

Rare earth element geochemistry of the Insizwa lobe of the Mount Ayliff Complex, Eastern Cape, South Africa

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New rare earth element (REE) data from all lithologies of the Insizwa lobe, Mount Ayliff Complex, are presented. On the basis of size and type of Eu anomaly, the geochemical subdivision of the complex as previously described is sustained and, additionally, the Top Gabbronorite of the Central Zone is shown to have formed from a magma that was compositionally distinct from other Central Zone magmas. The Basal Zone crystallized from magmas with large negative Eu anomalies probably acquired through crustal contamination. Previously recognized compositional heterogeneity in the contact rocks is also a feature of the REE. Overall, the Insizwa magmas had higher La/Sm ratios and, to a lesser extent, higher Gd/Yb ratios than Karoo basalts and appear to have no representatives in the basalt lava sequence of Lesotho.

Introduction

The Mount Ayliff Complex of Karoo age is a large dissected, transgressive intrusive sheet, up to 1.2 km thick, which is noteworthy for its strongly differentiated nature and associated Ni-Cu-PGE mineralization, which occurs at various places along the lower contact of the Insizwa lobe (see Maske and Cawthorn¹ and references therein). Between 1996 and 1998, several boreholes were drilled through the volumetrically dominant Central and Basal zones of the Insizwa lobe by Falconbridge Ventures of Africa. From detailed sampling of the core of borehole INS96-02 (Fig. 1), supplemented with samples from several other borehole cores, Marsh *et al.*² presented a large amount of geochemical data bearing on the overall structure and emplacement of the lobe. Their data suggested that the Insizwa intrusion was an open magmatic system in which the vertical sequence of gabbro-noritic and lherzolitic rocks was built from several intrusions of magma emplaced from the top down, i.e. Central Zone magmas intruded first, followed by the Basal Zone magmas. The data also suggest that the Central Zone rocks are plagioclase mesocumulates from which a significant proportion of intercumulus liquid has been lost as indicated by low incompatible element abundances and elevated Sr/Zr ratios. The Basal Zone rocks are olivine-enriched orthocumulates with low Sr/Zr ratio. In comparison with the basalt magma types building the main Lesotho volcanic sequence,³ Central Zone magmas have some geochemical affinity to the Senqu and Mothae chemical types in the upper part of the succession, but the Basal Zone magmas appear to have no volcanic equivalents. In this paper, I present rare earth element (REE) data which test and refine these results and extend the petrogenetic interpretation relating to the origin of the Insizwa lobe.

Sample material and analytical results

A subset of the samples in borehole INS96-02, and near-contact samples from boreholes INS98-05, INS96-01, INS98-08 and

INS98-04, studied in detail by Marsh *et al.*,² were analysed for REE and other elements by ICPMS at the University of Cape Town using techniques described in Le Roex *et al.*⁴ Analytical results are presented in Table 1 and summarized in Table 2 and Figs 1–5. Following convention, chondrite-normalized concentrations and ratios are indicated with an 'N' subscript, e.g. La_N and [La/Sm]_N. In the text and tables, samples are identified by borehole number and sample number, e.g. sample 56 from borehole INS98-08 is designated 08-56. The sequence in borehole INS96-02 is more complex than that encountered in other boreholes because the otherwise single lherzolite layer is 'split' by a package of gabbro-norites, and gabbro-noritic and sedimentary hornfels horizons.

Contact samples

All contact samples are from the Basal Zone and they exhibit a wide range in composition,² characterized by varying degrees of olivine enrichment as indicated by MgO ranging between 6.1% and 19.7%. On the basis of petrography, only one of the samples (05-110) has a true quench texture. To facilitate comparison, the REE concentrations in the olivine-enriched samples (05-110, 08-66, and 01-49) have been recalculated to an MgO content of 7% (typical of erupted Karoo basalt) by removing olivine with composition of Fo₈₆. The validity of this calculation arises from the demonstration that the contact samples lie on a mixing line between olivine of this composition and basalt with 7% MgO (ref. 2, fig. 14). The resulting chondrite-normalized REE patterns (Table 2 and Fig. 2) exhibit a wide range of REE contents, variable Eu anomalies, and some of the patterns cross one another. The absolute level of LREE concentration (as indicated by La_N in the contact 'liquids' at MgO = 7%) is within the range of Karoo basalt liquids.

