sub>2</sub><sup>3+</sup>Nb<sup>5+</sup> = 3Fe<sup>3+</sup>.

The apparent rarity of other high-Nb aenigmatite samples may be as much a consequence of not analyzing for Nb in microprobe analyses as is the actual absence of Nb-bearing aenigmatite, although Larsen (1977) reports only 310–430 ppm Nb in aenigmatite from the Ilmaus-saq intrusion, south Greenland. Small amounts of Nb have also been detected in other aenigmatite examined in the course of this study, including specimens from the Nandewar Volcano and the Mount Warning intrusive complex in northern New South Wales, the Peak Range Province, central Queensland, and the Dunedin Volcano, New Zealand (Table 3).

#### X-RAY DIFFRACTION DATA

Extremely fine grain size and intimate intergrowth with other phases preclude acquisition of single-crystal X-ray diffraction data on wilkinsonite, and apparent overlap of values of magnetic susceptibility and density with those of clinopyroxene prevent concentration by conventional mineral-separation techniques. However, a minute but sufficient amount of wilkinsonite for X-ray powder-diffraction study was separated from specimen 83260100 by hand-picking of a 38–53 μm fraction from a heavy concentrate ( $D > 3.3$  g/cm<sup>3</sup>). All grains were composite

(with adhering pyroxene, feldspar, or feldspathoids), but the purity was estimated to be at least 70%. The X-ray diffraction pattern of the concentrate was obtained using a 114.6-mm-diameter powder camera, FeK $\alpha$  radiation, and an exposure time of 36 hours, with Si as an internal standard. The powder diffraction pattern (Table 5) is essentially identical to that of synthetic and natural aenigmatite. It should be noted that the separate is a bulk sample of wilkinsonite from specimen 83260100 and, as such, is not the pure end-member but comprises a range of composition with up to about 2 wt% TiO<sub>2</sub> (average about 1 wt% TiO<sub>2</sub>).

Cell dimensions (Table 6) were determined using the Appleman-Evans cell-refinement program as modified for microcomputer by Benoit (1987). All reflections were satisfactorily indexed within the chosen  $2\theta$  tolerance (0.05°) except for (111), which is outside the range ( $\Delta 2\theta = 0.092^\circ$ ). The cell parameters are very similar to those of natural aenigmatite (Kelsey and McKie, 1964) and synthetic aenigmatite (Thompson and Chisholm, 1969). This suggests that the dominant substitution Fe<sup>2+</sup>Ti = 2Fe<sup>3+</sup> has a minimal effect on cell dimensions. It may be that any decrease in unit-cell dimensions resulting from the smaller Fe<sup>3+</sup> ion is partly compensated by the addition of minor Nb<sup>5+</sup> (0.69 Å) and of some tetrahedrally coordinated Fe<sup>3+</sup> and Al. Alternatively, the cell parameters may be primarily dependent on the anion framework and therefore not sensitive to minor cation variations.

#### PHYSICAL AND OPTICAL PROPERTIES

Wilkinsonite is black with a brown streak and displays a vitreous luster and conchoidal fracture. It is very brittle with a Mohs' hardness of about 5. Small grain size and the ubiquitous presence of adhering feldspar and pyroxene prevent density determination. The calculated density is 3.89 g/cm<sup>3</sup>.

Intense absorption colors, strong dispersion, fine grain size, and intergrowth with other minerals hinder precise measurement of refractive indices and  $2V$ . Best available determinations ( $\lambda = 589$  nm) give  $\alpha = \beta = 1.79(1)$ ,  $\gamma = 1.90(1)$  with  $2V$  positive and very small ( $<10^\circ$ ). These properties are similar to those of aenigmatite (Deer et al., 1978), although  $2V$  is significantly higher in that mineral (27–55°).

