

Titanium-bearing oxide minerals of the Critical Zone of the Eastern Bushveld Complex

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Abstract

The principal titanium-bearing oxide minerals in the Critical Zone of the Eastern Bushveld Complex are chromite, the most abundant, and rutile, widely distributed as an accessory mineral. Ilmenite and a complex Ti-rich oxide are rare minerals in the zone.

The TiO₂ content of one chromite is 5.17 percent, but the range for all other chromites analyzed is 0.31 percent to 2.47 percent. Rutile occurs as acicular crystals in plagioclase or bronzite in some layers of the rock sequence, but mostly it is associated with chromite. Oriented acicular inclusions in chromite and anhedral marginal to chromite appear to have formed by subsolidus oxidation–exsolution from chromite. Prismatic crystals included in chromite, straddling chromite–silicate boundaries, or embedded in plagioclase or bronzite are interpreted as cumulus crystals formed more or less simultaneously with chromite. Rutile interstitial to chromite crystals in two chromitites apparently formed during the postcumulus stage.

Rutile and chromite were evidently stable as coexisting phases during accumulation of many units of the Critical Zone. The low TiO₂ contents of chromite thus represent saturation levels at time of formation. A miscibility gap may therefore have existed in the series chromite–titanomagnetite under the conditions of crystallization of the Critical Zone. The occurrence of cumulus rutile in a chromitite from the Muskox intrusion and another from the Fiskenaasset intrusion suggests a similar conclusion for those bodies.

Introduction

Two major groups of oxide mineral concentrations are present in the layered rocks of the Bushveld Complex. One group consists of vanadium-bearing titanomagnetite deposits in the upper part of the Complex. Titanium-bearing oxides in those deposits have been studied in some detail (Molyneux, 1972). The second group consists of chromitites in the Critical Zone. Titanium is known to be present in chromite in these rocks and in associated silicate-rich rocks, and other titanium-bearing oxide phases have occasionally been reported, but the occurrence of titanium in oxide minerals has not been systematically examined.

This paper describes the occurrence and compositions of titanium-bearing oxide minerals in the Critical Zone of the Eastern Bushveld Complex. The data help to explain the compositional and stratigraphic gap between the chromium-rich spinels of the lower part of the Bushveld and the iron–titanium spinels of the upper part.

Previous work

Available information on titanium in oxide minerals in the Critical Zone is of two kinds: (1) analyses reporting TiO₂ contents of chromites from various horizons, and (2) descriptions of titanium-rich oxide phases present in various rock units, mostly in chromite-bearing rocks. All complete analyses of chromites from the Eastern Bushveld Complex show TiO₂, the amounts reported ranging from 0.20 to 2.40 percent. Most analyses (*cf.* DeWet and Van Niekerk, 1952; Cameron, 1964; Heiligman and Mikami, 1960; Cousins and Feringa, 1964; Waal, 1975) are of samples from various chromitites, in which chromite is the principal mineral but silicates are present in various amounts. The exact significance of the reported values of TiO₂ is not indicated for any of the published analyses. Purification procedures used have been designed primarily to separate chromite from associated silicates by crushing, elutriation, or magnetic separation, and solution of remaining silicates

in hydrofluoric acid with or without sulfuric acid. The presence or absence of separate TiO_2 oxides in the analyzed concentrates has generally not been determined.

There are a few reports of titanium oxide minerals in various chromites of the Eastern Bushveld. Younger (1958) described bodies of ilmenite in chromite in chromitites from Dwars River (Fig. 1) and from the M unit (Fig. 2) on Winterveld 417 KS, and tiny irregular grains of rutile along grain boundaries of chromite. Cameron and Emerson (1959) mentioned the occurrence of rutile in certain chromitites, and Guilbert (1962) reported rutile as an accessory mineral (trace amounts to 0.2 percent) in rocks of the C and D units (Fig. 2) on Winterveld 417 KS and Jagdlust 418 KS. Rutile was also found in acicular crystals in labradorite and bronzite in feldspathic pyroxenite. Cameron and Glover (1973) briefly compared the TiO_2 contents of spinels in mafic pegmatites with TiO_2 contents of spinels in the normal rocks of the Eastern Bushveld.

Materials studied

Materials studied are outcrop samples and drill cores representing the full 1600-meter thickness of the Critical Zone on Farms Jagdlust 418 KS, Umkoanes Stad 412 KS, and Winterveld 417 KS (Figs. 1 and 2), plus collections from numerous other farms in the Eastern Bushveld. Polished sections representing all major units of the Critical Zone, as well as many individual layers within units, have been examined in the course of the present study.

Occurrence of titanium in oxide minerals

General statement

In rocks of the Critical Zone, titanium occurs in four oxide minerals—rutile, chromite, ilmenite, and an oxide of complex composition (Cameron, 1978). Chromite and rutile are by far the most widely distributed, and chromite is by far the most abundant.

Rutile

Rutile is readily recognized by means of its white color, reflectivity, anisotropism, bireflectance, twinning in larger crystals, crystal habit, and internal reflections (yellow to amber, less commonly reddish). Rutile occurs in the Critical Zone in seven different ways:

1. As acicular inclusions in chromite, parallel to (111) of chromite (Fig. 3A). Most such inclusions are 5 μm or less in length and are less than 1 μm in

diameter, but crystals 20 to 50 μm in length are found.

