Ti-rich chromite from the Mount Ayliff Intrusion, Transkei: Further evidence for high Ti tholeiitic magma

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ABSTRACT

Four profiles through the lower picritic portion of the Mount Ayliff Intrusion from the Karoo Igneous Province of South Africa have been studied. Many analyses of chromite grains enclosed in olivine show major differences from those found in most tholeiitic rocks, in that they are very high in Ti and Cr and are low in Al. Typical ranges for these elements are (as cation proportions recalculated to 32 O anions) Ti = 0.2-1.8 (0.8-8.8 wt% TiO₂); Cr = 6.3-11.1 (26-51 wt% Cr₂O₃); and Al = 2.2-5.0 (6.7-15.7 wt% Al₂O₃). Some of these are the most Ti-rich chromites recorded from any tholeiitic suite. The lowest Ti contents occur in the olivine gabbros immediately adjacent to the floor contact. Their compositions are typical of tholeiitic chromite and cannot be related by fractional crystallization to the Ti-rich chromite trends in the overlying picrite, as that would require an increase in Ti and Cr.

Models involving exsolution, postcumulus modification of chromite composition by infiltrating residual magma, or subsolidus reequilibration are rejected for the following reasons. The required Cr content of original olivine would have been unrealistically high. Most analyses are of grains totally embedded in olivine; therefore, the potential for reaction with residual magma is restricted. Analyses of chromite grains interstitial to the olivine and enclosed in postcumulus phases, and therefore exposed to residual magma, do not show trends of increasing Cr and Ti. In examples where reaction with residual liquid have been documented in detail (Jimberlana and Rhum Intrusions), there are no analyses of chromite with high Ti and Cr content comparable to those reported here.

Comparison of these Ti- and Cr-rich chromite samples with other intrusive and extrusive tholeiitic suites, and experimental studies indicate that these compositions could not form from a typical continental tholeiite, but probably crystallized from a magma with high Ti content. The closest analogues to these chromite compositions in tholeiitic rocks are high-Ti tholeiites found in Hawaiian lava lakes. It is suggested that the Mount Ayliff Intrusion formed from at least two injections of magma of different compositions, one being enriched in Ti.

Chromite compositions from the different profiles through the intrusion show different trends. In the Mount Evelyn profile, the effects of differentiation and mixing can be identified and distinguished, whereas, in the Siroqobeni and Ingeli profiles, the chromite compositions reflect a prolonged period of slow mixing. Data from a restricted interval of the Waterfall Gorge profile at the base of the picrite indicate that the chromite formed from a typical continental tholeiite. This interpretation of multiple intrusion and mixing of geochemically distinct magmas is consistent with previously published data on Mg-rich ilmenite compositions.

INTRODUCTION

An extensive province of intrusive and extrusive basaltic magmatic activity occurs in southern Africa (Cox, 1983; Bristow and Saggerson, 1983; Eales et al., 1984). The dolerite sheets are now known to extend at least as

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Fig. 1. Simplified geological map of the Mount Ayliff Intrusion (from Maske and Cawthorn, 1986), showing localities of the profiles sampled at Mount Evelyn, Waterfall Gorge, Siroqobeni, and Endageni.

far north as Malawi (Woolley et al., 1979; MacDonald et al., 1983). The Mount Ayliff Intrusion, which is approximately 600 m thick and crops out over an area of approximately 1000 km², is one of the thickest of these intrusive sheets. It has been the focus of considerable interest for over 100 years because of the presence of magmatic nickel-copper-platinum sulphide mineraliza-

tion at the base of the intrusion (Du Toit, 1910; Scholtz, 1936; Dowset and Reid, 1967; Tischler et al., 1981; Lightfoot et al., 1984; Groves et al., 1986; Maske and Cawthorn, 1986). Based on its silicate mineralogy and differentiation sequence from picrite, through hypersthene gabbro to quartz diorite (Scholtz, 1936), it has been regarded as the product of fractional crystallization



Fig. 2. Typical sections through the Mount Ayliff Intrusion, including mineral compositions. Data for the lower part of Waterfall Gorge from Lightfoot et al. (1984); other data from Maske and Cawthorn (1986) and Cawthorn et al. (1986).

of a typical continental tholeiitic magma, referred to as the Lesotho-type by Marsh and Eales (1984). However, Cawthorn et al. (1985, 1988) have documented the presence of ilmenite containing up to 10 wt% MgO in the lower, ultramafic portion of the intrusion, and suggested that the magma was possibly analogous to the Letaba basalt type that is enriched in incompatible elements, recognized by Bristow and Saggerson (1983) from the Lebombo and Nuanetsi regions of the Karoo Province. This interpretation has been debated by Lightfoot and Naldrett (1984) and Lightfoot et al. (1987), who suggest that the unusual ilmenite composition is the result of subsolidus reequilibration with olivine.

In this study, we document the composition of Ti-rich chromite in the lower units of this intrusion as it places further constraints on the nature of the parental magma or magmas and crystallization history.

MOUNT AYLIFF INTRUSION

The Insizwa body is the largest of four adjacent bodies: Insizwa, Tonti, Tabankulu, and Ingeli (Fig. 1), collectively referred to as the Mount Ayliff Intrusion (Scholtz, 1936; Cawthorn et al., 1988). Typical sections are shown in Figure 2. They have a marginal medium-grained olivine gabbro, overlain by laterally variable layers of picrite and troctolite, together referred to as the basal zone. Above this occurs a central zone of hypersthene gabbro with minor olivine- and quartz-bearing horizons. A discontinuous upper zone of quartz diorite and monzonite is located above the central zone.

