

Petrogenesis of the Swaziland and Northern Natal Rhyolites of the Lebombo Rifted Volcanic Margin, South East Africa

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RECEIVED JANUARY 30, 2006; ACCEPTED SEPTEMBER 20, 2006;
ADVANCE ACCESS PUBLICATION NOVEMBER 16, 2006

The Jozini and Mbuluzi rhyolites and Oribi Beds of the southern Lebombo Monocline, southeastern Africa, have geochemical characteristics that indicate they were derived by partial melting of a mixture of high-Ti/Zr and low-Ti/Zr Sabie River Basalt Formation types. Compositional variations within the different rhyolite types can largely be explained by subsequent fractional crystallization. The Sr- and Nd-isotope composition of the rhyolites is unique amongst Gondwana silicic large igneous provinces, having ϵ_{Nd} values close to Bulk Earth (-0.94 to 0.35) and low, but more variable, initial $^{87}Sr/^{86}Sr$ ratios (0.7034 – 0.7080). Quartz phenocryst $\delta^{18}O$ values indicate that the rhyolite magmas had $\delta^{18}O$ values between 5.3 and 6.7‰ , consistent with derivation from a basaltic protolith with $\delta^{18}O$ values between 4.8 and 6.2‰ . The low- $\delta^{18}O$ rhyolites ($<6.0\text{‰}$) come from the same stratigraphic horizon and are overlain and underlain by rhyolites with more 'normal' $\delta^{18}O$ magma values. These low- $\delta^{18}O$ rhyolites cannot have been produced by fractional crystallization or partial melting of mantle-derived basaltic material. The rhyolites have low water contents, making it unlikely that the low $\delta^{18}O$ values are the result of post-emplacement alteration. Modification of the source by fluid–rock interaction at elevated temperatures is the most plausible mechanism for lowering the $\delta^{18}O$ magma value. It is proposed that the low- $\delta^{18}O$ rhyolites were derived by melting of earlier altered rhyolite in calderas situated to the east, which were not preserved after Gondwana break-up.

KEY WORDS: rhyolite; Lebombo; stable and radiogenic isotopes; low- $\delta^{18}O$ magmas; partial melting

INTRODUCTION

Large Igneous Provinces (LIPs) located near present-day continental margins provide an important record of

crustal and mantle geodynamics during the pre- to syn-rift stages of the break-up and dispersal of supercontinents. Most studies of LIPs have tended to focus on the extensive and generally better preserved mafic sequences along volcanic rifted margins; however, LIPs can also contain aereally and volumetrically significant amounts of silicic volcanic rocks. Understanding the relative timing of the eruptions and petrogenetic characteristics of the silicic volcanic rocks with respect to the flood basalts provides important constraints on the contribution of crustal material to LIP magmatism and the role of ancient subduction episodes in generating hydrous lower crustal source materials as well as environmental and climatic impacts during LIP emplacement (Wignall, 2001; Bryan *et al.*, 2002). Other studies have emphasized the stratigraphic importance of the silicic eruptive units in constraining the volcanic stratigraphy over several hundred kilometres within often monotonous and internally complex flood basalt lava successions, and for reassembling volcanic provinces now isolated by continental break-up and seafloor spreading (Milner *et al.*, 1995; Bryan *et al.*, 2002; Ukstins *et al.*, 2002).

The Mesozoic break-up of Gondwana was associated with four LIPs emplaced across southern Africa, Antarctica, and southern South America: the Ferrar (~180 Ma; Encarnacion *et al.*, 1996), the Karoo (183–180 Ma; Allsopp *et al.*, 1984; Duncan *et al.*, 1997; Riley *et al.*, 2004), the Chon Aike (188–178 Ma; VI of Pankhurst *et al.*, 2000); and the Paraná–Etendeka (~135–130 Ma; Hawkesworth *et al.*, 1992) provinces. The Ferrar, Karoo and Paraná–Etendeka provinces are dominated by mafic volcanic rocks with less than 5%

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by volume silicic material, usually in the form of ignimbrites–rheoignimbrites, rhyolitic lavas, or tuff deposits. In contrast, the Chon Aike province is dominated by silicic volcanic rocks with only rare basalts. Previous geochemical and isotopic studies of the above LIPs have established a reasonably extensive database for the basaltic and rhyolitic components of these provinces. Geochemical studies of the basaltic rocks have been used to identify the potential mantle source(s) involved (e.g. Erlank *et al.*, 1984; Hawkesworth *et al.*, 1984; Peate *et al.*, 1992), whereas the silicic volcanic rocks have been used to evaluate the contribution of crustal material in the petrogenesis of the magmas. Based on these geochemical studies, models for the generation of silicic magmas in LIPs have generally fallen into two groups. The first has invoked either fractional crystallization of basalt accompanied by varying amounts of crustal assimilation (e.g. Garland *et al.*, 1995; Ewart *et al.*, 2004), whereas the second requires partial melting of the crust with superimposed fractional crystallization (e.g. Cleverly *et al.*, 1984; Piccirillo *et al.*, 1988; Pankhurst & Rapela, 1995; Harris *et al.*, 1990; Harris & Milner, 1997).

The rhyolites of the Lebombo Monocline form part of the Karoo volcanic province and show two unusual characteristics compared with compositionally similar rocks from other LIPs: first, their initial Sr- and especially Nd-isotope ratios are not elevated in comparison with the associated basalts, which indicates little or no input of old continental crust (Hawkesworth *et al.*, 1984; Harris & Erlank, 1992); second, some of the Lebombo rhyolites appear to have crystallized from low- $\delta^{18}\text{O}$ magmas (Harris & Erlank, 1992). Since the Harris & Erlank (1992) study was undertaken, identifying the low- $\delta^{18}\text{O}$ character of the rhyolites, there has been considerable progress in quantifying oxygen isotope fractionation between phenocryst phases and melts of different compositions (e.g. Stolper & Epstein, 1991; Matthews *et al.*, 1994; Palin *et al.*, 1996; Zhao & Zheng, 2003; Bindeman *et al.*, 2004) and in our understanding of the generation of low- $\delta^{18}\text{O}$ primary rhyolite magmas (e.g. Balsley & Gregory, 1998; Bindeman & Valley, 2001, 2003; Broughs *et al.*, 2005). Whereas low- $\delta^{18}\text{O}$ rhyolite magmas are relatively common in some caldera systems, they are still a relatively rare phenomenon world-wide (Balsley & Gregory, 1998). In this sense, the Lebombo rhyolites are significant because, although not all of them have low $\delta^{18}\text{O}$ values, and the $\delta^{18}\text{O}$ values are not as low as in some other examples (e.g. Yellowstone Plateau volcanic field, Wyoming; Hildreth *et al.*, 1984), they are the only low- $\delta^{18}\text{O}$ magmas associated with a large igneous province.

Harris & Erlank (1992) analysed a comparatively small number of samples from a wide geographical area along the Lebombo Monocline and hence had little or no information on the stratigraphic variation in both the

radiogenic and stable isotope data. Those workers suggested that the low $\delta^{18}\text{O}$ values of the Lebombo rhyolites resulted from high-temperature interaction between circulating meteoric water and the source prior to partial melting. In this study, a much more expanded geochemical and isotope dataset has been compiled, along three stratigraphic sections through the rhyolites of Swaziland and northern Natal. These sections represent the thickest sequences of rhyolites in the Lebombo Monocline and can be used to assess stratigraphic and spatial variations in their major- and trace-element and isotope geochemistry. In addition, the original dataset of Harris & Erlank (1992) has been re-evaluated in light of the more recent information on oxygen isotope fractionation in rhyolite magmas and within the context of the new data obtained in this study. This new expanded dataset is then used to assess the petrogenetic processes that produced the rhyolite magmas and to reach some conclusions about the physical environment in which they formed. In addition, we have attempted to constrain further the composition of the underplated material to determine if it is represented by any of the exposed basalt lavas.

RHYOLITES OF THE LEBOMBO MONOCLINE

The Karoo continental flood basalt province of southern Africa represents the earliest phase of igneous magmatic activity associated with initial continental thinning and subsequent break-up of Gondwana during the Mesozoic (Eales *et al.*, 1984). The Lebombo Monocline, which represents the rifted volcanic margin of SE Africa, is a 600 km long, north–south-trending, linear feature parallel to the eastern margin of the Archaean Kaapvaal Craton (Cleverly *et al.*, 1984; Watkeys, 2002), containing the most extensive rhyolite sequences associated with the Karoo volcanic province (Fig. 1a). Together with the Save–Mwenezi rift arm located in southern Zimbabwe, the total preserved volume of rhyolite is thought to be $\sim 35\,000\text{ km}^3$ (Cleverly *et al.*, 1984). The Lebombo Monocline probably marks the transition from normal thickness continental crust in the west to thinned continental crust in the east, associated with rifting of Antarctica from Africa during Gondwana break-up. The rhyolites are thought to have been produced by decompression partial melting during the initiation of rifting (Cleverly *et al.*, 1984). The voluminous Karoo eruptions consist predominantly of mafic rocks (tholeiitic basalts), with the main phase of volcanism dated by the Ar–Ar method at $\sim 182\text{ Ma}$ (Duncan *et al.*, 1997). Lesser amounts of silicic rocks were erupted slightly later at 178–180 Ma (Duncan *et al.*, 1997; Marsh *et al.*, 1997). These ages were confirmed by Riley *et al.* (2004), who showed that U–Pb sensitive high-resolution ion microprobe (SHRIMP)

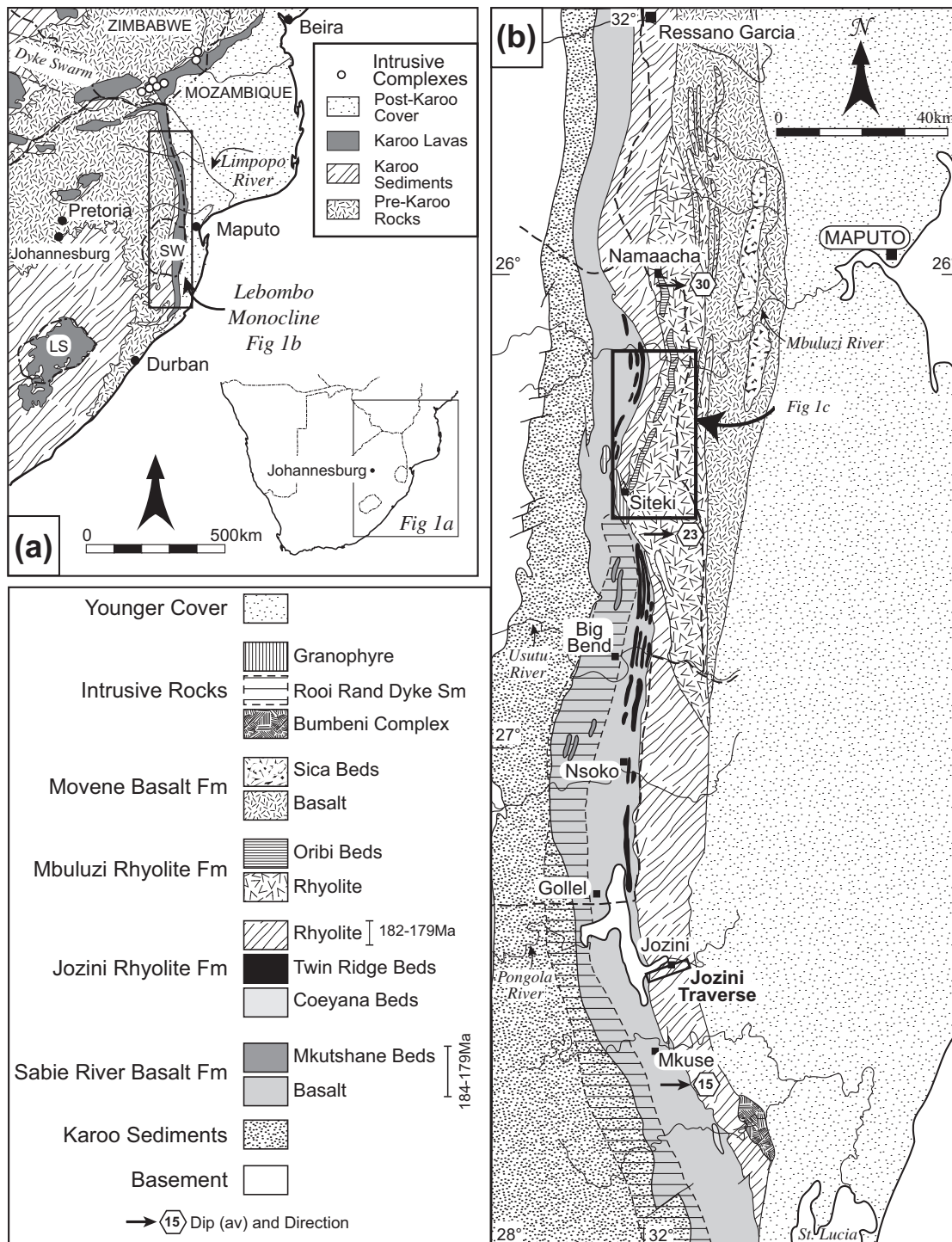


Fig. 1. (a) Location of the Lebombo Monocline within southern Africa; redrawn from Eales *et al.* (1984). SW, Swaziland; LS, Lesotho. (b) Geological map of the central and southern parts of the Lebombo Monocline in Swaziland and South Africa showing the location of the three rhyolite traverses sampled and their relationship to the distribution of the Sabie River Basalt Formation and extent of the Rooi Rand dyke swarm; redrawn from Eales *et al.* (1984). (c) Detail of the Mbuluzi traverse along the Mbuluzi river and the Siteki traverse between Siteki and the Mozambique border showing the location of MB and SR samples; redrawn from Cleverly (1977). Dates given in stratigraphic legend are from Duncan *et al.* (1997) and Riley *et al.* (2004).

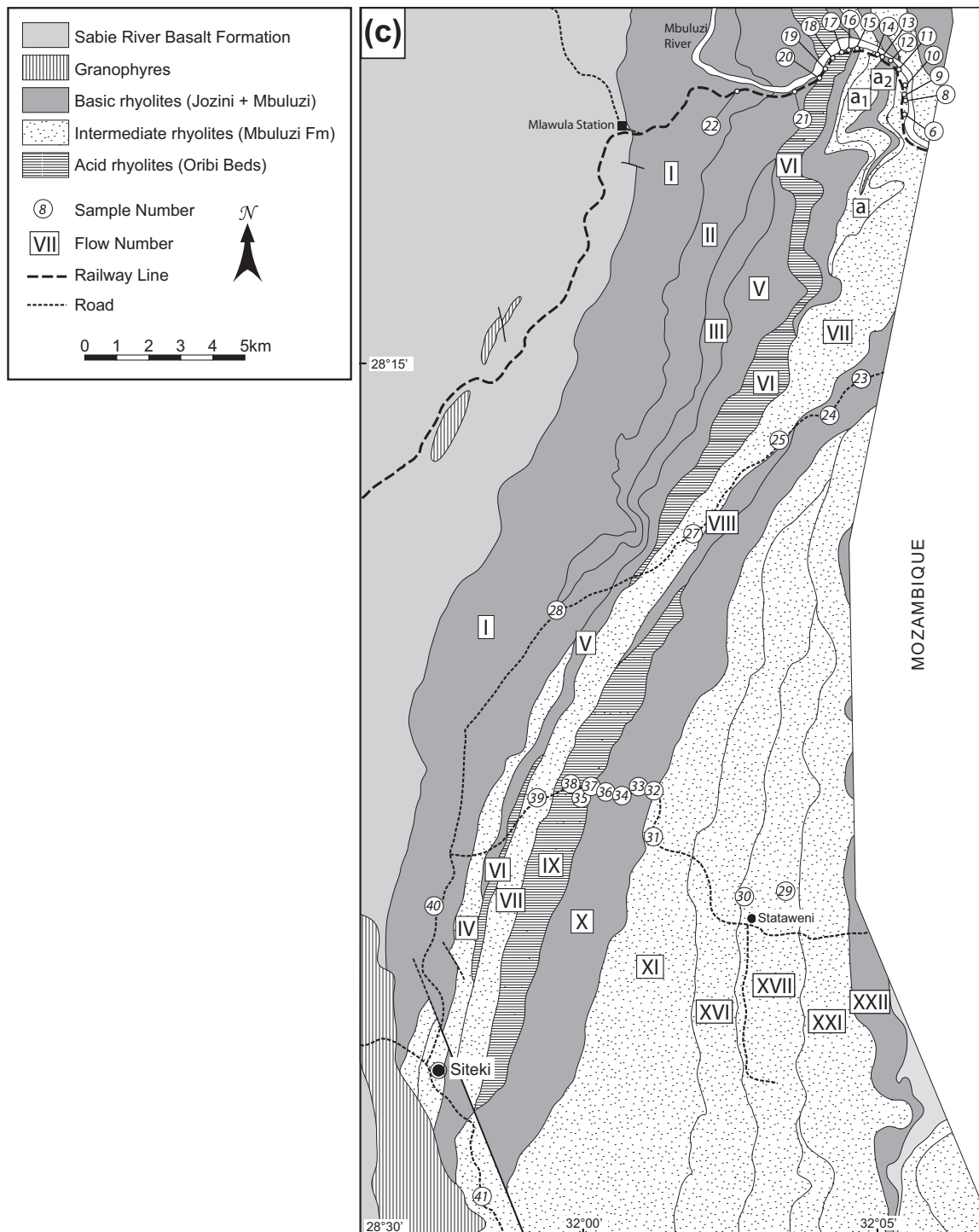


Fig. 1. Continued.

ages for rhyolites interbedded within the Sabie River Basalt Formation (SRBF) and the overlying Jozini rhyolites were the same within error, with the latter being 182.1 ± 2.9 Ma.

Stratigraphic relationships

The stratigraphy of the Karoo sequence in the Lebombo can be summarized as a thick sequence of basalts of the Sabie River and Letaba formations that overlie

sedimentary rocks of the Karoo Supergroup (Cox, 1972; Cox & Bristow, 1984; Eales *et al.*, 1984). These basalts are overlain by rhyolites of the Jozini and Mbuluzi formations (hereafter termed Jozini and Mbuluzi rhyolites), which are in turn overlain by the Moveene Basalt Formation, which is in turn capped by Cretaceous sedimentary rocks (Fig. 1b); Eales *et al.*, 1984). Both the Jozini and Mbuluzi rhyolites occur as sheets representing individual cooling units, which have features characteristic of both lavas and ignimbrites, and are considered to have formed as anhydrous, high-temperature (1000–1100°C) ash-flow tuffs (Betton, 1978; Cleverly, 1979). Textures typical of ignimbrites are preserved at the top and base of each unit (Bristow, 1976; Cleverly, 1977) and the lava-like features are considered to have formed in response to post-eruptive welding and remobilization of the degassed ignimbrite deposits (Cleverly, 1979). The plagioclase-phyric Jozini rhyolites, which are volumetrically the more significant unit, directly overlie the Sabie River basalts along most of the length of the Lebombo. Together with the sparsely quartz-phyric Mbuluzi rhyolites (and associated subsidiary quartz-phyric Oribi Beds), which are laterally discontinuous and occur principally in Swaziland, the two formations comprise a maximum thickness of around 5000 m of continuous rhyolite with no interbedded basalts. Cleverly (1977), in his original mapping in NE Swaziland, distinguished basic, intermediate and acid rhyolite types (on the basis of wt % SiO₂ and phenocryst populations) and mapped more than 20 distinct flows up to 200 m thick, which pinch and swell and extend laterally in excess of 60 km (Fig. 1c). Flow I, which is a relatively continuous flow in the region of this study and directly overlies the Sabie River Basalt Formation, was mapped as a basic rhyolite and probably equates to the Jozini rhyolites. Flows II and upwards (Fig. 1c) were mapped as both basic and intermediate rhyolites but probably largely represent Mbuluzi rhyolites. The interbedded and lenticular acid rhyolites (Flows VI and IX) are known as the Oribi Beds and are quartz-phyric. Of the other minor subsidiary rhyolite units, the most distinctive are the Mkutshane Beds, which occur towards the bottom of the Sabie River Basalt Formation. They are geochemically distinct from either the Jozini or the Mbuluzi rhyolites and in particular have elevated radiogenic isotope signatures indicative of crustal input (Cleverly *et al.*, 1984).