2. As stout to elongate prisms included in chromite, 1 to 4 inclusions per chromite grain (in section). Control of orientation by the lattice of host chromite may or may not be evident (Fig. 3B). Crystals range up to 0.73 mm in length.

3. As anhedral along margins of chromite crystals (Fig. 3C) or at intergrain boundaries of chromite. At triple junctions of chromite grains, rutile may appear to occupy grain interstices (Fig. 3D).

4. As euhedra along margins of chromite crystals; the chromite is molded against rutile. Some rutile crystals straddle chromite-silicate boundaries (Fig. 4A).

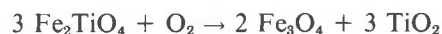
5. As independent crystals up to 0.32 mm in length (Figs. 4B, 4C), mostly associated with chromite but largely or completely detached from it and embedded in postcumulus plagioclase, less commonly biotite.

6. As aggregates interstitial to chromite (Fig. 4D).

7. As acicular crystals in plagioclase, less commonly in bronzite.

Acicular inclusions in chromite and marginal anhedral (1 and 3 above) are commonly associated and are found in various chromitic rocks from the B unit to the top of the Critical Zone. Prismatic euhedral inclusions in chromite, marginal anhedral, and independent crystals (2, 3, and 5 above) occur together at a number of horizons from the D unit upward. They are especially abundant from the F unit upward. Acicular and prismatic inclusions may occur in a single grain of chromite; in such grains the portions adjacent to large inclusions are devoid of acicular inclusions. Types 1, 2, 4, 5, and 6 may all occur in the same rock, but type 6 is the least common and has been noted thus far only in two chromitites.

The acicular, oriented inclusions in chromite are presumably due to separation of TiO_2 from the chromite structure. The process is not simple exsolution, however, since charge imbalance in the spinel (cation excess) would result. More likely is an oxidation-exsolution similar to that proposed as the origin of ilmenite-titanomagnetite intergrowths (Verhoogen, 1962; Buddington and Lindsley, 1964). In terms of a hypothetical ulvöspinel component of the chromite solid solution, the reaction



may be written.

The separation of TiO_2 from chromite appears to have been very uneven. Chromite-rutile intergrowths have been observed in polished sections of rocks rep-

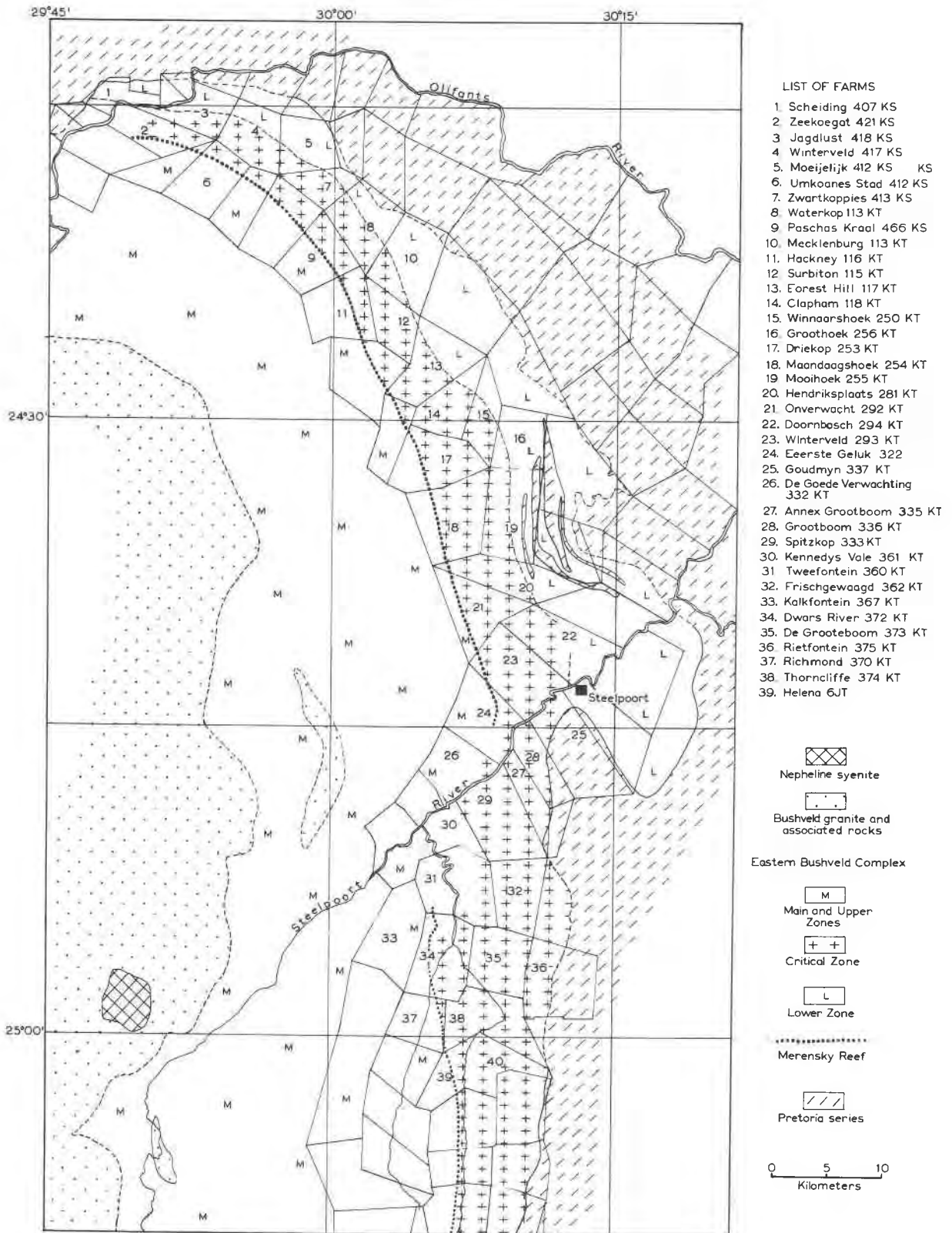


Fig. 1. Generalized geologic map of the Eastern Bushveld Complex.