The exact age of this intrusion is unknown but is assumed to be comparable to the geographically related dolerite sills approximately 190 m.y. old (Bristow and Saggerson, 1983). Attempts to date this intrusion by Rb/ Sr and Sm/Nd isotope techniques merely demonstrated that there had been multiple intrusion or variable contamination or both (Lightfoot et al., 1984).

In this study, chromite analyses from the picrite and under- and overlying olivine hypersthene gabbro are reported. Vertical profiles (Fig. 1) have been taken through the north end of the Tonti lobe (Mount Evelyn profile), through the Insizwa lobe, 8 km northeast of the mineralized Waterfall Gorge area (Siroqobeni profile), and through the Ingeli lobe (Endageni profile). Samples were also obtained from the mine workings at Waterfall Gorge covering a vertical section of only 10 m from the mineralized horizon at the base of the picrite (Waterfall Gorge profile). These profiles offer the most nearly continuous sections through the picrite. Additional data have been included from the Tabankulu lobe (Lightfoot and Naldrett, 1983).

The lower contact is poorly exposed and can usually only be located to within a few meters in the field. However, at Waterfall Gorge and at Mount Evelyn, the basal contact is exposed and a thin zone of olivine gabbro is developed; this zone is 10 m thick at the first locality and only 2 m thick at the second. In some sections, the lower contact of the picrite with this olivine gabbro is sharp, but in both instances examined here it is gradational. The upper contact of the picrite is not exposed on any of the specific profiles traversed, but an extremely sharp contact was located about 2 km southwest of the Mount Evelyn profile. At this boundary, the modal content of olivine drops abruptly from 65 to 24 vol%. This differs from previous inferences regarding this contact (Scholtz, 1936; Lightfoot et al., 1984), where plots of modal proportions suggest a thick, gradational contact.

PETROGRAPHY

Nearly all of the samples studied are picrites. The only exceptions are the lowest (21/1) and three uppermost (21/9)to 21/11) samples from the Mount Evelyn profile. Although sample 21/1 comes from within 1 m of the floor contact, it is medium grained. Olivine shows extensive corrosion features even when in contact with, or enclosed by, plagioclase; however, enclosure by clinopyroxene and orthopyroxene is more common (Tischler et al., 1981; Lightfoot and Naldrett, 1984). Orthopyroxene, clinopyroxene, and plagioclase are generally anhedral to subhedral, although there are a few euhedral plagioclase laths which develop an ophitic texture with the pyroxenes. The grain size of these matrix grains is typically from 0.1 to 0.2 cm. Chromite occurs as small euhedral grains embedded in olivine and all of the intercumulus minerals. A few show minor exsolution of ilmenite. Biotite, ilmenite, and sulfides are present as very minor constituents.

Picrite samples typically contain between 60 and 70 modal% olivine. With increasing height in the sections, the olivine grains take on an equant shape. Plagioclase, orthopyroxene, and clinopyroxene are present as poikilitic grains up to 0.5 cm in size. The pyroxenes show slight exsolution. Ilmenite is a minor phase and is euhedral when enclosed in plagioclase and pyroxene; whereas, biotite is considerably more common but anhedral.



Fig. 3. Plot of Cr-Al-Fe³⁺ + 2Ti for compositions of chromite in olivine. Lines of constant Cr/Al ratio are shown. The encircled field for Mount Evelyn refers to samples from the picrite only. In this and subsequent plots many data points are excluded because of overlap.

Toward the top of the picrite, plagioclase becomes more abundant, but remains poikilitic and intercumulus. The upper contact of the picrite is taken as the point where the plagioclase becomes a cumulus phase. Where this contact is exposed, the modal plagioclase content increas-



Fig. 4. Plot of cation Cr + Al vs. Ti for chromite compositions, based on 32 O anions. Symbols as in Figure 3.

es abruptly from 26 to 46 vol%. The olivine content decreases to 20% at this level in the Mount Evelyn profile, and then olivine gradually disappears over a height of 50 m. Subhedral orthopyroxene and clinpyroxene crystals are present in approximately equal proportions throughout the olivine hypersthene gabbro facies above the picrite. In the Siroqobeni profile, olivine grains devoid of chromite are present a short distance above the top of the picrite; therefore, there are no analyses from this ho-