Petrography

Previous studies have revealed that, with the exception of the phenocryst populations, there are few petrographic differences between the different rhyolite units occurring in the Lebombo (Cleverly, 1977; Cleverly *et al.*, 1984). In general, all the rhyolites are porphyritic and contain phenocrysts of one or more of plagioclase, clinopyroxene, magnetite, quartz and sanidine, as well as apatite, zircon, olivine and ilmenite (Cleverly *et al.*, 1984).

Phenocrysts are present in varying amounts but rarely exceed 30% by volume and more commonly make up 15–20% by volume of the rhyolites (Cleverly *et al.*, 1984). The phenocrysts are usually set in a fine-grained groundmass of devitrified glass and, in the case of plagioclase and clinopyroxene, show complex zoning patterns and compositional differences specific to the individual rhyolite sample, confirming their origin as phenocrysts and not xenocrysts (Cleverly, 1977, 1979; Betton, 1978; Cleverly *et al.*, 1984). Minor secondary hydrous phases are present as alteration products of both phenocrysts and groundmass (Harris & Erlank, 1992).

Plagioclase is the most common as well as dominant phenocryst, occurring as subhedral crystals 1–5 mm in size, with cores of oligoclase-andesine strongly zoned to more sodic rim compositions. Clinopyroxene phenocrysts occur in all but the most silica-rich rhyolites and exhibit complex zoning patterns (Betton, 1979; Cleverly *et al.*, 1984). They are much smaller than the plagioclase phenocrysts, being only 0.1–1 mm in length, and make up a much smaller proportion of the phenocryst population. Quartz phenocrysts are usually subhedral but clearly show the outline of pyramid faces. In some rocks, grains are partially resorbed and small magmatic inclusions are visible, clearly indicating that the quartz is igneous in origin. Quartz phenocrysts are not uncommon in the Mbuluzi rhyolites, ranging from trace amounts to just over 5% in sample SR24 (Table 1). Quartz phenocrysts are more abundant in the Oribi Beds, ranging from 4.1 to 8.3 vol.% but are almost completely absent from the Jozini rhyolites. The presence or abundance of quartz phenocrysts is one of the main tools used to distinguish between the rhyolite units and is particularly important in identifying the units from within the Mbuluzi rhyolites that can be classified as the Oribi Beds. The Oribi beds (samples MG16–20 and SR35) have a distinctive texture, with large phenocrysts of quartz (up to 3 mm diameter), plagioclase and alkali feldspar (up to 4 mm diameter) set in a fine-grained groundmass.

SAMPLING TRAVERSES

A total of 46 samples were collected for geochemical analysis from three sample traverses made approximately perpendicular to the north–south strike of the rhyolites (Fig. 1c). These samples are made up of 27 samples from the Mbuluzi rhyolites, six from the Oribi Beds and 12 from the Jozini rhyolites. One sample of the Mkutshane Beds was also collected. The most northerly traverse was made along the Mbuluzi River between Mlawula Station in Swaziland and the Mozambique border (Fig. 1c), and is referred to as the Mbuluzi section (all samples prefixed MB). To the south of this, a second traverse was made to the north and west of the town of Siteki (Fig. 1c), and is referred to as the Siteki

Table 1: Whole-rock major and trace element geochemistry for Mbuluzi, Jozini and Oribi Bed rhyolites from the Lebombo Monocline

Sample:	MG6	MG8	MG9	MG10	MG11	MG12	MG13	MG14	MG15	MG16	MG17	MG18
Fm:	Mb	Mb	Mb	Mb	Mb	Mb	Mb	Mb	Mb	Or	Or	Or
Flow no.:	VII	VII	VII	VII	VII	a	a	a	a	VI	VI	VI
Vol. % Qtz:	1.22	1.00	2.67	1.22	tr	0	tr	0	0	6.02	7.87	7.56
<i>XRF majors elements wt% oxide</i>												
SiO ₂	70.26	70.59	69.47	70.47	69.61	64.02	70.91	71.47	68.64	73.92	74.57	74.47
TiO ₂	0.53	0.56	0.53	0.53	0.66	0.67	0.42	0.42	0.59	0.24	0.20	0.22
Al ₂ O ₃	12.07	12.29	11.62	12.14	12.60	12.84	12.26	12.30	12.20	11.72	12.06	11.37
Fe ₂ O ₃	6.14	6.56	6.11	6.11	6.85	6.68	5.58	6.01	6.33	3.99	3.38	3.48
MnO	0.10	0.06	0.12	0.08	0.09	0.11	0.12	0.08	0.12	0.07	0.05	0.04
MgO	0.21	0.06	0.12	0.15	0.18	0.33	0.12	0.04	0.39	0.01	0.00	0.00
CaO	0.61	0.57	1.79	0.46	0.38	2.35	1.00	0.67	1.93	0.29	0.40	0.50
Na ₂ O	2.96	3.00	3.19	3.22	2.81	3.50	3.44	3.14	3.56	2.95	2.76	3.00
K ₂ O	4.68	4.66	4.41	4.23	4.44	4.20	4.66	5.01	4.26	4.86	5.58	5.02
P ₂ O ₅	0.13	0.06	0.13	0.12	0.11	0.18	0.09	0.09	0.16	0.03	0.02	0.03
H ₂ O ⁻	0.88	0.68	0.52	0.88	0.64	0.46	0.49	0.47	0.65	0.46	0.35	0.45
LOI	0.86	0.45	1.66	0.62	1.28	3.95	0.64	0.58	0.89	0.66	0.38	0.53
Total	99.42	99.53	99.67	99.01	99.65	99.36	99.72	100.28	99.73	99.19	99.75	99.10
SiO ₂ anh	71.93	71.74	71.25	72.27	71.23	67.42	71.92	72.03	69.91	61.55	70.51	70.66
<i>XRF trace elements ppm</i>												
Nb	71	67	69	66	66	64	76	74	66	87	82	86
Zr	844	835	808	877	946	961	849	871	1024	662	506	570
Y	158	173	134	137	179	142	148	136	127	150	142	128
Sr	81	126	116	201	144	171	129	138	138	85	87	91
Rb	148	138	128	126	134	105	135	139	120	141	156	140
Rb/Sr	1.83	1.10	1.10	0.63	0.93	0.61	1.05	1.01	0.87	1.66	1.79	1.54
<i>ICP-MS trace elements ppm</i>												
Sc	8.59	7.81	8.27	8.30	10.5	8.38	6.14	5.29	9.91	2.41	1.67	2.17
V	9.95	10.5	9.44	6.62	8.38	7.21	5.66	7.37	6.17	2.87	1.11	1.41
Cr	10.8	9.57	9.99	7.63	7.89	6.60	8.90	17.3	8.20	4.37	6.25	7.07
Co	4.03	2.87	3.75	2.97	3.67	2.87	2.78	2.08	3.53	0.63	0.58	0.67
Ni	7.78	4.53	5.12	3.41	3.58	3.22	4.71	6.33	3.83	2.04	3.51	3.42
Cu	19.7	15.0	18.3	14.8	13.6	14.7	16.0	18.3	20.9	6.98	9.75	13.8
Ba	1572	1306	1309	1311	1459	1252	1444	1313	1148	1425	1311	1593
Hf	12.3	11.7	11.3	12.4	14.8	16.6	12.3	12.5	12.6	7.9	8.8	9.0
Ta	4.12	4.18	4.06	4.18	4.04	4.06	4.46	4.50	3.86	4.97	4.94	4.98
Th	13.4	13.2	12.9	13.3	12.5	12.6	14.3	13.7	12.1	15.7	15.7	15.8
U	2.97	3.04	2.87	2.45	2.74	2.66	2.84	2.66	2.57	2.91	2.44	2.60
Pb	18.1	16.9	16.2	16.3	15.5	15.8	18.4	15.2	14.5	19.4	20.2	20.6
<i>ICP-MS REE ppm</i>												
La	143	123	102	98.6	149	95.3	122	101	90.9	113	126	141
Ce	252	247	231	220	264	222	294	198	200	266	269	260
Pr	34.6	31.9	27.1	26.1	37.8	25.9	32.5	26.9	24.2	30.4	32.2	35.2
Nd	149	140	116	113	162	112	138	115	105	131	139	152
Sm	28.5	28.6	23.6	22.8	31.0	22.9	26.9	23.2	21.0	26.2	27.4	29.2
Eu	6.09	6.15	5.05	4.94	6.70	4.96	5.29	4.59	4.50	4.85	4.37	5.12

(continued)

Table 1: Continued

Sample:	MG6	MG8	MG9	MG10	MG11	MG12	MG13	MG14	MG15	MG16	MG17	MG18
Fm:	Mb	Mb	Mb	Mb	Mb	Mb	Mb	Mb	Mb	Or	Or	Or
Flow no.:	VII	VII	VII	VII	VII	a	a	a	a	VI	VI	VI
Vol.% Qtz:	1.22	1.00	2.67	1.22	tr	0	tr	0	0	6.02	7.87	7.56
Gd	30.3	30.8	24.6	23.5	31.7	23.8	26.9	23.5	21.6	26.9	28.3	29.2
Tb	4.41	4.55	3.68	3.50	4.65	3.53	4.05	3.48	3.16	4.09	4.15	4.08
Dy	27.8	29.3	23.8	22.6	29.2	22.8	26.1	22.1	20.3	26.9	26.5	25.2
Ho	5.32	5.66	4.56	4.34	5.52	4.43	4.98	4.19	3.86	5.14	4.96	4.60
Er	15.5	16.6	13.5	13.0	16.0	13.2	14.7	12.5	11.4	15.3	14.4	13.3
Tm	2.11	2.25	1.85	1.79	2.16	1.84	2.02	1.73	1.56	2.07	1.92	1.78
Yb	14.1	14.9	12.3	12.2	14.4	12.6	13.5	11.7	10.7	13.6	12.7	11.8
Lu	1.96	2.09	1.72	1.70	1.98	1.78	1.84	1.64	1.49	1.86	1.72	1.62
REE _{tot}	715	683	591	568	756	567	713	549	520	667	692	713
Eu/Eu*	0.63	0.63	0.64	0.65	0.65	0.65	0.60	0.60	0.65	0.56	0.48	0.54
Ce/Ce*	0.88	0.97	1.08	1.06	0.86	1.10	1.14	0.93	1.05	1.12	1.04	0.90
(La/Yb) _N	7.28	5.95	5.93	5.81	7.42	5.44	6.48	6.18	6.11	5.93	7.11	8.55
Sample:	MG19	MG20	MG21	MG22	SR23	SR24	SR25	SR27	SR28	SR29	SR30	SR31
Fm.:	Or	Or	Mb	Jz	Mb	Mb	Mb	Mb	Mb	Mb	Mb	Mb
Flow no.:	VI	VI	II	I	X	X	VII	VII	I	XVII	XVII	XI
Vol.% Qtz:	6.09	4.08	0	0	0	5.04	3.21	tr	n.d.	tr	2.26	1.35
<i>XRF major elements wt% oxide</i>												
SiO ₂	72.02	74.20	65.34	60.14	68.90	68.92	70.44	69.98	71.36	68.91	68.67	70.11
TiO ₂	0.27	0.25	0.71	1.37	0.62	0.60	0.54	0.41	0.27	0.55	0.61	0.48
Al ₂ O ₃	12.13	11.75	12.24	12.22	12.99	12.97	12.93	12.32	12.39	13.42	12.75	12.67
Fe ₂ O ₃	4.07	4.11	6.56	11.66	6.86	7.22	5.34	5.51	5.15	4.93	6.87	5.94
MnO	0.07	0.04	0.17	0.21	0.03	0.03	0.03	0.12	0.04	0.02	0.09	0.13
MgO	0.03	0.01	0.49	0.97	0.05	0.04	0.12	0.28	0.10	0.12	0.41	0.32
CaO	1.11	0.34	2.16	4.50	0.62	0.66	0.91	1.09	0.12	0.45	1.33	1.62
Na ₂ O	3.13	2.76	3.30	2.96	2.73	2.75	3.07	3.15	3.10	2.95	2.99	3.36
K ₂ O	5.11	5.34	4.21	3.17	4.72	4.23	4.66	4.63	4.89	3.88	3.98	4.34
P ₂ O ₅	0.03	0.04	0.21	0.52	0.16	0.12	0.14	0.09	0.07	0.13	0.16	0.11
H ₂ O ⁻	0.37	0.50	0.39	0.63	0.61	0.33	0.37	0.79	0.44	3.26	0.07	0.28
LOI	0.68	0.58	3.32	0.85	1.54	1.58	0.83	0.99	1.14	1.28	1.39	0.26
Total	99.00	99.92	99.12	99.19	99.87	99.45	99.39	99.39	99.08	99.92	99.32	99.64
SiO ₂ anh	75.37	75.31	75.89	73.52	75.07	68.48	71.73	71.70	73.18	72.25	70.17	70.74
<i>XRF trace elements ppm</i>												
Nb	84	80	69	56	76	79	78	84	89	71	77	80
Zr	659	655	1048	923	1029	974	938	921	1045	897	940	903
Y	153	167	136	138	300	301	144	193	158	145	133	147
Sr	119	117	192	233	130	192	141	112	101	117	338	128
Rb	145	152	115	87	139	124	128	137	146	117	127	128
Rb/Sr	1.22	1.30	0.60	0.37	1.07	0.64	0.91	1.22	1.44	1.00	0.38	1.00
<i>ICP-MS trace elements ppm</i>												
Sc	2.66	2.16	12.3	22.0	10.40	9.41	8.39	6.11	7.53	9.30	11.8	10.6
V	1.38	2.83	3.89	10.9	11.89	9.97	9.06	5.91	2.49	11.6	9.4	6.5

(continued)

Table 1: Continued

Sample:	MG6	MG8	MG9	MG10	MG11	MG12	MG13	MG14	MG15	MG16	MG17	MG18
Fm:	Mb	Mb	Mb	Mb	Mb	Mb	Mb	Mb	Mb	Or	Or	Or
Flow no.:	VII	VII	VII	VII	VII	a	a	a	a	VI	VI	VI
Vol.% Qtz:	1.22	1.00	2.67	1.22	tr	0	tr	0	0	6.02	7.87	7.56
Cr	8.68	8.15	8.58	7.00	6.08	11.9	7.78	10.1	6.99	12.1	6.8	5.8
Co	0.84	0.83	3.68	9.79	3.75	1.54	2.24	2.67	0.94	3.80	4.1	2.98
Ni	3.58	4.44	3.95	4.22	6.22	5.25	7.47	4.37	3.74	5.31	4.4	3.91
Cu	10.9	9.44	16.6	18.7	20.4	17.9	14.6	15.6	12.7	15.8	10.6	15.5
Ba	1532	1563	1084	1058	2571	2027	1393	1402	1287	1225	1485	1306
Hf	10.3	9.69	21.5	20.0	17.9	12.9	9.87	11.9	12.9	8.31	9.85	10.3
Ta	4.90	4.69	4.03	3.55	4.44	4.13	4.34	4.48	4.73	3.92	4.07	4.27
Th	15.5	13.7	11.7	10.1	13.6	12.9	13.0	14.4	14.4	12.5	13.9	14.0
U	3.28	2.64	2.70	2.29	2.94	2.75	2.61	2.77	2.86	2.67	2.32	2.33
Pb	19.4	15.3	13.7	13.3	17.0	16.4	16.6	17.6	12.0	15.2	17.3	18.3
ICP-MS REE ppm												
La	121	93.6	86.6	84.2	270	251	101	135	114	96.1	106.1	105
Ce	273	117	201	199	412	254	221	252	180	220	226.2	235
Pr	31.5	24.3	24.0	23.6	61.7	58.6	26.6	32.5	30.0	25.7	27.00	27.7
Nd	136	106	106	107	260	245	113	138	128	110	115.0	118
Sm	26.9	21.2	21.3	22.0	47.8	43.9	22.9	27.4	25.8	22.5	22.9	23.8
Eu	5.15	4.76	5.03	5.56	10.6	10.1	4.83	5.69	5.15	5.06	5.08	4.94
Gd	28.2	24.5	22.5	23.8	51.5	49.0	23.5	30.7	26.1	23.7	24.3	24.6
Tb	4.21	3.77	3.32	3.45	7.21	6.83	3.50	4.60	3.90	3.61	3.58	3.78
Dy	27.9	25.6	21.6	22.4	44.7	41.9	22.5	29.7	24.8	23.2	21.9	24.0
Ho	5.34	5.05	4.15	4.27	8.53	8.15	4.36	5.86	4.81	4.57	4.22	4.73
Er	15.8	15.0	12.2	12.6	23.2	22.9	12.3	16.5	13.6	13.1	11.8	13.6
Tm	2.16	2.03	1.67	1.70	3.15	3.08	1.72	2.29	1.92	1.83	1.64	1.93
Yb	14.5	13.1	11.4	11.5	19.2	19.0	11.2	14.4	12.4	12.0	10.5	12.4
Lu	1.99	1.82	1.62	1.64	2.73	2.71	1.57	2.02	1.78	1.72	1.46	1.75
REE _{tot}	693	457	522	523	1223	1016	569	697	572	563	582	601
Eu/Eu*	0.57	0.64	0.70	0.74	0.65	0.67	0.64	0.60	0.61	0.67	0.66	0.62
Ce/Ce*	1.09	0.60	1.08	1.09	0.78	0.51	1.05	0.93	0.76	1.09	1.04	1.07
(La/Yb) _N	5.98	5.14	5.44	5.26	10.1	9.47	6.43	6.77	6.57	5.76	7.23	6.07
Sample:	SR32	SR33	SR34	SR35	SR36	SR37	SR38	SR39	SR40	SR41	SR45	
Fm:	Mb	Mb	Mb	Or	Mb	Mb	Mb	Mb	Mb	Mb	Mb	
Flow no.:	X	X	X	IX	X	X	IXS	VII	I	XI	n.a.	
Vol.% Qtz:		0	tr	8.30	tr	n.d.	3.98	0.64	tr	0.95	tr	
XRF major elements wt% oxide												
SiO ₂	69.15	66.41	68.57	76.25	71.85	73.47	72.26	74.38	74.87	69.62	65.55	
TiO ₂	0.51	0.65	0.49	0.17	0.49	0.31	0.30	0.28	0.29	0.51	1.15	
Al ₂ O ₃	12.75	13.05	12.44	11.94	14.34	11.83	12.65	12.40	13.44	12.48	12.45	
Fe ₂ O ₃	6.13	6.85	6.27	2.15	2.34	4.93	4.91	2.94	1.50	6.34	8.22	
MnO	0.11	0.20	0.13	0.01	0.01	0.06	0.02	0.02	0.01	0.13	0.11	
MgO	0.39	0.55	0.47	0.06	0.07	0.06	0.00	0.02	0.03	0.30	0.73	
CaO	1.94	1.44	1.71	0.04	0.14	0.05	0.11	0.14	0.06	2.16	2.41	

(continued)

