Zirconium-rich sodic pyroxenes in felsic volcanics from the Warrumbungle Volcano, Central New South Wales, Australia

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Abstract

Soda-rich pyroxenes in felsic rocks from the Warrumbungle Volcano, central New South Wales, contain up to 14.5 wt.% ZrO_2, which is more than double the previously reported maximum ZrO_2 in pyroxene. Zr is believed to enter aegirine as the component $Na(Fe^{2+},Mn,Mg)_{0.5}Zr_{0.5}Si_2O_6$ via the coupled substitution: $(Fe^{2+},Mn,Mg)^{VI}+Zr^{VI} = 2(Fe^{3+})^{VI}$. This component exceeds 50 mol.% in some analyses.

Pronounced pyroxene Zr-enrichment is restricted to rocks in which sodic amphibole is the major ferromagnesian mineral, with pyroxene only a minor late-stage phase. The Zr-rich pyroxenes resulted from a combination of host lava peralkalinity, low oxygen fugacity, rapid disequilibrium crystallization and low mobility of the Zr ion. These factors collectively led to the development of interstitial Zr-enriched microdomains in the felsic hosts during their final stages of crystallization.

KEYWORDS: zirconium, pyroxenes, felsic rocks, Warrumbungle Volcano, New South Wales, Australia.

Introduction

RECENT studies have shown that significant amounts of Zr may enter the structure of sodic pyroxenes in certain peralkaline rocks. In particular, Jones and Peckett (1980) report up to 7 wt.% ZrO_2 in aegirines in nepheline syenites from the Motzfeld Centre, South Greenland. Other Zr-bearing sodic pyroxenes have also been reported by Larsen (1976), Neilson (1979), Ewart (1981) and Stolz (1986). Jones and Peckett (1980) suggested that the Zr is present predominantly as an end-member component $NaFM_{0.5}Zr_{0.5}Si_2O_6$ for which they proposed the acronym FM-NAZ based on the scheme of Papike *et al.* (1974). Jones and Peckett used the symbol FM to denote (Fe^{2+},Mg). In this paper, FM will be used to denote (Fe^{2+},Mn,Mg) since, in the case of Fe-rich sodic pyroxenes, there appears to be no valid reason to distinguish between (Fe^{2+},Mg)-bearing components and their Mn analogues. The FM-NAZ component represents entry of Zr^{4+} into aegirine via the coupled substitution

$$(Fe^{2+},Mg,Mn)^{VI}+(Zr^{4+})^{VI} = 2(Fe^{3+})^{VI}$$

and is analogous to the formation of Ti-rich aegirines in some alkaline rocks (Ronsbo *et al.*, 1977; Ferguson, 1977; Neilson, 1979).

In the course of a detailed petrological study of the Warrumbungle Volcano in central New South Wales, very high Zr contents have been measured in aegirines from several peralkaline trachytes and comendites. The data considerably extend the known range of substitution of Zr in sodic pyroxenes.

Occurrence

The Warrumbungle Volcano, located approximately 500 km northwest of Sydney and immediately west of the township of Coonabarabran (31.3° S, 149.0° E), is a mildly alkaline intraplate volcano of mid-Miocene age (17–13 Ma; Wellman and McDougall, 1974). The volcanic suite, which ranges from hawaiite through mugearite to mafic trachyte, peralkaline trachyte and minor comendite, is very similar to that of the Nandewar Volcano some 180 km to the north (Stolz, 1985, 1986) except that, in the Warrumbungle Volcano, silica-undersaturated as well as oversaturated rocks are represented throughout the range hawaiite–peralkaline trachyte. A detailed account of the mineralogy and petrology of the volcano will be presented elsewhere (Duggan and Knutson, in prep.).

