

Oxide Minerals in a Layered Kimberlite-Carbonate Sill from Benfontein, South Africa

Nabil Z. Boctor and F.R. Boyd

Geophysical Laboratory, Carnegie Institution of Washington, 2801 Upton Str., N.W., Washington, DC 20008, USA

Abstract. The lower sill at Benfontein, South Africa, shows a high degree of magmatic sedimentation to kimberlite, oxide-carbonate, and carbonate layers. The iron-titanium oxide minerals are similar in the carbonate-rich and silicate-rich layers and are represented by titaniferous Mg-Al chromite, Mg-Al titanomagnetite, magnesian ilmenite, rutile, and perovskite. The spinel crystallization trend was toward enrichment in Mg and Ti and depletion in Cr; this trend is similar to that observed in many kimberlites. The ilmenite has Mg and Cr contents within the range observed in kimberlites and lacks the Mn enrichment observed in ilmenites from carbonatites. Perovskite in silicate-rich and carbonate-rich layers shows similar total REE contents and LREE enrichment and lacks the remarkable Nb enrichment observed in perovskite from carbonatites. These new data on the iron-titanium oxide minerals in the lower Benfontein sill do not support a genetic relationship between kimberlites and carbonatites.

Introduction

The relation between kimberlite and carbonatite has been a subject of controversy among petrologists for many years. The occurrence of calcite in the groundmass of kimberlites and the coexistence of primary carbonate and kimberlite in sills and dikes are commonly considered as evidence of a genetic relationship between kimberlite and carbonatite (Dawson and Hawthorne 1973; Gittens et al. 1975). On the basis of a study of the Oka carbonatite, Quebec, McMahon and Haggerty (1979) concluded that "although the regional relationships between kimberlites and carbonatites remain enigmatic, these two rock types appear to have some cogenetic association." Haggerty et al. (1979) noted that the Mn enrichment in ilmenite associated with carbonate segregations in the Monastery diatreme, South Africa, was similar to that observed in ilmenite from carbonatites; they considered such enrichment to represent the hallmark of carbonatitic differentiation from kimberlite magma. Mitchell (1979), however, argued against a genetic relationship between kimberlites and carbonatites on the basis of (1) mineralogical dissimilarity between the carbonate-rich residuum of kimberlites and carbonatites, (2) the absence of kimberlites in alkaline igneous complexes, and (3) the lack of similarity between the tectonic setting of carbonatites and kimberlites.

In no other South African kimberlite is the occurrence of primary magmatic carbonate and kimberlite so well demonstrated as in the Benfontein layered kimberlite-carbonate sills.

They have been commonly cited as evidence of a genetic relation between kimberlites and carbonatites (Dawson 1966; Dawson and Hawthorne 1973; Basu 1978). They provide, therefore, an ideal occurrence where the relationship between kimberlite and carbonatite could be tested.

Carbonatites are characterized by an assemblage of iron-titanium oxide minerals that differ from those observed in kimberlites (Prins 1972; Mitchell 1978, 1979; Boctor and Svisero 1978). In addition to their significance as indicators of compositional variations, redox condition, and temperature during progressive crystallization, these minerals remain relatively unaltered even when the associated silicate minerals undergo extensive alteration.

The present investigation deals with the mineralogy and chemistry of the iron-titanium oxide minerals in the lower sill from Benfontein, South Africa, and how they bear on the kimberlite-carbonatite relationship. The samples available for this study are from the lower sill, which shows the highest degree of magmatic sedimentation into kimberlite, oxide-carbonate, and carbonate layers observed in the three Benfontein sills. A brief summary of the mineral chemistry of spinels and ilmenite in the sill was given by Boctor and Boyd (1979a). Concurrent with the present investigation, McMahon et al. (1979) independently studied the oxide mineral compositions and oxygen fugacities of the Benfontein sills but placed emphasis in their investigation on the middle sill from which drill core specimens were available. The petrography and silicate mineral compositions of the layered kimberlite-carbonate sills were first investigated by Dawson and Hawthorne (1973).

Geological Setting

The kimberlite-carbonate sill complex occurs about 8 km southeast of Kimberley in the important zone of major kimberlite diatremes that strike NE-SE through Kimberley (Dawson and Hawthorne 1973). Three sills (1–1.5 m thick) intrude the Dwyka shales and the lower, well jointed parts of the overlying Karoo dolerite sheet. The sills display a layered appearance and are believed to represent multiple intrusions of kimberlite. Dawson and Hawthorne (1973) described various magmatic sedimentation features in the sills, such as layering, cross-lamination, and in situ settling. Sedimentation of cumulus phases gave rise to carbonate-rich layers that vary in thickness from 5 mm to 20 cm and are thickest near the upper contacts of the upper and middle sills. The sills are also cut by numerous vertical and horizontal veins of fibrous calcite that may reach up to 10 cm in thickness and fill joints and shrinkage cracks within the kimberlite. In the lower sill, migration of the carbonate, due to viscosity and density contrasts with the overlying layers, led to the formation of miniature diapiric structures within the carbonate layers. Dawson and Hawthorne (1973)

Table 1. Representative electron microprobe analyses of olivine from kimberlite^a