Table 1: Continued

Sample:	SR32	SR33	SR34	SR35	SR36	SR37	SR38	SR39	SR40	SR41	SR45
Fm:	Mb	Mb	Mb	Or	Mb	Mb	Mb	Mb	Mb	Mb	Mb
Flow no.:	X	X	X	IX	X	X	IXS	VII	I	XI	n.a.
Vol.% Qtz:		0	tr	8.30	tr	n.d.	3.98	0.64	tr	0.95	tr
Na ₂ O	3.48	4.25	3.52	1.34	4.08	2.12	3.01	3.02	2.95	3.37	3.69
K ₂ O	4.42	3.98	4.33	5.15	4.44	5.04	4.88	4.77	4.38	4.22	3.62
P ₂ O ₅	0.12	0.17	0.12	0.02	0.10	0.05	0.05	0.04	0.06	0.13	0.26
H ₂ O ⁻	0.23	0.53	0.37	0.38	0.81	0.28	0.24	0.33	0.32	0.17	0.40
LOI	0.42	1.25	1.07	1.69	1.07	1.04	0.99	0.94	1.39	0.19	1.14
Total	99.64	99.34	99.49	99.21	99.75	99.25	99.41	99.28	99.72	99.62	99.75
SiO ₂ anh	69.85	68.07	69.94	78.50	73.41	75.02	73.59	75.89	76.39	70.14	66.75
<i>XRF trace elements ppm</i>											
Nb	77	74	80	101	92	91	92	93	96	80	13
Zr	908	972	1011	483	1005	973	896	936	1133	945	253
Y	150	197	150	107	175	208	171	148	151	155	38
Sr	143	137	132	52	126	63	99	93	90	143	140
Rb	125	114	119	154	122	146	131	136	140	120	100
Rb/Sr	0.9	0.8	0.9	3.0	1.0	2.3	1.3	1.5	1.6	0.8	0.7
<i>ICP-MS trace elements ppm</i>											
Sc	10.1	12.9	10.3	2.91	8.76	5.79	3.35	3.85	6.73	8.11	10.5
V	7.98	8.49	6.49	1.07	6.42	3.30	1.42	1.28	2.56	6.67	69.4
Cr	7.16	15.1	8.32	8.68	14.9	8.95	5.03	3.46	10.5	9.05	15.9
Co	3.10	5.72	2.83	0.54	1.61	0.94	0.87	1.08	0.28	3.06	15.0
Ni	4.00	5.25	3.66	3.49	3.60	4.82	4.48	2.91	3.95	4.34	10.4
Cu	18.1	14.4	16.8	8.82	11.1	8.19	10.7	8.18	4.18	15.9	13.5
Ba	1293	1366	1270	923	1492	1683	1589	1500	7752	1202	496
Hf	10.5	12.6	13.7	9.45	14.9	11.2	9.04	11.8	11.6	10.6	5.11
Ta	4.16	3.88	4.15	5.30	4.55	3.79	4.46	4.69	4.74	4.08	0.83
Th	14.0	12.7	13.4	16.4	15.2	15.4	14.7	14.6	14.3	13.8	6.62
U	2.55	2.16	2.42	2.34	2.47	3.05	2.58	3.19	3.54	2.89	1.78
Pb	17.6	16.9	17.8	18.3	14.8	23.0	19.8	14.6	11.5	15.9	11.6
<i>ICP-MS REE ppm</i>											
La	104	131	106	18.5	167	114	102	111	138	104	31.0
Ce	230	257	236	51.7	293	260	246	260	276	223	67.6
Pr	27.3	33.6	28.1	3.90	38.3	30.9	28.2	30.0	35.2	27.3	7.79
Nd	116	146	120	15.0	166	132	120	128	145	116	31.6
Sm	23.3	29.7	24.2	3.13	32.3	27.4	24.7	26.1	27.0	23.6	6.36
Eu	4.91	6.95	4.99	0.50	7.17	5.85	5.12	5.27	5.22	4.78	1.79
Gd	24.2	32.5	25.0	4.51	35.5	29.8	25.6	25.7	27.6	24.5	6.94
Tb	3.73	4.95	3.78	1.18	4.98	4.85	3.98	3.83	4.02	3.72	1.03
Dy	23.9	31.5	24.1	11.7	28.3	32.6	26.1	24.2	24.4	24.1	6.42
Ho	4.76	6.28	4.74	3.06	5.08	6.63	5.20	4.67	4.48	4.76	1.20
Er	13.7	17.9	13.7	11.2	12.7	19.4	15.3	13.3	12.1	13.8	3.33
Tm	1.94	2.49	1.91	1.82	1.55	2.68	2.20	1.93	1.63	1.94	0.45
Yb	12.5	15.7	12.4	12.5	9.13	17.1	14.4	12.6	10.4	12.7	2.86
Lu	1.78	2.24	1.76	1.75	1.26	2.39	2.08	1.82	1.39	1.79	0.40
REE _{tot}	592	718	607	140	803	686	620	648	713	585	169
Eu/Eu*	0.63	0.68	0.62	0.40	0.65	0.62	0.62	0.62	0.58	0.61	0.82

(continued)

Table 1: Continued

Sample:	SR32	SR33	SR34	SR35	SR36	SR37	SR38	SR39	SR40	SR41	SR45
Fm:	Mb	Mb	Mb	Or	Mb	Mb	Mb	Mb	Mb	Mb	Mb
Flow no.:	X	X	X	IX	X	X	IXS	VII	I	XI	n.a.
Vol. % Qtz:		0	tr	8-30	tr	n.d.	3-98	0-64	tr	0-95	tr
Ce/Ce*	1-06	0-95	1-06	1-49	0-90	1-08	1-12	1-10	0-97	1-02	1-07
(La/Yb) _N	5-96	6-02	6-13	1-06	13-1	4-79	5-06	6-32	9-45	5-87	7-78
Sample:	J50	J51	J52	J53	J54	J55	J56	J57	J58	J59	J60
Fm:	Jz	Jz	Jz	Jz	Jz	Jz	Jz	Jz	Jz	Jz	Jz
Flow no.:	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
Vol. % Qtz:	0	0	0	0	0	0	0	0	0	0	0
<i>XRF major elements wt% oxide</i>											
SiO ₂	69-57	65-85	69-24	68-37	68-92	68-77	69-89	66-33	69-25	67-23	68-86
TiO ₂	0-49	0-71	0-52	0-50	0-37	0-39	0-47	0-76	0-48	0-81	0-38
Al ₂ O ₃	12-71	12-39	13-32	12-48	12-21	12-18	12-34	13-19	12-78	13-40	11-99
Fe ₂ O ₃	6-36	8-08	6-26	6-54	6-60	6-47	6-15	8-46	6-10	7-98	5-80
MnO	0-03	0-13	0-06	0-11	0-11	0-12	0-08	0-15	0-14	0-20	0-16
MgO	0-06	0-46	0-13	0-40	0-13	0-36	0-21	0-26	0-25	0-44	0-23
CaO	0-98	2-37	1-23	1-11	1-35	1-85	1-07	1-44	0-88	2-68	2-31
Na ₂ O	3-02	3-12	3-35	3-06	3-25	3-17	3-10	3-03	3-13	3-26	3-21
K ₂ O	4-35	4-21	4-78	4-45	4-54	4-63	4-55	4-82	4-72	3-63	4-53
P ₂ O ₅	0-15	0-24	0-15	0-16	0-11	0-12	0-15	0-24	0-11	0-25	0-10
H ₂ O ⁻	0-76	0-68	0-57	0-93	0-36	0-34	0-58	0-54	0-74	0-33	0-10
LOI	1-24	1-00	0-98	1-55	1-07	1-10	1-02	1-18	1-26	0-63	1-40
Total	99-72	99-25	100-59	99-66	99-04	99-50	99-62	100-41	99-81	100-84	99-07
SiO ₂ anh	71-19	67-50	69-92	70-35	70-61	70-13	71-31	67-21	70-79	67-31	70-57
<i>XRF trace elements ppm</i>											
Nb	82	79	87	84	85	82	78	77	84	73	83
Zr	1199	1194	1206	1206	1156	1168	1103	1160	1170	1113	1178
Y	211	124	110	204	141	131	138	127	90	141	134
Sr	197	181	152	159	147	151	153	175	155	195	138
Rb	121	114	128	136	132	123	122	130	128	103	119
Rb/Sr	0-62	0-63	0-84	0-85	0-90	0-81	0-80	0-75	0-82	0-53	0-86
<i>ICP-MS trace elements ppm</i>											
Sc	10-2	12-3	9-89	10-02	8-34	8-48	8-97	11-24	9-24	15-29	7-34
V	4-32	5-02	3-49	3-87	2-23	2-52	3-59	4-31	2-82	4-50	4-43
Cr	3-64	6-30	5-81	3-63	4-63	5-02	4-10	4-97	5-66	7-45	4-36
Co	2-10	4-43	2-64	2-85	1-96	2-19	2-66	3-47	2-02	5-02	1-27
Ni	3-84	3-14	3-03	3-34	3-57	3-77	3-52	3-26	3-39	3-46	3-39
Cu	13-9	27-1	18-0	17-3	13-6	15-4	17-6	18-4	13-4	19-8	15-8
Ba	1558	1138	1308	1449	1608	1270	1269	1176	1258	1422	1296
Hf	17-1	24-3	15-0	18-2	16-4	16-9	13-9	16-4	15-6	20-3	10-6
Ta	4-61	4-28	4-80	4-60	4-62	4-52	4-40	4-20	4-35	4-06	4-23
Th	13-3	12-8	14-2	13-4	13-6	13-0	13-2	11-4	11-5	11-8	11-7
U	3-36	2-67	2-40	2-93	2-64	3-02	2-60	2-38	2-16	2-51	2-59
Pb	17-4	16-1	18-3	17-2	17-9	16-5	16-6	14-9	15-9	13-9	16-0

(continued)

Table 1: Continued

Sample:	J50	J51	J52	J53	J54	J55	J56	J57	J58	J59	J60
Fm:	Jz	Jz	Jz	Jz	Jz	Jz	Jz	Jz	Jz	Jz	Jz
Flow no.:	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
Vol.% Qtz:	0	0	0	0	0	0	0	0	0	0	0
<i>ICP-MS REE ppm</i>											
La	166	99.3	115	118	109	101	107	93.8	89.7	99.5	94.9
Ce	374	222	235	256	231	226	238	198	172	224	211
Pr	46.2	26.7	30.6	34.3	28.8	27.4	29.1	25.7	23.5	27.0	25.6
Nd	198	113	130	150	123	117	125	110	98.1	116	109
Sm	39.7	22.5	25.1	30.5	24.3	23.0	24.3	21.6	18.7	23.6	21.9
Eu	8.89	5.14	5.27	6.91	5.32	5.20	5.46	5.06	4.14	5.47	5.09
Gd	38.4	22.1	23.0	32.0	24.6	22.7	24.1	20.8	16.5	24.0	21.2
Tb	5.73	3.29	3.23	4.72	3.62	3.37	3.51	3.07	2.32	3.54	3.17
Dy	35.8	21.1	19.4	30.1	23.0	21.5	21.6	19.4	14.1	22.4	20.0
Ho	6.85	4.10	3.67	5.95	4.48	4.18	4.26	3.73	2.59	4.40	3.81
Er	19.1	11.6	10.5	16.9	12.7	11.8	12.0	10.5	7.48	12.5	10.7
Tm	2.70	1.67	1.54	2.41	1.79	1.66	1.71	1.49	1.07	1.74	1.51
Yb	17.4	11.1	10.5	15.5	11.5	10.7	10.9	9.64	7.24	11.1	9.62
Lu	2.44	1.56	1.50	2.24	1.60	1.53	1.54	1.36	1.02	1.61	1.35
REE _{Tot}	961	566	614	706	606	577	608	524	458	577	539
Eu/Eu*	0.70	0.70	0.67	0.68	0.67	0.70	0.69	0.73	0.72	0.70	0.72
Ce/Ce*	1.05	1.06	0.97	0.99	1.01	1.05	1.05	0.99	0.92	1.06	1.05
(La/Yb) _N	6.85	6.43	7.84	5.48	6.83	6.74	7.05	6.98	8.88	6.43	7.08

All samples prefixed JM00. SiO₂ anh, SiO₂ recalculated to anhydrous totals; Mb, Mbuluzi Formation; J, Jozini Formation; Or, Oribi Beds. tr, trace; n.d., not determined; n.a., not applicable.

section (all samples prefixed SR). Samples from the two Swaziland traverses have been placed into their correct stratigraphic order using Global Positioning System (GPS) coordinates and the maps of Cleverly (1977). In this region between the Mbuluzi River and Siteki, the outcrop distribution of the individual rhyolite flows appears to be controlled by the pre-existing topography, and in some cases successive flows truncate previous flows, causing lateral discontinuities in some of the flows (Fig. 1c). As a result, all of the samples from the Mbuluzi section occur in flows that are stratigraphically below the flows from which the samples of the Siteki section were collected, with the exception of samples SR28 and SR40 (Fig. 1c). However, the actual stratigraphic thickness of rhyolite in the two areas is more or less equal (Fig. 1c). To the south, a third traverse was made through the Jozini rhyolites and the samples were collected along the road through Jozini (samples prefixed J) towards the Mozambique border, south of Swaziland (Fig. 1b).

ANALYTICAL TECHNIQUES

Quartz phenocryst volume percent was determined by point counting an average of ~3000 points per thin section. Whole-rock major- and some trace-elements (Nb, Zr, Y, Rb, and Sr) were determined by X-ray fluorescence (XRF) at the University of Cape Town (UCT) and the University of Stellenbosch using an X'unique spectrometer; errors and detection limits are equal to or lower than those of le Roex *et al.* (1981). All other trace element and rare earth element (REE) concentrations were determined by inductively coupled plasma mass spectrometry (ICP-MS), using a three-step HF-HNO₃ acid digestion procedure in sealed and heated Savilex vessels. Dried samples were taken up in a 5% HNO₃ solution containing 10 ppb Re, Rh, In and Bi as internal standards and analysed on a Perkin Elmer/Sciex Elan 6000 ICP-MS system in the Department of Geological Sciences at UCT. Further details of the analytical techniques have been given by le Roex *et al.* (2001). Unless stated otherwise, whole-rock

data plotted on the diagrams have been recalculated to anhydrous totals before plotting. Sample SR35, which has an unusual REE pattern, was run in duplicate, with no significant difference between the analyses.

Mineral separates (quartz, feldspar, and magnetite) for O-isotope analysis were hand-picked from sieved, jaw-crush material. Quartz phenocrysts were easily recognized as they are relatively large and equidimensional, and were cleaned in warm dilute HF to remove any adhering material. In one sample (MG17) it was possible to distinguish phenocryst quartz from quartz of secondary origin and both were analysed. The hand specimen contains narrow veins and small cavities lined with quartz crystals. The secondary quartz was distinct, as crystal fragments showed prism faces and lacked melt inclusions, which were typically visible in the phenocrysts. In all other samples where quartz was separated it was clearly of phenocryst origin. Although pyroxene phenocrysts are present in some of the samples, it was impossible to separate sufficient material for analysis.

Oxygen isotope ratios were determined at UCT following the method of Clayton & Mayeda (1963) using ClF_3 as the oxidizing reagent (Borthwick & Harmon, 1982). Samples were degassed under vacuum at 200°C for 2 h prior to addition of ClF_3 . The samples were then reacted for at least 4 h at 550°C and the liberated O_2 was converted to CO_2 using a hot platinized carbon rod. Isotope ratios were measured on a Finnigan MAT 252 mass spectrometer. Data are reported in the familiar δ notation where $\delta^{18}\text{O}$ is $(R_{\text{sample}}/R_{\text{standard}} - 1) \times 10^3$ and R is the ratio of $^{18}\text{O}/^{16}\text{O}$. At UCT, a quartz standard (MQ) calibrated against NBS-28 was analysed in duplicate with each run of eight samples and used to convert the raw data to the SMOW scale using the $\delta^{18}\text{O}$ value of 9.64‰ for NBS-28 recommended by Coplen *et al.* (1983). The average difference between duplicates of MQ analysed during the course of this study is 0.15‰.

Hydrogen isotopes were determined at UCT using the method of Vennemann & O'Neil (1993). Whole-rock samples were degassed on the vacuum line at 200°C prior to pyrolysis. An internal water standard (CTMP, $\delta\text{D} = -9\text{‰}$) was used to calibrate the data to the SMOW scale and a second water standard (DML, $\delta\text{D} = -300\text{‰}$) was used to correct for scale compression (e.g. Coplen, 1993). Typical reproducibility of internal biotite standards during the period of analysis was $\pm 2\text{‰}$ (1 σ). Water contents were determined either from the voltage measured on the mass 2 collector or (in the case of large samples) from the pressure measured during sample inlet using identical inlet volume to standards of known number of micromoles. Repeated measurements of water standards of known mass suggest that the typical relative error for the water content is 3% at the 2 mg level.

The Sr- and Nd-isotope data were obtained using a VG Sector mass spectrometer in the Department of Geological Sciences at UCT, following standard chemical separation procedures described by le Roex & Lanyon (1998). The standard SRM987 gave 0.71024 ± 1 and 0.71025 ± 9 during the Sr-isotope runs and the La Jolla Nd-isotope standard gave values of 0.51178 ± 1 , 0.51178 ± 1 , 0.51177 ± 1 during the Nd-isotope runs. The radiogenic isotope data were normalized to values of 0.71026 (SRM987) for Sr isotopes and 0.51184 (La Jolla) for Nd isotopes.

RESULTS

Major, trace and rare earth element data for the Mbuluzi rhyolites and Oripi Beds as well as one sample of Jozini rhyolite from Swaziland (Mbuluzi and Siteki Traverse) and the Jozini rhyolites in northern Natal (Jozini traverse) are presented in Table 1.

Major element geochemistry

The samples analysed in this study have SiO_2 contents (wt %) that vary between 60.14% and 76.25%, and almost all the samples are classified as rhyolites on a total alkalis-silica (TAS) diagram (Fig. 2a). The Oripi Beds have a significantly higher average wt % SiO_2 (74.24%) than the Mbuluzi and Jozini rhyolites (69.95% and 67.70%, respectively). As the loss on ignition (LOI) for all of the samples is relatively low, recalculation to anhydrous totals increases these averages only marginally (an average of 1.4 wt %). Six samples should be classified as high-K dacites rather than rhyolites (Fig. 2b), and one sample (MG22) of the Jozini rhyolite falls within the high-K andesite field.

Major element oxides vs SiO_2 are presented in Fig. 3 and show similar trends to those described and discussed by Cleverly *et al.* (1984). The new data illustrate several important features; in particular the good negative correlations between TiO_2 , Fe_2O_3^* , P_2O_5 and SiO_2 and less strong negative correlations between CaO and MgO and SiO_2 . The Jozini rhyolites generally plot at the low- SiO_2 , high- Fe_2O_3 end of the data array, whereas the Oripi Beds plot at the high- SiO_2 , low- Fe_2O_3 end of the data array. There is a general decrease in Na_2O with increasing SiO_2 whereas K_2O shows a positive correlation with SiO_2 . The weak negative correlation between Al_2O_3 and SiO_2 is probably due to the constant sum effect, with the Oripi Beds having lower Al_2O_3 than the other samples. One sample, MG22, has very high Fe_2O_3 , CaO , MgO and P_2O_5 (along with low Zr and Nb—see below) and plots in the high-K andesite field, possibly indicating less differentiated composition.

Trace element geochemistry

Comparison of trace element contents with wt % SiO_2 indicates that correlations within each of the three rhyolite

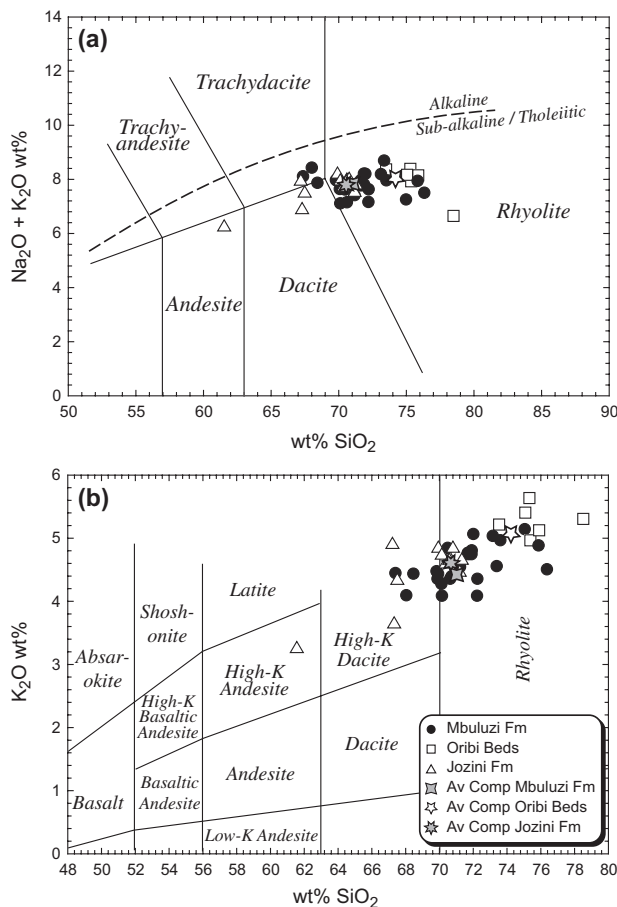


Fig. 2. Classification of the Lebombo Rhyolites. Total alkalis vs silica classification diagram of (a) Le Maitre *et al.* (1989); and (b) Peccerillo & Taylor (1976). The dashed line represents the division between the tholeiitic and alkaline series (Irvine & Baragar, 1971).

groups are rather poor, especially for the Jozini rhyolites. In general, SiO₂ correlates negatively with Sr and Zr and positively with Nb and Rb. However, there is no clear distinction between the three rhyolite groups except in the case of Zr, which acts as an effective discriminator (Fig. 4a). The Jozini rhyolites have consistently higher Zr contents (1100–1220 ppm) than the Mbuluzi rhyolites (800–1150 ppm), with the Oribi Beds having the lowest Zr concentrations (450–700 ppm). One sample of the Jozini rhyolite with a lower SiO₂ content also has a lower Zr content (923 ppm). Overall, there is a strong negative correlation between Rb and Sr (Fig. 4c, Table 1). Although there is considerable overlap in the ranges of the three rhyolite types, in general the Jozini rhyolites have the lowest Rb/Sr ratios (average ~0.7) whereas the Oribi Beds have the highest Rb/Sr ratios (average ~1.7), indicating that Rb/Sr generally increases with increasing silica content. Correlations within the three rhyolite types

between Zr and Y (Fig. 4b) or Nb (Fig. 4d) are poor and serve mainly to highlight the usefulness of Zr in distinguishing between the rhyolites. Although the Oribi Beds have relatively low and constant Zr/Y of around four, the Jozini rhyolites have a wide range of Zr/Y because of the relatively constant Zr content combined with variable Y contents, with a similar although less pronounced pattern also being observed in the Mbuluzi rhyolites (Fig. 4c). Figure 4d indicates that the Jozini rhyolites have a relatively constant Zr/Nb of slightly less than 15, whereas the Oribi Beds and the Mbuluzi rhyolites show a fair degree of scatter in Zr/Nb, but have average Zr/Nb of 6.9 and 12.3, respectively.