The ferromagnesian assemblage of the meta-

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luminous mafic trachytes is dominated by ferroaugite, with minor Fe-rich olivine and titanomagnetite (often mantled by aenigmatite). In some interstitial patches the ferroaugite is strongly zoned to hedenbergite and then towards aegirine. Zr enrichment is restricted to the Na-rich portions of these zoned grains. Silica undersaturated peralkaline trachytes are characterized by a mafic assemblage dominated by Fe-rich pyroxenes, often accompanied by Ti-depleted aenigmatite (Duggan, in prep.). In rare instances, traces of eudialyte and possibly other complex Zr-silicates are present in these trachytes. In contrast, silica-oversaturated (quartz-bearing) trachytes and comendites contain arfvedsonite as the dominant ferromagnesian phase, sometimes with minor aenigmatite, and with aegirine usually restricted to small interstitial late-stage grains. Other Zr-bearing species are absent. It is in these quartz-bearing trachytes and comendites that Zr sometimes reaches abnormally high levels in the late-crystallizing interstitial pyroxenes.

Microprobe data

Microprobe analyses have been carried out on a Camabex (Cameca) Microbeam electron probe microanalyser using an accelerating voltage of 15 kV, a beam current of 30 na (measured on barium titanate) and employing full ZAF corrections. Primary standards were Fe, Zr, and Nb metal, synthetic $CaSiO_3$ (Ca and Si), $CaAl_2O_4$ (Al), TiO_2, MgO and MnO, and natural anorthoclase (K and Na). A variety of natural mineral samples (olivine, pyroxenes, garnet, and zircon) were used as secondary standards to monitor analytical quality.

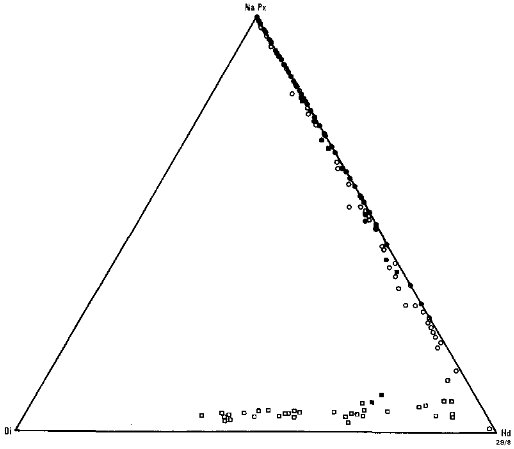

FIG. 1. Diopside–hedenbergite–Na pyroxene (= Na $Fe^{3+}Si_2O_6 + NaFe^{2+}_{0.5}Zr_{0.5}Si_2O_6$) diagram for pyroxenes in felsic rocks from the Warrumbungle Volcano. Squares—mafic trachytes; circles—peralkaline trachytes and rhyolites. Open symbols indicate pyroxenes with less than 1.0 wt. % ZrO_2. Some overlapping data points in Figs 1 to 4 omitted for clarity.

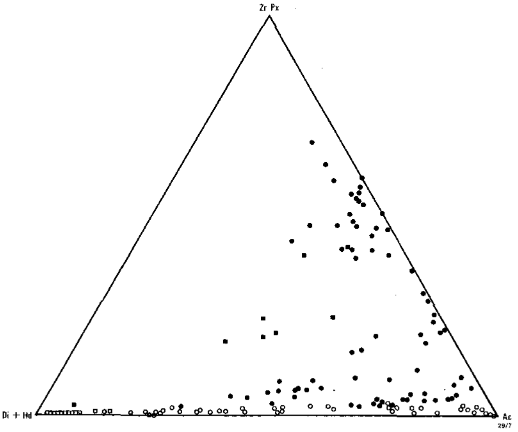

FIG. 2. (Diopside + hedenbergite)–acmite–Zr pyroxene (= $NaZrAlSiO_6 + NaFe^{2+}{}_{0.5}Zr_{0.5}Si_2O_6$) diagram for pyroxenes in felsic rocks from the Warrumbungle Volcano. Symbols as in Fig. 1.