Oxide, wt%	1	2	3	4	5	6
SiO ₂	40.25	41.11	39.99	40.01	40.14	39.84
TiO ₂	0.04	<0.01	<0.01	<0.01	<0.01	<0.01
Al ₂ O ₃	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Cr ₂ O ₃	<0.01	0.04	<0.01	0.14	0.24	0.29
FeO	9.25	6.74	10.80	10.17	10.00	10.03
NiO	0.26	0.27	0.18	0.24	0.27	0.29
MnO	0.02	<0.01	0.13	0.09	0.11	0.15
MgO	49.46	52.55	48.14	49.03	49.59	49.70
CaO	<0.01	0.08	0.04	0.04	0.01	0.01
Total	99.32	100.84	99.28	99.92	100.37	100.35
Fo	90.5	93.3	88.9	89.6	89.8	89.9
Fa	9.3	6.7	11.1	10.4	10.2	10.1

^a Analyses 1–3, olivine megacrysts; analyses 4–6, idiomorphic olivine

considered the carbonate layers at Benfontein as carbonatite on the basis of their magmatic origin and trace element content as well as oxygen and carbon isotope data.

Petrography

The kimberlite is composed of olivine, rare phlogopite, spinel, ilmenite, and perovskite in a groundmass of calcite. Olivine occurs mainly as rounded megacrysts of variable sizes and as idiomorphic crystals in the groundmass. The megacrysts have a forsterite content in the range 93.3–88.9 and show a weak tendency to be more iron rich toward their peripheries. The idiomorphic crystals of olivine overlap in composition (Fo 90–89) with the megacryst, but show higher Cr content in comparison to the megacrysts (Table 1). Olivine shows idiomorphic inclusions of spinel or ilmenite. Phlogopite is very rare in the kimberlite specimens investigated, in agreement with Dawson and Hawthorne's (1973) observation of the scarcity of this mineral in the lower sill relative to the upper sills at Benfontein.

The samples from the carbonate-oxide layers studied during the course of this investigation contain between 80 and 30% by volume cumulate oxide minerals and show mineral graded layering due to change in the ratio of the cumulate minerals to the intercumulus calcite. Oxide-free carbonate layers formed near the top. In all specimens, miniature diapirs similar to those described by Dawson and Hawthorne (1973) are present. The diapiric structures occur where a layer of calcite is overlain by a relatively large oxide-perovskite layer. The diapirs may be composed of clear rhombohedral calcite crystals in optical continuity with the calcite of the root layer or as randomly oriented tabular crystals of calcite. Detached diapirs are also common.

Oxide Mineralogy and Composition

The oxide minerals in the layered kimberlite-carbonate sills at Benfontein are represented by members of the spinel solid solution series, ilmenite, perovskite, and rutile.

Spinel

In the kimberlite, two types of spinel are present: small idiomorphic crystals of titaniferous Mg–Al chromite that occur as inclusions in the olivine crystals (Fig. 1a) and larger, subhedral to euhedral unzoned crystals of Mg–Al titanomagnetite that are abundant in the calcite groundmass. The titaniferous magnetite commonly occurs as mantles on corroded crystals of ilmenite. The Mg–Al chromite contains 4.77–10.72 wt% TiO₂, and the titanomagnetite contains 0.2–4.5 wt% Cr₂O₃ (Table 2). Spinel

of intermediate composition were not encountered in the kimberlite layers in the lower sill.

The spinels in the carbonate-oxide layers occur as both zoned and unzoned crystals. The zoned crystals have Cr-bearing cores (Cr₂O₃ 5.23–21.08 wt%) and rims of Cr-bearing Mg–Al titaniferous magnetite (TiO₂ 19.5–22.6 wt%). The cores have Mg and Al contents comparable to those of the rims, but contain less Ti (TiO₂ 13.8–18.7 wt%). The unzoned crystals are Mg–Al titaniferous magnetite (Fig. 1b) and are similar in composition to those observed in the kimberlite though they tend to contain more Cr₂O₃ in comparison. Perovskite mantles on spinel crystals in the carbonate layers are very common, and in some places thin intervening layers of calcite separate the two minerals.

Ilmenite

In the kimberlite, ilmenite occurs (1) as discrete rounded crystals that are occasionally mantled by perovskite and may reach up to 0.5 mm in diameter (Fig. 1c), (2) as inclusions mantled by spinel, and (3) as rare idiomorphic inclusions in olivine. Discrete ilmenite shows inclusions of rutile. The MgO content of discrete ilmenite is in the range 13.54–17.34 wt%. Individual crystals are compositionally homogeneous (Table 2) and do not show the strong zonation with respect to Mg observed by McMahon and Haggerty (1979) in ilmenite megacrysts from the middle sill (from pure FeTiO₃ to ≈14 wt% MgO). The ilmenite inclusions in spinel are irregular and are corroded by reaction with the liquid from which the spinels crystallized (Fig. 1d). They display a narrower range in MgO content (16.38–18.10 wt%). The ilmenite inclusions in olivine are commonly idiomorphic and contain 15.0–15.80 wt% MgO in solid solution. If the olivine-ilmenite geothermometer of Andersen and Lindsley (1979) is applied to the olivine with ilmenite inclusions in the Benfontein lower sill, an equilibration temperature of 1010° C (pressure raises temperature by 4° C/kbar) is estimated. This equilibration temperature, however, should be considered tentative because the effect of Cr and Mn on the geothermometer is still unknown. The Cr₂O₃ content of ilmenite from the kimberlite (1.3–2.5 wt%) is within the range observed in ilmenite from other kimberlites. The kimberlite from the Benfontein lower sill differs from other South African kimberlites (e.g., Monastery, Liphobong, Frank-smith, and DeBeers) in the lack of large nodules of ilmenite and in the lack of any spinel exsolution lamellae in ilmenite.