The Main Insizwa sequence

Figure 1 shows chondrite-normalized REE profiles for the different units recognized by Marsh *et al.*² in the core of borehole INS96-02. For comparison, the REE profiles for fine-grained contact rocks in INS96-02 (samples 02-139 and 02-140) and for the olivine-corrected composition of contact sample 05-110 (see above) are also shown. Salient features of the REE data are summarized in Table 2, where comparisons can be made with contact samples and Karoo basalt data. Apart from the Interleaved Gabbro-norites, which will be discussed separately below, all other rocks have lower total REE than the contact rocks and the Karoo basalts (compare La_N in Table 2). Insizwa rocks (including most of the contact samples) have much higher [La/Sm]_N and overlapping or higher [Gd/Yb]_N values than Karoo basalts (Table 2). Eu anomalies are variable, ranging from distinctly negative to positive. On the basis of these anomalies, the previously recognized² subdivision of the sequence is confirmed with the Top Gabbro-norite having no Eu anomaly, the Cu-poor and Upper Gabbro-norite having positive Eu anomalies, and the Basal Zone lherzolites and gabbro-norites all having negative

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Table 1. Rare earth element analyses of Insizwa gabbronorites and lherzolites.

Borehole sample:	INS96-02	INS96-01	INS98-04	INS98-05	INS98-08
MgO (%)	6.81	19.55	6.78	17.75	11.36
Depth (m)*	-29.5	-460.3	-249.2	-1103.5	-818
La (ppm)	8.83	5.07	12	7.11	11.8
Ce	18.8	10.9	23.2	15.6	25.2
Pr	2.31	1.32	2.72	1.94	2.97
Nd	10.5	5.92	11.7	8.64	13
Sm	2.45	1.46	2.61	2.13	2.9
Eu	0.91	0.52	0.69	0.63	0.85
Gd	3.02	1.95	2.93	2.6	3.54
Tb	0.46	0.32	0.47	0.42	0.56
Dy	3.13	2.18	3.04	2.85	3.68
Ho	0.63	0.45	0.61	0.58	0.75
Er	1.81	1.35	1.81	1.73	2.18
Tm	0.25	0.19	0.25	0.24	0.3
Yb	1.66	1.31	1.7	1.61	2.04
Lu	0.24	0.19	0.24	0.24	0.29
[La/Sm] _N	2.325	2.242	2.968	2.155	2.548
[Gd/Yb] _N	1.51	1.23	1.43	1.34	1.43
Eu/Eu*	1.03	0.942	0.762	0.818	0.811

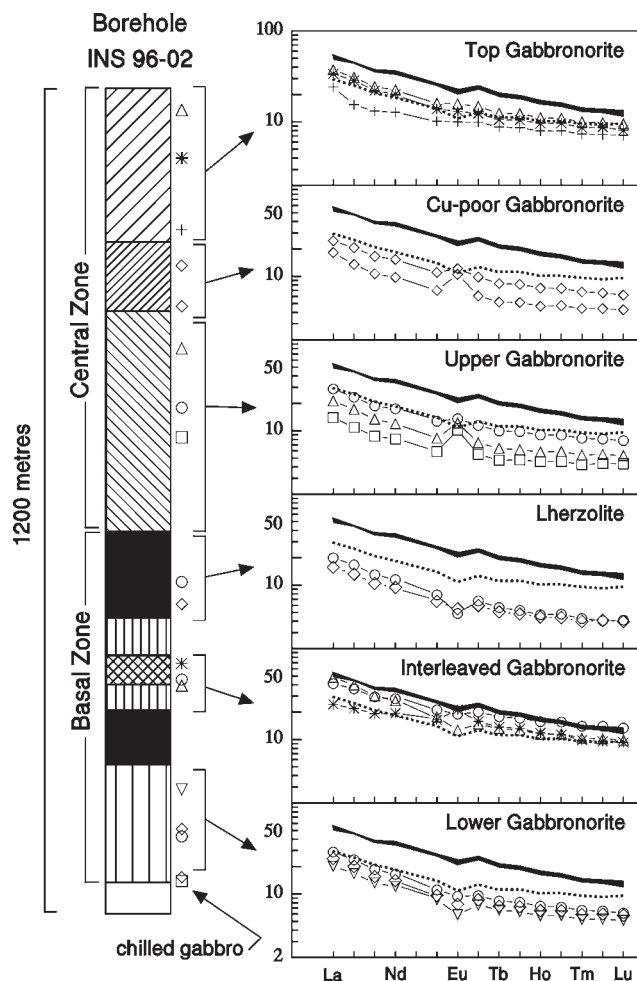


Fig. 1. Stratigraphic sequence in borehole INS96-02, showing sample locations and associated chondrite-normalized REE patterns. On the REE profiles the shaded pattern is for the two chilled gabbro samples (02-139 and 02-140) at the base of the core and the heavy dotted line is the profile for the olivine-corrected contact sample 05-110 (see text).