Chondrite-normalized REE patterns (Fig. 5) for the three rhyolite types are approximately parallel, moderately light REE (LREE)-enriched with distinct negative Eu anomalies (average Eu/Eu* = 0.64). The magnitude of the Eu anomaly decreases with increasing silica content (Fig. 6) for the rhyolites as a whole, but the correlation within the Jozini and Mbuluzi rhyolites is poor. One Oribi Bed rhyolite (SR35) has an extremely unusual REE pattern with strongly depleted middle REE (MREE), a strong negative Eu anomaly and a slightly positive Ce anomaly (Fig. 5d). A repeat analysis of this sample gave the same concentrations and it is, therefore, concluded that REE pattern is not an artefact of incomplete dissolution of the sample and is possibly related to secondary alteration processes. The Jozini rhyolites have slightly lower REE contents than the Mbuluzi rhyolites. The Oribi Beds samples (excluding sample SR35) have similar REE patterns. Figure 5d highlights the similarity in the REE patterns for the three rhyolite groups. A minority of samples show negative Ce anomalies, with four samples having Ce/Ce* < 0.8, whereas one sample had a pronounced positive Ce anomaly of 1.49.

Oxygen and hydrogen isotopes

Oxygen and hydrogen isotope data are presented in Table 2. The $\delta^{18}\text{O}_{\text{Ow}}$ values show a considerably larger range (4.2–8.5‰) than the $\delta^{18}\text{O}$ quartz values (5.9–7.3‰) or the $\delta^{18}\text{O}$ plagioclase values, except for one sample (J60) with a very high $\delta^{18}\text{O}$ feldspar value of 13.0‰. Unfortunately, most of the rhyolites did not contain more than one separable phenocryst phase. In only three samples was it possible to determine the $\delta^{18}\text{O}$ values of both quartz and plagioclase and the erratic values of $\Delta_{\text{quartz-feldspar}}$ (1.9, -0.3 and -1.1‰) indicate that equilibrium was not maintained, as a result of differential resetting of the feldspar. For sample MG17 both phenocryst quartz and vein quartz were analysed. The former had a $\delta^{18}\text{O}$ value of 6.7‰ whereas the latter had a $\delta^{18}\text{O}$ value of 8.7‰. The whole-rock δD values range from -67 to -111‰, with an average of $-96 \pm 12\text{‰}$ (1 σ). The water content (wt % H₂O⁺) determined during the H-isotope

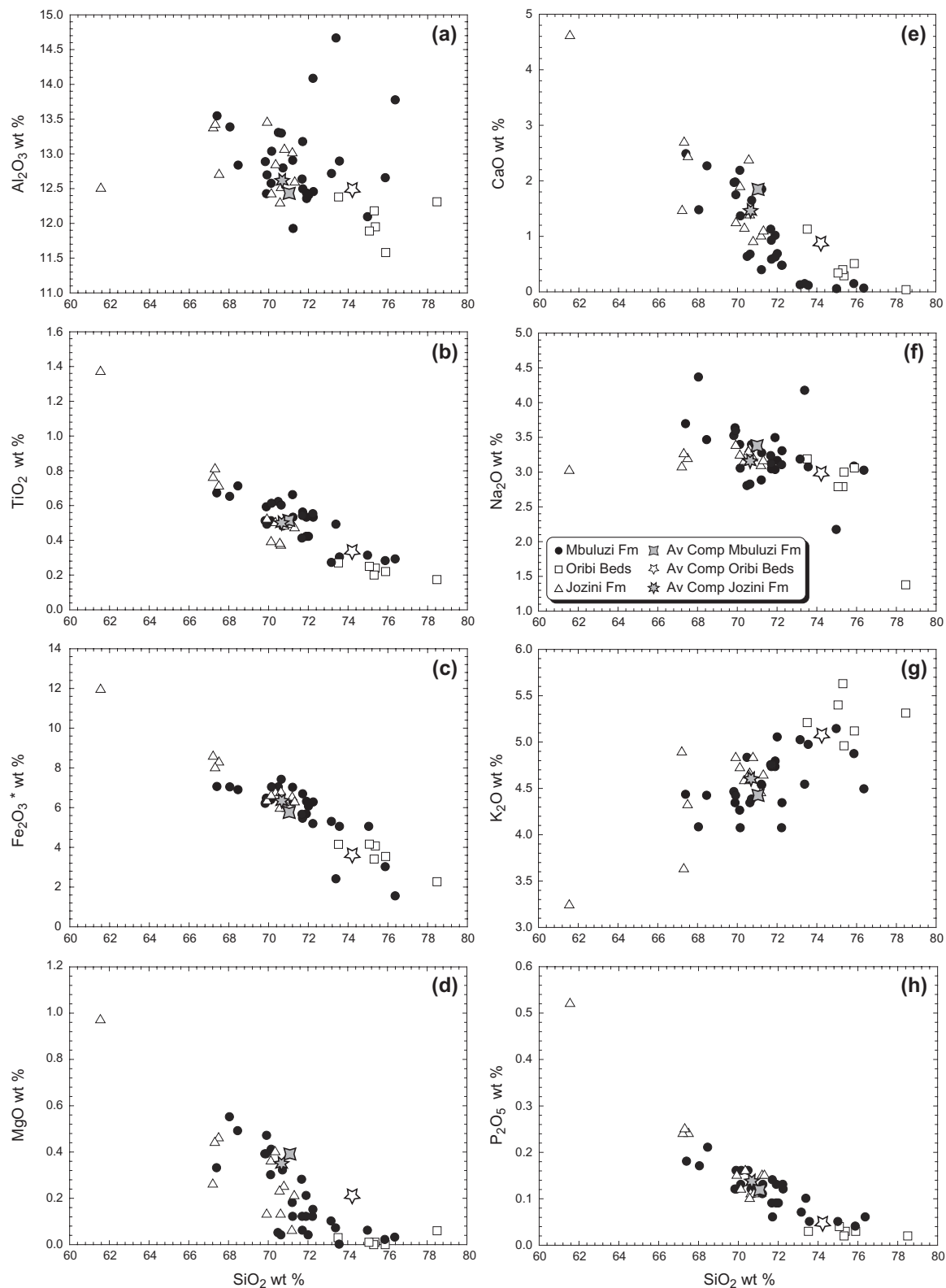


Fig. 3. Major element variation diagrams: (a) Al_2O_3 , (b) TiO_2 , (c) Fe_2O_3^* , (d) MgO , (e) CaO , (f) Na_2O , (g) K_2O and (h) P_2O_5 vs SiO_2 (wt%) for the Lebombo Rhyolites. Also shown for comparison are the average values for the Mbuluzi and Jozini Formation rhyolites and the Oribi Beds from Cleverly *et al.* (1984). Fe_2O_3^* is all Fe reported as Fe_2O_3 .

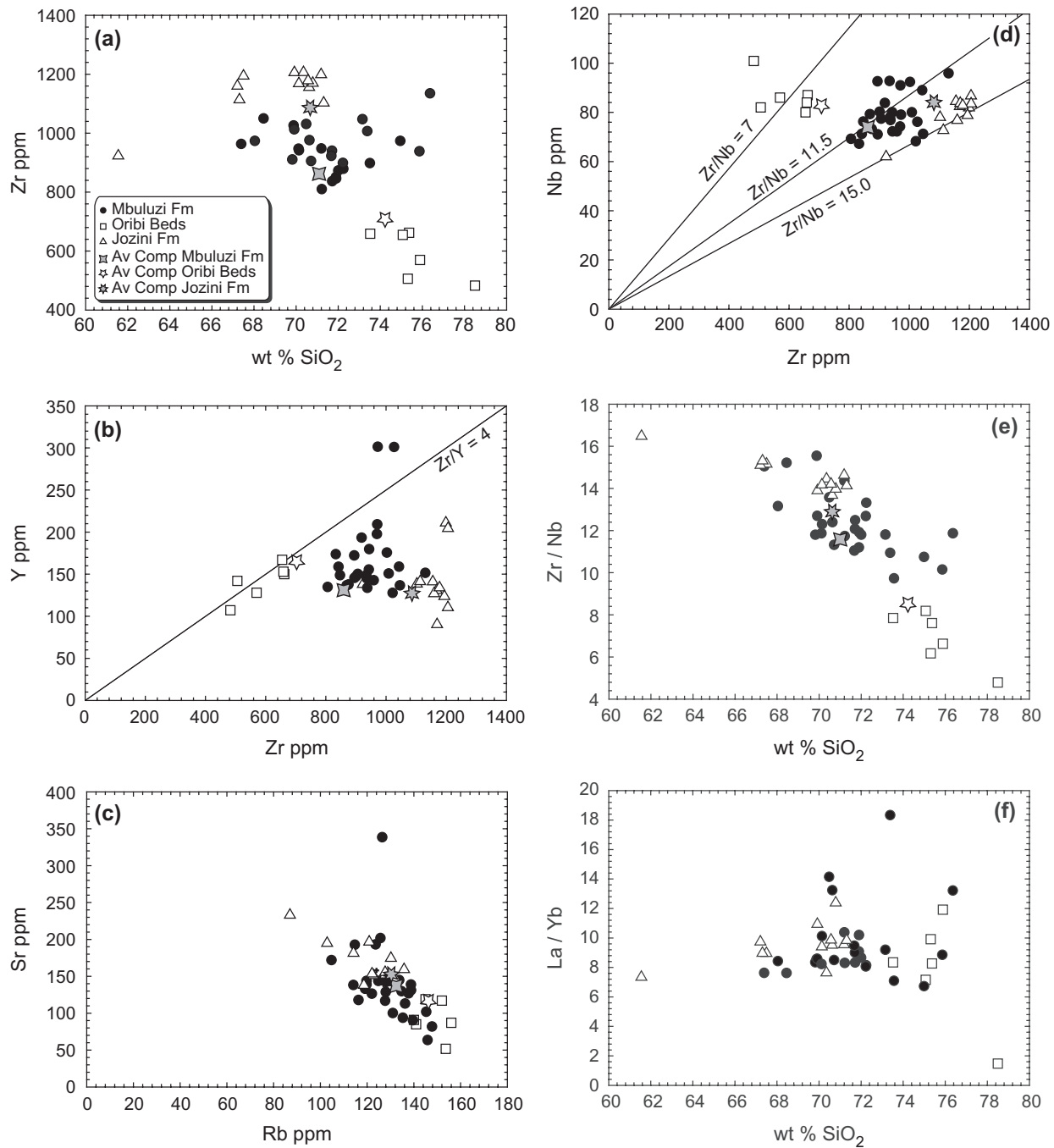


Fig. 4. Trace element variations for the Mbuluzi and Jozini rhyolites and the Oribi Beds. (a) Zr ppm vs wt% SiO_2 ; (b) Y ppm vs Zr ppm; (c) Sr ppm vs Rb ppm; (d) Nb vs Zr ppm; (e) Zr/Nb ratio vs wt% SiO_2 ; (f) La/Yb ratio vs wt% SiO_2 . Also shown for comparison are the average values for the Mbuluzi and Jozini Formation rhyolites and the Oribi Beds from Cleverly *et al.* (1984). It should be noted that REE were not analysed by Cleverly *et al.* (1984) and hence no average composition is shown for (f).

determination ranges from 0.3 to 1.2 wt %, with an average of 0.62 ± 0.27 (1σ).

The stable isotope data show several important features. $\delta^{18}\text{O}_{\text{wr}}$ values plotted against wt % SiO_2 (Fig. 7a) indicates that the Jozini rhyolites have higher $\delta^{18}\text{O}_{\text{wr}}$

values [average $\delta^{18}\text{O} = 9.9\text{‰} \pm 0.6$ (1σ)‰] than the Mbuluzi rhyolites or the Oribi Bed rhyolites [combined average $\delta^{18}\text{O} = 6.4 \pm 1.9$ (1σ)‰] at a given SiO_2 content. No correlation exists between $\delta^{18}\text{O}_{\text{wr}}$ and $\delta^{18}\text{O}$ quartz values (Fig. 7b), with the bulk of the variation occurring

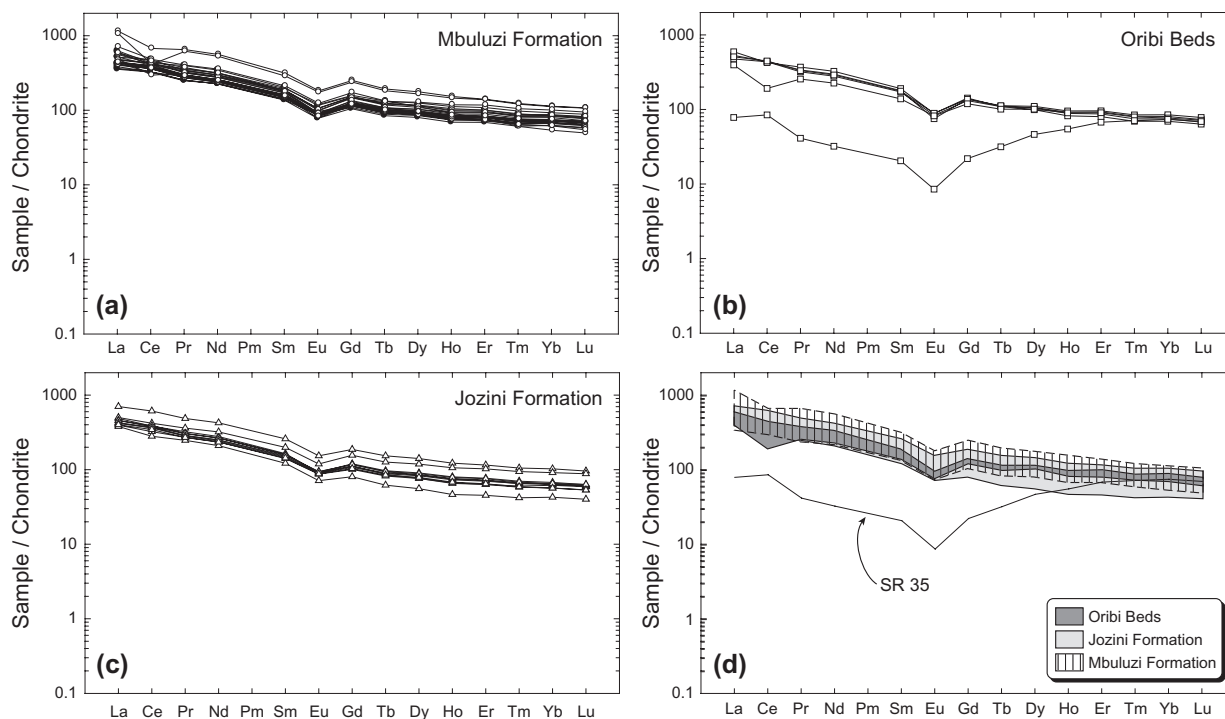


Fig. 5. Chondrite-normalized REE diagrams for rhyolites of (a) the Mbuluzi Formation, (b) the Oribi Beds and (c) the Jozini Formation. Samples of the Mbuluzi Formation from both the Mbuluzi and Siteki traverses are shown on the same diagram (a) and exhibit no differences in REE patterns. (d) REE patterns for the three rock groups superimposed, illustrating the similarity of REE patterns. The unusual REE pattern for one sample of the Oribi beds is SR35. Chondrite normalization factors taken from Sun & McDonough (1989).

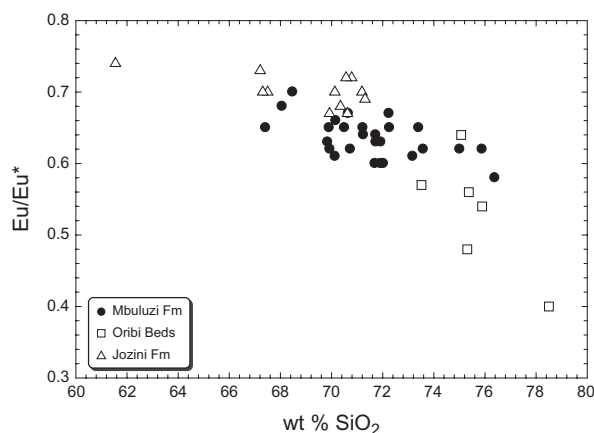


Fig. 6. Relationship between Eu anomaly (Eu/Eu^*) and wt% SiO_2 , where $\text{Eu}^* = \text{Eu}_N / \sqrt{[\text{Sm}_N \times \text{Gd}_N]}$. Chondrite normalization factors are from Sun & McDonough (1989).

in whole-rock rather than quartz values. $\delta^{18}\text{O}_{\text{wr}}$ also shows no correlation with either wt % H_2O^+ (Fig. 7c) or whole-rock δD (Fig. 7d). Figure 7e indicates that rocks with <0.4 wt % H_2O^+ have consistently low δD values, with values between -90 and -116‰ , whereas samples with >0.4 wt % H_2O^+ have a much larger range of δD values.

Although there is a lack of correlation generally between $\delta^{18}\text{O}_{\text{wr}}$ values and wt % SiO_2 , the Oribi beds show

a fairly good positive correlation (Fig. 7a). This cannot be related to the $\delta^{18}\text{O}$ value of the magma because the correlation between $\delta^{18}\text{O}$ values for whole-rocks and quartz is, if anything, negative (Fig. 7b). Positive correlations between $\delta^{18}\text{O}_{\text{wr}}$ values and wt % SiO_2 as a result of low-temperature alteration are to be expected (Harris, 1989) in glassy rocks because glass is susceptible to low-temperature exchange, and the amount of glass increases with increasing silica content. This would also explain the weak positive correlation between whole-rock δD values and SiO_2 (Fig. 7f) in that hydration water might be expected to have less negative δD values.