In the carbonate-oxide layers, no discrete ilmenite crystals are present, and ilmenite is represented only by inclusions that are mantled by spinel (MgO 16.9–17.7 wt%). The ilmenite does not display any Mn enrichment such as that reported by Haggerty et al. (1979) for ilmenite associated with immiscible carbonate liquid in the Monastery diatreme or in ilmenite from carbonatite (Mitchell 1978; Boctor and Svisero 1978; McMahon and Haggerty 1979). The Cr₂O₃ content of ilmenite (1.2–2.6 wt%) is comparable to that of ilmenite in the kimberlite.

Perovskite

In the kimberlite, perovskite occurs as discrete crystals disseminated in the intercumulus calcite or as mantles on ilmenite and spinel. In the carbonate-oxide layers, perovskite occurs as a discrete phase, as crystals perched on spinels, and as thin, continuous mantles on the majority of spinel crystals. The perovskite mantles are similar to the perovskite rims on titanomagnetite described by El Goresy and Yoder (1974) from melilite nephelinites. The modal proportions of perovskite vary from one layer to another, but there is no indication that the carbonate layers are enriched in perovskite relative to the kimberlite layers. Per-

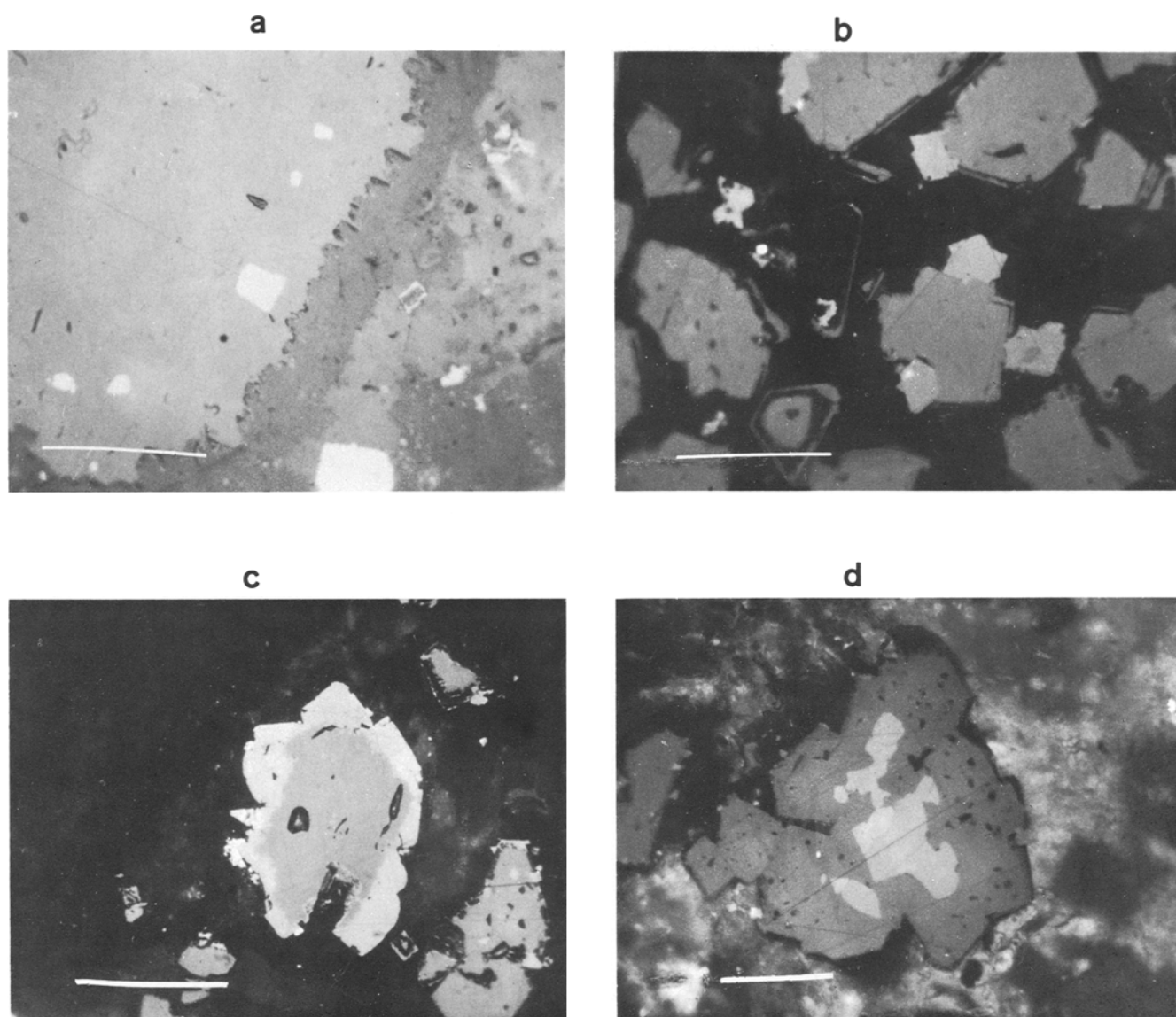


Fig. 1. **a** Titaniferous Mg–Al chromite inclusions in olivine. Reflected light, bar=0.1 mm. **b** Titanomagnetite crystals in oxide-rich carbonate layer. Perovskite occurs as crystals (*light gray*) and as rims on most spinel crystals. Reflected light, bar=0.1 mm. **c** Discrete ilmenite crystals in kimberlite, mantled by perovskite. Reflected light, bar=0.1 mm. **d** Relics of ilmenite (*medium gray*) mantled by titanomagnetite (*dark gray*) in carbonate-oxide layer. Reflected light, bar=0.1 mm