TABLE 1. Analyses of chromite in olivine from the Mount Ayliff Intrusion

Profile Moun Sample	t Evelyn 21/1	21/1	21/2	21/2	21/3	21/3	21/4	21/4	21/5	21/5	
	,.		- 9-		- 110	=1/0	=.,.	= 17 1	21/0	21/0	
Height (m)	1	1	3	3	7	7	12	12	17	17	
TiO ₂	0.7	3.8	4.7	7.0	5.2	6.0	3.0	4.5	3.3	5.1	
Cr_2O_3	43.0	41.4	47.1	44.4	46.8	45.5	48.5	46.2	51.6	43.9	
Al ₂ O ₃	15.7	12.8	9.1	7.7	10.6	8.8	11.7	11.3	8.5	9.0	
Fe ₂ O ₃	6.5	6.6	3.2	3.5	2.0	3.3	2.2	2.7	2.6	5.9	
FeO	22.8	29.0	28.9	30.1	25.8	29.8	26.1	26.3	27.7	28.5	
MnO	0.3	0.3	0.3	0.4	0.3	0.4	0.3	0.3	0.3	0.4	
MgO	7.1	5.0	5.2	5.6	7.9	5.4	6.2	6.9	5.3	5.6	
Total	96.1	98.9	98.5	98.7	98.6	99.2	98.0	98.2	99.3	98.4	
Ti	0.14	0.78	0.99	1.47	1.06	1.26	0.61	0.92	0.69	1.07	
Cr	9.32	8.98	10.40	9.85	10.04	10.01	10.56	10.00	11.33	9.71	
AI	5.08	4.15	3.00	2.54	3.41	2.86	3.81	3.66	2.78	2.96	
Fe ³⁺	1.32	1.29	0.61	0.67	0.42	0.61	0.41	0.50	0.50	1.17	
Fe ²⁺	5.25	6.73	6.82	7.13	5.86	7.03	6.06	6.08	6.50	6.72	
Mn	0.07	0.07	0.07	0.09	0.07	0.09	0.07	0.07	0.07	0.09	
Mg	2.89	2.05	2.17	2.33	3.20	2.22	2.56	2.83	2.19	2.35	
Profile Moun	Profile Mount Evolution										
Sample	21/6	21/6	21/7	21/7	21/8	21/8	21/9	21/9	21/11	21/11	
- an option	=.,•	2110	21/7	- 1//	21/0	21/0	21/3	21/3	21/11	21/11	
Height (m)	23	23	39	39	58	58	62	62	93	93	
TiO ₂	3.2	6.3	3.4	3.4	4.8	8.8	3.6	5.2	5.1	4.3	
Cr ₂ O ₃	47.9	43.8	46.6	45.8	44.4	38.2	41.0	37.4	33.8	27.9	
AI ₂ O ₃	10.5	9.4	11.5	12.5	6.9	7.3	10.5	9.2	9.8	9.7	
Fe ₂ O ₃	3.9	3.9	3.9	4.0	8.4	8.7	9.1	11.0	14.6	20.9	
FeO	26.1	29.2	26.6	25.8	30.3	28.5	29.7	31.1	31.9	32.1	
FeO	26.1	29.2	26.6	25.8	30.3	28.5	29.7	31.1	31.9	32.1	
MnO	0.3	0.4	0.3	0.3	0.4	0.3	0.3	0.3	0.4	0.4	
MgO	6.3	6.1	6.1	6.9	4.4	7.9	4.2	3.9	3.5	2.9	
Iotal	98.2	99.1	98.4	98.7	99.6	99.7	98.4	98.1	99.1	98.2	
11	0.67	1.30	0.70	0.69	1.02	1.80	0.76	1.11	1.09	0.93	
UT AL	10.46	9.58	10.14	9.83	9.91	8.28	9.10	8.39	7.55	6.34	
AI Ea3t	3.43	3.06	3.72	4.02	2.28	2.37	3.47	3.09	3.27	3.28	
Fe ³⁺	0.75	0.75	0.73	0.77	1.76	1.74	1.89	2.30	2.99	4.51	
Fe ²⁺	6.10	6.80	6.20	5.91	7.18	6.57	7.02	7.45	7.64	7.70	
Min	0.07	0.09	0.07	0.07	0.09	0.07	0.07	0.07	0.09	0.09	
Mg	2.58	2.50	2.50	2.78	1.84	3.23	1.75	1.66	1.45	1.24	

rizon. In contrast, in the Mount Evelyn profile, chromite is present in the olivine grains throughout the entire 50 m-thick olivine-bearing horizon from which samples 21/9-21/11 are taken.

The picrite contains approximately 1-1.5 wt% of chromite (although point counting is statistically imprecise at such low abundances), the proportion of chromite inside olivine grains being less than that in the interstitial phases. The chromite grains tend to be clustered both within the olivine grains and interstitial to them. In the gabbroic rocks, the abundance decreases both within the olivine and interstitial to it. The chromite is always subhedral to euhedral and appears to be the same size whether inside or outside the olivine grains.

CHROMITE CHEMISTRY

Only chromite grains embedded in olivine are reported here. Analyses with the highest and lowest Cr content for each sample are given in Table 1. At least eight grains per sample have been analyzed. Multiple analyses of single grains indicate little variation: typically less than 0.6 wt% for Al_2O_3 , Cr_2O_3 , and Fe_{tot} . Different grains of chromite within a single olivine grain may show slight differ-

TABLE 1—Continued

ences. Such variations have been examined to see if chromite grains closer to the edge of olivine grains are systematically different from those nearer the center, analogous to the findings of Evans and Moore (1968), or to see if there is any variation as a function of size, as reported by Wilson (1982). Neither pattern could be established in our data. In some of the samples, large differences exist among chromite analyses from different olivine grains.

Chromite compositions are plotted in Figure 3, which shows the cation proportions of Cr-Al-(Fe³⁺ + 2Ti). The three complete profiles through the picrite occupy partially overlapping, but distinct fields. The samples from the picrite from Mount Evelyn have the highest combined Cr + Al contents; whereas, those from Siroqobeni have lower Cr + Al contents. The samples from the Ingeli profile generally have lower Cr/Al ratios than those from the Mount Evelyn profile. Chromite from Waterfall Gorge shows the widest range of compositions even though samples come from a restricted vertical section.