Strontium and neodymium isotopes

Strontium and neodymium isotope data for 15 of the rhyolites are reported in Table 3 and shown graphically in Fig. 8. Samples were selected on the basis of the presence of quartz phenocrysts and include four samples of the Oribi Beds, 10 samples of the Mbuluzi rhyolites and one sample from the Mkutshane Beds. No samples of the Jozini rhyolites were analysed as these were analysed previously by Harris & Erlank (1992). An important feature of the data from this study is that there is very little variation in initial $^{143}\text{Nd}/^{144}\text{Nd}$ ratios (0.51236 – 0.51243), with ϵ_{Nd} values close to Bulk Earth

Table 2: Stable isotope data for the Lebombo rhyolites

Sample	Fm	$\delta^{18}\text{O}_{\text{wrr}}$	$\delta^{18}\text{O}_{\text{qtz}}$	$\delta^{18}\text{O}_{\text{fsp}}$	$\delta^{18}\text{O}_{\text{mt}}$	$\delta^{18}\text{O}_{\text{magma}}^*$	δD	wt% H_2O^+
JM00MG6	Mb	6.7	7.0			6.4		
JM00MG8	Mb	8.2	6.9			6.3		
JM00MG9	Mb	8.4	7.1			6.5	−101	0.54
JM00MG10	Mb	7.1						
JM00MG11	Mb	7.6						
JM00MG12	Mb	5.3						
JM00MG13	Mb	4.3	6.3			5.7	−92	0.45
JM00MG14	Mb	3.9					−101	0.40
JM00MG15	Mb	4.7						
JM00MG16	Or	5.3	7.1			6.5		
JM00MG17	Or	6.1	6.7			6.1		
JM00MG17	Or		8.7 (secondary vein quartz)					
JM00MG18	Or	5.3	7.0			6.4	−98	0.30
JM00MG19	Or	4.4	7.1			6.5	−97	0.36
JM00MG20	Or	5.0	6.7	4.8		6.1	−92	0.30
JM00MG21	Mb	4.3					−111	0.70
JM00MG22	Jz	7.3						
JM00SR23	Mb	8.7					−73	1.17
JM00SR24	Mb	7.8					−112	0.93
JM00SR25	Mb	8.2						
JM00SR27	Mb	6.6					−82	0.53
JM00SR28	Mb	4.8		6.1				
JM00SR29	Mb	8.7					−96	0.91
JM00SR30	Mb	8.1			5.8			
JM00SR31	Mb	6.5	7.3			6.7	−93	0.29
JM00SR32	Mb	4.7	5.9			5.3	−100	0.36
JM00SR33	Mb	8.2					−102	0.54
JM00SR34	Mb	6.5						
JM00SR35	Or	7.3	6.2	6.5		5.6	−85	1.18
JM00SR36	Mb	9.0						
JM00SR37	Mb	7.6	6.3	7.4	7.3	5.7		
JM00SR38	Mb	7.2	6.3			5.7		
JM00SR39	Mb	9.7		6.4		6.7	−78	0.71
JM00SR40	Mb	3.4					−67	0.87
JM00SR41	Mb	2.1					−106	0.27
JM00SR45	Mkt	6.9					−102	0.64
JM00J50	Jz	9.6		6.3		6.6	−105	0.66
JM00J51	Jz	8.9		6.0		6.3		
JM00J52	Jz	10.7		6.0		6.3	−107	0.58
JM00J53	Jz	11.1		6.3		6.6	−102	0.79
JM00J54	Jz	10.0						
JM00J55	Jz	10.1						
JM00J56	Jz	9.3						
JM00J57	Jz	9.9					−94	0.68
JM00J58	Jz	9.4					−103	0.62
JM00J59	Jz	9.7		6.3		6.6		
JM00J60	Jz	10.3		13.0				

* $\delta^{18}\text{O}$ magma calculated assuming $\Delta_{\text{quartz-melt}}$ and $\Delta_{\text{plagioclase-melt}}$ values of +0.6‰ and −0.3‰, respectively (Matthews *et al.* 1994; Zhao & Zheng, 2003). Formation abbreviations are as in Table 1; and Mkt, Mkutshane Beds.

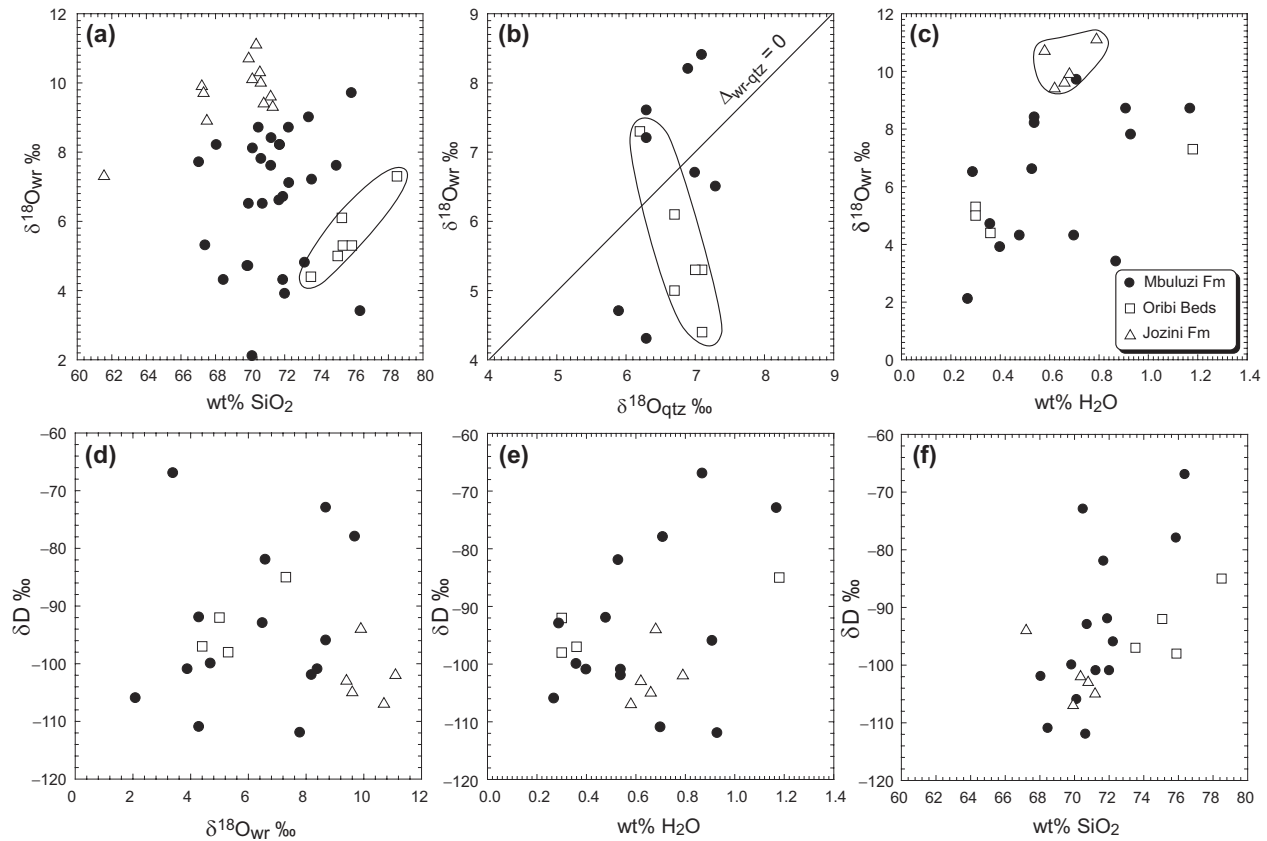


Fig. 7. (a) $\delta^{18}\text{O}_{\text{wr}}$ values vs wt% SiO_2 content; (b) $\delta^{18}\text{O}_{\text{wr}}$ value vs $\delta^{18}\text{O}$ quartz value; (c) $\delta^{18}\text{O}_{\text{wr}}$ values vs wt% H_2O^+ ; (d) whole-rock δD values vs $\delta^{18}\text{O}_{\text{wr}}$ value; (e) whole-rock δD vs wt% H_2O^+ ; (f) whole-rock δD vs anhydrous wt% silica contents.

Table 3: Sr and Nd radiogenic isotope data for selected Lebombo rhyolites

Rock formation	Flow no.	Sample no.	Rb (ppm)	Sr (ppm)	$^{87}\text{Rb}/^{86}\text{Sr}$	$^{87}\text{Sr}/^{86}\text{Sr}$ measured	$^{87}\text{Sr}/^{86}\text{Sr}$ (179 Ma)	$\varepsilon_{\text{Sr}(179)}$	Sm (ppm)	Nd (ppm)	$^{147}\text{Sm}/^{144}\text{Nd}$	$^{143}\text{Nd}/^{144}\text{Nd}$ measured	$^{143}\text{Nd}/^{144}\text{Nd}$ 179 Ma	$\varepsilon_{\text{Nd}(179)}$
Mbuluzi Fm	VII	JMOOMG6	148	81	5.2876	0.71691	0.70345	-11.83	28.5	149	0.11594	0.512560	0.512424	0.32
Mbuluzi Fm	VII	JMOOMG9	128	116	3.1919	0.71244	0.70432	0.46	23.6	116	0.12332	0.512570	0.512426	0.35
Mbuluzi Fm	a	JMOOMG13	135	129	3.0272	0.71244	0.70474	6.41	26.9	138	0.11815	0.512560	0.512422	0.27
Mbuluzi Fm	a	JMOOMG14	131	118	2.9135	0.71212	0.70470	5.97	23.2	115	0.12228	0.512520	0.512377	-0.60
Oribi Beds	VI	JMOOMG16	141	85	4.8001	0.71611	0.70389	-5.55	26.2	131	0.12123	0.512540	0.512398	-0.19
Oribi Beds	VI	JMOOMG19	145	119	3.5250	0.71341	0.70444	2.19	26.9	136	0.11989	0.512530	0.512390	-0.35
Oribi Beds	VI	JMOOMG20	152	117	3.7588	0.71470	0.70513	12.06	21.2	106	0.12123	0.512550	0.512408	0.01
Mbuluzi Fm	X	JMOOSR23	139	130	3.0936	0.71480	0.70693	37.52	47.8	260	0.11143	0.512490	0.512359	-0.94
Mbuluzi Fm	X	JMOOSR24	124	192	1.8652	0.71274	0.70799	52.55	43.9	245	0.10861	0.512540	0.512413	0.10
Mbuluzi Fm	I	JMOOSR28	146	101	4.1827	0.71541	0.70477	6.83	25.8	128	0.12217	0.512560	0.512417	0.18
Mbuluzi Fm	XI	JMOOSR31	128	128	2.8924	0.71172	0.70436	1.06	23.8	118	0.12225	0.512540	0.512397	-0.21
Mbuluzi Fm	XI	JMOOSR32	125	143	2.5285	0.71223	0.70579	21.45	23.3	116	0.12175	0.512550	0.512407	0.00
Mbuluzi Fm	X	JMOOSR33	114	137	2.4067	0.71097	0.70484	7.96	29.7	146	0.12330	0.512560	0.512426	0.35
Oribi Beds	IX	JMOOSR35	154	52	8.5788	0.72700	0.70517	12.53	3.1	15	0.12648	0.512570	0.512422	0.28
Mkutshani Beds	n.a.	JMOOSR45	100	140	2.0677	0.71994	0.71468	147.57	6.4	32	0.12197	0.511730	0.511587	-16.01

Initial ratios calculated using the program Geodate for Windows (Eglington & Harmer, 1999); ε values calculated using values for CHUR from Faure (1986). n.a., not applicable.

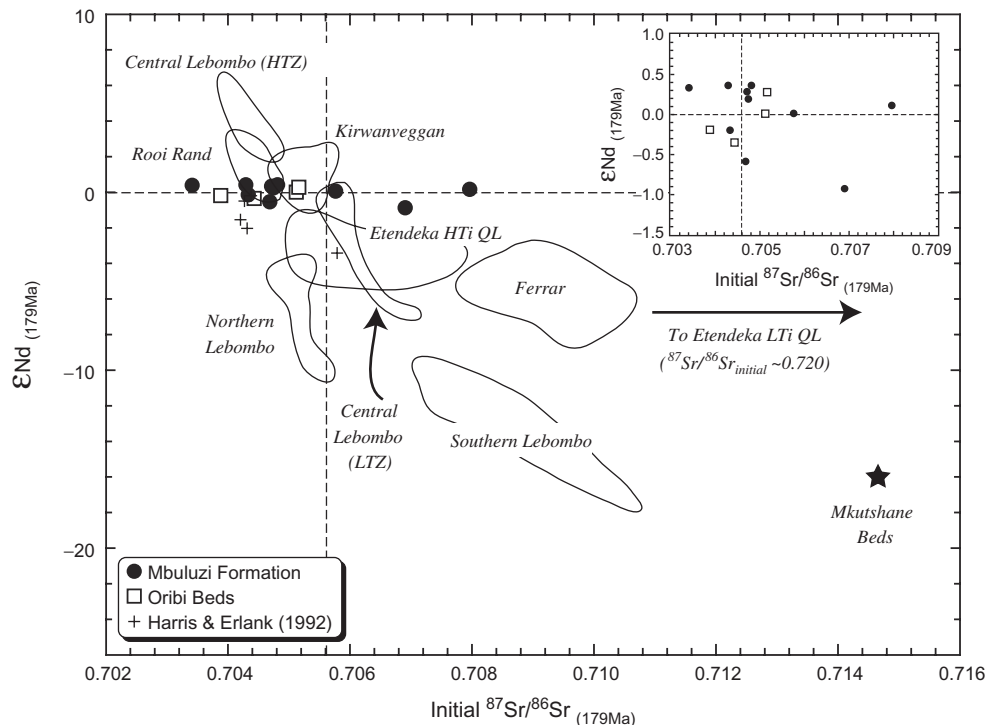


Fig. 8. Variation of ϵ_{Nd} vs ϵ_{Sr} showing the initial isotopic compositions of selected samples of the Mbuluzi Formation and Oribi Beds. Samples were selected on the basis of the presence of quartz phenocrysts. Epsilon values calculated at 179 Ma. Also shown for comparison are the fields for the Rooi Rand (Hergt *et al.*, 1991), the northern, central and southern Lebombo SRBF (Sweeney *et al.*, 1994), Kirwanveggen basalts (Harris *et al.*, 1990) and the Ferrar basalts (Fleming *et al.*, 1995). Fields for the Etendeka high-Ti and low-Ti rhyolite (Ewart *et al.*, 2004) are also shown. Also plotted is the single sample of the Mkutshane beds analysed as part of this study.

(average $\epsilon_{\text{Nd}} = -0.03$). Initial $^{87}\text{Sr}/^{86}\text{Sr}$ values are much more varied, ranging from 0.7035 to 0.7080. With two outlying samples omitted, the Rb–Sr data form an isochron that yields an age comparable with those found in previous studies, indicating that the Rb–Sr system has been relatively undisturbed since the time of eruption. The four Oribi Beds samples show substantially less variation in initial $^{87}\text{Sr}/^{86}\text{Sr}$ ratios (0.7039–0.7052) than the Mbuluzi rhyolites (0.7035–0.7080). The single sample of the Mkutshane Beds has highly radiogenic initial $^{87}\text{Sr}/^{86}\text{Sr}$ and $^{143}\text{Nd}/^{144}\text{Nd}$ isotope ratios (0.7147 and 0.51159, respectively) and is clearly crustal in origin, as shown by Betton (1979) on the basis of Pb and Sr isotope data. There is no correlation between Sm/Nd and measured $^{143}\text{Nd}/^{144}\text{Nd}$, indicating that there is no isochron relationship for this system. The inset diagram in Fig. 8 has an expanded ϵ_{Nd} scale and shows that there is no correlation between ϵ_{Nd} and initial Sr-isotope ratio. The initial $^{87}\text{Sr}/^{86}\text{Sr}$ and ϵ_{Nd} composition of a variety of basaltic and felsic magma types from southern African and adjacent Gondwana volcanic provinces is also shown in Fig. 8 for comparison. The compositional variation of the Lebombo rhyolites is unlike that of any of the other magma types and this feature will be discussed in more detail below.

DISCUSSION

Stratigraphic variations

Lateral variations in the thickness and continuity of the individual rhyolite flows (Fig. 1c) make the assessment of systematic variations in geochemistry with stratigraphic height problematic. Figure 9 shows data from the combined Mbuluzi and Siteki traverses for various geochemical parameters as a function of flow number. On first pass there seems little evidence for systematic changes in the chemical composition of the various rhyolite flows with stratigraphic height. The samples of Oribi rhyolite from Flows VI and IX indicate differences that would be consistent with an increasing degree of fractional crystallization between the flows, in particular higher SiO_2 contents (Fig. 9a) coupled with lower Fe_2O_3 contents (Fig. 9b), although it should be noted that this is based on the one sample of the Oribi beds from Flow IX. The Rb/Sr ratios show a small variation in that the middle flows have slightly elevated ratios compared with the flows at the base and top of the sequence examined (Fig. 9c). The Zr/Nb ratios are constant and illustrate again the different Zr/Nb ranges for the Oribi, Mbuluzi and Jozini rhyolites (Fig. 9d).

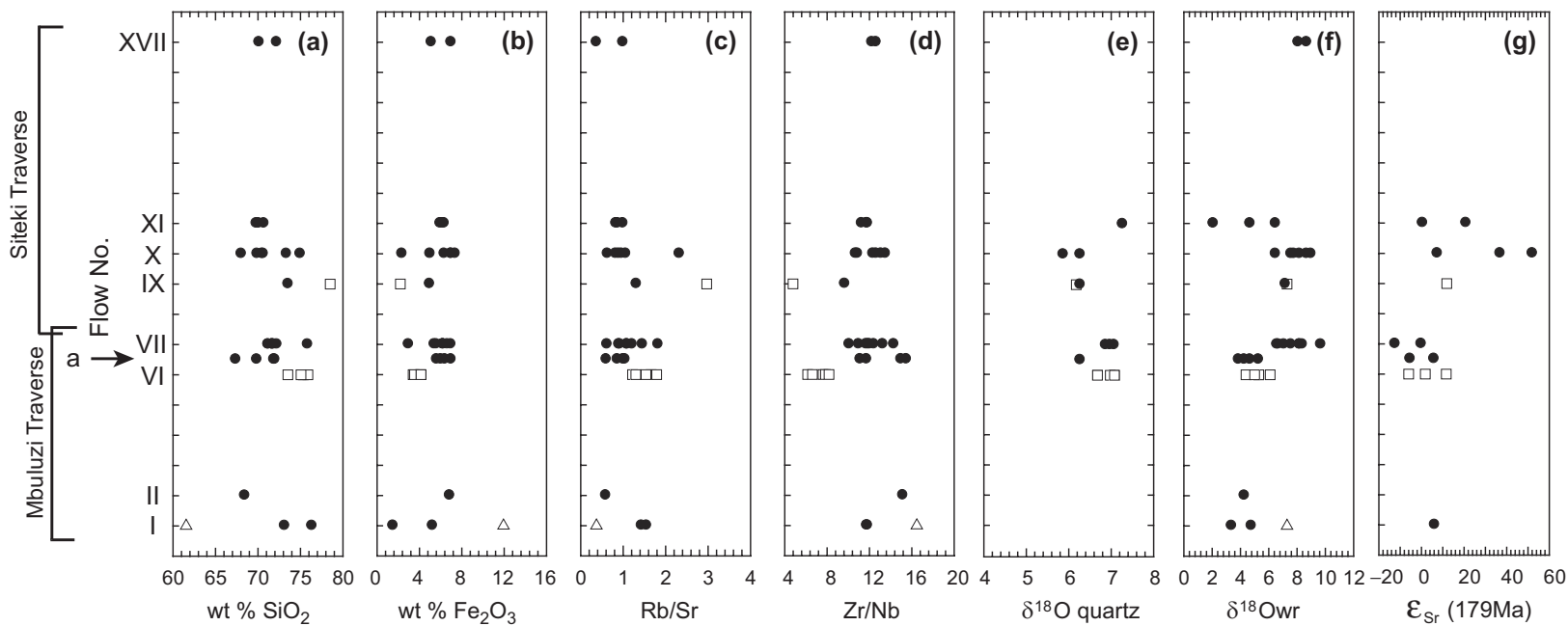


Fig. 9. Selected major and trace element abundances and ratios vs flow number for samples from the Mbuluzi and Siteki traverses: (a) wt% SiO_2 ; (b) wt% Fe_2O_3 ; (c) Rb/Sr; (d) Zr/Nb; (e) $\delta^{18}\text{O}$ quartz ‰; (f) $\delta^{18}\text{O}$ wr ‰; (g) ϵ_{Sr} (179 Ma). It should be noted that for Flow I, the two samples of the Mbuluzi Formation belong to the Siteki Traverse (see Fig. 1c).

