

## Intrinsic Oxygen Fugacity Measurements on Chromites From the Bushveld Complex and Their Petrogenetic Significance

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**Abstract.** Oxygen Fugacity measurements were carried out on chromites from the Eastern Bushveld Complex (Maandagshoek) and are compared with former measurements on chromites from the western Bushveld Complex (Zwartkop Chrome Mine). These results together with those of Hill and Roeder (1974) yield the following conditions of formation for the massive chromitite layers:

Western Bushveld Complex (Zwartkop Chrome Mine)

Layer	$T(^{\circ}\text{C})$	$p_{\text{O}_2}(\text{atm})$
LG 3	1160–1237	$10^{-5} - 10^{-7.6}$
LG 4	1175–1200	$10^{-6.35} - 10^{-7.20}$
LG 6	1162–1207	$10^{-6.20} - 10^{-7.50}$

Eastern Bushveld Complex (Farm Maandagshoek)

L XI	1115–1150	$10^{-7.80} - 10^{-8.80}$
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(=Steelpoort Seam)

L X	1125	$10^{-8.25}$
V	1120	$10^{-8.55}$
L II	1120–1145	$10^{-8.0} - 10^{-8.60}$

The comparison of the data shows, that the chromitite layers within each particular sequence were formed under approximately identical  $p_{\text{O}_2}$ - and  $T$ -conditions. The chromites from the western Bushveld Complex, however, were formed at higher temperatures and higher oxygen fugacities than the chromites from the eastern Bushveld Complex.

From  $p_{\text{O}_2}$ - $T$ -curves of disseminated chromites and the temperatures derived above, the following conditions of formation for the host rocks were obtained:

Western Bushveld Complex

$$T = 1200^{\circ}\text{C}; \quad p_{\text{O}_2} = 10^{-7.25} - 10^{-7.50}$$

Eastern Bushveld Complex

$$T = 1125^{\circ}\text{C}; \quad p_{\text{O}_2} = 10^{-8.50} - 10^{-9.25}$$

Consequently, the host rocks in the Zwartkop-Chrome-Mine, were formed under higher temperatures and higher oxygen fugacities than the host rocks at Maandagshoek. The rock sequence in the Zwartkop-Chrome-Mine therefore originated in an earlier stage of the differentiation of the Bushveld magma.

Comparison of the chromites from the host rocks with the chromites from massive layers supports Ulmer's (1969) thesis that an increase of the oxygen fugacity is responsible for the formation of massive chromitite layers. The values in this investigation show that increases of only about 0.5–1.0 log units are necessary to enhance chromitite layer formation.

### A. Introduction

Because of the limited solubility of  $\text{Cr}^{3+}$ -ions in silicate magmas (e.g., Irvine, 1974) chromite separates early during fractional crystallization. In many ultrabasic and basic intrusions chromite is frequently concentrated in the form of massive layers. The reason for the repetitive formation of chromitite layers has been discussed in several publications, three of which are briefly referred to here:

– Jackson (1961) explained the typical cyclic occurrence of certain cumulus minerals of the ultrabasic part of the Stillwater Complex as being due to a mechanism of “variable depth convection” in the magma, which can be comprehended by the interaction between the adiabatic temperature gradient and the melting point gradient.

– Irvine (1977) on the basis of observations in synthetic systems suggested that the contamination of magma which has differentiated to relatively silicious compositions by fresh magma of the same type can

be held responsible for the formation of massive chromitite layers.

— Ulmer (1969), reported that a pulsating oxygen fugacity could have been the controlling factor. In the same publication he also pointed out, that by means of oxygen fugacity measurements it should be possible to get some basic information about the genesis of chromites.

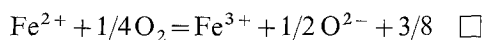
For the oxygen fugacity measurements, chromite samples from the Western (Zwartkop-Chrome-Mine, ca. 100 km north of Rustenburg) and from the Eastern Bushveld Complex (Farm Maandagshoek) were available.