Clinopyroxenes in the felsic peralkaline volcanics of the Warrumbungle Volcano are predominantly hedenbergite–acmite solid solutions in which Na enrichment was suppressed until extreme Fe enrichment and Mg depletion had occurred (Fig. 1). This trend is also common to other eastern Australian central-type volcanoes (Ewart *et al.*, 1976; Stolz, 1986) and has been attributed to very low oxygen fugacities during crystallization (Ewart *et al.*, 1976; Ewart, 1981).

Some representative analyses of Zr-bearing pyroxenes from the Warrumbungle Volcano are presented in Table 1 and Zr data on pyroxenes in several rocks from the Warrumbungles are summarized in Table 2. Analyses in Table 1 have been recast into end-member pyroxene components after Jones and Peckett (1980), except that measured Fe has been recalculated as FeO and Fe_2O_3 on the basis of stoichiometry (4 cations and 6 oxygen atoms) prior to recasting, and Mn has been combined with (Fe^{2+} + Mg). The analyses show very low abundances of most minor elements other than Zr (and, in two cases, Ti) and are strongly dominated by the $NaFe^{3+}Si_2O_6$, Ca(FM) Si_2O_6, $Na(FM)_{0.5}Zr_{0.5}Si_2O_6$ (and sometimes $Na(FM)_{0.5}Ti_{0.5}Si_2O_6$) components.

Zr enrichment is restricted to highly Mg-depleted pyroxenes (Fig. 1) and is more pronounced in Na-rich (acmitic) than Ca-rich (hedenbergitic) types (Fig. 2). Thus in the mafic trachytes, earlier-crystallized more Mg-rich pyroxenes have no detectable Zr, whereas later interstitial Fe-rich

TABLE 1. Analyses of Zr-bearing Pyroxenes from the Warrumbungle Volcano.

	(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)
SiO_2	50.49	50.18	49.63	50.39	50.32	50.69	50.39	52.24	50.77
TiO_2	0.36	0.55	0.18	0.09	0.05	0.09	3.77	9.95	0.75
ZrO_2	14.30	13.53	11.71	2.86	10.08	5.33	11.49	3.88	11.19
Al_2O_3	0.35	0.10	0.08	0.48	0.24	0.44	0.13	0.08	0.13
FeO*	18.62	19.45	21.18	27.62	23.14	25.55	17.90	18.82	21.08
MnO	1.13	1.29	0.67	0.44	0.60	0.48	0.95	0.16	0.99
MgO	-	-	-	-	0.03	0.05	-	-	-
CaO	1.22	1.23	3.96	5.88	4.91	3.62	0.59	0.81	1.43
Na_2O	11.98	12.45	10.65	9.72	10.07	10.98	12.86	13.26	11.96
K_2O	0.16	0.05	0.04	0.02	0.07	0.03	0.07	0.08	0.02
Nb_2O_5	-	-	-	-	-	-	0.10	0.23	0.59
Total	98.61	98.83	98.10	97.50	99.51	97.26	98.25	99.51	98.91
Fe_2O_3#	9.26	13.15	11.23	20.82	12.12	19.97	10.02	8.70	12.10
FeO	10.29	7.62	11.07	8.89	12.23	7.58	8.89	10.99	10.19
Total	99.54	100.15	99.23	99.59	100.72	99.26	99.25	100.38	100.12
					Cations Based on 6 Oxygen Atoms				
Si	2.031	2.003	2.009	1.994	2.006	2.009	2.006	2.002	2.022
Al^{IV}	-	-	-	0.006	-	-	-	-	-
Al^{VI}	0.017	0.005	0.004	0.016	0.011	0.021	0.006	0.004	0.006
Ti	0.011	0.017	0.005	0.003	0.001	0.003	0.113	0.287	0.022
Zr	0.281	0.263	0.231	0.055	0.196	0.103	0.223	0.073	0.217
Fe^{3+}	0.280	0.395	0.342	0.620	0.364	0.596	0.300	0.251	0.363
Fe^{2+}	0.346	0.254	0.375	0.294	0.408	0.251	0.296	0.352	0.339
Mn	0.039	0.044	0.023	0.015	0.020	0.016	0.032	0.005	0.033
Mg	-	-	-	-	0.002	0.003	-	-	-
Ca	0.053	0.053	0.172	0.249	0.210	0.154	0.025	0.033	0.061
Na	0.935	0.964	0.836	0.746	0.778	0.844	0.993	0.985	0.924
K	0.008	0.003	0.002	0.001	0.004	0.002	0.004	0.004	0.001
Nb	-	-	-	-	-	-	0.002	0.004	0.011
					End Member Molecules (Mole %)				
$KFe^{3+}Si_2O_6$	0.86	0.25	0.21	0.10	0.36	0.16	0.36	0.39	0.10
$NaZrAlSiO_6$	1.74	0.47	0.39	2.27	1.14	2.12	0.62	0.36	0.63
$NaZr_{½}FM_{½}Si_2O_6$	55.20	51.60	46.24	6.65	37.27	16.97	43.79	13.82	43.31
$NaTi_{½}FM_{½}Si_2O_6$	2.28	3.29	1.11	0.54	0.30	0.55	22.78	57.52	4.61
$NaFe^{3+}Si_2O_6$	28.46	39.14	34.58	62.72	36.34	61.14	29.92	24.77	37.09
$Ca(FM)Si_2O_6$	5.50	2.27	16.79	25.27	21.16	15.82	-	0.18	6.26
$(FM)_2Si_2O_6$	5.98	-	-	2.44	3.42	3.24	-	-	-
$Ca_2Si_2O_6$	-	2.97	0.68	-	-	-	2.54	3.15	-

