

THE CHEMISTRY AND GENESIS OF OPAQUE MINERALS IN KIMBERLITES.

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A detailed reflection microscopy study and over 500 electron microprobe analyses of an extensive suite of kimberlites from some 30 southern and west African localities has been undertaken in an attempt to characterize the opaque mineralogy of kimberlites. The results of this study indicate that in addition to the ubiquitous occurrence of geikielite-rich ilmenite that an exotic and chemically variable suite of other opaque minerals are also commonly present. The oxides include members of the spinel mineral group, armalcolite $(\text{FeMg})\text{Ti}_2\text{O}_5$, the polymorphs of TiO_2 , perovskite, and two new minerals, a primary Ba-Fe-Ti-Cr-vanadate, and a phase that is essentially intermediate between CaTiO_3 and Fe_2O_3 , and of secondary origin. The sulfides identified are restricted to pyrite, pyrrhotite, chalcopyrite and pentlandite; and the native metals, aside from graphite, are Cu and Ni-Fe alloys. Subsolidus reactions that include oxidation, reduction and solid state decomposition of the primary assemblages are widespread. The effects of solid-liquid, solid-solid, solid-gas and hydrothermal alteration are also recognised. The variable intensity of these reactions coupled with non-systematic chemical trends within the reaction assemblages and superimposed or indeterminate paragenesis of minerals of identical or related composition in different samples from the same pipe preclude a uniform interpretation of the conditions that prevailed during crystallization or during subsequent crystallization events. However, these effects contrast strongly with the primary mineralogy which in most cases are clearly defined as liquidus phases.

Spinel. Five distinct petrogenetic types of spinels are recognised and these are classified as follows: 1) xenocrystic spinels; 2) primary groundmass spinels; 3) secondary spinels associated with (1) and (2), and in association with perovskite in ilmenite reaction mantles; 4) secondary spinels in garnet kelyphitic rims and in partially serpentinized olivine; and 5) exsolved spinels in ilmenite. Compositionally, the xenocrystic and primary spinels are in the system $\text{MgCr}_2\text{O}_4\text{-FeCr}_2\text{O}_4\text{-MgAl}_2\text{O}_4\text{-FeAl}_2\text{O}_4$, whereas the secondary spinels are more typically in the system $\text{Fe}_2\text{TiO}_4\text{-Mg}_2\text{TiO}_4\text{-FeAl}_2\text{O}_4\text{-Fe}_3\text{O}_4$. There is however considerable overlap of these subsystems and a further characteristic feature of both types is that the spinels are strongly zoned. Zonal trends are either of a clearly defined nature from Mg-Al to Fe-Cr, and from Fe-Cr to Fe-Ti, in which the role of Fe^{+3} is limited, or alternatively one in which $\text{Fe}_2\text{TiO}_4\text{-Fe}_3\text{O}_4$ is dominant. Apart from the complexity of zonal patterns the single outstanding chemical characteristic of kimberlitic spinels is the presence of extensive Mg_2TiO_4 solid-solubility; the outstanding textural characteristics are skeletal spinels in garnet reaction rims and a variety of exsolved spinels in ilmenite. Typical analyses are listed in Table 1.

Ilmenite. The compositions of the ilmenites determined range from 10-70 mole % MgTiO_3 and from <1-40 mole % Fe_2O_3 . Cr_2O_3 ranges from <0.5 wt% to a maximum of 5.6 wt%; and Al_2O_3 varies between <0.1 wt% to 1.3 wt%. The paragenetic types of ilmenite are classified as follows: 1) xenocrystic ilmenite; 2) groundmass primary ilmenite; 3) subsolidus oxidation ilmenite in titanomagnetite; 4) ilmenite-spinel-perovskite mantles on xenocrystic ilmenite; and 5) ilmenite-rutile and ilmenite-rutile-armalcolite intergrowths. The xenocrystic ilmenites fall within two groups: those that are non-magnetic are typically high in MgO (e.g. 15 wt%), contain <10 mole % Fe_2O_3 , and Cr_2O_3 contents close to 1.5 wt%; those that are magnetic contain 25-40 mole % Fe_2O_3 , variable Cr_2O_3 contents and <5

wt% MgO. Groundmass ilmenites and oxidation ilmenites are characterized by low MgO and Cr_2O_3 contents (1 wt% and <0.5 wt% respectively), whereas ilmenites associated with rutile or with armalcolite may contain up to 4 wt% Cr_2O_3 and 9-12 wt% MgO. Exsolution-like and crystallographically oriented spinel lamellae in ilmenite are chromite, titanian-chromite, or aluminian-titanomagnetite; these phase intergrowths are considered to be the result of subsolidus reduction. The ilmenite-rutile assemblages, although bearing some relationship to exsolved FeTiO_3 from TiO_2 are more likely the result of armalcolite decomposition ($\text{FeMgTi}_2\text{O}_5 \rightarrow \text{FeMgTiO}_3 + \text{TiO}_2$).

Armalcolite. The first terrestrial occurrence of armalcolite ($\text{FeMgTi}_2\text{O}_5$) is reported from DuToitspan, in discrete crystals 25-50 μm in dimension, and in association with rutile + MgO-rich ilmenite. This mineral is comparable in optical properties and major element chemistry to the type armalcolites present in the Lunar samples, although within the precision of the analyses the presence of Fe^{+3} cannot be unambiguously excluded (Table 1).