Further differences between the profiles are apparent in the cation plot of Cr + Al vs. Ti (Fig. 4). (These and all subsequent cation abundances quoted and presented in

Profile Siroo	obeni								Ingeli	
Sample	16/3	16/3	16/4	16/4	16/5	16/5	16/7	16/7	NGL/9	NGL/9
Height (m)	23	23	36	36	59	59	105	105	14	14
TIO ₂	2.5	4.7	4.0	6.4	2.4	3.6	4.3	3.3	2.7	4.1
Cr ₂ O ₃	40.3	33.1	38.3	31.2	40.0	35.7	37.4	25.3	41.7	38.5
Al ₂ O ₃	7.1	7.3	6.3	6.4	7.0	6.8	9.1	12.7	12.8	11.1
Fe ₂ O ₃	16.9	20.6	15.7	18.5	16.6	20.2	14.4	23.5	9.8	11.1
FeO	28.3	28.3	29.4	32.2	27.6	29.1	27.9	28.1	23.9	27.2
MnO	0.4	0.4	0.4	0.4	0.4	0.5	0.4	0.4	0.4	0.4
MgO	4.2	5.5	4.0	3.8	4.3	4.3	5.7	4.9	7.7	6.3
Total	99.7	99.9	98.1	98.9	98.3	100.2	99.2	98.2	99.0	98.7
Ti	0.53	0.98	0.87	1.39	0.52	0.77	0.90	0.70	0.55	0.85
Cr	9.03	7.34	8.74	7.09	9.07	7.98	8.21	5.56	8.86	8.40
AI	2.38	2.40	2.15	2.17	2.38	2.26	2.98	4.16	4.05	3.61
Fe ³⁺	3.53	4.29	3.36	3.95	3.50	4.23	2.97	4.84	1.98	2.30
Fe ²⁺	6.77	6.70	7.16	7.77	6.70	6.94	6.51	6.63	5.37	6.27
Mn	0.09	0.09	0.09	0.09	0.09	0.11	0.09	0.09	0.08	0.09
Mg	1.75	2.28	1.71	1.61	1.82	1.83	2.36	2.04	3.10	2.58
Profile Ingeli	Profile Ingeli				Waterfa	all Gorge				
Sample	NGL/11	NGL/11	NGL/54	NGL/54	WG/1	WG/1	GC692	GC692	GC697	GC697
Height (m)	28	28	110	110						
TiO ₂	2.3	1.4	1.8	3.8	2.6	2.8	0.6	0.9	2.7	4.4
Cr ₂ O ₃	44.2	43.0	43.7	38.5	45.0	39.8	42.3	39.6	38.7	29.8
Al ₂ O ₃	12.9	15.7	13.7	10.8	13.4	16.8	12.7	15.2	8.9	6.6
Fe ₂ O ₃	7.1	6.9	8.8	12.2	4.7	6.0	10.8	10.3	15.5	23.7
FeO	24.0	24.0	23.4	27.3	28.9	26.9	25.7	26.3	31.2	33.0
MnO	0.4	0.4	0.4	0.5	0.4	0.4	0.4	0.4	0.5	0.4
MgO	7.3	7.2	7.7	5.7	4.7	6.2	5.6	5.7	3.5	3.0
Total	98.2	98.6	99.5	98.8	99.7	98.9	98.1	98.4	101.0	100.9
Ti	0.47	0.29	0.36	0.78	0.54	0.55	0.11	0.18	0.56	0.94
Cr	9.49	9.08	9.22	8.40	9.67	8.41	9.20	8.50	8.49	6.65
AI	4.13	4.95	4.29	3.51	4.28	5.29	4.12	4.87	2.90	2.20
Fe ³⁺	1.44	1.39	1.76	2.53	0.97	1.20	2.44	2.27	3.49	5.27
Fe ²⁺	5.45	5.34	5.22	6.31	6.56	6.01	5.70	5.79	7.00	7.57
Mn	0.09	0.08	0.08	0.11	0.09	0.08	0.10	0.09	0.11	0.10
Mg	2.93	2.86	3.06	2.36	1.88	2.46	2.30	2.29	1.46	1.25

Note: For each sample, the chromite analysis with the highest and lowest Cr₂O₃ content is presented. Ferrous and ferric contents are calculated assuming stoichiometry, and cation proportions are calculated for 32 O anions per unit formula. Details of analytical techniques are presented in Cawthorn et al. (1988).

figures have been calculated to 32 O anions per formula unit.) This diagram is designed to illustrate the relationship between elements in chromite that tend to concentrate in the early stages of differentiation (Cr and Al) and Ti, which usually increases in more evolved compositions. Chromite grains in picrite from Mount Evelyn, Endageni, and Siroqobeni occupy distinct subparallel trends. In contrast, the data for Waterfall Gorge show a more rapid decrease in Cr + Al in the range 0.2–0.7 cations of Ti. Chromite analyses from the upper olivine hypersthene gabbro of the Mount Evelyn profile have values straddling the gap between the Mount Evelyn picrite and Waterfall Gorge trends.

DISCUSSION

Dick and Bullen (1984, p. 54) regard chromite as "petrological litmus paper, being extremely sensitive to host rock petrogenesis." We concur with this view and suggest that the composition of the chromite provides further insights into the origin and evolution of the Mount Avliff Intrusion. The most notable feature of some of these chromite compositions is their high Ti content, the highest value recorded being 1.8 cations of Ti per 32 O anions for a grain with 8.1 cations of Cr. Combined high Ti and Cr is anomalous for chromite formed from tholeiitic magmas. For example, chromite in continental layered intrusions, such as the Bushveld Complex, the Great Dyke, and the Stillwater Complex, has Ti values generally less than 0.2 cations (Jackson, 1969; De Waal, 1975; Cameron, 1977; Wilson, 1982; Eales and Reynolds, 1983). In extrusive continental tholeiites chromite is very scarce. It occurs in picritic rocks such as those at Baffin Island (Clarke, 1970) and Deccan Traps (Krishnamurthy and Cox, 1977) where the chromite contains less than 0.4 cations Ti. Similarly low Ti values are reported in chromite in MORB (Dick and Bullen, 1984; Allan et al., 1988) and ophiolites (Malpas and Strong, 1975).