1,2. Zr-rich aegirines in peralkaline quartz trachyte 83260141, Mt Naman (855266)[+].
3. Zr-rich aegirine in peralkaline trachyte 82260007, Timor Rock (053388).
4. Zr-bearing aegirine in peralkaline nepheline trachyte 83260100, Mt Bingie Grumble (079333).
5. Zr-rich aegirine in mafic trachyte 84260150, Mopra Creek (928379).
6. Zr-bearing aegirine in peralkaline nepheline trachyte 84260154, The Breadknife (898320).
7. Zr-rich aegirine in comendite 84260165, Western High Tops (874332).
8. Zr-bearing titanian aegirine in peralkaline quartz trachyte 84260199, Bridget Peak (881319).
9. Zr-rich aegirine in comendite 84260181, Danu Saddle (866336).

FM = Fe^{2+} + Mn + Mg.

* Total Fe as FeO.

\# Fe_2O_3 and FeO calculated on the basis of stoichiometry (4 cations and 6 oxygens).

\+ Grid references refer to the Australian Map Grid on 1:100,000 sheets 8635 (Tenandra) and 8735 (Coonabarabran).

TABLE 2. Zr Contents of Sodic Pyroxenes and Their Host Rocks

Spec. No.	Rock Type	Zr in Host (ppm)	Range of ZrO_2 in Pyroxene (wt %)
84260158	mafic trachyte	545	0.00 - 6.13
84260150	mafic trachyte	585	0.00 - 10.46
86260228	peralk. qz trachyte	585	0.00 - 10.24
86260235	comendite	1250	0.00 - 1.82
82260007	peralk. trachyte	1280	0.58 - 11.71
83260141	peralk. qz trachyte	1280	4.59 - 14.30
84260165	comendite	1580	0.18 - 11.42
84260169	peralk. ne trachyte	1870	0.36 - 0.67
83260093	peralk. ne trachyte	1900	0.00 - 4.50
84260199	peralk. qz trachyte	1910	0.38 - 3.92
84260181	comendite	2230	0.37 - 11.19
83260100	peralk. ne trachyte	3660	0.44 - 2.86