In contrast, the variation in stable isotope data with respect to stratigraphic height clearly indicates lower $\delta^{18}\text{O}$ quartz values associated with Flows IX, X and a_2 (Fig. 9e). Although Flows IX and X do not appear to be connected to Flow a_2 , all three flows occur at the same stratigraphic position, towards the base of the Mbuluzi Formation (Fig. 1c). $\delta^{18}\text{O}$ quartz values in these flows vary between 5.9 and 6.3‰. In the case of Flows X and IX, the flows immediately above and below have $\delta^{18}\text{O}$ quartz values of 7.3‰, whereas for Flow a_2 , the surrounding flows have $\delta^{18}\text{O}$ quartz values around 7.1‰. Moreover, the $\delta^{18}\text{O}$ quartz values appear to record a bimodal $\delta^{18}\text{O}$ distribution, as the higher $\delta^{18}\text{O}$ quartz values all fall between 6.9 and 7.3‰, although two samples have $\delta^{18}\text{O}$ quartz values of 6.7‰. In comparison, the $\delta^{18}\text{O}_{\text{Owr}}$ values (Fig. 9f) show both high and low values that seem to oscillate with stratigraphic height (see Table 1 and Fig. 1c). This is particularly clear when looking at the Mbuluzi section, where from east to west the $\delta^{18}\text{O}_{\text{Owr}}$ values start at 6.7‰, increase to 8.4‰, decrease to 3.9‰, increase again to 6.1‰, before decreasing again to 4.3‰ and ending at 7.3‰. This last sample is of the Jozini rhyolite, which, in general, has higher $\delta^{18}\text{O}_{\text{Owr}}$ values than the Mbuluzi rhyolite and Oriibi Beds. This pattern of oscillating $\delta^{18}\text{O}_{\text{Owr}}$ values in part explains the range in $\delta^{18}\text{O}_{\text{Owr}}$ values for some individual flows, and is best illustrated in Flow VII, which incorporates the topmost section of the Mbuluzi traverse. The difference in the pattern of $\delta^{18}\text{O}_{\text{Owr}}$ and $\delta^{18}\text{O}$ quartz values indicates that whereas the $\delta^{18}\text{O}$ quartz values reflect original magmatic values, the $\delta^{18}\text{O}_{\text{Owr}}$ values reflect hydrothermal alteration processes whose timing with respect to rhyolite eruption must be determined. The significance of these features is discussed in more detail below. The rhyolite ε_{Sr} values are higher in the Siteki traverse than in the Mbuluzi traverse (Fig. 9f). However, this pattern is obscured by the within-flow variation, which is often considerable, and the small number of data points. Likewise, the samples from the Jozini traverse do not show any significant stratigraphic variation, although there are some indications that samples from near the base of individual flows (J51, J57 and J59) have lower than normal SiO_2 contents.

Geochemical modelling

Origin of the rhyolites by partial melting

Cleverly *et al.* (1984) pointed out that the Lebombo rhyolites form a coherent group of rocks, a fact borne out by the new extended dataset, and considered that the close association with the underlying basalts indicates a clear petrogenetic link. Derivation by partial melting of pre-Mesozoic crust was rejected on the basis of radiogenic isotope data, and Cleverly *et al.* (1984) considered the possibility that the rhyolite magmas formed either by partial melting of a basaltic source or by prolonged

fractional crystallization of a basaltic magma. They further considered the possibility that the range in chemical composition within the rhyolites might be due to varying degrees of partial melting of a basaltic parent or by fractional crystallization of the rhyolite magma once formed. Cleverly *et al.* (1984) concluded that the rhyolite magmas were produced by decompression partial melting of a basaltic sill complex that was coeval with the basalt magmatism. During crustal thinning prior to continental separation at 155 Ma (Watkeys, 2002), the base of the crust would have been uplifted by as much as 20 km. Provided the sill complex had not cooled significantly below its solidus, the drop in pressure would have been sufficient to initiate partial melting. Since 1984, the geochronological database on the Lebombo volcanic rocks has been greatly expanded. The most recent age determinations (Riley *et al.*, 2004) favour the eruption of the entire 12 km sequence of basalts and rhyolites within 1–2 Myr at about 180–182 Ma. Although this would require rapid crustal thinning, it would also mean that the basaltic sill complex remained close to its solidus, rendering it susceptible to decompression partial melting.

It is not the purpose of this study to repeat the partial melting and fractional crystallization modelling of Cleverly *et al.* (1984) and Betton (1979). Nevertheless, various questions remain unanswered. First, Cleverly *et al.* (1984) did not discuss in any detail the composition of the source material and its relationship with the exposed basalt types and intrusions. Second, the petrogenetic relationships between the Jozini and Mbuluzi Formation rhyolites and the Oriibi beds require further consideration, in the light of the greatly expanded dataset from this study, in particular the addition of detailed REE data.

Comparison of basalt and rhyolite magma types

The SRBF forms the major thickness of basalts that underlie the rhyolites along the entire length of the Lebombo (Fig. 1b). If the rhyolites were derived by partial melting of underplated basaltic material, the SRBF is the most likely surface representative of this basaltic source. Based on major and trace element geochemistry, previous studies (e.g. Duncan *et al.*, 1984; Sweeney & Watkeys, 1990; Sweeney *et al.*, 1994) have shown that there are various basaltic magma types in the Lebombo, the most significant division being between the high- and low-Ti/Zr (HTZ and LTZ) types. Sweeney *et al.* (1994) further subdivided the HTZ basalts into a high- and low-Fe type (HTZ-HF and HTZ-LF). These basalt types are geographically distinct in that the HTZ types are found in the northern Lebombo whereas the LTZ type is confined to the southern Lebombo. The transition from LTZ to HTZ basalts is apparently gradational and occurs north of Swaziland along the Sabie River (Sweeney *et al.*, 1994). In that region, the general sequence of eruption is first HTZ-LF, followed by LTZ, followed by HTZ-HF, although

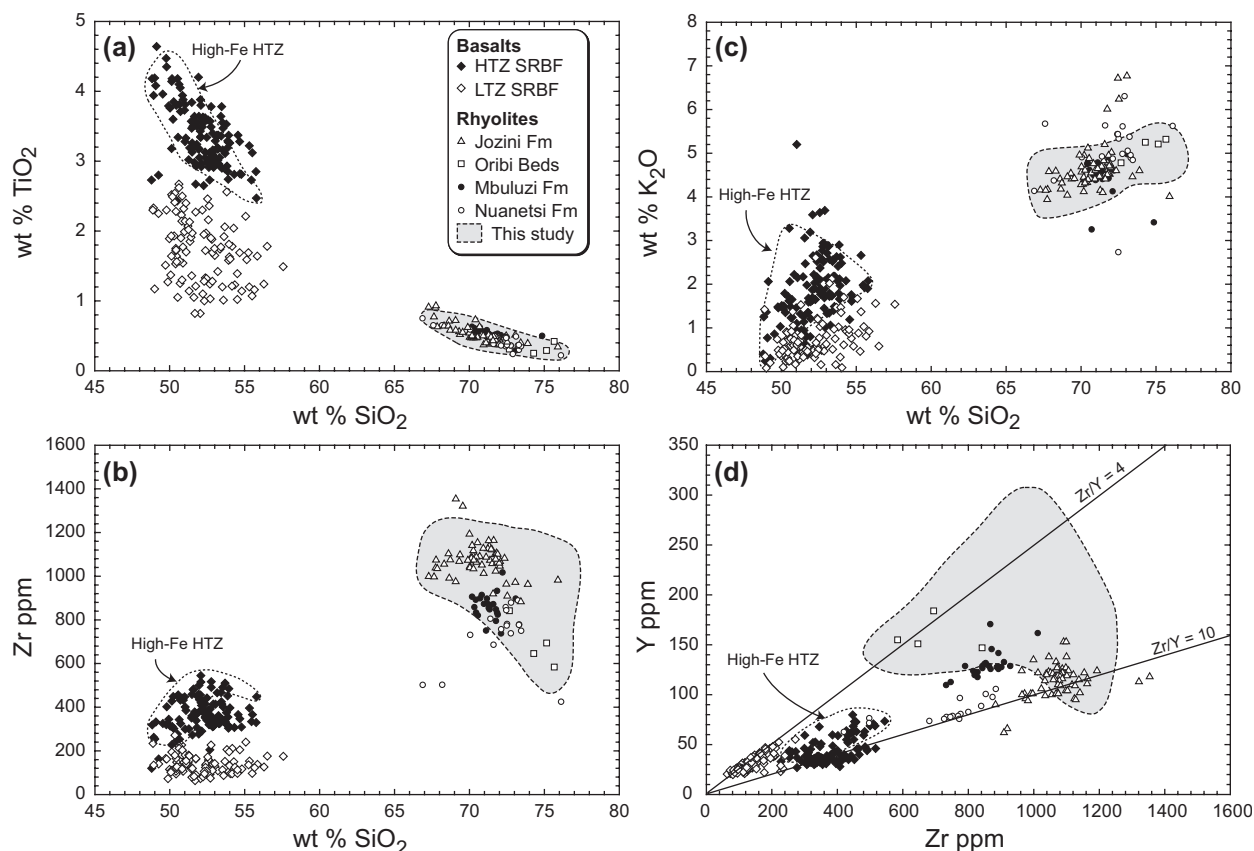


Fig. 10. Comparison of basalt and rhyolite compositions from Karoo database (courtesy of A. R. Duncan). The new data presented in this paper are shown as the grey field. (a) TiO_2 vs wt% SiO_2 ; (b) Zr vs wt% SiO_2 ; (c) K_2O vs wt% SiO_2 ; (d) Y vs Zr (ppm).

in some areas the presence of interbedded basalt types indicates that simultaneous eruption occurred at times (Sweeney *et al.*, 1994).

The geochemical differences between the basaltic magma types are clearly illustrated using a combination of trace element and major element data in Fig. 10. The HTZ and LTZ basalt types have distinct TiO_2 and K_2O contents (Fig. 10a and c), whereas the distinction between HTZ-HF and HTZ-LF as well as that with the LTZ type are shown more clearly by comparing Zr/Y ratios (Fig. 10d). In contrast to the basalt magma types, the rhyolite magma types show no clear difference in TiO_2 or K_2O (Fig. 10a and c). However, the distinct differences between the Jozini and Mbuluzi rhyolites, in terms of Zr and Zr/Y (Fig. 10b and d), mirror the differences seen in the different basalt types. The relationship between Zr and Y (Fig. 10d) is particularly interesting in that the Jozini rhyolites have $\text{Zr/Y} \sim 10$, as is the case for the low-Fe variant of the HTZ basalts (Sweeney *et al.*, 1994). On the other hand, the Oribi beds have similar Zr/Y ratios to the LTZ basalts, whereas the Mbuluzi

rhyolites have fairly consistent Zr/Y ratios that are similar to those of the HTZ-HF type. The Mwenezi rhyolites have lower Zr and Y contents, but similar Zr/Y to the Jozini rhyolites (Fig. 10d). If the rhyolites were produced by partial melting of underplated basalt without subsequent modification of their trace element compositions by fractional crystallization or crustal contamination, an obvious first-order conclusion is that the high-Zr/Y Jozini and Nuanetsi rhyolites were produced by partial melting of the HTZ-LF basalts whereas the Mbuluzi rhyolites were produced by partial melting of the HTZ-HF basalts, and only the Oribi beds were derived by partial melting of an LTZ basalt source. However, given that the concentration of Zr has probably been affected by fractional crystallization of zircon, this hypothesis should be treated with caution and will be discussed further below.

Variation in rhyolite composition

Cleverly *et al.* (1984) successfully modelled the variation within the Mbuluzi rhyolites from 70 to 72 wt % SiO_2 by about 9% crystallization of an assemblage consisting

of 69% plagioclase (An_{34}), 11% pyroxene, and 20% magnetite. The proportions of plagioclase to pyroxene match the typical phenocryst assemblages in the rhyolites, but magnetite is much less abundant in the rhyolites themselves. On the basis of their modelling, Cleverly *et al.* (1984) suggested that either substantial thicknesses of magnetite cumulates must exist beneath the Lebombo, or that fractional crystallization is not a viable mechanism for generating the variation in chemical composition. In focusing on the Mbuluzi rhyolites, Cleverly *et al.* (1984) did not model the compositional variation in the various rhyolite types as products of different amounts of fractional crystallization of a single parental felsic magma.

Quantitative modelling of major elements as part of this work concentrated on producing a silica-rich Oriibi bed from a typical Mbuluzi Formation rhyolite. Sample SR32 was chosen as a typical Mbuluzi rhyolite as it is petrographically fresh and has relatively low wt % SiO_2 (70.28% normalized to 100% volatile-free with total Fe as FeO) compared with the Mbuluzi rhyolites as a whole. Compositionally, it is very similar to a number of the Jozini rhyolites and therefore no attempt was made to relate the Jozini and Mbuluzi rhyolites by fractional crystallization. Sample MG16 (SiO_2 75.68%), which was chosen to represent the Oriibi beds, contains ~6 vol.% quartz phenocrysts. This sample has an LOI of 0.66 wt %, suggesting that alteration had little or no effect on the major element composition. Consideration of the relationship between bulk-rock and phenocryst compositions (Fig. 11) indicates that the strong negative correlation between Fe_2O_3 and SiO_2 (Fig. 11a) is due to fractionation of clinopyroxene $\pm$ magnetite. The strong positive correlation between TiO_2 and Fe_2O_3 (Fig. 11b) also requires some fractionation of Ti-magnetite, although the proportions of pyroxene and magnetite depend strongly on the exact composition of the pyroxene chosen. A combination of pyroxene and plagioclase fractionation accounts for the weak negative correlation between Na_2O and SiO_2 (Fig. 11c), whereas the positive correlation between K_2O and SiO_2 (Fig. 11d) indicates that some fractionation of K-rich alkali feldspar was also involved. The results of one model are shown in Table 4 and indicate that Oriibi rhyolite could be generated from Mbuluzi rhyolite by 44.6% fractional crystallization of an assemblage consisting of 19% Fe-rich clinopyroxene, 59% plagioclase (An_{20}), 14% sanidine (Or_{93}), 7% Ti-magnetite, and 1% apatite. This is compatible with the phenocryst assemblage observed in the rhyolites, and in particular the magnetite content is more appropriate than the original model of Cleverly *et al.* (1984). The addition of quartz as a fractionating phase did not result in more tightly constrained models, and it would therefore appear that quartz fractionation was not important.

The trace element variations are more difficult to explain in terms of fractional crystallization. Qualitatively, the major element model described above is consistent with the negative correlation between Sr concentrations and SiO_2 contents and the positive correlation between both Rb and Nb concentrations and wt % SiO_2 . On the other hand, Zr concentrations show a generally negative correlation with wt % SiO_2 (Fig. 4a), as does Zr/Nb. This suggests that Nb is behaving as an incompatible element whereas Zr is not, presumably because of fractionation of zircon. Numerous small crystals of zircon are visible in many of the rhyolites. The Zr saturation concentration for rhyolites depends on chemical composition and temperature (Watson & Harrison, 1983). Application of the equations of Watson & Harrison (1983) shows that the M-value [mole fraction $Na + K + 2Ca/(Al \times Si)$] of the three rhyolite types is between 1.0 and 1.7 (mean 1.44). None of the rhyolites would have been zircon saturated at 1020°C, which is close to the proposed eruption temperature of the rhyolite magmas (Betton, 1978). Nearly all of the rhyolites would have been saturated in zircon at 930°C, for which the Zr concentration is about 600 ppm for an M-value of 1.44. It therefore seems feasible that zircon fractionation occurred during fractional crystallization of the rhyolite magmas. The Zr/Y ratios show a scattered relationship with SiO_2 but also suggest that Y is behaving more incompatibly than Zr. The positive correlation between Rb/Sr ratio and SiO_2 (Fig. 4b) and the positive correlation between the size of the negative Eu-anomaly and SiO_2 (Fig. 6) is consistent with the importance of plagioclase fractionation throughout the evolution of the rhyolites.

In the light of the above discussion, it is clear that the high Zr/Nb ratios (~15) and Zr/Y ratios (~10) that characterize the Jozini rhyolites and the low Zr/Nb (~7) and Zr/Y (~4) ratios that characterize the Oriibi Beds are probably the result of fractional crystallization of zircon and do not reflect derivation from source materials of different compositions. The calculated trace element concentrations of MG16 based on the major element fractional crystallization model are shown in Table 4. Good matches were obtained for Sr and Ba, but the match for Rb was poorer, which might be due to the susceptibility of this element to alteration. The concentrations of incompatible elements such as La and Y (but not Ce) and Nb are overestimated by the model and Zr is underestimated by a factor of more than two. Fractionation of zircon and other accessory minerals could potentially explain the lack of fit of the trace element model. Zircon is present in most of the rocks and, as reported by Riley *et al.* (2004), a very small proportion of the zircons are inherited. However, there is no correlation between La/Yb and SiO_2 , indicating that zircon fractionation had a minimal effect on trace element abundances, other than Zr. The K_d values for the heavy REE (HREE) in

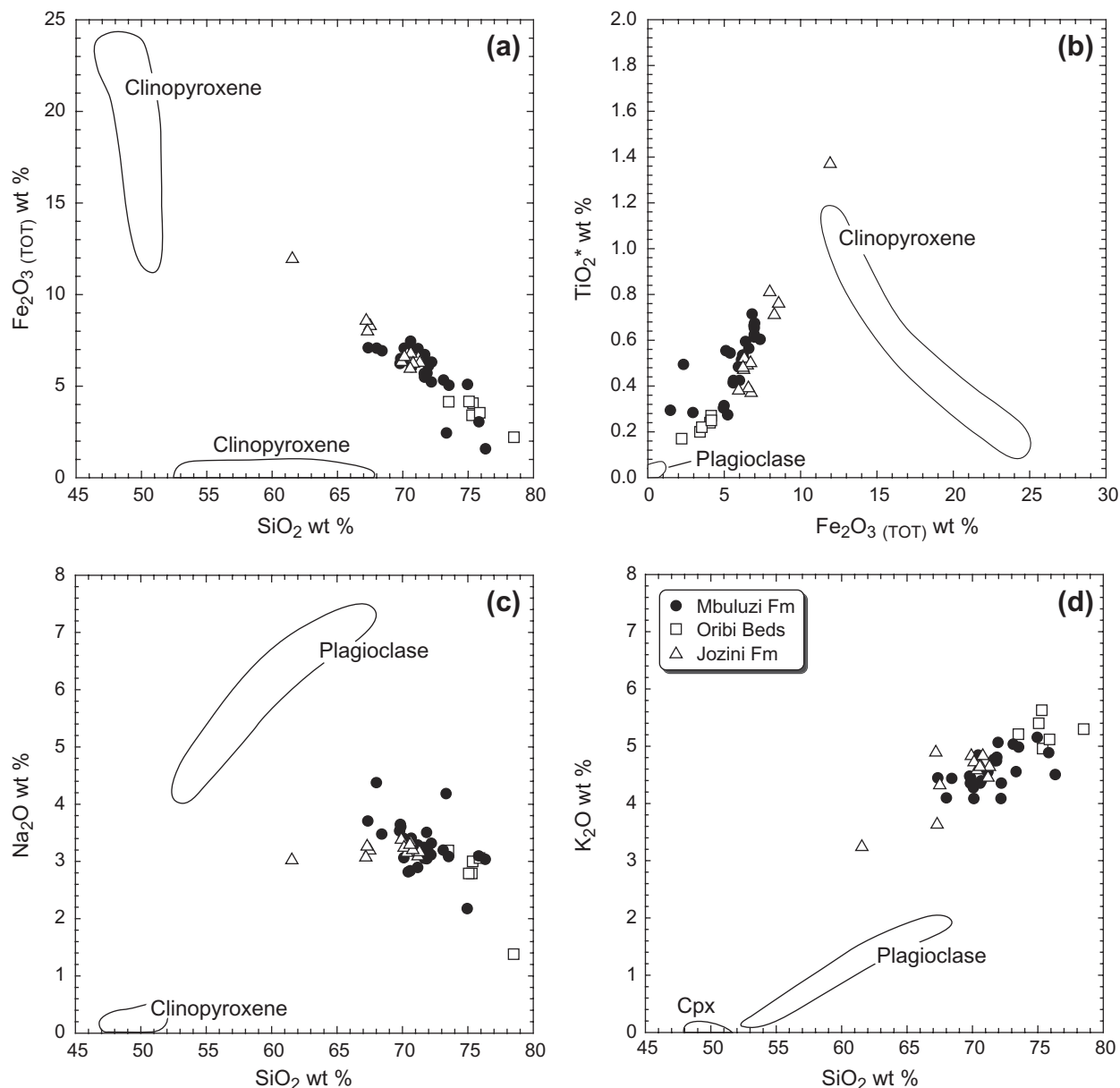


Fig. 11. Variation of (a) Fe_2O_3 (TOT) vs SiO_2 , (b) TiO_2 vs Fe_2O_3^* , (c) Na_2O vs SiO_2 , and (d) K_2O vs SiO_2 for rhyolites, with fields for phenocryst data (from Betton, 1979) shown.