In order to assess the significance of these chromite compositions, it is necessary to consider what processes may have affected their chemistry. Their composition may reflect the effects of (1) exsolution, (2) subsolidus reequilibration with host olivine, (3) reaction with interstitial liquid, and (4) the parental magma composition(s).

Exsolution

Barnes et al. (1988) suggested that chromite inclusions in olivine in very thick komatiitic flows were the result of exsolution from the olivine host. In this study, the percent of chromite included in olivine is approximately 1.5 wt%. The average chromite analysis contains 45 wt% Cr_2O_3 . Hence, to produce 1.5% of chromite by exsolution, the original olivine must have contained at least 0.68% Cr_2O_3 . Estimates of the Cr_2O_3 contents in komatiitic olivine range up to 0.3 wt% (Arndt et al., 1977). Donaldson (1982) suggested that this may be attributed to the very high temperatures of crystallization of forsteritic olivine in komatiite. This was partially confirmed by the experimental study of Murck and Campbell (1986) who showed that at 1400 °C, under reducing conditions, olivine (Fo₉₀) could contain up to 0.3% Cr₂O₃, but only up to 0.15% Cr₂O₃ (for Fo₈₅) at 1250 °C. The olivine crystallizing in the picrite of the Mount Ayliff Intrusion has a composition in the range Fo₈₅-Fo₇₉ (Lightfoot et al., 1984; Cawthorn et al., 1986) and, hence, would definitely not have contained the 0.68% Cr₂O₃ required to produce the proportion of chromite observed in olivine. Furthermore, the chromite in the olivine is euhedral and tends to be clustered and is, therefore, typical of magmatic processes rather than of exsolution.

Subsolidus reequilibration

Reaction between chromite and host silicate minerals in slowly cooled intrusions is well documented, although extremely variable (e.g., Cameron, 1975; Hamlyn and Keays, 1979; Wilson, 1982; Hatton and von Gruenewaldt, 1985). Lightfoot and Naldrett (1983) demonstrated this effect for chromite from the Tabankulu lobe of the Mount Ayliff Intrusion. In order to simplify this discussion, only chromite as inclusions in olivine is considered here. This does not imply that there is no reaction between chromite and olivine; indeed, a geothermometer has been determined for these phases (Jackson, 1969; Evans and Frost, 1975; Fabries, 1979; Roeder et al., 1979; Sack, 1982; O'Neill and Wall, 1987). However, the major exchange will be between Fe and Mg, not between Fe and Ti. If Ti were to increase during slow cooling, then there should be a systematic increase in Ti as a function of height in Figure 5, but the variation in Ti within one sample is greater than the variation in Ti in chromite samples from the bottom to the top of the sections.

Analyses of chromite enclosed in olivine from the Bushveld Complex (Hulbert and von Gruenewaldt, 1985) and the Great Dyke (Wilson, 1982) indicated extremely low Ti content. These are probably the most slowly cooled ultramafic intrusions and, as these show no evidence of increased Ti in chromite, it can be inferred that high Ti content in the chromites of the Mount Ayliff Intrusion cannot be attributed to subsolidus reequilibration with the host olivine.

Reaction with interstitial liquid

Several studies have shown that chromite will react rapidly with interstitial liquid (Henderson, 1975; Ridley, 1977; Henderson and Wood, 1981). Roeder and Campbell (1985) further suggested that interstitial liquid could penetrate into olivine grains along fractures to promote such reaction. In the latter study, it was suggested that the reaction involved an increase in Fe and Ti and a decrease in Mg and Cr in the chromite. Our data are compared with those reported by Roeder and Campbell (1985) in Figure 6. No individual analyses were presented, but the average for all of the chromite grains embed-



Fig. 5. Plot of Ti and Al cations, based on 32 O atoms, vs. stratigraphic height for all four profiles. Symbols as in Figure 3. The horizontal line indicates the range of compositions (56 analyses) found in the Waterfall Gorge section from a vertical interval of less than 10 m.

ded in olivine was quoted and is plotted on Figure 6. As the Jimberlana Intrusion is a large, slowly cooled body, there should have been a longer period of time for reaction to occur between chromite enclosed in olivine and interstitial liquid in this body than in the body of magma represented by samples taken a few tens of meters above the base of the much thinner (and hence more rapidly cooled) Mount Ayliff Intrusion. The low Ti content of the average analysis from Jimberlana suggests that the Ti enrichment of chromite enclosed in olivine caused by infiltrating magma is minimal, even in that intrusion, and can be expected to be even less in the Mount Ayliff Intrusion.

A further test for reaction with interstitial liquid may be made by comparing compositions of chromite enclosed in olivine with those enclosed in the interstitial phases. This is demonstrated for the Tabankulu lobe in Figure 6, where chromite from olivine, plagioclase, and pyroxene in three samples are presented. One sample shows chromite to be slightly enriched in Ti when enclosed in plagioclase and pyroxene relative to chromite enclosed in olivine. However, in the other two cases, the chromite enclosed in olivine actually contains significantly more Ti than the chromite enclosed in plagioclase and pyroxene. This suggests that, if there has been any reaction with interstitial liquid, then this reaction has decreased the Ti content of chromite that is unprotected by enclosure in cumulus olivine. Thus, the data for these samples argue against an increase in Ti caused by reaction with interstitial liquid.