Eu anomalies.

REE data of cumulate rocks, particularly those with small fractions of trapped melt, may not accurately reflect the relative abundances of REE (La/Sm, Gd/Yb and Eu/Eu*) in the liquids from which they crystallized. With decreasing amounts of trapped liquid relative to cumulus minerals, the REE content of the rock is increasingly influenced by the REE content of the latter and, hence, by the mineral cumulus mode and their mineral/melt partition coefficients (*D*) for the REE. Thus the

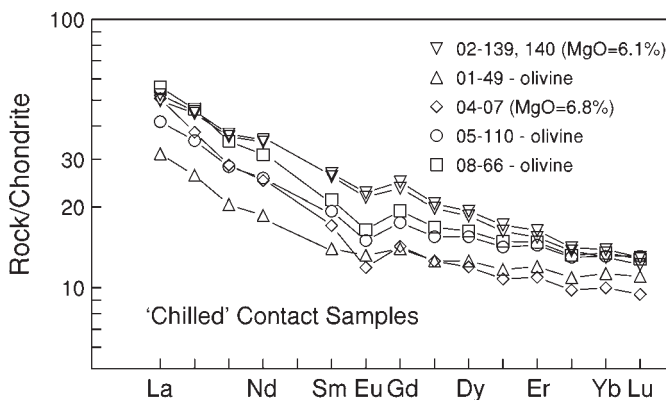


Fig. 2. Chondrite-normalized patterns for near-contact samples. For samples 01-49, 05-110 and 08-66 — all olivine-rich samples — the plotted patterns are for compositions recalculated to MgO = 7% as described in the text.

*Depth below borehole collar.

Table 2. Summary of REE data for Lesotho basalts and Insizwa.

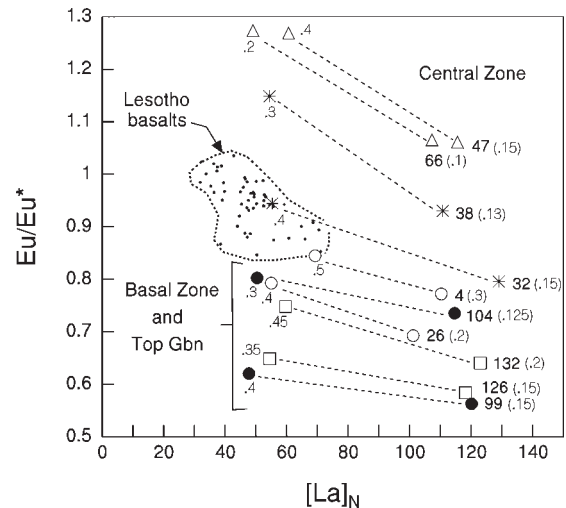
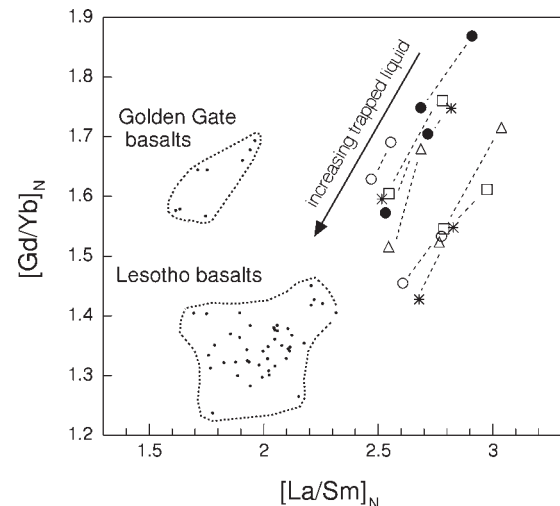
Unit	MgO	[La] _N	[La/Sm] _N	[Gd/Yb] _N	Eu/Eu*
Lesotho basalts in stratigraphic order					
Mothae (5)*	5.3–6.0	44–71	1.62–1.96	1.57–1.69	0.85–0.91
Senqu (10)	5.4–7.0	40–53	1.83–2.12	1.32–1.38	0.92–0.98
Maloti (8)	6.8–7.5	39–50	2.05–2.18	1.27–1.36	0.94–0.98
Mafika Lisiu (8)	7.4–8.6	32–43	1.77–1.98	1.24–1.41	0.97–1.02
Sani (2)	6.8–7.0	39–44	1.69–1.75	1.40	0.90–0.95
Wonderkop (5)	5.8–7.3	39–56	1.94–2.21	1.38–1.45	0.94–1.02
Golden Gate (8)	5.6–7.7	44–71	1.62–1.96	1.57–1.69	0.85–0.91
Insizwa borehole INS96-02					
Top Gbn (3)	6.8–11.4	24–37	2.33–2.43	1.36–1.51	0.99–1.03
Cu-poor Gbn (2)	6.6–10.9	18–25	2.23–2.61	1.38–1.50	1.17–1.61
Upper Gbn (3)	8.6–12.5	14–29	2.27–2.57	1.26–1.41	1.12–1.79
Lherzolite (2)	33–34	16–20	2.36–2.54	1.45–1.65	0.67–0.88
Lower Gbn (3)	13.5–25.8	20–29	2.35–2.61	1.43–1.47	0.73–0.91
Contact (2)	6.1–6.2	50–52	1.92–1.96	1.80	0.88
Other chilled contact samples**					
05–110 - ol	7	42	2.15	1.34	0.82
01–49 - ol	7	32	2.25	1.24	0.94
08–66 - ol	7	56	2.63	1.44	0.81
04–07	6.8	51	2.96	1.43	0.76