Absorption is intense and the pleochroic scheme is only observable in minute grains or very thin wedges that overlap colorless, transparent minerals. In Ti-free portions of grains, absorption colors ( $X =$  olive green,  $Y =$  gray-brown,  $Z =$  dark brown) differ from those of aenigmatite, but closely match those of the Ti-free synthetic phase (olive drab to reddish brown: Ernst, 1962). Absorption colors change with increasing Ti content. Portions of grains with minor Ti (1–2 wt% TiO<sub>2</sub>) have  $X =$  gray-green to pale greenish brown,  $Y =$  gray-brown to brown, and  $Z =$  very dark brown, whereas grains with measured TiO<sub>2</sub> in excess of about 2–3 wt% assume colors transitional from the reddish brown to very dark brown absorption characteristic of aenigmatite.

TABLE 6. Cell parameters of wilkinsonite and aenigmatite

	Wilkinsonite Bingie Grumble Mtn.	Aenigmatite* (synthetic)	Aenigmatite** Kola Peninsula
$a$ (Å)	10.355(2)	10.35	10.406
$b$ (Å)	10.812(2)	10.81	10.813
$c$ (Å)	8.906(2)	8.94	8.926
$\alpha$ (°)	105.05(1)	105.28	104.93
$\beta$ (°)	96.63(1)	96.25	96.87
$\gamma$ (°)	125.20(1)	125.57	125.32
$V$ (Å <sup>3</sup> )	741.07(16)	739.8	744.5

Note: Standard errors (in parentheses) refer to last digit.

\* Synthetic aenigmatite parameters are taken from JCPDS file (22-1453) and based on the powder diffraction data of Thompson and Chisholm (1969).

\*\* Kelsey and McKie (1964).

## DISCUSSION

### Site occupancy

It has already been emphasized that all published analyses of aenigmatite have Ti as an essential component of their empirical formula (Ti > 0.5 atoms per formula unit). Moreover, there are no known examples of Ti significantly in excess of one atom per formula unit. For example, 14 aenigmatite analyses listed in Deer et al. (1978) have TiO<sub>2</sub> in the range 6.8–10.2 wt% (ave. 8.67) and Ti in the range 0.73–1.10 atoms per formula unit (ave. 0.933), whereas some 52 analyses compiled from the literature (post-1970) and the author's unpublished data have TiO<sub>2</sub> in the range 6.4–10.2 wt% (ave. 8.17) and Ti in the range 0.68–1.10 atoms per formula unit (ave. 0.882).

It is therefore suggested that one atom of Ti is an essential component of aenigmatite, as indicated by the formula Na<sub>2</sub>Fe<sub>5</sub><sup>2+</sup>TiSi<sub>6</sub>O<sub>20</sub>, and, further, that a particular octahedral site is favored by Ti over Fe<sup>2+</sup>. The structure and cation-site populations of aenigmatite were determined by Cannillo et al. (1971), who showed that Fe<sup>2+</sup> and Ti occupy seven octahedral sites [M(1)–M(7)]. The major proportion of Ti (54%) occupies the M(7) site. The remaining Ti is distributed among five of the other six sites with only M(4) containing more than 10% Ti. This is consistent with the smaller average interatomic distance of the M(7) site (1.99 Å) relative to M(1) to M(6) (2.10–2.16 Å). Thus, although not exclusively confined to one octahedral site, the M(7) site is clearly the predominant location for Ti in aenigmatite, and substitution of Ti in the remaining octahedral sites is relatively limited. If the configurations of octahedral sites in aenigmatite and wilkinsonite are similar, it is probable that the smaller M(7) site will also be dominated by Fe<sup>3+</sup>. However, the coupled substitution 2Fe<sup>3+</sup> = Fe<sup>2+</sup>Ti also entails a concomitant substitution of some Fe<sup>3+</sup> into the Fe<sup>2+</sup>-dominated M(1)–M(6) sites.