In the Rhum Intrusion, the reaction of chromite with

interstitial liquid and postcumulus minerals has been documented by Henderson (1975) and Henderson and Wood (1981); in the Bushveld Complex, by Hulbert and von Gruenewaldt (1985) and Hatton and von Gruenewaldt (1985); in the Great Dyke, by Wilson (1982); and in the Panton Sill, by Hamlyn and Keays (1979). In none of these studies was Ti enrichment caused by the processes noted above. These intrusions are much thicker than the Mount Ayliff Intrusion, and therefore the time for, and the extent of, the reaction should have been greater. There appear to be no reported analogues to the Ti-rich chromites documented here in any of the olivinerich layered complexes, even when the reaction with interstitial magma has been specifically investigated. Although these arguments do not disprove any contribution from interstitial magma to changes in the composition of chromite embedded in olivine, such reaction does not explain the distinctive compositions observed.

Primary chromite compositions

The distinctive features of the chromite compositions are the association of high Cr and Ti, and relatively low Al, which are very unusual for tholeiitic rocks. However, these characteristics are reported in lunar spinels (Reid, 1971) and kimberlites (Haggerty, 1976; Pasteris, 1982).

The low Al values in some of the chromite analyses are anomalous for chromite in tholeiites. Experiments on tholeiitic compositions produce chromite with at least 3 cations Al per formula unit, and usually much higher (Hill and Roeder, 1974; Barnes, 1986; Murck and Campbell, 1986). Similarly, naturally occurring chromite in in-



Fig. 6. Plot of cations $Fe^{3+} + Fe^{2+}$ vs. Ti, based on 32 O atoms. Symbols as in Figure 3. The star indicates the average composition of chromite enclosed in olivine from the Jimberlana Intrusion (Roeder and Campbell, 1985). The three sets of tie lines joining points labeled FPA refer to analyses of chromite enclosed in olivine, pyroxene, and plagioclase, respectively, in single samples from the Tabankulu lobe (Lightfoot and Naldrett, 1983).

trusive and extrusive tholeiitic rocks ranges from 3-7 cations Al (Haggerty, 1976). Some of the chromite compositions shown in Figure 5 indicate that values as low as 2 Al cations per formula unit are found, and that in the picritic rocks, the Al content generally does not exceed 4 cations. Allan et al. (1988) suggested that Ti and Al demonstrate a strong negative correlation in spinels, and this is well demonstrated in our data.

Eales and Snowden (1979) suggested that the high Ti content in spinels could be attributed to rapid quenching and preservation of the true chromite composition, but exsolution of ilmenite during slow cooling could significantly change such compositions. In none of the samples studied does the grain size or texture suggest rapid cooling or disequilibrium crystallization of chromite. Moreover, there is no increase in Ti content close to the base of the profiles (Fig. 5), as would be expected if this process had occurred. In fact, the highest Ti content in chromite recorded for the Mount Evelyn profile is from a sample 58 m above the base and close to the contact of the upper picrite and olivine gabbro.

The Ti content of magmatic magnetite-rich spinels is influenced by f_{O_2} (Buddington and Lindsley, 1964). In order to test whether anomalously reducing conditions could have caused the crystallization of Ti-rich chromite, the ratio of 100 × Fe³⁺/Fe_{tot} is plotted against the Ti content of chromite in Figure 7. There is a considerable range in 100 × Fe³⁺/Fe_{tot} ratios, but there is no negative correlation, as predicted if f_{O_2} had influenced the chromite composition. In fact, for each profile, there appears to be a different range of 100 × Fe³⁺/Fe_{tot} ratios for similar Ti content. Furthermore, the experimental studies of Murck and Campbell (1986) and Barnes (1986) indicate



Fig. 7. Plot of $100 \times \text{Fe}^{3+}/\text{Fe}^{2+} + \text{Fe}^{3+}$ against Ti, based on 32 O anions for different profiles through Mount Ayliff Intrusion. Symbols as in Figure 3. All profiles show a similar range of Ti values, but $100 \times \text{Fe}^{3+}/\text{Fe}^{2+} + \text{Fe}^{3+}$ varies markedly.

no correlation between the Ti content of the chromite and f_{O_2} .

The extent of magmatic differentiation in these vertical sections may be evaluated by reference to the ratio of 100 \times Mg/(Mg + Fe) in both the olivine and chromite. The former has been presented by Cawthorn et al. (1986), who showed that the maximum range was from Fo₈₅ to Fo₇₉ in the picrite, but was more Fe-rich in the gabbro. The $100 \times Mg/(Mg + Fe^{2+})$ ratio of the chromite is shown in Figure 8. The general trends for the Ingeli and Siroqobeni profiles in which the samples are all picrites show little change in $100 \times Mg/(Mg + Fe)$ with height. However, for each individual sample, the range of values for different chromite grains is comparable to that of the total vertical range. Hence, there are no obvious differentiation trends for these profiles. Similarly, the trend for the picrites from Mount Evelyn shows little variation in the Mg/ (Mg + Fe) ratio with height, but samples from the overlying olivine gabbro display decreasing values. As the chromite from the gabbro from the Mount Evelyn profile is not enriched in Ti compared to chromite from the picrite (Fig. 5), the high Ti content observed for chromite in the picrite is not related to differentiation. The high Ti content of chromite associated with relatively forsteritic olivine indicates that the former is related more to the composition of the parental magma than the effects of differentiation.

Ti-rich chromite in other tholeiitic suites

No other examples of chromite with such high Cr and Ti contents in tholeiitic suites are known to the authors. The closest analogues are some spinels from Hawaii (Evans and Moore, 1968; Helz, 1987; Nicholls and Stout, 1988; Wilkinson and Hensel, 1988). They occur in lavas and lava lakes that contain relatively high TiO₂ (1.6 wt% TiO₂ at 16 wt% MgO; Wilkinson and Hensel, 1988). From a single sample, Nicholls and Stout (1988) reported two



Fig. 8. Plot of $100 \times Mg/(Mg + Fe^{2+})$ vs. height for profiles. The data from Waterfall Gorge are shown at constant height as the horizontal line.

chromite analyses with a range of composition from 0.38 to 0.92 cations Ti. This is not necessarily the total range in Ti for this sample; nonetheless, it illustrates that the range in Ti contents for individual samples shown in Figure 5 could be largely the result of magmatic processes.