Table 2. Representative electron microprobe analyses of spinels and ilmenite in kimberlite and carbonate layers

Oxide, wt%	Kimberlite						Carbonate					
	Titaniferous Mg–Al chromite		Mg–Al titanomagnetite		Ilmenite		Zoned Spinel Core	Spinel Rim	Mg–Al titanomagnetite		Ilmenite	
SiO ₂	0.18	0.11	0.11	0.14	<0.01	0.13	0.13	0.14	0.21	0.04	<0.01	<0.01
TiO ₂	4.86	9.05	21.09	20.32	53.63	52.72	13.21	20.31	19.52	22.59	52.48	52.72
Al ₂ O ₃	7.56	8.18	8.86	8.14	0.34	0.37	8.28	8.61	9.53	7.80	0.62	0.58
Cr ₂ O ₃	47.44	34.36	0.27	4.56	1.92	1.82	21.08	1.84	0.03	0.86	2.40	2.58
Fe ₂ O ₃	8.96	14.96	26.66	23.86	10.02	7.70	20.86	25.86	28.67	25.60	11.12	11.04
FeO	17.42	18.99	26.94	25.46	17.48	23.11	26.39	26.39	24.70	27.22	15.71	15.98
NiO	0.05	0.16	0.11	0.01	0.11	0.02	<0.01	0.09	<0.01	0.02	0.03	0.05
MnO	0.48	0.47	0.58	0.64	0.70	0.48	0.33	0.54	0.54	0.45	0.43	0.27
MgO	12.78	13.75	16.27	16.49	16.04	13.54	14.23	15.92	16.74	16.80	17.34	17.45
CaO	0.03	0.02	<0.01	<0.01	<0.01	<0.01	0.13	0.33	0.08	0.16	0.18	0.16
Total	100.01	99.73	100.73	99.62	100.64	99.88	100.38	100.03	100.02	100.03	100.33	100.76

Table 3. Representative electron probe analyses of perovskite^a

Oxide, wt.%	1	2	3	4	5	6
TiO ₂	54.11	54.41	54.48	52.10	52.43	52.71
FeO	1.07	1.46	1.68	1.67	1.54	1.40
MgO	n.d.	0.06	n.d.	0.82	0.83	0.84
CaO	37.07	37.45	36.04	36.64	37.60	37.56
Na ₂ O	0.55	0.36	0.56	0.59	0.53	0.48
La ₂ O ₃	0.68	0.84	0.82	0.64	0.93	1.00
Ce ₂ O ₃	3.29	2.50	3.25	2.61	2.70	2.79
Pr ₂ O ₃	0.31	0.33	0.20	0.52	0.16	0.31
Nd ₂ O ₃	1.25	0.65	1.46	1.06	0.98	0.91
Sm ₂ O ₃	n.d.	0.04	0.02	0.02	0.05	0.03
Eu ₂ O ₃	n.d.	n.d.	n.d.	n.d.	0.03	n.d.
Gd ₂ O ₃	0.78	0.34	0.55	0.49	0.54	0.59
Yb ₂ O ₃	n.d.	n.d.	n.d.	0.04	0.05	n.d.
Lu ₂ O ₃	0.09	n.d.	0.03	n.d.	n.d.	0.09
Cr ₂ O ₃	0.10	0.09	0.05	0.08	0.03	n.d.
Nb ₂ O ₅	1.29	1.93	1.02	1.08	0.55	1.18
	100.25	100.46	100.16	98.36	98.95	99.89

Atomic proportions on the basis of 24 oxygens

Ti	7.641	7.617	7.254	7.420	7.451	7.492
Fe	0.168	0.227	0.266	0.270	0.246	0.223
Mg	0.000	0.016	0.000	0.234	0.234	0.238
Ca	7.457	7.469	7.699	7.488	7.576	7.523
Na	0.203	0.129	0.207	0.219	0.195	0.176
Y	0.000	0.000	0.000	0.000	0.000	0.000
La	0.047	0.059	0.059	0.047	0.066	0.068
Ce	0.227	0.172	0.230	0.184	0.188	0.195
Pr	0.023	0.023	0.016	0.035	0.012	0.016
Nd	0.082	0.043	0.098	0.074	0.066	0.063
Sm	0.000	0.004	0.002	0.000	0.001	0.001
Eu	0.000	0.000	0.000	0.000	0.000	0.000
Gd	0.047	0.020	0.035	0.031	0.035	0.039
Yb	0.000	0.000	0.000	0.000	0.000	0.000
Lu	0.000	0.000	0.001	0.002	0.000	0.004
Cr	0.016	0.012	0.008	0.012	0.004	0.000
Nb	0.109	0.164	0.086	0.089	0.047	0.102
	16.020	15.955	15.961	16.099	16.086	16.120

^a Analyses 1–3, perovskite in carbonate-oxide layers; analyses 4–6, perovskite in kimberlite layers

Si, Tb, Dy, Ho, Er, and Tm not detected

ovskite in both carbonate and kimberlite is Nb-bearing (1.06–1.9 wt% Nb₂O₅) and is characterized by a low FeO content (1.05–1.7 wt%). Perovskite (Table 3) is rich in rare earth elements (5.6–7.4 wt% RE₂O₃) and shows a remarkable enrichment in the light rare earth elements (LREE) relative to the heavy rare earth elements (HREE). The total REE contents and LREE enrichment are similar in both kimberlite and carbonate layers.