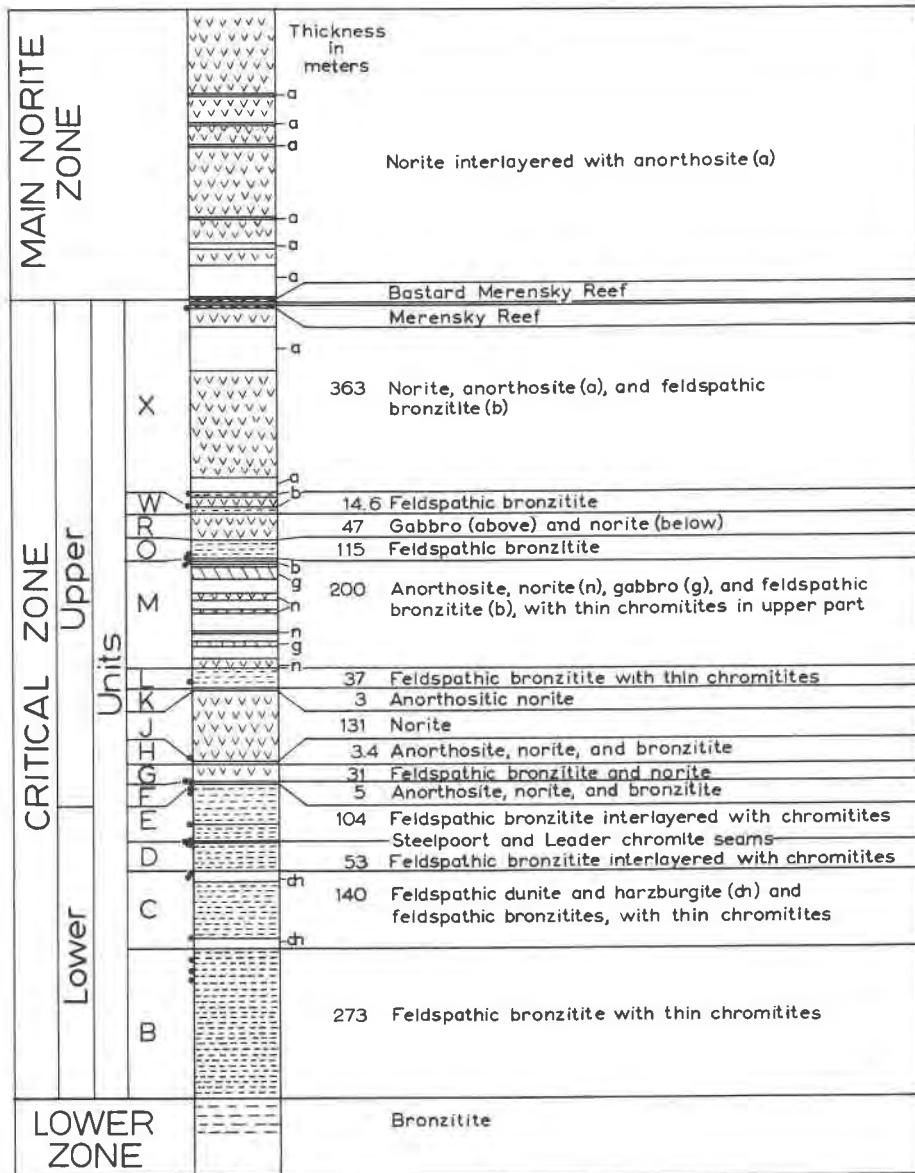


Fig. 2. Section of the Critical Zone on Farms Jagdlust, Winterveld 417 KS, and Umkoanes Stad.

representing more than 100 different layers in the Critical Zone. In every section, there are numerous chromite grains devoid of rutile; e.g., in a chromitic anorthosite from the lower part of the F unit, 79 percent of the grains are rutile-free. Also, intergrowths typically are present only in parts of grains and are randomly disposed. In some rocks, this heterogeneity may be apparent, not real, for exsolved rutile crystals in chromite are mostly very small, with sizes extending to the limits of optical resolution with a 105X oil immersion objective. Some apparently

homogeneous chromite may thus contain sub-microscopic rutile.

In rocks in which acicular rutile forms the only inclusions in chromite, marginal rutile anheda or subhedra are almost invariably present. In part, at least, the latter may represent "exsolution" of TiO_2 to the margins of chromite grains.