Seeing that these samples belong to coherent profiles over about 300 m of vertical rock sequence, oxygen fugacity measurements will not only yield possible information on the genesis of the chromitite layers but also on the differentiation of the magma and the genetic position of both profiles in the total rock sequence.

The oxygen fugacity measurements were carried out in galvanic high temperature cells with  $ZrO_2(CaO)$  as solid electrolyte. By this way the oxygen fugacities of the separated chromite fraction and partially of the total silicate fraction were determined.

## B. Theoretical Considerations

As already pointed out by Sato (1972) in the case of oxygen fugacity measurements on single oxides, the reaction which determines the oxygen fugacity is not an equilibrium reaction between two crystalline phases and a gas phase, but rather an oxygen buffering equilibrium between only one crystalline phase (the natural chromite sample) and the gas phase. This equilibrium can only be understood in regard to the vacancy concentrations. For pure  $Fe_3O_4$ , the reaction which is also applicable for the problem discussed here can be described in the following way (Flood and Hill, 1957):



This reaction describes the formation of 3/8 vacancies ( $\square$ ) by oxidation at constant total Fe-content. In the range  $Fe^{3+} \gg Fe^{2+}$ , the range of sufficiently great non-stoichiometry, the equilibrium constant can be given with good approximation as

$$K = \frac{n_{Fe^{3+}}}{n_{Fe^{2+}} \cdot p_{O_2}^{1/4}} \left( \frac{n_{Fe^{3+}} - 2n_{Fe^{2+}}}{8 \sum n_i} \right)^{3/8}$$

with  $n_i$  = number of moles of ionic species.

This reaction can be applied to natural spinel solid solutions considering  $Fe_3O_4$  as the component with the maximum non-stoichiometry which determines the  $p_{O_2}^1$  of the specimen. This assumption is supported by the results obtained on all spinel systems investigated up to now, which clearly show, that at 1300°C the essential end members  $MgCr_2O_4$ ,  $FeCr_2O_4$ ,  $MgAl_2O_4$ , and  $FeAl_2O_4$  are nearly ideally stoichiometric (see Ulmer, 1969). In  $MgFe_2O_4$ , as well as in  $Fe_3O_4$  there is a range of solid solution with  $Fe_2O_4$  (Ulmer and Smothers, 1968). But  $MgFe_2O_4$  is a subordinate solid solution compound. Following De Waal (1975) the Bushveld-chromites cannot be classified as a simple solid solution type  $M^{2+}M_2^{3+}O_4$ , but rather as a mixture containing additional amounts of  $M_2^{3+}O_3$  molecules, so that the above-mentioned reaction should reflect the oxygen buffering cell reaction in a good approximation.

## C. Experimental Conditions

### 1. Sample Preparation

After crushing, the sieve-fraction  $0.25 > x > 0.10$  mm was separated into chromite- and silicate fraction by means of a magnetic separator. When necessary the purity of the sample was brought up to better than 99% by selection under the stereo microscope. Directly before the measurement, the specimen was ground in acetone down to  $< 5 \mu m$ . After vaporization of the acetone, the powdered sample was placed in the  $ZrO_2$ -tube, which was immediately closed and evacuated.

### 2. Measuring Equipment

The solid electrolyte tube  $ZrO_2(CaO)$  of the equipment is 400 mm long with an inner diameter of 3 mm. By exactly fitting alumina tubes the free volume of the sample chamber could be minimized. (For details see Snelthage and Klemm, 1977.) At 1000°C the Kanthal tube furnaces have a temperature-constant zone of 8 cm.

The EMF was recorded by an automatically compensating mV-recorder and, additionally, controlling measurements were made by a voltmeter with high resistance.

### 3. Methods of Measurements

The EMF of the galvanic cells were measured at 1000, 1100, and 1200°C approaching from both sides. Ni/NiO was used as reference buffer (data after Charette and Flengas, 1968). Because of kinetical reasons a stepwise adjustment of the temperature was practiced. A constant EMF-reading for 1/2 h was assumed to be the equilibrium.