TiO_2 polymorphs. Rutile is the most commonly occurring polymorph, it is present typically as a groundmass phase and is generally associated with lamellar or mantled overgrowths of picro-ilmenite. The purity of these rutiles is variable, particularly with respect to Fe, Cr and Al. The limited solid-solubility of Fe in TiO_2 , the widespread ilmenite association, the identification of armalcolite, and broad-beam analyses of $(\text{FeMg})\text{TiO}_3\text{-TiO}_2$ intergrowths that approximate armalcolite in composition, suggests that the majority of rutile-ilmenite intergrowths may be derived by armalcolite thermal decomposition. Anatase (+ hematite) is restricted to ilmenite decomposition in deeply weathered pipes, and brookite is positively identified only in concentrates - both tend to be compositionally stoichiometric.

Rare minerals. In addition to armalcolite the following minerals have been identified, a complex vanadate (Table 1) from De Beers; intermediate members of a proposed series between perovskite and hematite (Table 1) from KaO, the Ti-rich garnet schorlomite (Table 1) from both of above localities, and Ni-Fe alloys from Ramatseliso. The vanadate is a primary mineral included in phlogopite, the $\text{CaTiO}_3\text{-Fe}_2\text{O}_3$ phase forms a secondary mantle on microxenocrystic picroilmenite, schorlomite (+ sphene) replaces titanomagnetite-ilmenite intergrowths, and Ni-Fe is included in olivine.

Distinctive assemblages such as graphite + pyrrhotite, rutile + ilmenite, titanomagnetite + ilmenite, picroilmenite + chromite, and rhythmically mantled zones of alternating ilmenite and spinel on xenocrystic picroilmenite, suggest that prevailing redox conditions, rates of cooling, and the physiochemical kinetics of solid-solid, solid-liquid and solid-gas reactions during kimberlite emplacement and specifically during groundmass crystallization are widely variable. The outstanding examples that underscore the extremes of these variabilities are: (1) Redox conditions. The presence of native metals and armalcolite, in contrast to the occurrence of subsolidus oxidation of titaniferous magnetite; (2) fO_2 -Cooling rate. Homogeneous chromian-rich picroilmenite and low- Cr_2O_3 picroilmenite but with exsolved chromite; and (3) Reactions. Alteration rims on picroilmenite of variable thickness and widely varying chemistry in contrast to pristine picroilmenite. Groundmass enrichment trends as exhibited by spinel core-mantle relationships (i.e. from Mg-Al to Fe-Cr, and from Fe-Cr to Fe-Ti, and culminating in Ca-Ti, perovskite, in the outermost border zones) are compatible with crystal fraction models and

provide unambiguous evidence for the existence of late stage Ti-rich liquids in the majority of the kimberlites examined.

Table 1

Spinels (KaO: 1947, 2229)

	Core	Int.	Mantle	Core	Int.	Mantle	Core	Mantle
TiO ₂	4.07	5.42	10.96	0.60	1.89	4.37	0.18	0.23
MgO	16.11	13.19	11.75	11.66	13.37	16.13	16.40	9.26
MnO	0.44	0.52	0.54	0.27	0.32	0.04	0.20	0.37
CaO	0.08	0.06	0.15	0.07	0.04	0.02	0.02	0.11
FeO	13.88	17.82	23.53	15.57	14.84	14.28	10.88	19.79
Fe ₂ O ₃	9.26	29.33	43.62	5.35	6.73	9.37	0.95	1.06
Al ₂ O ₃	17.69	7.40	6.36	5.59	9.50	17.63	25.11	10.93
Cr ₂ O ₃	39.18	25.30	2.50	60.05	53.48	37.89	46.02	59.04
SiO ₂	0.28	0.27	0.29	0.38	0.27	0.29	0.06	0.13
Total	100.99	99.31	99.70	99.54	100.44	100.02	99.82	100.92

Spinels (Lipelaneng: 1363)

	Core	Mantle	Core	Mantle	Core	Mantle	Core	Mantle
TiO ₂	0.06	0.27	0.01	16.08	8.19	12.21	0.13	0.70
MgO	15.98	12.82	16.67	13.75	14.30	13.04	14.05	9.08
MnO	0.08	0.30	0.04	0.39	0.28	0.78	0.23	0.30
CaO	0.14	0.01	0.01	0.02	0.05	0.08	0.01	0.02
FeO	15.57	16.63	15.71	26.36	21.07	24.15	15.61	23.20
Fe ₂ O ₃	2.65	2.66	7.38	27.37	15.84	32.30	3.81	7.66
Al ₂ O ₃	50.36	32.20	52.70	12.52	23.13	6.38	30.91	29.47
Cr ₂ O ₃	15.69	35.63	7.51	2.95	17.41	11.01	35.64	29.45
SiO ₂	0.05	0.15	0.01	0.23	0.22	0.68	0.13	0.13
Total	100.58	100.67	100.04	99.67	100.49	100.63	100.52	100.01

	Armal- colite	Phase 1	Phase 2	Schorlo- mite	Sphene	Rutile	Perovskite
TiO ₂	76.92	53.16	36.31	20.35	40.64	96.49	57.39
MgO	7.08	3.66	3.96	2.35	0.02	0.63	0.19
MnO	0.54	0.14	0.33	0.05	0.02	0.01	0.02
CaO	0.06	0.39	23.78	31.96	28.90	0.31	38.93
BaO		4.07					
FeO	13.47*	11.28*		16.79*	0.25*	1.04*	1.21*
Fe ₂ O ₃			33.22**				
Al ₂ O ₃	0.02	0.27	1.09	0.13	0.89	0.00	0.24
Cr ₂ O ₃	1.64	17.98	0.36	0.00	0.00	1.87	0.16
V ₂ O ₃		8.46					
SiO ₂	0.28	0.20	0.18	27.94	29.55	0.20	0.21
Total	100.01	99.61	99.23	99.57	100.27	100.55	98.35

* Fe as FeO

** Fe as Fe₂O₃