Prismatic inclusions (Fig. 3B) appear first in a chromitic pyroxenite layer in the upper part of the D unit and are found in chromitic rocks at intervals to the Merensky Reef. The distinction between acicular

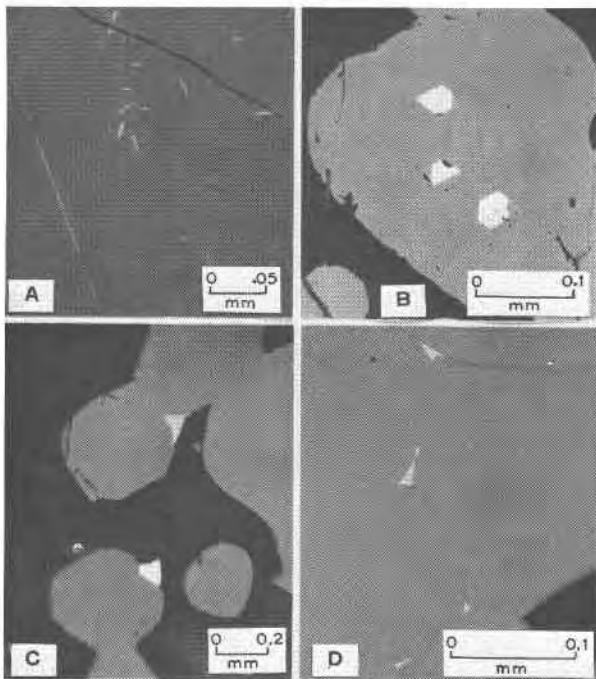


Fig. 3. Photomicrographs, reflected light, oil immersion. (A) Acicular inclusions of rutile (light gray) in chromite (medium gray). F unit, Jagdlust. (B) Prismatic inclusions of rutile (white) in chromite (gray). H unit, Jagdlust. (C) Anhedral and subhedral rutile (white) at margins of chromite grains. Chromitite in Merensky Reef, Umkoanes Stad. (D) Rutile (white) at triple junctions of chromite grains (gray). Steelpoort chromitite, Jagdlust.

and prismatic inclusions is clearcut in most rocks in which the two types of inclusions occur. In a few there is a gradation between the two in size and in habit, and in such rocks the larger inclusions, like the smaller, may be due to exsolution. However, small crystals of chromite are common as inclusions in cumulus olivine and bronzite, and these inclusions are best interpreted as crystals trapped during growth of the host crystals (Cameron, 1975). In the same way, most of the large inclusions of rutile in chromite appear to represent trapped crystals.

Three features support this interpretation. First, there seems to be no systematic relation between size of inclusion and size of host crystal. Second, in any given sample, most chromite grains lack such inclusions; in a polished section of chromitic anorthosite from the H unit, for example, only 15 of 321 chromite crystals intersected by parallel traverses contain large rutile inclusions. Third, rocks in which prismatic inclusions are present in chromite also contain independent rutile, and commonly there is a range from crystals that appear totally enclosed to

those that are only partially enclosed, as in Figure 4A, to those that are completely detached from chromite. Some apparent inclusions undoubtedly are the ends of crystals that are partly embedded in silicates but project into the margins of the host chromite crystals.

The textural relations, taken together, strongly indicate that in such rocks rutile preceded both chromite and silicates on the liquidus. Crystallization of rutile may have ceased when chromite crystallization began, but the sharp outlines of the inclusions indicate that rutile remained stable in the presence of chromite. The bulk TiO_2 contents of the chromites thus represent saturation for TiO_2 under the conditions prevailing.

The textural relations of rutile of type (6) are also pertinent to the question of saturation. This type consists of aggregates of rutile crystals interstitial to

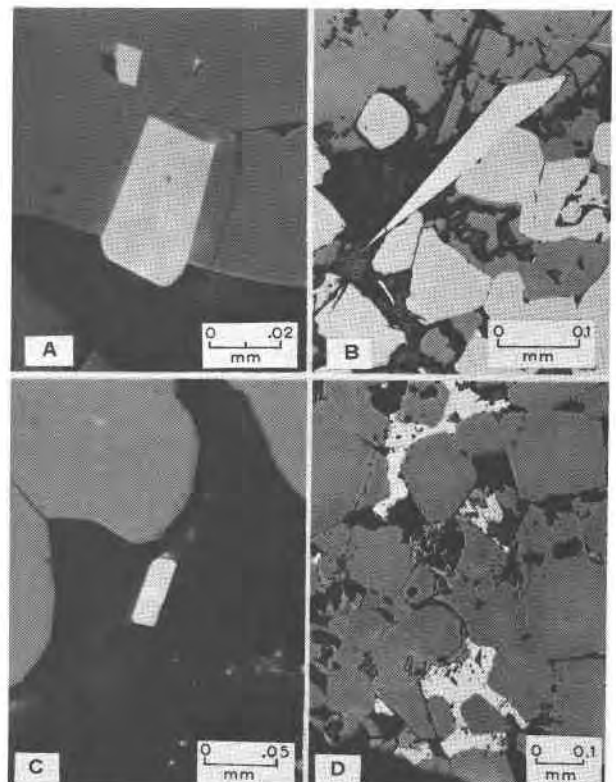


Fig. 4. Photomicrographs, reflected light. A, C, and D in oil immersion. (A) Two rutile crystals (light gray), one partly enclosed in chromite (medium gray), one completely enclosed. H unit, Jagdlust. (B) Cumulus rutile crystal (white) associated with chromite (light gray) and bronzite (medium gray). Base of F chromitite, Annex Grootboom. (C) Rutile crystal (light gray) in plagioclase (black). Medium gray—chromite. F unit, Jagdlust. (D) Postcumulus rutile (white) interstitial to chromite (medium gray). Footwall chromitite, Winterveld.

chromite (Fig. 4D). The aggregates are very irregularly distributed. Rutile is very abundant in places, absent in others. The erratic distribution of rutile and the local high rutile/chromite ratios cannot be explained in terms of exsolution. Rutile of this type evidently formed at the postcumulus stage. In both chromitites in which such rutile occurs, the chromites contain less than 1 percent TiO_2 , and saturation of chromite at low levels is again indicated.