### Conditions of formation

As already noted, recorded instances of very low Ti contents in aenigmatite are very rare. Aenigmatite with Ti less than one atom per formula unit (two atoms per unit cell) is known (Yagi and Souther, 1974; Larsen, 1977;

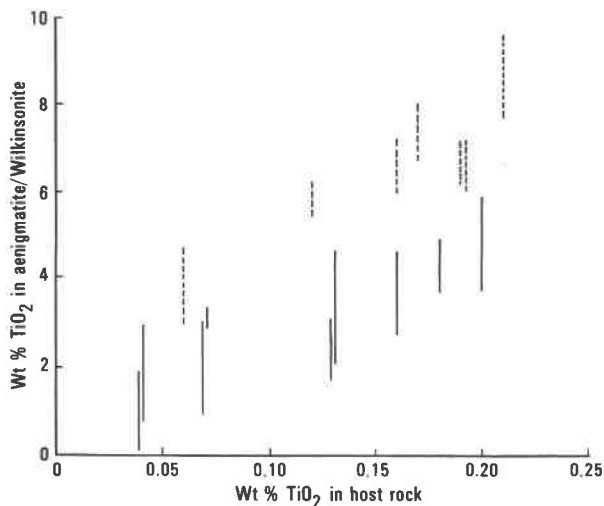


Fig. 4. Range of  $\text{TiO}_2$  contents of aenigmatite and wilkinsonite vs.  $\text{TiO}_2$  content of respective host rocks for Ti-poor felsic rocks from the Warrumbungle Volcano. Solid lines represent silica-undersaturated hosts and dashed lines represent silica-oversaturated hosts.

Grapes et al., 1979; Howie and Walsh, 1981), but the only documented occurrence of aenigmatite with Ti less than 0.5 atoms per formula unit is in the Sierra Prieta nepheline-analcime syenite and other intrusions of the Diablo Plateau, Texas, where aenigmatite  $\text{TiO}_2$  contents as low as 1.7 wt% have been reported (Hodges and Barker, 1973). The present account therefore represents the first report of a naturally occurring aenigmatite-type mineral which is essentially free of Ti. The extreme rarity of such compositions indicates that very specific and unusual conditions are required for their formation.

Hodges and Barker (1973) suggested that the Ti activity of the host melt was the prime control of Ti content in aenigmatite. The Sierra Prieta nepheline-analcime syenite host rocks contain 0.04–0.11 wt%  $\text{TiO}_2$ , which is lower than  $\text{TiO}_2$  concentrations in most aenigmatite-bearing felsic rocks reported in the literature. Wilkinsonite-bearing trachytes in the Warrumbungle Volcano are similarly Ti-poor (<0.2 wt%  $\text{TiO}_2$ ). The influence of low Ti activities on the Ti content of Warrumbungle wilkinsonite is demonstrated by the relationship between the Ti contents of wilkinsonite and aenigmatite and those of their respective host rocks (Fig. 4). At low values of host rock  $\text{TiO}_2$  (less than approximately 0.1 wt% for quartz trachytes and 0.2 wt% for nepheline trachytes), Ti in wilkinsonite is directly proportional to Ti in the host, suggesting that Ti is acting as a trace component and displaying behavior consistent with Henry's Law in its substitution. Figure 4 also demonstrates the relationship of host-rock Si activity and the Ti content of wilkinsonite; that in silica-undersaturated rocks has significantly lower Ti content relative to that in silica-saturated rocks. By contrast, aenigmatite in more Ti-rich rocks from the