<sup>1</sup> In the low pressure range of these experiments the measured oxygen fugacity  $f_{O_2}$  is equal to the oxygen partial pressure  $p_{O_2}$

#### 4. Accuracy of Measurement

The accuracy of the temperature measurement can be estimated as  $\pm 5^\circ\text{C}$ . In spite of an accuracy of 0.1 log units for the  $p_{O_2}$ -measurement it was found in practice that values within a range of 0.2 log units were reproducible in runs of normal duration, so that this accuracy can be regarded as realistic for the  $p_{O_2}$ -determination.

### D. Petrography

#### 1. Western Bushveld Complex

A columnar section of the rock sequence at the Zwartkop Chrome Mine is given in Figure 1. The thicker chromitite layers are numbered LG 1-LG 6. Some petrographic details of the investigated layers, LG 3, LG 4, and LG 6 are reproduced in Figure 3. It is interesting to recognize that the sharp footwall contacts of the layers LG 3 and LG 6 are in contrast to the gradational footwall contact of LG 4, which has a sharp hanging contact. Furthermore it should be noted that olivine is present in the host-rock of LG 4, whereas it is absent in the pyroxenite of the other chromitite layers.

Seeing that a relatively detailed geochemical discussion of these chromitite layers is presented by Snethlage and Gruenewaldt (1978), only a short review of these results is given here.

The chemical analysis of all three layers shows that MgO and FeO in chromite behave antithetically (Table 1), i.e., the sudden increase in MgO at the sharp footwall contact of LG 3 and LG 6 contrasts with a sudden decrease of FeO, while at the gradational contact of LG 4 a gradual increase of MgO and a gradual decrease of FeO are observed. On the other hand, the chemical behaviour of  $\text{Cr}_2\text{O}_3$  and  $\text{Al}_2\text{O}_3$  differ significantly. In LG 3 an increase of both  $\text{Cr}_2\text{O}_3$  and  $\text{Al}_2\text{O}_3$  can be observed in contrast to LG 4 in which  $\text{Cr}_2\text{O}_3$  increases and  $\text{Al}_2\text{O}_3$  decreases and to LG 6 where only  $\text{Al}_2\text{O}_3$  increases and  $\text{Cr}_2\text{O}_3$  does not show any remarkable variation.

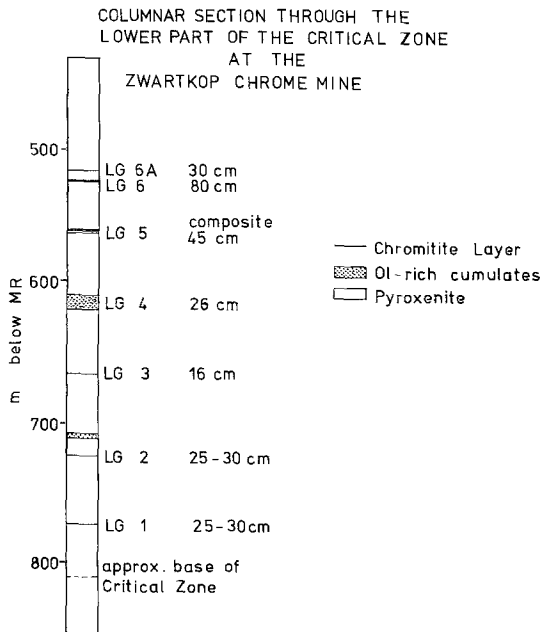


Fig. 1. The layered sequence in the Zwartkop-Chrome-Mine, Western Bushveld Complex (notation after Cousins and Feringa, 1964)