Irvine (1974) reported that in chromite from the Muskox intrusion rutile occurs as inclusions in chromite, but more commonly as primary rodlike crystals scattered among the chromite grains. A sample of chromite collected by the writer from unit 17 south of Transition Lake (see Smith *et al.*, 1967) shows the two types of rutile occurrence described by Irvine. In addition, rutile occurs as anhedral marginal to chromite grains, and as minute oriented needles within chromite grains, both types presumably representing oxidation-exsolution. Finally there is one occurrence (Fig. 5) of what appears to be postcumulus rutile.

The normal TiO_2 content of chromite in the Muskox sample is 4.6 percent. Crystals in contact with the postcumulus rutile, however, have only 3.4 percent TiO_2 . Partial depletion during formation of rutile is indicated, but it is not enough to account for all the rutile present.

Rutile has also been reported by E. D. Jackson

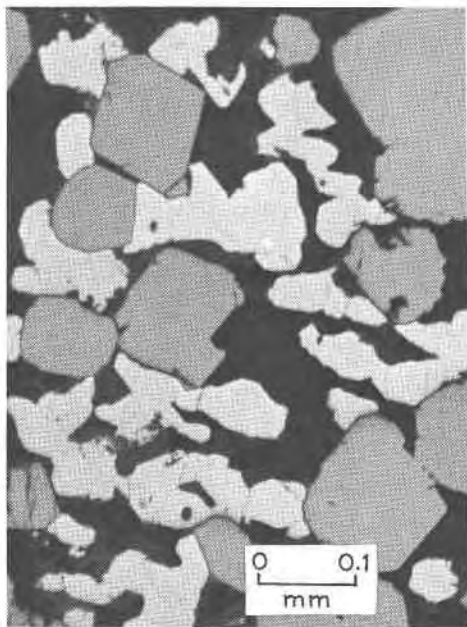


Fig. 5. Photomicrograph in reflected light, oil immersion. Rutile (light gray) interstitial to chromite (medium gray). Chromitite, Muskox intrusion, N.W.T., Canada.

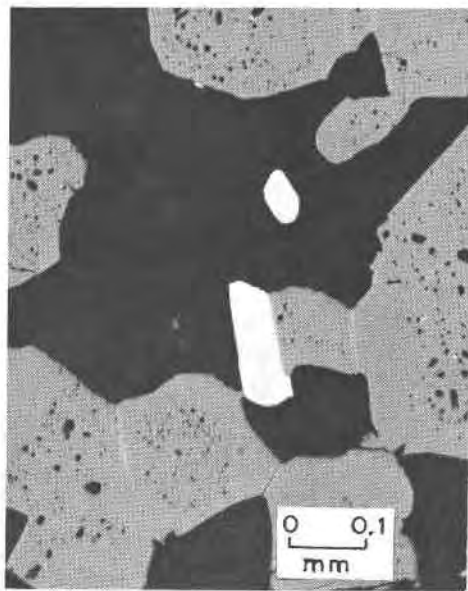


Fig. 6. Photomicrograph in reflected light, oil immersion. Two cumulus crystals of rutile (white) associated with chromite (gray) and plagioclase (black). Minute inclusions of rutile in chromitite appear due to oxidation-exsolution. Chromitite, Fiskenaasset complex, Greenland.

(Irvine, 1974, p. 1009) as inclusions in Stillwater chromite. From Campo Formoso, Brazil, Hedlund *et al.* (1974) reported rutile and ilmenite in chromitite, apparent as unoriented inclusions in chromite grains. Ghisler (1970) found rutile in chromitites in the Fiskenaasset complex, Greenland, in intergrowths with chromite, as small marginal anhedral, and as large anhedral between chromite grains. He concluded that rutile was produced by exsolution during metamorphism, although the evidence for this does not appear persuasive. In a section of chromitite from Fiskenaasset, the writer found rutile that appears to have formed independently of chromite (Fig. 6). Associated chromite contains only 0.07 percent TiO_2 . Chromite from the Sittampundi Complex, India (Subramanian, 1956) contains both exsolved oriented rutile, and separate large anhedral grains. Both were regarded by Subramanian as metamorphic in origin. The complex is metamorphosed; the anorthositic rocks enclosing the chromitites now fall in the amphibolite facies. An analysis of a chromite from the complex shows 0.36 percent TiO_2 .

It thus appears that the stable association of rutile with chromite low in TiO_2 is not unique to the Bushveld Complex. In the Bushveld, in the Muskox intrusion, and possibly in the Fiskenaasset intrusion, rutile and chromite are associated in part as cumulus minerals.

Table 1. Electron microprobe analyses of rutile and ilmenite

	1.	2.	3.	4.	5.
TiO ₂	98.51	98.91	99.24	98.37	52.44
Al ₂ O ₃	0.05	0.04	0.08	0.05	0.01
Cr ₂ O ₃	0.87	0.65	0.69	0.86	0.49
MgO	0.06	0.06	0.04	0.05	2.77
MnO	n.d.	n.d.	n.d.	n.d.	2.36
FeO*	<u>0.41</u>	<u>0.17</u>	<u>0.23</u>	<u>0.47</u>	<u>41.38</u>
	99.90	99.83	100.28	99.75	99.45

*Total Fe as FeO.