Rutile

Rutile occurs rarely as discrete tabular crystals disseminated in the carbonate layers or as discontinuous mantles on spinel crystals. An intervening zone of carbonate occurs between the spinel crystals and rutile. Rutile is niobium-bearing, and the discrete rutile crystals are enriched in Nb (0.90–1.22 wt% Nb₂O₅) relative to the rutile rims (0.01–0.25 wt% Nb₂O₅). Perovskite, another Nb-bearing phase in the carbonate layers, is generally more enriched in Nb relative to rutile. In addition to niobium, iron seems to be the other major impurity in rutile (Table 4).

Table 4. Representative electron microprobe analyses of rutile from carbonate layers^a

Oxide, wt%	1	2	3	4	5	6
SiO ₂	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
TiO ₂	96.02	96.37	96.71	98.10	97.23	96.77
Al ₂ O ₃	0.23	0.18	0.12	0.23	0.20	0.19
Cr ₂ O ₃	0.04	0.01	<0.01	<0.01	0.01	0.02
Nb ₂ O ₅	1.22	1.05	0.89	<0.01	0.13	0.25
FeO	1.50	1.41	1.32	0.78	1.42	1.67
NiO	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
MnO	0.05	0.07	0.09	0.02	<0.01	<0.01
MgO	0.12	0.14	0.20	0.14	0.15	0.14
CaO	0.16	0.15	0.14	0.30	0.19	0.13
Total	99.39	99.38	99.47	99.57	99.39	99.17

^a Analyses 1–3, discrete crystals; analyses 4–6, rutile rims on spinels

Discussion

The characteristic iron-titanium minerals in carbonatite from alkaline igneous complexes are magnetite, ilmenite, spinel, perovskite, and pyrochlore (Mitchell 1978, 1979; Boctor and Svisero 1978; McMahon and Haggerty 1979). The magnetite may be homogeneous or may contain lamellar intergrowths of ilmenite. The magnetite-ilmenite intergrowths apparently formed by the mechanism suggested by Buddington and Lindsley (1964). Manganese and magnesium partition in ilmenite relative to the coexisting magnetite in agreement with the experimental data of Mazzullo et al. (1975) and Pinckney and Lindsley (1976). Homogeneous magnetite in carbonatite is generally Ti poor and may belong to the magnetite-magnesioferrite solid solution series as in Jacupiranga carbonatite or the magnetite-jacobsite solid solution series as in Oka, Quebec, carbonatite. Ilmenite is remarkably enriched in Mn and is virtually Cr free. It may be an ilmenite-pyrophanite-hematite solid solution as in Oka or an ilmenite-geikelite-pyrophanite-hematite solid solution as in Jacupiranga. Spinel, when present, belong to the hercynite-pleonaste solid solution series and occur as exsolution lamellae or rounded inclusions in magnetite (Mitchell 1978). Perovskite in carbonatites is enriched in REE and may show remarkable substitution of Ti by Nb (Nickel 1962). The bulk of Nb, however, concentrates in pyrochlore-group minerals, which may show a preferential fractionation of Ti resulting in a low Ti content of magnetite and low modal concentrations of ilmenite (McMahon and Haggerty 1979).

In the following discussion an attempt will be made to point out the similarities and differences between the oxide minerals in the Benfontein lower sill and those in carbonatites.

Spinel

When the electron microprobe analyses of the spinels (Table 2) from the kimberlite and carbonate layers from the Benfontein lower sill are plotted in the reduced spinel prism (Fig. 2), the Mg–Al chromites plot at the base of the spinel prism bound by the end members MgAl₂O₄–FeAl₂O₄–FeCr₂O₄–MgCr₂O₄. The Mg–Al titanomagnetites fall within the front rectangular face bound by the end members Fe₂TiO₄–Mg₂TiO₄–MgAl₂O₄–FeAl₂O₄. The cores of the zoned spinels in the carbonate layers have compositions intermediate between the Mg–Al chromite and Mg–Al titanomagnetite and plot mainly in the front rectangular face close to the FeAl₂O₄–Fe₂TiO₄ and the MgAl₂O₄–FeAl₂O₄ joins with few exceptions