Fig. 9. Plot of Cr vs. Ti for chromite from different profiles from the Mount Ayliff Intrusion compared with analyses from elsewhere in the Karoo, from other intrusions, and from Hawaii. For reference, the trend for chromite from certain Hawaiian lavas (Wilkinson and Hensel, 1988) is shown as a heavy line. (A) Data for Waterfall Gorge (crosses) and Mount Evelyn, each sample from Mount Evelyn is designated separately and grouped stratigraphically. (B) Data for Sirogobeni profile. (C) Chromite from other Karoo intrusive rocks is shown by open circles (Eales and Snowden, 1979; Eales et al., 1980). Analyses from Rhum Intrusion are shown as crosses, those designated I are inclusions in olivine, E are external to olivine (Henderson and Suddaby, 1971; Henderson and Wood, 1981). Analysis of chromite in olivine from the Jimberlana Intrusion is denoted by a star (Roeder and Campbell, 1985). Samples joined and denoted F, A, and P are chromites enclosed in forsteritic olivine, plagioclase, and pyroxene, respectively, from individual samples from the Tabankulu lobe (Lightfoot and Naldrett, 1983). (D) Schematic and simplified trends for different suites of tholeiitic rocks. Karoo, Hawaii, and Mount Evelyn refer to typical trends displayed by chromites from these localities. Dashed trends 1, 2, and 3 refer to trends in the Mount Evelyn and Sirogobeni profiles (see text).

Spinels from the Snake River Plain Basalts provide another possible analogue (Thompson, 1973), although none are as Cr-rich as those reported here. Again, the magmas had high TiO₂ contents (3-4 wt% TiO₂ at 5-7 wt% MgO).

A model for the crystallization of the Mount Ayliff Intrusion

Lightfoot et al. (1984, 1987) argued that the Mount Ayliff Intrusion had formed by olivine fractionation and accumulation from a typical continental basalt. This was debated by Cawthorn et al. (1988), based on the fact that the coexistence of olivine and highly magnesian ilmenite is unlikely in such a magma. They suggested that the variable Mg content of the ilmenite resulted from the





Fig. 10. Schematic sections through the intrusion depicting its evolution, by crystal accumulation, magma addition, and fractionation. In stage A, magma type 1 (low in Ti) is intruded and produces low-Ti chromite in olivine (hexagons with a black dot). This produces a significantly thick layer at Waterfall Gorge but is thin at Mount Evelyn. Stage B results when type 2 magma (high Ti) is added. The model requires it to be less dense than type 1 possibly because it is enriched in incompatible elements and volatiles. Inputs of less dense magma follow the fluid dynamic constraints discussed by Huppert et al. (1986). High-Ti chromite embedded in olivine (circles with black dots) crystallizes from this magma. It may remain suspended in the upper layer by turbulent convection (Tait, 1985) and eventually dump a thick succession of relatively homogeneous chromite and olivine (stage C, circles with dots). In the Mount Evelyn profile, the nearly constant composition of the chromite from 7 to 39 m (Fig. 9A) may result from this process. The density (σ) and temperature relationships of the two magmas are shown qualitatively on the right of each figure. The upper magma is required to be hotter than the lower so that heat will diffuse downward and, therefore, terminate crystallization of low-Ti chromite, at least while olivine is accumulating. Stage C shows the temper-

ature in the upper layer decreasing and the bulk density increasing to approach that of the lower layer. Crystallization of olivine will decrease the density of the residual liquid. However, if the olivine remains suspended in the upper magma, the bulk density will increase. Alternatively, olivine and plagioclase may be coprecipitating causing the density of the residual liquid to increase, but the plagioclase remains suspended in the upper liquid layer while olivine sinks, as suggested by Wilson et al. (1989) in the Great Dyke. At stage D, the densities of the two layers are now equal, so mixing is initiated. The chromite and olivine from this mixing process are denoted in stage E by the square symbol enclosing a dot, and these chromite grains will be intermediate between the high and low Ti compositions, as shown by the trends in Figure 9D (dashed lines 2 and 3) and corresponding to the compositions at 58 to 73 m in the Mount Evelyn profile. Stage F represents an alternative scenario to stages D and E, where further addition of and entrainment by more magma similar to type 1 composition (here denoted 3) occurs. The numbers (1-3; 7-39; 58-93) in stage F correspond to the heights, in meters, in the Mount Evelyn profile where such chromite inclusions in olivine occur.

mixing of a low-Ti and a high-Ti magma, the latter being analogous to the Letaba Basalts documented from several localities in the Karoo Volcanic Province (Bristow and Saggerson, 1983). It can also be argued that the occurrence of coexisting chromite and ilmenite is unknown in low-Ti tholeiitic magmas but was reported by Evans and Moore (1968) from the high-Ti lavas at Hawaii. The presence of magnesian ilmenite and the high Ti content of chromite both suggest that the magma from which they formed was Ti rich. These distinctive features are here integrated into a model for the crystallization of the Mount Ayliff Intrusion, with special emphasis on the origin of the chromite compositional relationships. The geochemical constraints imposed by the chromite compositions are shown in Figure 9 and the proposed processes operating within the magma chamber are illustrated in Figure 10.