1-4, Rutile. 1. Chromitic pyroxenite, upper part of D unit,

Jagdlust. Independent crystal. 2. Chromitite, top of H unit,

Jagdlust. Independent crystal. 3. As for 2, inclusion in chromite. 4. Chromitite, F unit, inclusion in chromitite.

5. Ilmenite from norite below Main Chromite Subzone, De Grooteboom.

Although in part rutile and chromite have crystallized as separate phases, the two minerals are closely associated. In the part of the Critical Zone from the base to the top of the M unit, rutile is lacking or rare in non-chromitic rocks thus far examined. It is relatively abundant in chromitic rocks of the F, H, and L units but is notably absent from non-chromitic rocks of the G and J units and the lower two-thirds of the M unit.

Acicular rutile in bronzite or plagioclase is found mostly in chromite-free rocks of the O and higher units. Swarms of rutile crystals appear to have been trapped in crystals of the two silicates.

The history of crystallization of rutile in the chromitic rocks of the Critical Zone is analogous to that of ilmenite in many titanomagnetite-bearing rocks (Vincent, 1960; Buddington and Lindsley, 1964). In these, a first generation of ilmenite was deposited as discrete (independent) crystals, more or less contemporaneously with titanomagnetite solid solution. Subsequently, at relatively high temperatures, a second generation of ilmenite was formed by oxidation of titanomagnetite_{ss} and exsolution of ilmenite to the margins of the titanomagnetite grains. Finally, at lower temperatures, hence lower diffusion rates, ilmenite lamellae within the magnetite grains were produced by further oxidation-exsolution. In the rocks of the Critical Zone, the independent rutile crystals and most of the large inclusions in chromite correspond to the first generation of ilmenite. The rutile anhedral marginal and interstitial to chromite and the acicular oriented inclusions of rutile in chromite correspond, respectively, to the second and third generations of ilmenite. In a few rocks, however, interstitial

rutile of type 6 appears to represent still another generation formed very locally from the magma during the postcumulus stage.

Analyses of rutiles from various samples are given in Table 1. Small amounts of iron and chromium are invariably present.

Ilmenite

Ilmenite associated with chromite, locally in a reaction relation, has been reported by Legg (1969) from chromitites in the Merensky Reef at the Union Mine, Western Bushveld Complex. Macdonald (1967) reported the occurrence of ilmenite and rutile in chromitites on Farm Ruighoek in the Western Complex. Ilmenite is an uncommon mineral in the normal layered rocks of the Eastern Complex. I have not found it in any of hundreds of samples of chromitic rocks from various localities north of the Steelpoort River, including samples of chromitite from the Merensky Reef on farms Winnarshoek and Umkoanes Stad. Reexamination of the ilmenite reported by Younger (1958) indicates that it is rutile. South of the Steelpoort River, however, ilmenite has been observed in a few samples of chromitic rocks from the Main Chromite Subzone on Annex Grootboom, and in two thin chromitites below the Main Chromite Subzone on De Grooteboom. In all these samples it occurs as tiny grains interstitial to chromite. In chromitite from the Merensky Reef on Grootboom, it forms scattered grains interstitial to chromite, with or without associated rutile, and a few inclusions in chromite. Rutile is much more abundant in the chromitite, however, than ilmenite.

The chemistry of ilmenite has not been investigated fully. One analysis is given in Table 1. The MgO and MnO contents are noteworthy.

The great preponderance of rutile over ilmenite in the chromitic rocks is somewhat surprising in the light of experimental investigations. Lindsley (1976) has recently reviewed phase relations in the system FeO-Fe₂O₃-TiO₂. Muan *et al.* (1972) summarized known phase relations in the systems FeO-Al₂O₃-TiO₂, MgO-Al₂O₃-TiO₂, Fe₂TiO₄-FeAl₂O₄-FeCr₂O₄, and Mg₂TiO₄-MgAl₂O₄-MgCr₂O₄. Muan *et al.* (1971) described studies of simplified ternary systems involving TiO₂, Al₂O₃ or Cr₂O₃, and MgO or FeO as components. In all systems studied thus far, at temperatures of 1000° to 1300°C, the spinel field is separated from the rutile field by a pseudobrookite field, a rhombohedral oxide_{ss} field, or both. In systems containing FeO or Fe₂O₃, ilmenite is the stable phase coexisting with spinel. The assemblage magnetite-

rutile is apparently stable only at temperatures well below the magmatic range (Lindsley, 1976). Additional experimental work is evidently needed to understand relations in the complex system $\text{FeO-MgO-Fe}_2\text{O}_3\text{-Al}_2\text{O}_3\text{-Cr}_2\text{O}_3\text{-TiO}_2$ represented by Bushveld chromites.

Complex Ti-rich oxide

At certain horizons, tiny grains of a Ti-rich mineral have been found. The mineral is either a member of the pseudobrookite series or the senaite-crichtonite series, containing Cr, Fe, Al, Mg, Mn, Zr, Sc, Y, and rare earths. Description and analyses are given in a separate paper (Cameron, 1978a).