zircon are much larger than those for the LREE (e.g. Mahood & Hildreth, 1983). The rhyolites in this study have Zr contents between 1200 and 500 ppm. If it is assumed that the difference of 700 ppm is due to zircon fractionation, 1400 ppm zircon has to be lost, which equates to 0.14 wt %. Most of the rhyolites contain 1–2 ppm Lu. If the K_d for Lu between melt and zircon is 648 (Mahood & Hildreth, 1983), a zircon in a melt with 2 ppm Lu will contain ~1300 ppm Lu. The removal of 0.14 wt % zircon would therefore result in a decrease in Lu concentration of 1.82 ppm. Thomas *et al.* (2002) found

that K_d values for the HREE between zircon and rhyolite melt are significantly lower than those found by either Watson (1980) or Mahood & Hildreth (1983). No K_d values are given for Lu but the median value K_d for Yb is 40. This would mean about a 0.1 ppm decrease in Lu as a result of zircon fractionation. This is slightly greater than the analytical error but suggests that zircon fractionation did not make a significant difference to HREE concentrations. The failure of fractional crystallization models to adequately explain trace element abundances suggests that source composition and/or degree of partial

Table 4: Major element least-squares fractional crystallization model relating Mbuluzi rhyolite (SR32) to Oribi bed rhyolite (MG16) based on major element mixing model defined by Cleverly et al. (1984)

Major element mixing model								
		Major element compositions					Results for MG16	
	SR32	Cpx	Plag	San	TiMgt	Ap	Actual	Calc
SiO ₂	70.28	49.23	67.56	63.66	0.01	0.00	75.67	75.67
TiO ₂	0.52	0.20	0.02	0.01	20.78	0.00	0.25	0.25
Al ₂ O ₃	12.96	1.06	20.58	19.54	1.01	0.00	12.00	12.00
FeO*	5.61	22.43	0.29	0.10	76.56	0.00	3.73	3.73
MnO	0.11	0.11	0.01	0.01	0.56	0.00	0.13	0.13
MgO	0.40	6.75	0.04	0.01	0.67	0.00	0.00	0.00
CaO	1.97	18.40	3.27	0.10	0.01	55.84	0.28	0.28
Na ₂ O	3.54	0.34	7.23	0.80	0.01	0.00	3.14	3.14
K ₂ O	4.49	0.06	1.80	15.60	0.01	0.00	5.03	5.03
P ₂ O ₅	0.12	0.01	0.01	0.01	0.01	42.04	0.06	0.06
							Σ ²	0.06
FC model	100	−8.5	−26.3	−6.3	−3.1	−0.3 (44.6% fractional crystallization)		
% Phenocrysts	19	59	14	7	1			

Trace element fractional crystallization model									
		Distribution coefficients						Results for MG16	
	SR32	D _{Cpx}	D _{Plag}	D _{Ap}	D _{Mgt}	D _{San}	Bulk D	Actual	Calc
Nb	78	0.10	0.01	0.01	0.40	0.01	0.0544	89	136
Zr	918	0.10	0.01	0.01	0.20	0.01	0.0404	675	1617
Y	151	0.50	0.03	10.00	0.20	0.01	0.2281	153	238
Sr	144	0.12	1.83	0.01	0.05	8.00	2.2261	87	70
Rb	126	0.03	0.10	0.01	0.01	0.34	0.1131	144	213
Sc	10.2	4.00	0.01	0.01	25.00	0.01	2.5174	2.5	4.2
V	8.1	1.50	0.01	0.01	20.00	0.01	1.6924	2.9	5.4
Ba	1306	0.01	0.10	0.01	0.01	5.00	0.7617	1453	1504
La	105	0.76	0.01	5.00	1.70	0.01	0.3207	115	157
Ce	233	1.20	0.01	10.00	2.90	0.01	0.5383	272	306

All Fe recalculated to FeO and analyses normalized to 100% volatile free. Trace element calculation made for Rayleigh fractionation where $C_i/C_o = F^{(D-1)}$. Distribution coefficients from the GERM database (<http://earthref.org>).

melting are additional factors influencing the final rhyolite composition.

Source composition and partial melting

The similarity in REE profiles of all three rhyolite types (Fig. 5) supports the idea that they could be related by a combination of different degrees of partial melting and/or varying degrees of fractional crystallization,

but that the source was essentially the same. In Fig. 12 this idea is explored further by comparing both the REE and extended trace element profiles of average Mbuluzi, Oribi and Jozini rhyolite with potential basaltic source compositions, namely the Rooi Rand dolerites (Fig. 1b) and the HTZ (HF and LF types) and LTZ varieties of the underlying SRBF. The Rooi Rand dolerites crop out only in the southern part of

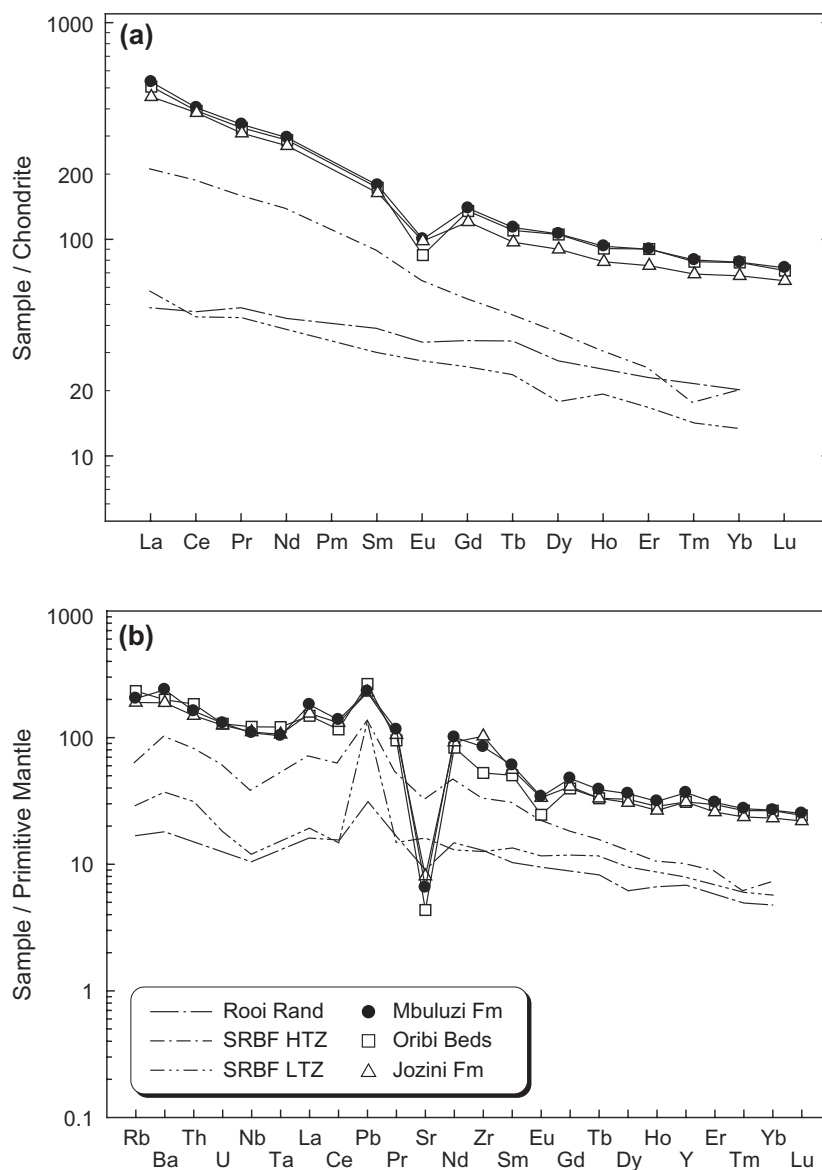


Fig. 12. (a) Chondrite-normalized REE diagram showing average Jozini and Mbuluzi Formations and Oribi Beds compositions (this study) plus patterns for average Sabie River Basalt Formation Low-Ti/Zr Type (SRBF LTZ), and High-Ti/Zr type (SRBF HTZ) and Rooi Rand (A. R. Duncan, unpublished database). (b) Primitive-mantle normalized trace-element diagrams for the same samples. Chondrite and primitive mantle normalizations factors taken from Sun & McDonough (1989).

the Lebombo Monocline, are thought to have been derived largely from the asthenosphere (Duncan *et al.*, 1990), and are characterized by relatively flat chondrite-normalized REE patterns ($\text{La}/\text{Yb}_N \sim 2$). The LTZ variety of the SRBF has similar LREE contents to the Rooi Rand dolerites but with a slightly steeper profile ($\text{La}/\text{Yb}_N \sim 4$), whereas the HTZ varieties of the SRBF have similar HREE patterns to the Rooi Rand but with much steeper LREE patterns ($\text{La}/\text{Yb}_N \sim 10$).

If partial melting of basaltic sources took place at relatively shallow depths (e.g. <20 km) it is unlikely that

the minerals present (plagioclase, clinopyroxene, minor olivine and magnetite) will have significantly different partition coefficients (e.g. Cox *et al.*, 1984) for the REE and melts will not be significantly more LREE-enriched than the source. Comparing the rhyolite profiles with the three basaltic magma types shows that the gradient of the rhyolite REE profile decreases from Gd to Lu. For the LREE part of the profile, the rhyolites have an almost identical gradient to the HTZ SRBF, whereas for the HREE the rhyolites are similar in gradient to the Rooi Rand and LTZ SRBF. This suggests that the source of the rhyolites might be a mixture of these basalt types whose

LREE is dominated by the HTZ SRBF, but whose HREE show the flatter profile of the other basalt types.

The major element model of Cleverly *et al.* (1984) suggested that the rhyolites could have been produced by ~10% batch melting of a basaltic source. Figure 13a shows the REE profiles of 10% batch melts of the three potential basaltic sources calculated using the parameters given in Table 5. It is evident that partial melting of average LTZ basalt provides the best fit to the observed data, although the model profile is less LREE-enriched than the observed data. An HTZ source would produce a rhyolite that is too REE-enriched and the Rooi Rand would produce a rhyolite with too flat a REE profile. The composition of the source for the rhyolite types is shown in Fig. 13b, and for any reasonable value of K_d for Eu, a positive Eu-anomaly is obtained. This suggests that the source material is a plagioclase-rich cumulate. The composition of the Mbuluzi source is compared with mixed LTZ and HTZ source material in Fig. 13c, and with mixed LTZ and Rooi Rand source material in Fig. 13d. The LTZ–Rooi Rand mixed source produces partial melts that have REE profiles that are too flat, whereas the 90% LTZ–10% HTZ mixture matches the profile of the Mbuluzi source. In terms of other

trace elements (Fig. 12b), the rhyolites have patterns that are consistent with such a source. For the most incompatible elements (Rb–Ce), the rhyolites are approximately parallel to the HTZ basalts, whereas for Nd–Lu, the rhyolite patterns are approximately parallel to the LTZ basalts. On this basis, it is suggested that the source composition is dominated by LTZ basaltic material with a small component (about 10%) of HTZ basalt, possibly as dykes in thick gabbroic cumulates formed from underplated LTZ basalt.

Low- $\delta^{18}\text{O}$ rhyolite magmas

In general, mantle-derived basalts have a very consistent $\delta^{18}\text{O}$ value of $5.7 \pm 0.2\text{‰}$ (Ito *et al.*, 1987; Eiler, 2001) and differentiation from basalt to rhyolite leads to a small increase in the $\delta^{18}\text{O}$ value (e.g. Muehlenbachs & Byerly, 1982; Taylor & Sheppard, 1986; Bindeman *et al.*, 2004). The magnitude of this change is still subject to debate, but most researchers are agreed that it is less than 1‰ (Taylor & Sheppard, 1986), with the most recent estimates suggesting values of less than 0.5‰ (e.g. Bindeman *et al.*, 2004). The change in $\delta^{18}\text{O}$ value of the magma with increasing degree of differentiation can be modelled assuming knowledge of the proportions of phenocryst

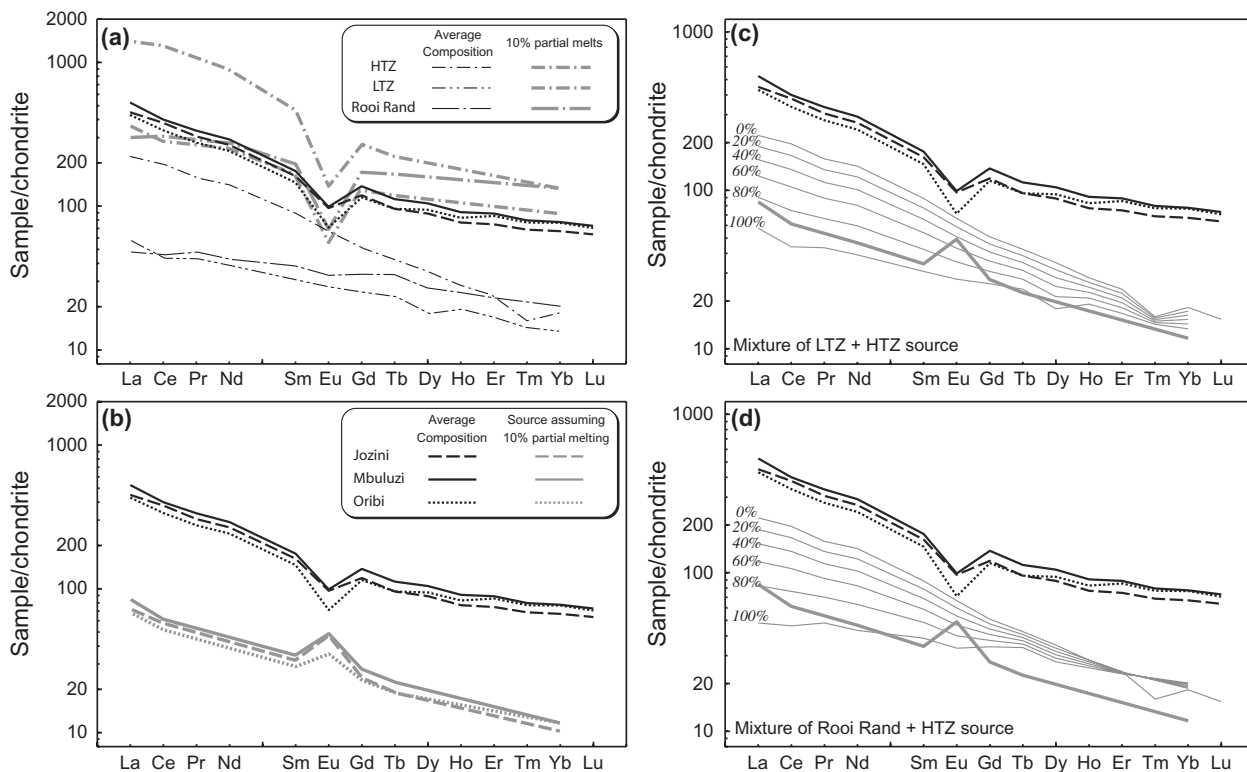


Fig. 13. Results of REE modelling of partial melting based on the major element model of Cleverly *et al.* (1984): (a) 10% batch melts of the three potential basaltic sources (data sources as in Fig. 12); (b) modelled source composition of the rhyolites assuming 10% partial melting; (c) comparison of modelled Mbuluzi source composition (thick grey line) with mixtures of LTZ and HTZ source material in increments of 20% from 100% LTZ at bottom (thin grey lines); (d) comparison of modelled Mbuluzi source composition with mixtures of Rooi Rand and HTZ source material in increments of 20% from 100% Rooi Rand at bottom (thin-grey lines). Average composition of Jozini, Mbuluzi Formations and Oribi Beds shown for comparison. Model parameters from Table 5.

Table 5: Partition coefficients, source mineral modes and melt modes for trace element partial melting model

	Opx	Cpx	Plag	Qtz	Mgt
La	0.001	0.069	0.25	0	0.24
Ce	0.003	0.098	0.2	0	0.28
Nd	0.0065	0.18	0.13	0	0.35
Sm	0.01	0.26	0.135	0	0.39
Eu	0.013	0.31	2	0	0.29
Gd	0.016	0.3	0.13	0	0.29
Tb	0.2	0.3	0.1	0	0.36
Yb	0.049	0.28	0.03	0	0.30
Mineral mode	0.05	0.38	0.45	0.02	0.10
Melt contribution	0.00	0.15	0.60	0.20	0.05

Partial melting calculations assuming batch melting according to the equation $C_i/C_o = 1/D^* + F(1 - P^*)$. Partition coefficients from the GERM database (<http://earthref.org>).

minerals and appropriate mineral–melt fractionation factors (e.g. Bindeman *et al.*, 2004) and result in downward-concave curves that flatten out with increasing silica content (Fig. 14). Rhyolites with $\delta^{18}\text{O}$ values that plot below this curve are referred to as low- $\delta^{18}\text{O}$ rhyolites and have $\delta^{18}\text{O}$ magma values $< \sim 6.2\text{‰}$ (Taylor & Sheppard, 1986; Bindeman *et al.*, 2004).

The $\delta^{18}\text{O}$ values of the Lebombo rhyolitic magmas in this study have been calculated assuming $\Delta_{\text{quartz-rhyolite melt}}$ values of $+0.6\text{‰}$ at 900°C (Zhao & Zheng, 2003). Using this value, $\delta^{18}\text{O}$ magma values for this study vary between 5.3 and 6.7‰ . The $\delta^{18}\text{O}$ values for the rhyolite magma fall into two groups, those with values less than 5.7‰ , and those with values higher than 6.1‰ . As pointed out above, the rhyolites with $\delta^{18}\text{O}$ magma values less than 5.7‰ all come from a very similar stratigraphic horizon towards the base of the Mbuluzi Formation. These values are considered to be representative of the magma from which the rhyolites crystallized. Re-equilibration of oxygen between minerals and host-rock is unlikely to be significant in the Lebombo because of the fast quenching of the rhyolitic magmas and, although $\delta^{18}\text{O}$ feldspar values can be reset by alteration, quartz is normally highly resistant and retains its primary magmatic value (e.g. Gregory & Taylor, 1981; Giletti, 1986; Bindeman & Valley, 2003). In sample MG17, secondary quartz from vugs and veins was analysed and was shown to have a $\delta^{18}\text{O}$ that was 2‰ higher than that of the quartz phenocrysts. This indicates that if regrowth of secondary quartz around phenocrysts occurred, it would have raised rather than lowered the phenocryst $\delta^{18}\text{O}$ values. Based on these $\delta^{18}\text{O}$ values and assuming $\Delta_{\text{rhyolite-basalt}} = 0.5\text{‰}$ (Zhao & Zheng, 2003; Bindeman *et al.*,

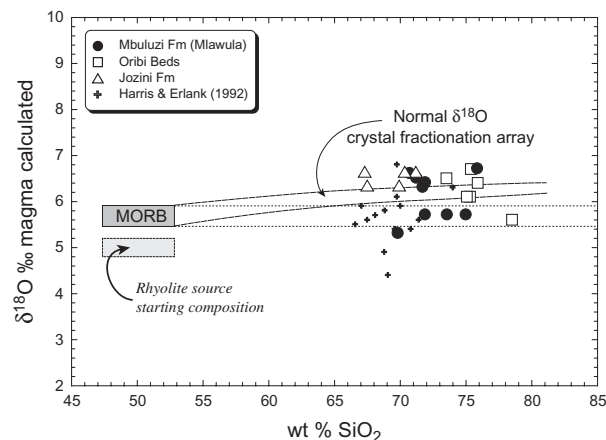


Fig. 14. Plot of $\delta^{18}\text{O}$ magma vs SiO_2 showing mid-ocean ridge basalt (MORB) field and data array expected for closed-system fractionational crystallization. The calculated normal $\delta^{18}\text{O}$ crystal fractionation array is from Bindeman *et al.* (2004). Rhyolite source starting composition is based on the oxygen isotope and major and trace element modelling from this study for the low- $\delta^{18}\text{O}$ group. The Harris & Erlank (1992) data have been calculated assuming a $\Delta_{\text{pyroxene-melt}}$ value of -0.7 from Taylor & Sheppard (1986), whereas data from this study are calculated assuming $\Delta_{\text{quartz-melt}}$ is 0.6‰ based on Matthews *et al.* (1994) and Zhao & Zheng (2003).

2004), the higher rhyolite magma values indicate derivation from a basaltic source material with $\delta^{18}\text{O}$ values between 5.6 and 6.2‰ , whereas the lower rhyolite magma values indicate derivation from a basaltic source material with $\delta^{18}\text{O}$ values between 4.8 and 5.2‰ . The first set of values is within the accepted range for mantle-derived basalts. However, the second group of values are lower than would be expected for mantle-derived basalts and indicate low- $\delta^{18}\text{O}$ magmas as defined by Bindeman *et al.* (2004). The results of this study, therefore, indicate that the low- $\delta^{18}\text{O}$ rhyolites are restricted to specific horizons.