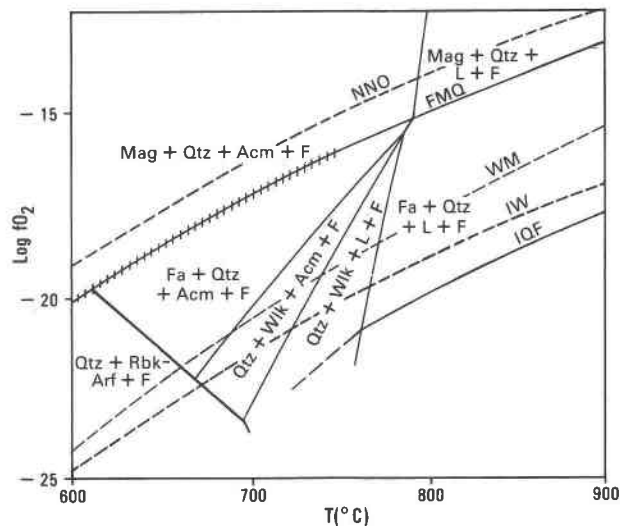


Fig. 5. Stability diagram ( $f\text{O}_2$  versus  $T$ ) of wilkinsonite for the composition  $\text{Na}_2\text{O} \cdot 5\text{FeO} \cdot 8\text{SiO}_2$  + excess  $\text{H}_2\text{O}$  at  $P(\text{H}_2\text{O}) = 500$  bars, after Ernst (1962). Oxygen-buffer curves, based on thermodynamic data of Robie et al. (1978): NNO = nickel-bunsenite, FMQ = fayalite-magnetite-quartz, WM = wüstite-magnetite, IW = iron-wüstite, IQF = iron-quartz-fayalite. Hatched portion of FMQ curve indicates the temperature range over which aenigmatite was synthesized by Lindsley (1971). The upper stability limit of aenigmatite was not determined. Mineral abbreviations: Qtz = quartz, Wlk = wilkinsonite, Acn = acmite, Rbk-arf = riebeckite-arfvedsonite, Mag = magnetite, Fa = fayalite, L = liquid, F = fluid.

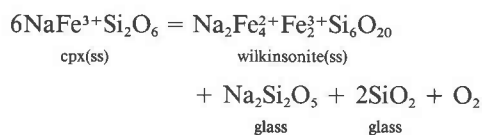
Warrumbungles displays no unusually low Ti content, regardless of the level of silica saturation.

A Ti-free aenigmatite-like phase (wilkinsonite) was synthesized by Ernst (1962) using the bulk composition  $\text{Na}_2\text{O} \cdot 5\text{FeO} \cdot 8\text{SiO}_2$  (plus excess water) and with  $f\text{O}_2$  controlled by the iron-wüstite (IW) and wüstite-magnetite (WM) buffer assemblages, but the full stability limits of the phase are unknown. On the WM buffer curve, the approximate stability range is 670 to 850 °C at  $P(\text{H}_2\text{O}) = 250$  bars, contracting to 690–775 °C at  $P(\text{H}_2\text{O}) = 500$  bars. Wilkinsonite was not observed in runs at  $P(\text{H}_2\text{O}) = 1000$  bars. The suggested stability field of wilkinsonite in  $f\text{O}_2$  space at  $P(\text{H}_2\text{O}) = 500$  bars, together with relevant O buffer curves, is shown in Figure 5. The phase was not detected in runs with  $f\text{O}_2$  controlled by the fayalite-magnetite-quartz (FMQ) buffer (Ernst, 1962), and that has often been interpreted to mean that it does not have a stability field under those conditions. However, the data indicate that no experiments were made on the FMQ buffer curve under the most favorable  $T$  and  $P(\text{H}_2\text{O})$  conditions as predicted from the IW and WM buffer-experiment data [ $P(\text{H}_2\text{O}) = 250$ –500 bars and 650–800 °C]. Furthermore, the starting material contained excess silica relative to the stoichiometric composition  $\text{Na}_2\text{Fe}_2^+ + \text{Fe}_3^{3+} + \text{Si}_6\text{O}_{20}$ ; wilkinsonite stability should be enhanced by a stoichiometric starting mixture or, as discussed below, reduced silica activity. Therefore the instability of wilkin-

sonite under FMQ buffer conditions, especially at reduced silica activities, has not been unequivocally demonstrated, and an expansion of the stability field in Figure 5 to intersect the FMQ buffer curve cannot be discounted. Nevertheless, it is clear that the stability field of wilkinsonite in  $T$ - $P(\text{H}_2\text{O})$ - $f\text{O}_2$  space must be greatly reduced relative to most aenigmatite.