Titanium in chromite

Chromites in samples representing 129 stratigraphic horizons from top to bottom of the Critical Zone of the sector of the Eastern Complex north of the Steelpoort River have been analyzed by the writer by means of the electron microprobe. Analyses of chromites from 64 horizons are reported in a separate paper (Cameron, 1977). In addition, chromites from 52 horizons in the Critical Zone south of the Steelpoort River have been analyzed by D. B. Furgason (1977) and chromites from three other horizons by the author. Results are summarized in Table 2. Only ranges are given. A more detailed presentation is hardly justified because the TiO_2 content of chromite does not vary systematically with stratigraphic position, and the TiO_2 content of a given chromite is not a reliable indicator either of stratigraphic position or of differentiation trends. In general, chromites from the Upper Critical Zone north of the Steelpoort River are higher in TiO_2 than chromites from the Lower Critical Zone, but in each of the two zones there is a considerable range of TiO_2 contents. It is also true that in general chromite in chromitites is lower in TiO_2 than chromite in associated silicate rocks, as indicated in the table, but again ranges overlap.

Not included in Table 2 is a spinel (Furgason,

Table 2. TiO_2 contents of chromites, in weight percent

	Chromites in Chromitites	Chromites in Silicate Rocks
North of Steelpoort valley		
Upper Critical Zone	0.52-1.29	0.64-2.24
Lower Critical Zone	0.48-0.90	0.31-2.10
South of Steelpoort valley	0.50-2.35	0.42-2.47

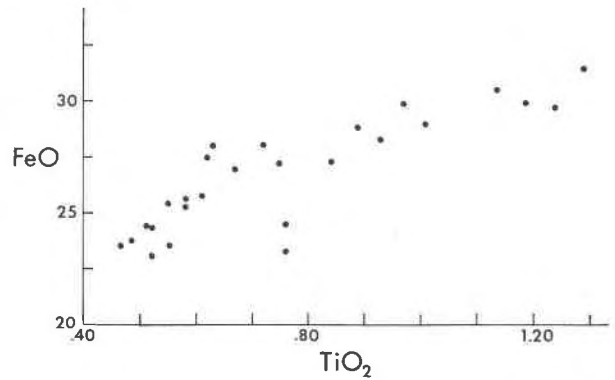


Fig. 7. Weight percent FeO (total iron calculated as FeO) plotted against weight percent TiO_2 for chromites in 26 chromitites of the Critical Zone. For complete analyses of the chromites see Cameron (1977).

1977) occurring in trace amounts in norite on Farm Grootboom. It is an aluminian ferrian chromite containing 5.17 percent TiO_2 .

The TiO_2 content of chromite might be expected to vary with its bulk composition, but plots show no correlation between TiO_2 content and proportions of various cations. There is, however, some correlation between TiO_2 content and total iron content of chromite, as displayed in Figures 7 and 8.

Discussion

Studies of spinels containing various proportions of Ti and Cr, along with other cations, have now been made for two principal groups of rocks—lunar basalts and associated rocks, and terrestrial rocks. In some lunar rocks a complete range of compositions from ulvöspinel to Cr-rich spinels has been found, with no evidence of a miscibility gap in the series

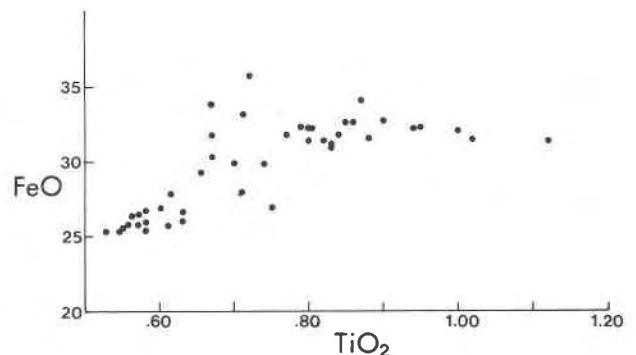


Fig. 8. Weight percent FeO (total iron calculated as FeO) plotted against weight percent TiO_2 for chromites in 38 layers of chromitic pyroxenites and chromitites in the upper part of the D unit. The sequence includes the Steelpoort and Footwall chromitites.

(Gibb *et al.*, 1970; Cameron, 1971; Champness *et al.*, 1971; El Goresy *et al.*, 1971; Keil *et al.*, 1971; El Goresy, 1976). In others, compositional gaps (Haggerty and Meyer, 1970) have been found.

In terrestrial extrusive rocks, spinels ranging from chromite to titanomagnetite have been reported. In basaltic lavas of Makaopuhi, Hawaii, Evans and Moore (1968) found a complete series between the two end members and inferred complete miscibility at temperatures not above 1200°C. Spinel intermediate between chromite and titanomagnetite have also been found in volcanic rocks by Gunn *et al.* (1970) and Thompson (1973), and a nearly complete series has been reported by Arculus (1974).

Chromite-titanomagnetite series in true intrusive rocks are apparently rare (Haggerty, 1976) but have been reported from kimberlites (Mitchell and Clark, 1976). A continuous series was found by Cameron and Glover (1973) in mafic pegmatites in the Eastern Bushveld Complex, but those bodies were formed by replacement of the normal layered rocks. In layered mafic intrusions in general, spinels are either Ti-rich and Cr-poor, or Cr-rich and Ti-poor, as in the Bushveld. Where both are present, they occur at widely separated stratigraphic horizons.