*Number of samples in brackets after unit name.

**Olivine corrected indicated by '- ol' where appropriate. See text for discussion.

apparent differences between the Insizwa rocks and Karoo basalts highlighted above need to be treated with caution. In order to understand the relationship of Insizwa liquids to the Karoo basalt magmas better, the REE content of liquids which were in equilibrium with the Insizwa cumulate rocks were calculated using the method of Bédard,⁵ which offers potential for examining the parental magmas of cumulate rocks.⁶ Similar calculations were advocated by Meurer and Boudreau.⁷ For Insizwa, the calculation utilizes modal data,² the whole-rock REE analyses (Table 1) and a set of mineral/melt partition coefficients which are very similar to those presented by Bédard⁵ but smoothed to eliminate irregularities between partition coefficients of adjacent REE (except, of course, for Eu). Importantly, the relative differences in the partition coefficients between LREE and HREE are very similar to those commonly used for modelling REE in mafic rocks. For each rock a number of calculations were made, assuming the presence of different amounts of trapped melt in the cumulate. Calculations were carried out assuming that the trapped melt crystallized minerals in the same modal proportions as in the individual rock. This is unrealistic and calculations were repeated using the non-modal 'back-stripping' proportions suggested by Bédard⁵ but results were similar to modal back-stripping. Calculations were also repeated using different sets of partition coefficients, particularly those for augite, within the range of commonly accepted values. These calculations do not significantly influence the overall results, which are summarized in Figs 3 and 4, where comparisons are also made with Karoo basalt data.

Figure 3 indicates that for calculated Insizwa liquids with La concentrations approaching those of Karoo basalts ($La_N = 30–60$), the Insizwa rocks would have to contain a significant fraction of trapped liquid (30–50%). Moreover, the Eu/Eu* values in these liquids vary widely and over a much greater range than found in the basalts. Specifically, the calculations indicate that Basal Zone rocks crystallized from liquids with distinctly negative Eu anomalies, whereas those from the Central Zone formed from liquids with slight negative or positive Eu anomalies. Figure 4 shows that calculated liquids have much higher $[Gd/Yb]_N$ and $[La/Sm]_N$ values than Karoo basalts and decrease on a steep trajectory with increasing amount of trapped liquid. Liquids at the left-hand end of the

**Fig. 3.** Calculated Eu/Eu* and La_N values in liquids in equilibrium with Insizwa gabbro (Gbn) cumulates compared to Karoo basalts of Lesotho (unpublished data). Bold font, sample numbers; light font, assumed fraction of trapped liquid in the calculation.**Fig. 4.** Comparison of relative fractionation amongst REE in calculated Insizwa liquids and in Karoo basalts from Lesotho. Symbols and trapped liquid fractions are the same as in Fig. 3.

calculated trajectories have La contents equivalent to typical Karoo basalt (see Fig. 3), yet $[Gd/Yb]_N$ and particularly $[La/Sm]_N$ remain significantly greater than in the basalts.