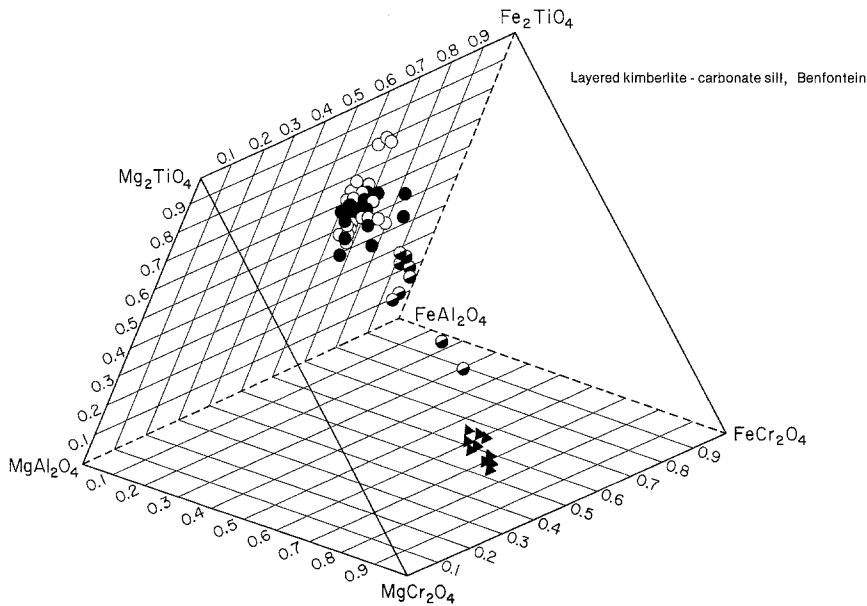


Fig. 2. Composition of spinels plotted in the spinel prism. *Triangles*, titaniferous Mg–Al chromite inclusions in olivine; *open circles*, unzoned Mg–Al titanomagnetite in kimberlite; *half-filled circles*, cores of zoned spinels in carbonate; *solid circles*, Mg–Al titanomagnetite rims of zoned spinels in carbonate

that plot at the base of the spinel prism. The crystallization trend of spinels involved a progressive decrease in Cr and an increase in Ti and Mg with the progress of crystallization. The $\text{Fe}^{3+}/\text{Fe}^{2+}$ and total iron also increased, and Al remained nearly constant during spinel crystallization. The spinel crystallization trend is similar to that observed in other kimberlites (Haggerty 1975; Mitchell and Clark 1976). The Mg–Al titanomagnetites in the Benfontein lower sill are members of the Fe_3O_4 – Mg_2TiO_4 – MgAl_2O_4 solid solution series and are characterized by substantially higher Mg, Ti, and Al contents relative to homogeneous magnetite from carbonatites.

Ilmenite

The Mg and Cr contents of ilmenite in the kimberlite and carbonate-oxide layers are similar to those observed in other kimberlites (Mitchell 1973, 1977), and their high Cr and low Mn contents distinguish them from those observed in carbonatites. The similarity between the ilmenite compositions in the kimberlite and carbonate layers is clearly demonstrated when they are plotted in terms of the molecular proportions of FeTiO_3 – MgTiO_3 and Fe_2O_3 (Fig. 3).

Coexisting ilmenite and spinel in both kimberlite and carbonate layers have similar Mg and Mn contents. The partitioning patterns observed for these elements in ilmenite and spinel phases from carbonatites in alkaline igneous complexes are lacking in the Benfontein lower sill. Thus, the coexisting ilmenite and spinel are not in equilibrium. Apparently the ilmenite either was incorporated in the magma as xenocrysts or crystallized earlier as a cumulate phase prior to the crystallization of spinel. The ilmenite was later partially resorbed by reaction with the liquid from which spinels crystallized, a phenomenon that seems to be more pronounced in the oxide-carbonate layers relative to the kimberlite layers.

Perovskite

The total REE content of perovskite at Benfontein is similar to that reported for other carbonate-bearing kimberlites, e.g., Monastery, though it is much lower than that reported for perovskite in micaceous kimberlite such as Bellsbank (Boctor and Boyd 1979b).

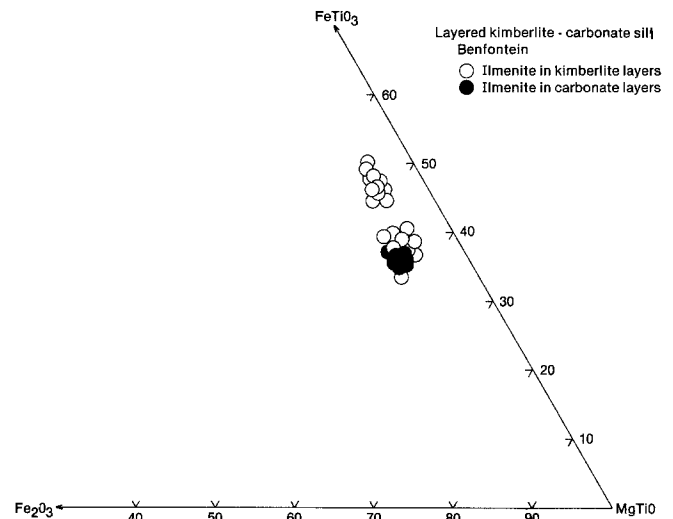


Fig. 3. Composition of ilmenite in terms of the MgTiO_3 , FeTiO_3 , and Fe_2O_3 contents

The REE contents of perovskite in both the carbonate-oxide layers and the silicate-rich layers are similar. Experimental investigation of the partitioning of REE between immiscible carbonate and silicate melts at 1,200° C and 1,300° C and at 5 and 20 kbar shows that they favor the carbonate melt by a factor of 2–3 for the LREE and 5–8 for the HREE (Wendlandt and Harrison 1979). Although the silicate melt compositions used in Wendlandt and Harrison's experiments differ from kimberlite melts, data on the distribution of REE between carbonatites and cogenetic alkaline rocks show that they favor carbonatites to the silicate rocks (Cullers and Medaris 1977). Similarly, carbonatites have a higher REE content in comparison to kimberlites (Haskin et al. 1966). If the partition coefficients for REE between perovskite, carbonate, and silicate melts are dependent on the activities of REE in the melts, then perovskite crystallizing from the carbonate melt is expected to be more enriched in REE relative