The stability field of most aenigmatite is also rather poorly constrained. It was synthesized by Thompson and Chisholm (1969) from a stoichiometric starting mixture of fired  $\text{Na}_2\text{O}$ - $\text{FeO}$ - $\text{SiO}_2$  gel plus Specpure  $\text{TiO}_2$  at 700 °C,  $P(\text{H}_2\text{O}) = 1000$  bars and  $f\text{O}_2$  defined by the IW buffer and by Lindsley (1971) from a stoichiometric mixture of crystalline starting materials at 500–750 °C,  $P(\text{H}_2\text{O}) = 500$  bars and  $f\text{O}_2$  defined by the FMQ buffer. The upper stability limit in  $f\text{O}_2$  space at 750 °C and  $P(\text{H}_2\text{O}) = 500$  bars lies between the Ni-NiO and the FMQ buffer curves. The upper temperature-stability limit of aenigmatite is unknown but is constrained by incongruent melting in vacuo at 880 to 900 °C.

The influence of Si activity as inferred from Figure 4 can be explained by reference to the equation



This equation indicates qualitatively that in a peralkaline melt, the stability of Ti-free aenigmatite is favored relative to acmite by relative low  $a\text{SiO}_2$ , low  $a\text{Na}_2\text{Si}_2\text{O}_5$  and low  $f\text{O}_2$ . Given the variability in pyroxene compositions (and hence  $a\text{NaFe}^{3+}\text{Si}_2\text{O}_6$ ), the absence of thermodynamic data on  $\text{Na}_2\text{Fe}_4^{2+}\text{Fe}_2^{3+}\text{Si}_6\text{O}_{20}$  and also the uncertainties in estimating  $a\text{SiO}_2$  and especially  $a\text{Na}_2\text{Si}_2\text{O}_5$ , it is not possible to evaluate this reaction in detail to assess the physicochemical conditions under which wilkinsonite forms. However, available mineralogical and chemical data are all consistent with low  $a\text{SiO}_2$ , relatively low  $a\text{Na}_2\text{Si}_2\text{O}_5$  and low  $f\text{O}_2$ . Thus, the host rocks are mildly undersaturated (note the presence of modal sodalite, analcime, or nepheline and of minor nepheline in the CIPW norm; Table 1) and only very mildly peralkaline with  $(\text{Na}_2\text{O} + \text{K}_2\text{O})/\text{Al}_2\text{O}_3 = 1.02$ . There is also independent evidence, especially from compositional trends in the pyroxenes (Duggan, 1988) that the host rocks crystallized at relatively low  $f\text{O}_2$ , probably substantially below the FMQ buffer curve. Indeed, in the absence of other oxygen-buffering phase assemblages, coexisting acmitic pyroxene and wilkinsonite will act as an oxygen-buffer assemblage according to the above reaction. Unfortunately, the practical application of this reaction to natural assemblages is minimized by difficulties in accurately assessing activities of the melt components and of the acmite component of clinopyroxene.

## ACKNOWLEDGMENTS

I am grateful to J.F.G. Wilkinson, J. Knutson, A. L. Jaques and K. L. Currie for valuable discussions and for perceptive and helpful reviews of the manuscript, to E. H. Nickel and W. D. Birch for advice, and to N. G. Ware for instruction and advice on operation of the Cameca microprobe. I also thank J. M. Hughes and an anonymous reviewer for their constructive reviews. The New South Wales National Parks and Wildlife Service is thanked for cooperation in obtaining specimens from remote areas of the Warrumbungle National Park. The paper is published with the permission of the Director, Bureau of Mineral Resources.

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MANUSCRIPT RECEIVED OCTOBER 23, 1989

MANUSCRIPT ACCEPTED JANUARY 29, 1990