The reasons for discontinuities in titanomagnetite-chromite and ulvöspinel-chromite series have been discussed by various authors (*e.g.* Kushiro *et al.*, 1970; Cameron, 1971; Busche *et al.*, 1972; Haggerty, 1972; Nehru *et al.*, 1974; El Goresy, 1976). A miscibility gap in the series is obviously one possible explanation. Irvine (1967), however, suggested that the onset of clinopyroxene crystallization in a mafic magma could terminate the crystallization of chromite, the incorporation of Cr in the clinopyroxene reducing the concentration of Cr in the magma below the saturation level for chromite. Spinel crystallization would not be resumed until the concentrations of Ti and Fe rose to levels at which titanomagnetite is a stable phase. This explanation has been applied to spinels in certain lunar rocks by Cameron (1971), Busche *et al.* (1972), and Nehru *et al.* (1974). Support is given by the experimental work of Hill and Roeder (1974), who studied the crystallization of a basaltic melt under varying conditions of temperature and oxygen fugacity. In the temperature range 1050° to 1200°C, at oxygen fugacities in the range $10^{-0.7}$ to 10^{-9} , they obtained a continuous series of spinels from chromite to titanomagnetite, the Cr-rich members forming at high temperatures and low oxygen fugacity. At still lower oxygen fugacities, however, spinel crystallization ceased with the appearance of

clinopyroxene and was resumed only when the FeO, Fe₂O₃, and TiO₂ contents of the residual liquid increased sufficiently to cause precipitation of titanomagnetite.

Hill and Roeder concluded that the crystallization of spinel from basaltic liquids in near-surface environments is a function of a combination of factors, the most important being Cr content of the liquid, oxygen content or ferrous-ferric ratio, MgO content, TiO₂ content, temperature, and the presence or absence of clinopyroxene as a stable phase. For intrusive rocks total pressure should be added to these, because Osborn and Watson (1977) have shown that total pressure significantly influences the compositions of spinels.

As pointed out by Cameron and Glover (1973), Irvine's explanation seems applicable to the Eastern Bushveld Complex in a broad sense. Bronzite was the stable cumulus pyroxene during crystallization of the Lower Critical Zone and most of the Upper Critical Zone. In the few units of the Upper Critical Zone in which cumulus clinopyroxene is present, there is no spinel. Chromite crystallization terminated with formation of the Merensky Reef, above which cumulus clinopyroxene is prominent. Spinel crystallization was not resumed until thousands of feet of rock had accumulated, and Fe and Ti contents of rest magma permitted crystallization of titanomagnetite.

The present study indicates, however, that this general explanation may not account for the low contents of TiO₂ in chromites of the Critical Zone. The presence of coexisting cumulus rutile, and, locally, postcumulus rutile indicates that chromite was saturated with TiO₂, hence under the conditions prevailing, a miscibility gap may have existed in the series chromite-titanomagnetite. Furthermore, the presence of oxidation-exsolution intergrowths of chromite and rutile indicates that the solubility of Ti in chromite decreased during the subsolidus stage, presumably because the system became more oxidizing with fall in temperature.

The nature of conditions in the Bushveld magma is partly indicated. Using the Sato cell, Flynn and Ulmer (1972) obtained 1075°C and $10^{-12.2}$ as the equilibration temperature and oxygen fugacity for the assemblage at the contact of the Lower Critical Zone and Upper Critical Zone. It is not certain, however, whether these values represent cumulus, post-cumulus, or subsolidus equilibration. Guilbert (1962) studied the crystallization of melts of mixtures of labradorite, bronzite, and chromite with proportions and compositions appropriate to the D unit of the

Critical Zone. The temperature range of the experiments was 1100° to 1550°C. Oxygen fugacity was controlled over a range from 10^{-12} atm at 1100° to 10^{-7} atm at 1550°C, so as to avoid changes in the Fe^{2+}/Fe^{3+} ratios of the phases. A labradorite-orthopyroxene-plagioclase eutectic was found at 1215°C, at 36 percent orthopyroxene, 61 percent plagioclase, 3 percent chromite. In view of uncertainties about the composition of the Critical Zone magma, these values cannot be taken literally, but they probably are not far from the actual values. Guilbert calculated that for precipitation of chromite alone, a minimum content of about 1200 ppm Cr was required in the melts. Cameron (1978b) has calculated that the Cr content of the Bushveld magma was at least 1000 ppm. This is within the range of 540–1600 ppm calculated by Irvine (1977) for the Muskox magma during crystallization of chromite and olivine.

Calculations of total pressure rest on known data for thickness of roof rocks, about 14,000 feet, and uncertain inferences as to the height of the column of magma present between the roof and the top of the cumulate pile at the time the Critical Zone was forming. The problem with the latter is that recent work (Gruenewaldt, 1973) has indicated a heave of magma during the formation of the Main Zone. The best estimate is that total pressure was between 3 and 4 kbar.

Conclusions

1. Chromite and rutile were stable as coexisting phases during accumulation of many chromitic units of the Critical Zone of the Eastern Bushveld Complex.

2. Chromite was saturated with TiO_2 at levels of 2.5 percent TiO_2 or less, hence a miscibility gap may exist in the series chromite-titanomagnetite under the conditions of crystallization of the Critical Zone.

3. In general, rutile content and TiO_2 content of chromite increase upward in the Critical Zone.

4. During the subsolidus stage, there was loss of TiO_2 from chromites due to oxidation-exsolution.

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