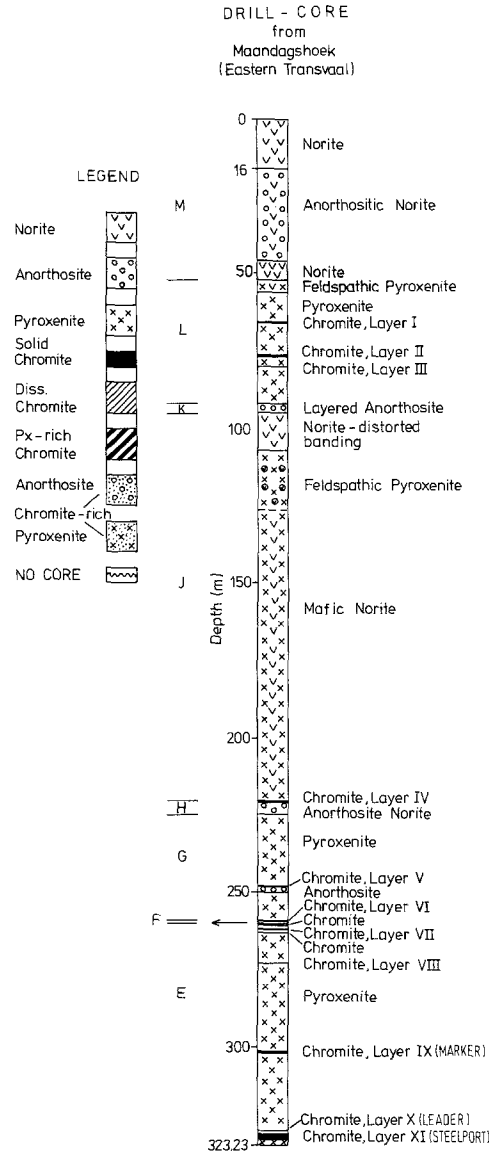


Fig. 2. The layered sequence in the area of the farm Maandagshoek, eastern Bushveld Complex (notation of the rock units after Cameron and Desborough, 1969; the thicker chromitite layers are numbered from L I to L XI = Steelpoort Seam)

#### 2. Eastern Bushveld Complex

Figure 2 shows the sequence of rock types as intersected in a borehole drilled on the farm Maandagshoek. Of petrographic significance are the thick mafic norite (unit 'J') and the 'F' unit (notation after Cameron and Desborough, 1969) in which cumulus plagioclase appears for the first time in the sequence. For convenience the chromitite layers of this drill core were numbered L I-L XI from the top down. According to this scheme the Marker layer would be L IX, the Leader Seam = L X and the Steelpoort Seam = L XI.

(a) Chromitite Layers L XI and L X. Layer XI is known as Steelpoort Seam, which has a strike length of 90 km in the eastern Bushveld Complex. Its thickness on the farm Maandagshoek is

**Table 1.** Chemical composition and molar ratios in the investigated chromites. The MgO/MgO+FeO ratio increases systematically from the host rock to the massive chromitite layer. The chemical analyses of LV and LII are still incomplete and will be reported later. FeO-values are mean values of a wet-chemical and a gravimetric (oxidation in air) determination.  $N$  = mole fraction

Sample	$N_{Cr_2O_3}$	$N_{Al_2O_3}$	$N_{MgO}$	$N_{FeO}$	$N_{Fe_2O_3}$	$\log Fe^{2+}/Fe^{3+}$	MgO/ MgO+FeO
LG 3, -7	0.3314	0.0977	0.1817	0.2755	0.058	0.3708	0.398
LG 3, -4	0.3432	0.1190	0.2631	0.2254	0.044	0.3247	0.539
LG 3, +2	0.3508	0.1170	0.2869	$\sum FeO.2980$	—	—	—
LG 3, +8.5	0.3425	0.1132	0.2886	0.1905	0.048	0.2976	0.602
LG 4, -67	0.3087	0.1508	0.2537	0.241	0.056	0.21	0.513
LG 4, -43	0.3194	0.150	0.2971	0.2029	0.051	0.2126	0.500
LG 4, -20	0.3387	0.1277	0.2991	0.1908	0.043	0.1826	0.610
LG 4, -6	0.3472	0.1215	0.3335	0.167	0.051	0.2115	0.666
LG 6, -4	0.3097	0.0904	0.1464	0.307	0.073	0.6184	0.322
LG 6, +1	0.3092	0.1329	0.2465	0.241	0.061	0.2921	0.505
LG 6, +40	0.3091	0.1389	0.2514	0.2409	0.058	0.3173	0.510
LG 6, +87	0.3164	0.0932	0.1567	0.2712	0.085	0.2191	0.366
LG 6, +91	0.3084	0.1368	0.2271	0.2570	0.064	0.2171	0.378
L XI, 1	0.3129	0.0978	0.1555	0.306	0.075	0.3096	0.336
L XI, 2	0.3147	0.1296	0.2554	0.2602	0.065	0.298	0.495
L XI, 3	0.3226	0.1364	0.2859	0.247	0.052	0.3756	0.537
L XI, 4	0.2970	0.1263	0.1932	0.2672	0.059	0.3316	0.419
L X, 1	0.3124	0.1349	0.2666	0.272	0.081	0.2250	0.494
L X, 3	0.3031	0.1481	0.2624	0.2459	0.058	0.3218	0.516
L X, 4	0.3110	0.1418	0.2648	0.2339	0.056	0.3072	0.531