Discussion

The Central Zone

The Central Zone rocks were distinguished by elevated Sr/Zr and Sr/Al₂O₃ and lower Ni/MgO ratios and overall lower olivine content compared to the Basal Zone gabbroites.² Other criteria (e.g. Cu/Zr) allowed subdivision into Top, Cu-poor and Upper Gabbroite units. The Sr/Zr ratio is useful to identify rocks in which plagioclase ($D_{Sr}^x \approx 2$) has accumulated relative to the melt fraction, whose abundance can be monitored by the concentration of an incompatible element (e.g. either large ion lithophile elements such as K and Rb or high field strength elements such as Zr, P and Nb). In Insizwa rocks, Zr is strongly correlated with K, P, etc. and, given its well-known immobility during alteration and weathering as well as the precision with which it can be determined by X-ray fluorescence spectrometry, it is an ideal element to monitor the liquid fraction in tholeiitic cumulate rocks. Thus, the overall elevated Sr/Zr ratio (>4) and

low Zr concentrations suggest that plagioclase was an important cumulus phase in the Central Zone and the gabbronorites were probably mesocumulates from which the intercumulus liquid had been expelled. The REE data for samples of the Upper and Cu-poor gabbronorites support these conclusions in that they have lower REE contents and distinct positive Eu anomalies.

The lack of an Eu anomaly ($\text{Eu}/\text{Eu}^* = 0.99\text{--}1.03$) clearly distinguishes the Top Gabbronorite from the other units in the Central Zone. This feature seems inconsistent with the elevated Sr/Zr (>4) and the interpretation of this feature offered above. There are two possibilities. First, the Top Gabbronorites are indeed mesocumulates depleted in intercumulus liquid but they crystallized from a more evolved liquid with a significant negative Eu anomaly and 'normal' Sr/Zr ratio. Loss of intercumulus liquid increased Sr/Zr and Eu in the residue to the extent that the Eu anomaly was fortuitously eliminated in the cumulates. Alternatively, the Top Gabbronorite is an orthocumulate sequence crystallized from a liquid which is compositionally distinct from those forming other Central Zone rocks in having elevated Sr relative to other incompatible elements (LREE, Zr, etc.). The REE data indicate, however, that the Top Gabbronorite formed from a magma which was compositionally distinct from other Central Zone magmas.

The Basal Zone (excluding the Interleaved Gabbronorites)

Marsh *et al.*² demonstrated that the diverse lithologies in the olivine-enriched Basal Zone exhibit a coherent set of compositional characteristics, specifically low Sr/Zr (1–4), which coincides with the range for Karoo basalts (97% of 443 basalts have Sr/Zr = 1–3). They interpreted this to mean that the rocks were essentially orthocumulates determined largely by sorting of mafic phases relative to liquid with no significant loss of intercumulus liquid relative to plagioclase. In a few samples with slightly higher Sr/Zr, there is petrographic evidence of early crystallization of plagioclase and possible cumulus enrichment of this phase. The lack of positive Eu anomalies in the Basal Zone rocks is consistent with this interpretation. However, it is notable that the size of the negative Eu anomalies in the lherzolite and Lower Gabbronorite is significantly larger than in Karoo basalts. As shown in Fig. 3, the implication is that Basal Zone magmas had a distinctly negative Eu anomaly, but the question remains how this feature was acquired.

Negative Eu anomalies can be generated if the Basal Zone magmas were initially 'normal' with respect to Eu/Eu^* (Eu/Eu^* approximately 1) but fractionated significant plagioclase prior to emplacement at Insizwa. Studies on differentiation of Karoo basaltic magma⁸ indicate that significant negative Eu anomalies of the magnitude of those in the Basal Zone rocks develop only by plagioclase fractionation in evolved magmas where olivine is no longer a liquid phase. In the case of Insizwa, it is difficult to understand how such differentiated magmas could then generate the abundant olivine-enriched rocks of the Basal Zone. Alternatively, the magmas could have equilibrated with feldspathic rocks prior to intrusion. Basal Zone rocks have high initial Sr-isotopic compositions (0.7067–0.7099).^{9,10} These have been interpreted²⁹ in terms of interaction of Insizwa magmas with metamorphic rocks, including feldspathic gneisses, of the underlying Namaqua-Natal Mobile Belt that underlies the Karoo sequence at Insizwa. The most likely form of such interaction is one where the mafic magmas are contaminated with partial melts from such gneisses.