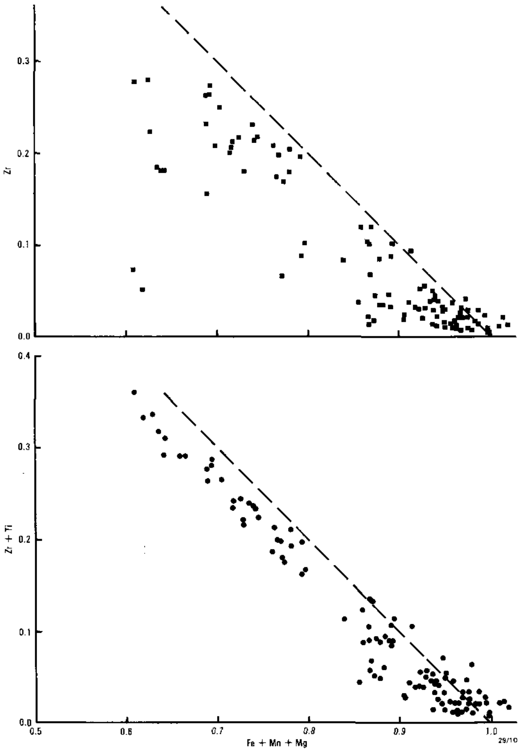

FIG. 3. [Fe + Mn + Mg] *vs.* Zr (filled squares) and [Fe + Mn + Mg] *vs.* [Zr + Ti] (filled circles) for pyroxenes in felsic rocks from the Warrumbungle Volcano. Dashed lines indicate substitution between $NaFe^{3+}Si_2O_6$ and $Na(Zr,Ti)_{0.5}Fe^{2+}{}_{0.5}Si_2O_6$.

pyroxenes contain up to 10 wt. % ZrO_2. In pyroxenes from peralkaline trachytes and comendites (essentially Mg-free hedenbergite-acmite solid solutions), enrichment in Zr and/or Ti tends to be more pronounced in more hedenbergite-depleted variants.

There is a strong negative correlation between Zr and [Fe + Mn + Mg] and, to an even greater extent, between [Zr + Ti] and [Fe + Mn + Mg] in the Zr-bearing pyroxenes (Fig. 3). By contrast (Fig. 4), Zr and [Zr + Ti] correlate positively with [Fe^{2+} + Mn + Mg − Ca] (representing divalent Fe other than that required for quadrilateral components). These trends clearly support the view that the coupled substitution

$$(Fe^{2+},Mn,Mg)^{VI} + (Zr,Ti)^{VI} = 2(Fe^{3+})^{VI}$$

is the major control on entry of Zr (and Ti) into Na-rich pyroxenes and that other possible substitutions such as

$$(Fe^{3+})^{VI} + Si^{IV} = Zr^{VI} + Al^{IV}$$

($NaZrAlSiO_6$ component) or

$$(Fe^{3+})^{VI} + Si^{IV} = Zr^{VI} + (Fe^{3+})^{IV}$$

($NaZrFe^{3+}SiO_6$ component) are only minor. The data also preclude the (unlikely) possibility of Zr entering tetrahedral sites (note that, in all analyses in Table 1, Si is close to the 'ideal' 2 atoms per formula unit).

Among the minor elements, Nb is sometimes present in small amounts (usually less than 0.1 wt. %, but up to 0.6 wt. % Nb_2O_5), especially in aenigmatite-free rocks. When aenigmatite is present, Nb is strongly partitioned into this phase.