to that crystallizing from the silicate melt. In the absence of data on the concentration dependence, temperature, and pressure effects on the partition coefficients of REE between perovskite, carbonate, and silicate melts, however, only speculation on the causes of similar enrichment of REE in perovskite can be attempted. A possible explanation is that perovskite crystallized as an early liquidus phase from a carbonate-rich kimberlite magma prior to carbonate-silicate liquid immiscibility. The presence of intervening layers of calcite between spinel crystals and their perovskite mantles, however, suggests that perovskite continued to crystallize after the beginning of carbonate crystallization. An alternative explanation for the similarity in total REE contents and LREE enrichment in perovskite from carbonate and kimberlite is that it nucleated from the intercumulus carbonate liquid after silicate-carbonate liquid immiscibility took place and that the LREE were incorporated preferentially in perovskite. A third possible explanation for the similar total REE contents and LREE enrichment in perovskite is that the partition coefficients of REE between carbonate or silicate liquids and perovskite are independent of the initial activities of these elements in the melt and that the LREE enrichment is primarily controlled by crystal-chemical factors. The LREE elements can replace Ca easily in the perovskite structures, whereas the HREE are less favored because their ionic size is significantly smaller than Ca (Boynton 1975). Experimental investigations on the partitioning of REE between perovskite, carbonate, and silicate melts are needed to clarify this problem.

Rutile

The presence of Nb-bearing rutile in the oxide-carbonate layers in the Benfontein lower sill is an indication that the activity of Ti was much higher in the residual liquids in the Benfontein lower sill than the activity of Nb. Therefore, the formation of pyrochlore minerals and the extensive substitution of Ti by Nb in perovskite that are characteristic of carbonatites are lacking in the Benfontein lower sill.

When the oxide mineralogy of the lower sill is compared with that of the middle sill (McMahon and Haggerty 1979), some differences are noted. The ilmenite crystals in the lower sill are not zoned and do not show the lamellar intergrowths of titanomagnetite observed in ilmenite megacrysts from the middle sill. These intergrowths were interpreted by McMahon and Haggerty (1979) as products of subsolidus reduction. The lack of any titanomagnetite lamellar intergrowths in ilmenite from the lower sill suggests that the conditions were unfavorable for exsolution of its Fe_2O_3 content and its subsolidus reduction to titanomagnetite. Apparently the degree of supersaturation of Fe_2O_3 in ilmenite from the lower sill was much lower than that in the ilmenite from the middle sill, and quenching conditions may have been faster in the lower sill relative to the middle sill. The spinel compositional trends in the lower sill are similar to those reported by McMahon and Haggerty in the middle sill although Mg enrichment with progressive crystallization seems to be more pronounced in the middle sill relative to the lower sill. The occurrence of Cr-rich spinels in the carbonate layers in the lower sill cannot be attributed, however, solely to the degradation of olivine crystals and the liberation of their Mg-Al chromite inclusions into the matrix as proposed by McMahon and Haggerty (1979) for the middle sill. The Cr-bearing spinels in the lower sill commonly occur in carbonate layers that contain no olivine or none of its alteration products. In such cases, the Cr-bearing spinel apparently crystallized as an early cumulate phase.

Implications to the Kimberlite-Carbonatite Relations

Data on the oxide minerals in silicate and carbonate layers from the lower sill from Benfontein, South Africa, do not support a genetic relationship between kimberlites and carbonatites. The mineral composition and crystallization trends of the spinels in the lower sill are similar to those observed in kimberlites and differ from those in carbonatites from alkaline igneous complexes. Ilmenite lacks the Mn enrichment observed in ilmenite from carbonatites, and unlike the latter, it is Cr-bearing. Furthermore, perovskite does not show the remarkable enrichment of Nb observed for this mineral in carbonatites (Mitchell 1979; McMahon and Haggerty 1979), and pyrochlore was not found in the Benfontein lower sill.

The major argument raised by advocates of a genetic relationship between carbonatites and kimberlites is the occurrence of magmatic carbonates formed by liquid immiscibility from kimberlite magma. Experimental investigations (Wyllie and Huang 1975; Egger 1976) show that a primary carbonatitic melt can form by partial melting of carbonated mantle peridotite at 1,200°C and a pressure above 25 kbar. With the increase in the degree of partial melting, the melt compositions become progressively richer in silicate components (Wendlandt and Mysen 1980). Magmas of variable composition and variable carbonate content can be generated, therefore, by partial melting of carbonated peridotite. Silicate-carbonate liquid immiscibility takes place at low pressures, but it is not solely restricted to carbonate-bearing kimberlite magma. Moreover, it has been shown experimentally that a carbonatitic magma can be generated at high pressures without recourse to liquid immiscibility (Egger and Wendlandt 1979). The separation of an immiscible carbonate liquid from kimberlite magma, therefore, does not necessarily imply a genetic relationship between kimberlites and carbonatites.

Acknowledgements. The authors wish to thank Drs. J.B. Dawson, S.E. Haggerty, H.S. Yoder Jr., and an anonymous reviewer for critical comments on the manuscript.