Interleaved Gabbronorites

This is a complex zone characterized by a 50-m-thick sequence of thermally metamorphosed (hornfelsed) gabbronorites with

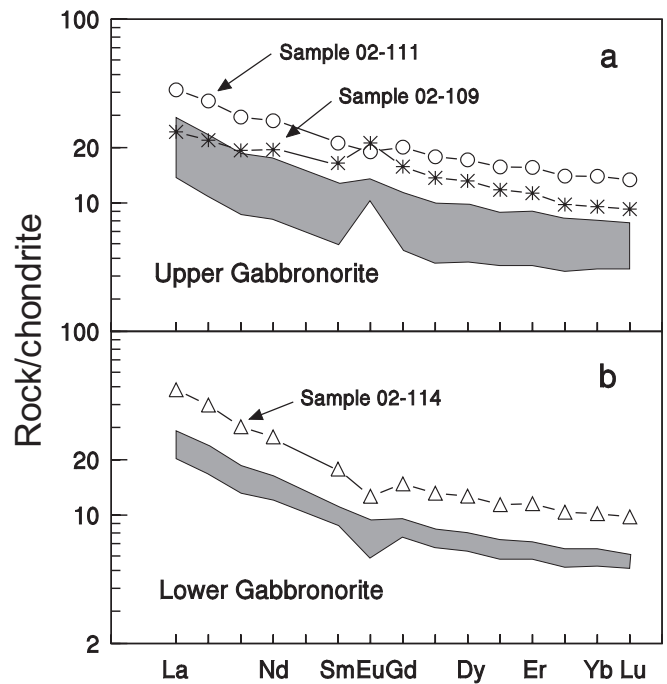


Fig. 5. Comparison of REE profiles for gabbronorites in the Interleaved Gabbronorite sequence with those of rocks in (a) the Upper and (b) the Lower Gabbronorite sequence (shaded field).

distinctive granoblastic and poikiloblastic textures, interleaved with two sedimentary hornfels screens and displaying three internal chilled horizons (evidence of multiple intrusion). The metamorphosed sequence is sandwiched between olivine-rich gabbronorites which are chilled against them and grade into the upper and lower lherzolite of the Basal Zone — see fig. 6 in Marsh *et al.*² These authors showed that the metamorphosed sequence has chemical characteristics of the Central Zone gabbronorites, whereas the enclosing olivine-rich gabbronorites were chemically similar to the Lower Gabbronorite below the lherzolite. These chemical correlations are the basis for their conclusion² that the Central Zone was emplaced before the Basal Zone.

The REE profiles for two samples of the internal chilled zones in the hornfelsed gabbronorites (02-109 and 02-111) and a sample of the chilled olivine-rich gabbronorite below the metamorphosed sequence (02-114) are shown in Fig. 5. The REE concentrations in these samples are similar to those of the chill zone reference samples, indicating that these rocks are probably not cumulates but represent crystallized liquids. Figure 5b compares the REE profile for 02-114 with those of the Lower Gabbronorites. Although 02-114 is enriched in REE, the profiles are parallel and 02-114 also has a distinct Eu anomaly ($\text{Eu}/\text{Eu}^* = 0.78$). A liquid with these characteristics could have given rise to the Lower Gabbronorites through accumulation of mafic phases and in some cases a little plagioclase. The distinct negative Eu anomaly in 02-114 is consistent with interpretations made above that the Basal Zone magmas had distinctly larger negative Eu anomalies than normal Karoo basalts.