Discussion

The conditions of formation of Zr-rich sodic pyroxenes were discussed in relation to the Motzfeldt Centre, South Greenland, by Jones and Peckett (1980) who concluded that the crystallization of potential Zr-bearing phases (zircon in

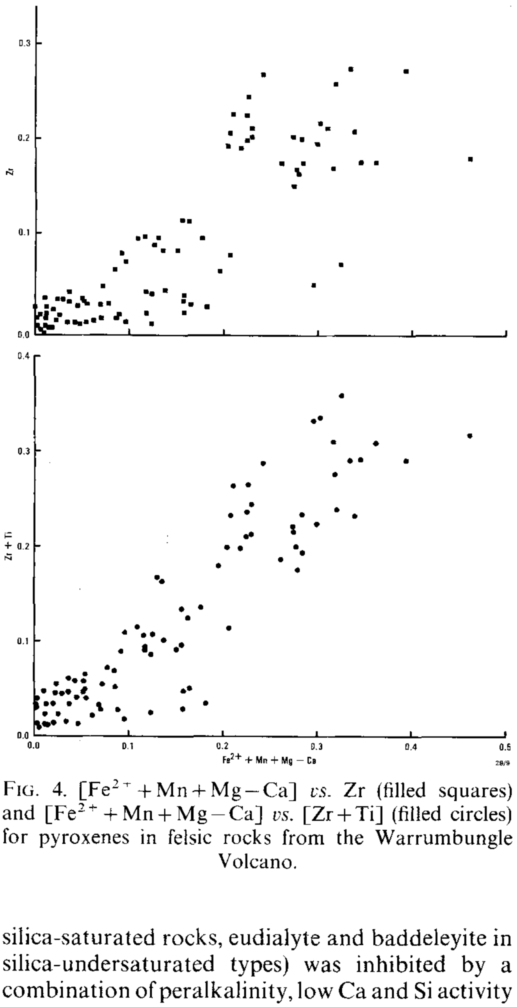

FIG. 4. $[Fe^{2+} + Mn + Mg - Ca]$ *vs.* Zr (filled squares) and $[Fe^{2+} + Mn + Mg - Ca]$ *vs.* $[Zr + Ti]$ (filled circles) for pyroxenes in felsic rocks from the Warrumbungle Volcano.

silica-saturated rocks, eudialyte and baddeleyite in silica-undersaturated types) was inhibited by a combination of peralkalinity, low Ca and Si activity and relatively low oxygen fugacity. This resulted in the concentration of Zr in late-formed sodic pyroxenes.

The physico-chemical conditions under which the Warrumbungle pyroxenes crystallized differed in some respects from the Motzveld Centre and further discussion of factors controlling the atypically high Zr abundances in some pyroxenes is therefore appropriate. Certainly the magmas of both centres were peralkaline, with low Ca activity and low f_{O_2} (see below). However the Warrumbungle pyroxenes occur in flows, lava domes, and very high-level plugs, rather than syenitic intrusions, and probably crystallized more rapidly. It is perhaps more significant that the Zr-rich pyroxenes occur in both silica-undersaturated and oversaturated hosts. In fact, the more extreme levels of Zr enrichment (over 4.5% and up to 14.5 wt. % ZrO_2) are restricted to the latter, which are characterized by relatively abundant sodic amphibole with only minor pyroxene compared with the silica-undersaturated rocks.

There is no apparent correlation between pyroxene Zr and host rock Zr (Table 2). Furthermore, the Zr contents of the hosts are not exceptionally high, compared with peralkaline rocks elsewhere. It is therefore clear that, although Zr of the parent melts must be high enough to enable significant Zr-enrichment in liquid residua, unusually high Zr in the peralkaline trachytes and comendites themselves was not a critical factor in the production of Zr-enriched pyroxenes.

The model proposed here for Zr-rich pyroxene crystallization is similar to that outlined by Jones and Peckett (1980). It is suggested that the principal control on entry of Zr into pyroxenes was the rapid crystallization of the sodic pyroxenes under disequilibrium conditions in interstitial microdomains. These were the sites of extreme Zr enrichment in the final stages of crystallization after most of the potential ferromagnesian component had crystallized as arfvedsonite. Such enrichment was controlled by a number of factors including advanced states of crystallization, relatively strong partitioning of Zr into the liquid relative to arfvedsonite, high viscosities of the felsic peralkaline liquids, the suppression of other crystallizing Zr-bearing phases due to the high solubility of Zr in peralkaline melts (Watson, 1979), and the low diffusion rate of the high field strength Zr^{4+} ion. Entry of Zr into the pyroxene structure would also have been enhanced by the effects of low f_{O_2} which would facilitate the coupled substitution

$$(Fe^{2+})^{VI} + (Zr^{4+})^{VI} = 2(Fe^{3+})^{VI}.$$

This model is supported by several observations.