In Figure 9, chromite from each sample is plotted separately so that trends, as a function of height, are seen. For reference, data from other Karoo intrusions (Eales, 1979; Eales and Snowden, 1979; Eales et al., 1980), the Rhum Intrusion (Henderson and Wood, 1981), and the Jimberlana Intrusion (Roeder and Campbell, 1985) are included. Collectively, these define the trend of typical low-Ti tholeiite, which is designated the Karoo trend, A, in Figure 9D. Also shown in Figure 9D is the Hawaii trend, C, based on data from Wilkinson and Hensel (1988) produced by the crystallization of chromite from a Tirich tholeiite.

The data from the limited section at Waterfall Gorge (Fig. 9A) plot close to the Karoo trend, and the chromite grains are interpreted to have crystallized from a low-Ti magma.

Analyses from the Mount Evelyn profile at 1 and 3 m are somewhat variable; several overlap the Karoo trend, whereas others are distinctly enriched in Ti and Cr relative to this trend. A model is suggested in Figures 10A, 10B, and 10C, whereby the injection of a low-Ti tholeiite is followed by a high-Ti tholeiite closer in composition to the tholeiite that produced the Ti-rich chromite from Hawaii. If it is related to the Letaba type of basalt, it would be enriched in incompatible elements including alkalis and H₂O, and, therefore, be less dense than the low-Ti magma. Coprecipitation of chromite and olivine from these two magmas leads to the range of chromite compositions observed (dashed line 1 in Fig. 9D). Samples from 7 to 39 m contain chromite with very high Ti and Cr content (Fig. 9A) and formed from the high-Ti magma. These samples show no systematic change as a function of height. With differentiation, the chromite composition evolves to lower Cr and higher Ti values, as shown by the sample at 58 m (Fig. 9A). The general Mount Evelyn trend, B, is shown in Figure 9D for samples from 7 to 58 m. From 62 to 73 m there is a change in trend with compositions becoming depleted in Ti at constant Cr. These compositions plot between those from the sample at 58 m and the middle of the Karoo trend. This is attributed to mixing between high-Ti and low-Ti magmas (dashed line 2 in Fig. 9D). The two magmas in the intrusion may mix as a result of changing densities (Figs. 10D and 10E), or there may be a second injection of low-Ti magma (Fig. 10F). Further differentiation of this mixed magma produced the chromite compositions observed for the sample at 93 m, which is relatively low in Cr and high in Ti (Fig. 9A).

The data for the Siroqobeni profile are shown in Figure 9B. These display a great variation in Ti with little range in Cr. Furthermore, there is no general trend of changing composition with height: the lowest sample at 16 m has high Ti content and the next sample at 23 m has one of the lowest Ti contents. The data are shown in Figure 9D as the trend denoted 3, a trend similar to, but more varied in composition than, that seen for the samples from 62 to 73 m in the Mount Evelyn profile. These data are interpreted as reflecting prolonged and incomplete mixing between a differentiated high-Ti magma (equivalent to the magma that produced the sample at 58 m in the Mount Evelyn profile) and a low-Ti magma. It is therefore possible that the lateral equivalent of the lowest part of the Mount Evelyn profile (below 58 m) is either missing or very compressed in the Siroqobeni section.

The general trend for samples from Ingeli is exactly the same as for those from Siroqobeni and, therefore, is not plotted in Figure 9. The slow mixing of magmas may also have taken place in this lobe of the intrusion.

The proposed intrusion relationships in Figure 10 are supported by evidence from the compositions of chromite interstitial to the olivine. The data from the Tabankulu lobe (Fig. 9C) show that chromite enclosed in olivine in two samples has a higher Ti content than spinel in the interstitial phases. If the chromite and its enclosing olivine formed from the high-Ti magma and sank into the basal layer of low-Ti magma (Fig. 10C), the intercumulus minerals would form from this latter magma. Specifically, the chromite interstitial to the olivine would be predicted to have a composition along the Karoo trend in Figure 9D, which is exactly what is observed. The same also applies to the pyroxene forming the interstitial component in the picrite. They also formed from the low-Ti magma and, hence, have low Ti contents.

CONCLUSIONS

The coexistence of chromite and ilmenite in picrite in the Mount Ayliff Intrusion is unique in tholeiitic intrusive suites. These are also the most Ti-rich chromite and Mg-rich ilmenite recorded in tholeiitic rocks. These features suggest that the chromite and ilmenite formed from Ti-rich magma. The chromites are also depleted in Al, which is consistent with the known incompatibility between Al and Ti in spinels.

Comparison with chromites in other intrusions that show evidence of reaction with interstitial liquid or of subsolidus reequilibration indicates that these unusual compositions cannot be attributed to such processes.

Low-Ti chromite grains with compositions typical of tholeiitic rocks occur as inclusions in olivine in gabbroic rocks above and below the picrite, suggesting that these formed from a low-Ti magma. It is therefore suggested that the intrusion is the product of multiple injection of contrasting magma types with different Ti contents. In one profile (Mount Evelyn), the chromite in the picrite shows evidence of restricted differentiation. In contrast, at the contact with gabbro and in two other profiles (Siroqobeni and Ingeli) there is a wide range in Ti content (with little change in Cr content of the chromite) which is thought to be caused by mixing between two magmas rather than by differentiation.

In another profile (Tabankulu), chromite interstitial to olivine is low in Ti, while chromite included in olivine is enriched in Ti. This is interpreted as the result of sinking of olivine with its included Ti-rich chromite from a higher stratified high-Ti magma into a low-Ti magma which then crystallized low-Ti chromite among the intercumulus phases.

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