Of the metamorphosed gabbronorites, sample 02-111 has a REE profile parallel to those of the Upper Gabbronorites but with slight negative Eu anomaly ($\text{Eu}/\text{Eu}^* = 0.92$). These features are consistent with this sample being representative of a magma from which the Upper Gabbronorites formed by accumulation of plagioclase and mafic phases as suggested previously.² Sample 02-109 is plagioclase phyrlic and in contact with sedimentary hornfels screens. The plagioclase phyrlic character is consis-

tent with the positive Eu anomaly, but $[La/Sm]_N$ is clearly lower than in the Upper Gabbonorites and 02-111. Despite the evidence of other chemical features, the REE data do not unambiguously confirm that the metamorphosed gabbonorites have an affinity to Central Zone magmas.

Conclusions

The REE data support and extend the conclusions (based on other compositional features) of Marsh *et al.*² Previously, the Top Gabbonorite was regarded as having strong geochemical affinities to the Upper Gabbonorite, albeit more evolved, but the REE data indicate that these rocks have crystallized from a magma which was geochemically distinct from that forming the Upper Gabbonorite. The previous suggestion that the Central Zone magmas had chemical affinities with the Senqu or Mothae chemical types in the basalt sequence is precluded by La/Sm and Gd/Yb data. The Basal Zone magmas had large negative Eu anomalies, which were most probably acquired through crustal contamination as suggested by high initial $^{87}Sr/^{86}Sr$. Overall, the Insizwa magmas were compositionally heterogeneous with regard to REE and do not correlate with any of the known major chemical types in the Lesotho basalt sequence, but may have been derived from one of these types by crustal contamination.

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The kaolinitic clay deposits on Beaconsfield, north of Grahamstown

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The Grahamstown clay deposits occur below the Grahamstown Formation silcrete, which forms a remnant of an extensive peneplain that developed on the African erosion surface during the Cretaceous–Tertiary period. This paper provides new data on the distribution of the kaolinitic clay deposits in the Beaconsfield area north of Grahamstown. These data include 23 borehole profiles through the deposits, and the chemistry and mineralogy of the clays. Relatively little information is available on this part of the peneplain. It was found that the thickness of the kaolin horizon varies considerably, but reaches 35 m in places. It generally occurs under a silcrete cover, which attains a thickness of 8 m in places. Lithological logs enable direct comparison across the Beaconsfield area. The clays are developed in both the Witteberg Group shale and Dwyka Group tillite. The contact between the clay and underlying bedrock is gradational and relatively uneven. Major-element X-ray fluorescence analyses revealed that there is chemical variation, both vertically and laterally. Al_2O_3 content is generally near 20%, but may reach 29%. SiO_2 content varies between 55 and 70+%. SiO_2 contents are highest in the silcretes occurring just below soil level. Fe_2O_3 is high locally in the top part of the profile. K_2O and Na_2O are generally low, but increase towards the unweathered bedrock as the primary feldspar content increases.

These compositional variations are compatible with residual concentrations of kaolinitic clays through deep weathering below the former African erosion surface.

Introduction

The Grahamstown area is situated in the eastern part of the Cape Fold Belt and is underlain by folded rocks of the Cape and Karoo supergroups (Fig. 1). The clay deposits are related to the Grahamstown Formation silcrete, an ancient pedogenic horizon which developed across the folded rock sequences on a broad, slightly concave, peneplain. Remnants of this peneplain owe their preservation to the resistant layer of silcrete, which hinders erosional destruction.^{1,2} Clay deposits underlie the peneplain and represent mainly the deeply weathered profile that developed during Cretaceous to Tertiary times.^{3–5}

This paper is concerned with the geology and mineralogy of the Beaconsfield area on the northern part of the peneplain. Recent mining and exploration activity has provided a number of vertical profiles through the deposits, and clay material for chemical and mineralogical analyses. No such data are presently available for this area.

Location and geology

The clay deposits described here are located about 7 km north of Grahamstown on Beaconsfield (33°51'S, 26°33'E), a subdivision of the farm Brakkefontein 243 (Fig. 2). The pit from which the clay is presently extracted lies at the northern edge of the Grahamstown Formation silcrete (also the edge of the peneplain).

The region is underlain mainly by rocks of the Witteberg Group of the Cape Supergroup, and the Dwyka and Ecga groups of the Karoo Supergroup (Fig. 1). In the general area, the oldest rocks of the Cape Supergroup are the shales and sandstones of the Weltevrede Formation, overlain by resistant quartz arenites of the Witpoort Formation. These quartzites are overlain by fine-grained shales and thin sandstones of the Lake Mentz and Kommadagga subgroups.⁴ The published geological map of the

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