1. Zr-rich pyroxene is a late-crystallizing interstitial phase in mafic trachytes containing less than 600 ppm Zr. However, earlier Ca-Mg-bearing pyroxenes in the same rock have negligible Zr.

2. Highest Zr concentrations occur in pyroxenes from amphibole-dominated trachytes. Compared with the sodic pyroxenes, sodic amphiboles apparently do not readily accept Zr and the Warrumbungle arfvedsonites rarely contain more than 1.5 wt. % ZrO_2.

3. Although precise estimates of f_{O_2} have not been possible, indirect evidence indicates that low oxygen fugacities prevailed during crystallization of the host rocks. Most important, the presence in some undersaturated rocks of aenigmatite strongly depleted in Ti (Ti below limit of detection in extreme cases) suggests that oxygen fugacities were below the fayalite-magnetite-quartz oxygen buffer curve, at least in the silica-undersaturated rocks (Duggan, in prep.). Ti-free aenigmatite has been

synthesized (Ernst, 1962) but its stability field appears to be very restricted relative to 'normal' aenigmatite (Thompson and Chisholm, 1969; Lindsley, 1971; Hodges and Barker, 1973) to a narrow range of relatively low f_{O_2} near the wüstite-magnetite and iron-wüstite oxygen buffer curves. Suppression of Na enrichment in the pyroxenes prior to extreme Mg depletion is also indicative of low oxygen fugacities (Ewart, 1981).

4. The highest Zr concentrations measured in pyroxenes from the Motzfeld Centre by Jones and Peckett (1980) are in a fine grained syenite in which amphibole is the dominant ferromagnesian phase and pyroxene only a minor interstitial phase.

5. The Zr content across individual pyroxene grains is relatively uniform (usually less than ±1 wt. % ZrO_2 but Zr varies widely from grain to grain throughout a thin section.

6. Many of the most Zr-rich pyroxenes contain small, but measurable amounts of K_2O, probably reflecting low diffusion rates and disequilibrium crystallization. By contrast, earlier-formed pyroxenes, where present, contain negligible Zr and K.

7. The scatter in the trend of Zr-enrichment on Fig. 2 is suggestive of entry of Zr into the pyroxenes under conditions of rapid cooling and disequilibrium.

The stability relations of Zr-pyroxene species, in particular $NaFe^{2+}{}_{0.5}Zr_{0.5}Si_2O_6$, are unknown. Formation of such phases in nature is inhibited because Zr is more readily accommodated in other phases (especially zircon, eudialyte and baddeleyite) except under strongly peralkaline conditions and, as illustrated by this study and by Jones and Peckett (1980), by the formation of solid solutions with other sodic pyroxene species. Nevertheless, the high Zr contents of some Warrumbungle pyroxenes indicate that such phases, especially $NaFe^{2+}{}_{0.5}Zr_{0.5}Si_2O_6$, may in fact be stable under certain conditions, even though disequilibrium has probably been an important factor in their formation. Indeed, the existence of pyroxenes with calculated contents of the $NaFe^{2+}{}_{0.5}Zr_{0.5}Si_2O_6$ component in excess of 50 mol. % suggests that $NaFe^{2+}{}_{0.5}Zr_{0.5}Si_2O_6$ may be a natural pyroxene species. However, at least in the rocks under discussion, the low abundance, very fine grain size and large compositional variability of the phase preclude its characterization as a valid species.

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