There are a number of ways in which low- $\delta^{18}\text{O}$ rhyolites can be produced (see below). However, the influence of any post-eruption alteration on the $\delta^{18}\text{O}$ values of the rhyolites must first be assessed, as post-eruption alteration can play an important role in generating low- $\delta^{18}\text{O}$ rocks. A simple way of assessing alteration effects is to consider the difference between the $\delta^{18}\text{O}_{\text{wr}}$ values and the calculated $\delta^{18}\text{O}$ magma values ($\Delta_{\text{wr-magma}}$). This difference varies largely as a function of alteration temperature (Fig. 15), assuming that mineral $\delta^{18}\text{O}$ values remain unchanged. A rock in which $\Delta_{\text{wr-magma}}$ is positive must have been affected by low-temperature alteration that caused the $\delta^{18}\text{O}_{\text{wr}}$ value to be raised. Conversely, a rhyolite where $\Delta_{\text{wr-magma}}$ is negative must have been affected by high-temperature alteration where the rock $\delta^{18}\text{O}$ value was lowered by exchange with water. The difference between high and low temperature, in this sense, corresponds to the temperature at which $\Delta_{\text{rock-water}}$

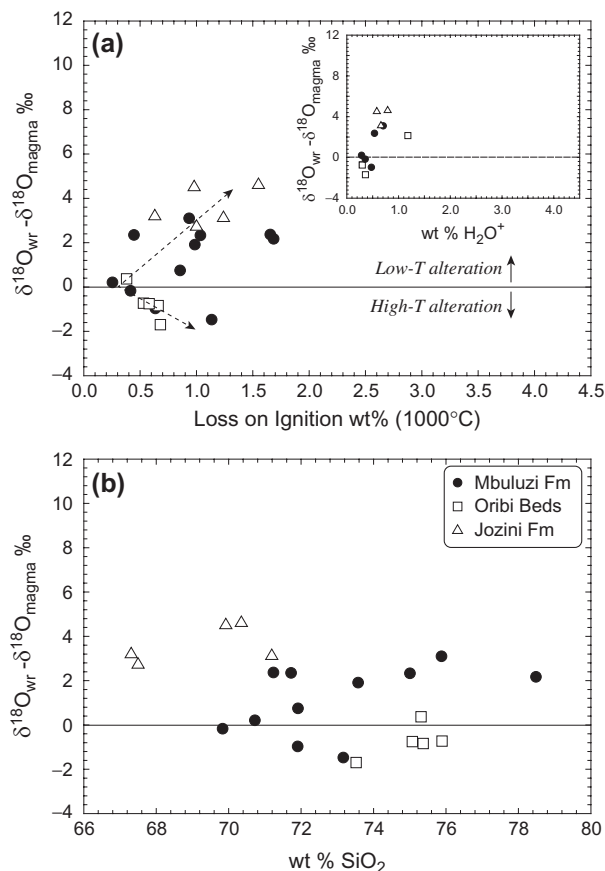


Fig. 15. Plot of (a) $\delta^{18}\text{O}_{\text{wr}} - \delta^{18}\text{O}_{\text{magma}}$ vs $\text{wt \%}$ loss on ignition at 1000°C (LOI) and (b) $\delta^{18}\text{O}_{\text{wr}} - \delta^{18}\text{O}_{\text{magma}}$ vs $\text{wt \% SiO}_2$. $\delta^{18}\text{O}_{\text{wr}}$ and $\delta^{18}\text{O}_{\text{magma}}$ values are from Table 2. Low-temperature alteration results in an increase in $\delta^{18}\text{O}_{\text{wr}}$ values and hence results in positive values of $\delta^{18}\text{O}_{\text{wr}} - \delta^{18}\text{O}_{\text{magma}}$. High-temperature alteration results in a decrease in $\delta^{18}\text{O}_{\text{wr}}$ values and hence results in negative values of $\delta^{18}\text{O}_{\text{wr}} - \delta^{18}\text{O}_{\text{magma}}$. Dashed arrows indicate visual best-fit lines.

is ~ 6 (about 280°C, assuming $\Delta_{\text{rock-water}} \sim \Delta_{\text{plagioclase-water}}$; O'Neil & Taylor, 1967). A simplified interpretation, which ignores water/rock ratios and the $\delta^{18}\text{O}$ value of the fluid, can be made with reference to Fig. 15, which plots $\Delta_{\text{wr-magma}}$ vs whole-rock $\text{wt \% SiO}_2$ and LOI (Fig. 15). The Oribi beds have $\Delta_{\text{wr-magma}}$ values that are all zero to negative, indicating that the Oribi beds have been affected largely by high-temperature alteration, whereas all of the Jozini rhyolites have positive $\Delta_{\text{wr-magma}}$ values and have therefore been affected largely by low-temperature alteration. Most Mbuluzi rhyolites have been affected by low-temperature alteration, but to a lesser extent than the Jozini rhyolites. There is, therefore, evidence for fluid-rock interaction in the Lebombo rhyolites, but $\delta^{18}\text{O}_{\text{wr}}$ values are not shifted significantly, which implies that there was not extensive post-eruption interaction between the rhyolites and meteoric water at either low or high temperatures. Furthermore, it has been

shown above that the rhyolites all have low $\text{wt \% H}_2\text{O}^+$ values (average 0.62 $\text{wt \%}$) and lack any correlation between δD and $\delta^{18}\text{O}_{\text{wr}}$ values (Fig. 9c), which would be expected if the rhyolites had undergone significant post-eruption interaction with fluids.

Formation of low- $\delta^{18}\text{O}$ rhyolites has been investigated by a number of workers and interpretations generally involve three main mechanisms: (1) interaction between the erupting rhyolitic magma and meteoric water at relatively high temperatures synchronously with eruption (Hildreth *et al.*, 1984, 1991); (2) assimilation of low- $\delta^{18}\text{O}$ material prior to eruption (Grunder, 1987); or (3) derivation from a low- $\delta^{18}\text{O}$ source (Condomines *et al.*, 1983; Bindeman *et al.*, 2004). Harris & Erlank (1992) concluded that derivation from a low- $\delta^{18}\text{O}$ source was the most likely mechanism for generating the low- $\delta^{18}\text{O}$ Lebombo rhyolites, and suggested that this source was underplated basalt affected by deep fluid-rock interaction. Before discussing whether this model can explain the data presented in this study, the relationship between the stable and radiogenic isotope data must be determined to assess the possibility of assimilation of low- $\delta^{18}\text{O}$ material.

Correlations between $\delta^{18}\text{O}$ and Sr and Nd isotopes

As discussed above, the $\delta^{18}\text{O}$ quartz values are unaffected by any alteration and the whole-rock initial Nd- and Sr-isotope ratios can reasonably be assumed to represent those of the original magma. The variation of $\delta^{18}\text{O}$ quartz values with ϵ_{Nd} and ϵ_{Sr} is shown in Fig. 16. For samples analysed in this study, ϵ_{Nd} values appear to be relatively constant (-0.5 to 0.5) regardless of the $\delta^{18}\text{O}$ quartz value (Fig. 16a). In comparison, the data of Harris & Erlank (1992) fall within two groups: two samples that have ϵ_{Nd} values in the same range as samples from this study, and five samples that have lower ϵ_{Nd} values (-3.7 to -1.6). However, comparison with Fig. 8 shows that ϵ_{Nd} values, which are close to Bulk Earth, show very little variation over a range of $\delta^{18}\text{O}$ quartz values, indicating that contamination by pre-Mesozoic crust was minimal. This suggests that the Nd-isotope composition of the rhyolites is a primary magmatic feature and that the process that caused modification of the rhyolite O-isotope values had no impact on the Nd-isotope values.

The relationship between ϵ_{Sr} and $\delta^{18}\text{O}$ quartz values is more complicated to interpret, and appear to show two data arrays highlighted in Fig. 16b. The first has constant ϵ_{Sr} with variable $\delta^{18}\text{O}$ quartz values. This group is defined by five samples of the Jozini rhyolite that come from south of the Sabie River (Fig. 1b). The second group involves the two samples of the Jozini rhyolites north of the Sabie River and the one sample of Oribi rhyolites analysed by Harris & Erlank (1992), as well as the Mbuluzi and Oribi rhyolite samples from this study. In this group, there is an overall negative correlation

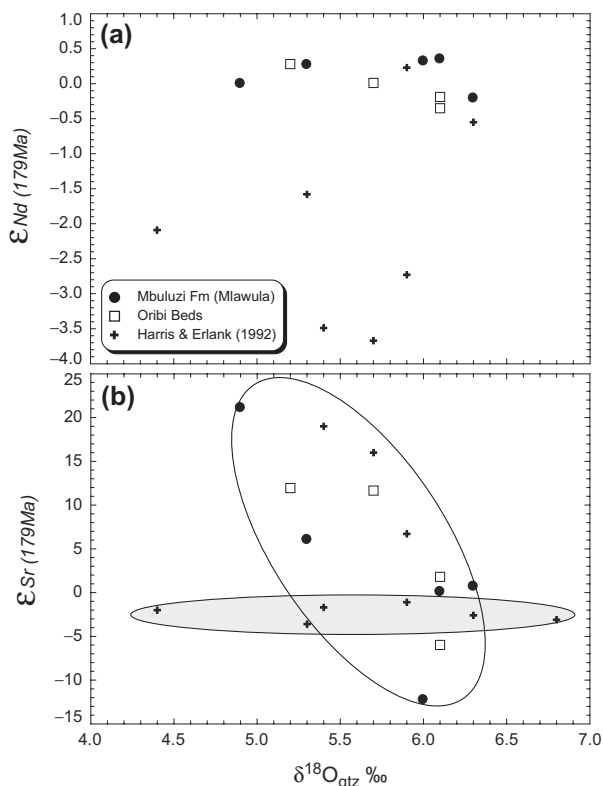


Fig. 16. (a) Variation of ϵ_{Nd} and (b) ϵ_{Sr} vs $\delta^{18}\text{O}$ quartz for the Jozini, Mbuluzi and Oribi Beds rhyolites as well as the data of Harris & Erlank (1992). Epsilon values calculated at 179 Ma using values for CHUR from Faure (1986).

between ϵ_{Sr} and $\delta^{18}\text{O}$ quartz values. The difference in the two data arrays probably reflects differences in the nature of fluid–rock interaction affecting the Jozini rhyolites as opposed to the Mbuluzi rhyolites (including the Oribi Beds) and lateral variations in the extent of fluid circulation. Negative correlations between O- and Sr-isotope values, especially when combined with constant Nd-isotope values, are often taken to indicate the effects of fluid–rock interaction at relatively high temperatures, because other possible mechanisms, such as the incorporation of older more radiogenic crustal material, should modify the Nd-isotope composition (e.g. McCulloch *et al.*, 1994; Dorendorf *et al.*, 2000; Bindeman *et al.*, 2004).

As the rhyolites are high-temperature magmas, their source must have been fairly dry and consequently fluid–rock interaction in the source must have occurred between 500 and 700°C. This would have decreased the $\delta^{18}\text{O}$ value of the source material without significant hydration. However, to elevate the Sr-isotope ratio, the fluid must have been Sr-bearing with a higher Sr-isotope ratio than 0.706, the initial Sr-isotope ratio of sample SR24, which has the highest initial Sr-isotope ratio. The two most likely sources for such a fluid are meteoric fluids that became enriched in ^{87}Sr by passing through

old-pre-Mesozoic rocks, or seawater that contained ~8 ppm Sr and that at 179 Ma had a Sr-isotope ratio of about 0.7074 (Faure, 1986).

The interaction of seawater with gabbroic and basaltic rocks of oceanic origin and its effects on Nd-, Sr- and O-isotope ratios has been discussed by McCulloch *et al.* (1980), who studied the variation of these isotope ratios with depth through the Cretaceous Samail ophiolite. Their findings were that Nd isotopes remained essentially unchanged, whereas O- and Sr-isotope ratios changed as a result of the fluid–rock interaction. The potential shift in Sr-isotope ratio is independent of temperature and interaction with seawater will always result in an increase in the Sr-isotope ratio. The magnitude of the shift depends on the water/rock (w/r) ratio. Interaction of seawater with gabbro can result in an increase or decrease in $\delta^{18}\text{O}_{\text{wr}}$ value, depending on the temperature of interaction. Below about 300°C, the $\delta^{18}\text{O}$ of the rock will increase as a result of interaction because $\Delta_{\text{rock-water}}$ is ~6. Above this temperature, the fractionation factor is smaller and interaction results in shifts to lower rock $\delta^{18}\text{O}$ values. The w/r ratio required to lower the $\delta^{18}\text{O}$ value of a gabbro from 5.7‰ (equivalent to a typical mantle-derived basalt) to 4.2‰ (rhyolite source) decreases from about 4 at 300°C, to 0.62 at 400°C, and to 0.26 at 800°C, assuming simple mass balance in a closed system (Taylor, 1977). If an open system is assumed, the w/r ratio is significantly lower at 300°C, but only slightly lower at 600°C. Much higher w/r ratios would have been required to increase ϵ_{Sr} from –15 to +19, assuming that the source material contained 136 ppm Sr (average value for SRBF LTZ). Simple mass-balance calculations using the equation of McCulloch *et al.* (1980) suggest w/r ratios ~200 times larger for Sr than the w/r ratio estimated for O isotopes at high temperature. Unless Sr exchange is much faster than O-isotope exchange, interaction between the source and seawater is not a viable way of producing the $\epsilon_{\text{Sr}}-\delta^{18}\text{O}$ quartz correlation. A seawater source for the fluids is also not supported by palaeogeographical reconstructions, which indicate that the closest seawater body was probably over 1000 km to the south of the Lebombo (Watkeys, 2002). Thus, on the basis of the geochemical data the most plausible mechanism for the generation of low- $\delta^{18}\text{O}$ source material and the relationship between the $\delta^{18}\text{O}$ quartz value and whole-rock initial Sr-isotope ratio is through high-temperature fluid–rock interaction of meteoric water that had passed through older continental crust prior to interacting with the source of the rhyolite magma. Because not all of the rhyolites have low $\delta^{18}\text{O}$ values, zones of fluid–rock interaction must have been unevenly distributed to account for the presence of both low- and normal- $\delta^{18}\text{O}$ rhyolite magmas. However, although the original model for the generation of the Lebombo rhyolites put forward by Cleverly *et al.* (1984) indicated the presence of pre-existing continental crust between the rhyolites and their source, it is not easy to explain how surface-derived fluids could

penetrate to such depths that they would be able to interact with the rhyolite magmas prior to eruption.

Nature and environment of fluid–rock interaction

A commonly invoked mechanism for generating low- $\delta^{18}\text{O}$ rhyolites is through recycling of older rhyolitic material that had interacted with meteoric fluids at high temperatures in large calderas (e.g. Lipman & Friedman, 1975; Grunder, 1987; Balsley & Gregory, 1998; Bindeman & Valley, 2000). Calderas are conducive to the production of low- $\delta^{18}\text{O}$ altered material (e.g. Taylor, 1987) because surface waters can penetrate down the ring faults and feed into convective hydrothermal systems. Harris & Erlank (1992) discounted this mechanism, first because of the lack of any geological evidence for calderas in the Lebombo, and second because of the lack of correlation between $\delta^{18}\text{O}$ magma values and the degree of fractional crystallization.

Although the locations of eruptive centres in the Lebombo are currently unknown, it is possible that the rhyolites were produced in large caldera systems that were not preserved because of opening of the Indian Ocean. The lack of preserved rhyolites with low $\delta^{18}\text{O}$ values is also difficult to reconcile with the caldera model, in that only nine out of 46 samples have $\delta^{18}\text{O}$ values $<5.0\text{‰}$ (Table 2). However, it is possible that rhyolites with appropriately low $\delta^{18}\text{O}$ existed only in the vicinity of the eruptive centres, where the degree of fluid–rock interaction is likely to be greatest and temperatures highest. The lack of correlation between the $\delta^{18}\text{O}$ values of the rhyolites and the degree of fractional crystallization suggests that the low- $\delta^{18}\text{O}$ rhyolite magmas were not produced by an assimilation–fractional crystallization (AFC) process. However, the absence of any AFC relationship can be explained if the low- $\delta^{18}\text{O}$ rhyolites were produced by mixing rhyolite magma with bulk melts of altered low- $\delta^{18}\text{O}$ rhyolite. Evidence for bulk melting or close to bulk melting of pre-existing rhyolite material has been found in other low- $\delta^{18}\text{O}$ rhyolite systems (e.g. Grunder, 1987; Balsley & Gregory, 1998) and cannot be excluded in the case of the Lebombo rhyolites. The Oribi Beds rhyolites record evidence for high-temperature fluid–rock interaction (as discussed above); these rhyolites form the flows at the base of the low- $\delta^{18}\text{O}$ horizon. Their presence is thus entirely consistent with the proposed model of high-temperature fluid–rock interaction driving the formation of the low- $\delta^{18}\text{O}$ rhyolite magmas. The increase in $\delta^{18}\text{O}$ values for younger rhyolite flows (Fig. 9e) has also been recognized in low- $\delta^{18}\text{O}$ rhyolite lavas formed in intracontinental caldera environments. In the case of low- $\delta^{18}\text{O}$ rhyolites from Yellowstone, this pattern has been ascribed to progressive remelting of later less ^{18}O -depleted rhyolite flows, as the earlier flows would have been closest to the magma

chamber and hence undergone the greatest degree of fluid–rock interaction (Bindeman & Valley, 2000).

CONCLUSIONS

Results of partial melting and fractional crystallization modelling, building on the original work of Cleverly *et al.* (1984), indicate that the Lebombo rhyolites represent 10% batch melts of a basaltic or gabbroic precursor. The modelling results in this study indicate that 10% batch melting of a mixture of 90% LTZ and 10% HTZ SRBF types best explains the observed trace-element patterns and that the differences between the three main rhyolite types, the Jozini and Mbuluzi rhyolites and Oribi Beds, can be explained by subsequent fractional crystallization of this partial melt. This is further supported by recent geochronological data, which indicate that there is little time difference between the formation of the basalt and rhyolite lavas (Riley *et al.*, 2004), and that the Rooi Rand dyke swarm may post-date the formation of both the basalts and the rhyolites. Stable isotope studies indicate that in the southern Lebombo both normal- and low- $\delta^{18}\text{O}$ rhyolites are present. A combination of stable and Sr- and Nd-isotope data suggests that the low- $\delta^{18}\text{O}$ rhyolites cannot have formed by combined fractional crystallization and assimilation of older crustal material with a low $\delta^{18}\text{O}$ value.

The previously proposed model of Harris & Erlank (1992) whereby the rhyolites are produced by the interaction of underplated basalt with deep circulating fluids is discounted because of the variability of $\delta^{18}\text{O}$ magma values, and the implausibility of fluids reaching such deep levels. Instead, the low $\delta^{18}\text{O}$ values of some of the rhyolite flows probably arose by remelting of early rhyolites whose $\delta^{18}\text{O}$ values had been lowered by fluid–rock interaction at high temperatures. The likely environment for this was in caldera systems to the east, which were not preserved after continental break-up. The stable and radiogenic isotope data combined indicate that fluid–rock interaction involved meteoric water, rather than seawater, that had passed through relatively young pre-Mesozoic crustal material, imparting a radiogenic Sr-isotope signature to the fluids but leaving the Nd-isotope composition unchanged. Crustal thinning facilitated fluid–rock interaction at the shallow-crustal levels, as the Lebombo rifted margin began to develop.

ACKNOWLEDGEMENTS

We are greatly indebted to Andy Duncan for the use of his unpublished Karoo database. Thanks go also to Fayrooza Rawoot, Andreas Späth, Dave Reid, Shireen Govender, Steve Richardson, John Lanham, Esmé Spicer and Johnny Smit for technical assistance. Jean-Francois Moyen improved the consistency and clarity of the

tables. This study was undertaken whilst J. A. Miller was a recipient of a University of Cape Town Postdoctoral Research Fellowship and a National Research Foundation Postdoctoral Fellowship. Funding was provided via an NRF core grant to C. Harris and a Stellenbosch University Young Researchers Fund Grant to J. A. Miller. The manuscript benefited from discussions with Scott Bryan and constructive and detailed reviews by Ilya Bindeman, Teal Riley and Richard Price.

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