References

- Andersen DJ, Lindsley DH (1979) The olivine-ilmenite thermometer. *Proc Lunar Sci Conf*, 10th, 1:493-507
- Basu JV (1978) Origin of kimberlites and carbonatites explained by Nd isotopes (abstract). *GAC/MAC, Abstr with Progr* 3:364
- Boctor NZ, Boyd FR (1979a) Oxide minerals in layered kimberlite-carbonate sills from Benfontein, South Africa. *Carnegie Inst Washington Yearb* 78:493-496
- Boctor NZ, Boyd FR (1979b) Distribution of rare earth elements in perovskite from kimberlites. *Carnegie Inst Washington Yearb* 78:572-574
- Boctor NZ, Svisero DP (1978) Iron-titanium oxide and sulfide minerals in carbonatite from Jacupiranga, Brazil. *Carnegie Inst Washington Yearb* 77:876-880
- Boynton WV (1975) Fractionation in the solar nebula: Condensation of yttrium and the rare earth elements. *Geochim Cosmochim Acta* 39:569-584
- Buddington AF, Lindsley DH (1964) Iron-titanium oxide minerals and synthetic equivalents. *J Petrol* 5:310-357
- Cullers RL, Medaris LG (1977) Rare earth elements in carbonatites and cogenetic alkaline rocks: Examples from Seabrook Lake and Callander Bay, Ontario. *Contrib Mineral Petrol* 65:143-153
- Dawson JB (1966) The kimberlite carbonatite relationship. *Mineral Soc India, IMA*, 1-22
- Dawson JB, Hawthorne JB (1973) Magmatic sedimentation and carbonatitic differentiation in kimberlite sills at Benfontein, South Africa. *J Geol Soc London* 129:61-85

- Eggler DH (1976) Does CO₂ cause partial melting in the low velocity layer of the mantle? *Geology* 4:69–72
- Eggler DH, Wendlandt RF (1979) Experimental studies on the relationship between kimberlite magmas and partial melting of peridotite. In: Boyd FR, Meyer HOA (eds) *Kimberlites, Diatremes and Diamonds: Their Geology, Petrology and Geochemistry*. Washington, DC, American Geophysical Union, pp 330–338
- El Goresy A, Yoder HS Jr (1974) Natural and synthetic melilite compositions. *Carnegie Inst Washington Yearb* 73:359–371
- Gittens J, Hewins RH, Laurin AF (1975) Kimberlitic-carbonatitic dikes of the Saquenay River Valley, Quebec, Canada. *Phys Chem Earth* 9:137–148
- Haggerty SE (1975) The chemistry and genesis of opaque minerals in kimberlites. *Phys Chem Earth* 9:295–307
- Haggerty SE, Hardie RB, III, McMahon BM (1979) The mineral chemistry of ilmenite nodule associations from the Monastery diatreme. In: Boyd FR, Meyer HOA (eds) *The Mantle Sample*. Washington, DC, American Geophysical Union, pp 249–256
- Haskin LA, Frey FA, Haskin MA, Schmitt RA, Smith RH (1966) Meteorite, solar and terrestrial abundances of rare earth distribution. *Phys Chem Earth* 7:167–321
- Mazzullo LJ, Dixon SE, Lindsley DH (1975) T - fO_2 relationship in Mn-bearing compositions (abstract). *Geol Soc Am, Abstr with Progr* 7:1192
- McMahon BM, Haggerty SE (1979) The Oka carbonatite complex: Magnetite compositions and the related role of titanium in pyrochlore. In: Boyd FR, Meyer HOA (eds) *The Mantle Sample*. Washington, DC, American Geophysical Union, pp 382–392
- McMahon BM, Haggerty SE, Bence RJ (1979) Oxide mineral chemistry and oxygen fugacities of the Benfontein sills, South Africa (abstr). *Cambridge Kimberlite Symposium*, Cambridge, England
- Mitchell RH (1973) Magnesian ilmenite and its role in kimberlite petrogenesis. *J Geol* 81:301–311
- Mitchell RH (1977) Geochemistry of magnesian ilmenites from kimberlites from South Africa and Lesotho. *Lithos* 10:29–37
- Mitchell RH (1978) Manganoan magnesian ilmenite and titanium clinohumite from the Jacupiranga carbonatite, Sao Paulo, Brazil. *Am Mineral* 63:544–547
- Mitchell RH (1979) The alleged kimberlite-carbonatite relationship: Additional contrary mineralogical evidence. *Am J Sci* 279:570–589
- Mitchell RH, Clark DB (1976) Oxide and sulfide mineralogy of the Peuyuk kimberlite, Somerset Island, NWT, Canada. *Contrib Mineral Petrol* 56:157–172
- Nickel EH (1962) Compositional variation in pyrochlore and niobian perovskite from a niobium deposit in the Oka district of Quebec. *Dept Mines Tech Surv, Canada, Tech Bull TB-31*:1–35
- Pinckney LR, Lindsley DH (1976) Effects of magnesium on iron-titanium oxides (abstract). *Geol Soc Am, Abstr with Progr* 8:1051
- Prins P (1972) Composition of magnetite from carbonatites. *Lithos* 5:227–240
- Wendlandt RF, Harrison WJ (1979) Rare earth partitioning between immiscible carbonate and silicate liquids and CO₂ vapor: Results and implications for the formation of light rare earth enriched rocks. *Contrib Mineral Petrol* 69:409–419
- Wendlandt RF, Mysen BO (1980) Melting phase relations of natural peridotite+CO₂ as a function of the degree of partial melting at 15 and 30 kbar. *Am Mineral* 65:37–44
- Wyllie PJ, Huang WL (1975) Peridotite, kimberlite and carbonatite explained in the system CaO–MgO–SiO₂–CO₂. *Geology* 3:621–624

Received August 7, 1980; Accepted in revised form February 9, 1981