about 1.50 m (see Fig. 4) where it has gradational footwall and hanging wall contacts as also described by Cameron and Desborough (1969) from other areas of the eastern Bushveld Complex. Pyroxenite, the host rock, contains about 4% chromite. The 40 cm thick Leader Seam (LX), has a sharp lower and a gradational upper contact and is separated from the underlying Steelpoort layer by a pyroxenite layer which contains a narrow zone of medium chromite enrichment.

The chemical analyses show that MgO and FeO in the chromite behave antithetic (see Table 1). The increase of MgO and the decrease of FeO correspond to the increase of the chromite concentration. The behaviour of  $Cr_2O_3$  and  $Al_2O_3$  can be compared with LG 6 at Zwartkop, in that increase of  $Al_2O_3$  can be observed, whereas  $Cr_2O_3$  shows no systematical variation. The  $Cr_2O_3$ -content reaches only 49% even in the massive parts. As in the layers LG 3, 4 and 6, the MgO/MgO+FeO ratio increases in the massive layer.

(b) *Chromitite Layer LV.* Layer LV is developed ca. 20 m above LXI and LX, i.e., about 10 m above unit 'F' (Cameron and Desborough, 1969). The modal analysis shows relative sharp contacts with the host rocks (Fig. 4). The underlying rock is anorthosite, whereas the chromitite layer is overlain by pyroxenite. At the basis of the massive layer chromite and plagioclase are associated cumulus minerals accompanied by noticeable mica content. These findings seem to be important for the interpretation of the  $p_{O_2}$ -measurements, as will be shown later.

(c) *Chromitite Layer LII.* Layer LII is located in the hanging wall of the thick mafic norite (unit 'J'). It consists of two approx. equal parts, separated from one another by 60 cm of chromite rich pyroxenite (Fig. 4). Up to now only samples from the lower part of the layer, which has gradational contacts with the underlying and overlying pyroxenites have been investigated.

### 3. Oxygen Fugacity Measurements

(a) *Possibilities of Interpretation.* The result of the oxygen fugacity measurements is only a  $p_{O_2}$ - $T$ -variation for every particular sample. Therefore, a direct interpretation with respect to the conditions of formation is not possible. For this reason some assumptions must be made.

Principally the interpretation can be restricted by every post-magmatic reaction as for example by the Mg/Fe<sup>2+</sup> exchange reaction between chromite and olivine resp. pyroxene (Irvine, 1965, 1967). However, the homogeneity of the chromites from LXI and LX (Schintgen, pers. comm.) as the absence of clear post cumulus or subsolidus formed reaction zones on the chromites from the eastern Bushveld Complex (Cameron, 1975) support the assumption that the  $p_{O_2}$ - $T$  behaviour of the chromites was fixed by the conditions during their formation.

Experimental investigations on basaltic liquids (Hill and Roeder, 1974) as well as models for the formation of layered intrusions (Jackson, 1961) suggest that the main spinel crystallization takes place in a small temperature range. Accordingly isothermal conditions can be assumed for the formation of a chromitite layer. This assumption can be supported, as will be shown later, by the results reported here. Because the  $p_{O_2}$ -curves do not intersect (see Figs. 5

## CHROMITITE LAYERS in the ZWARTKOP CHROME MINE

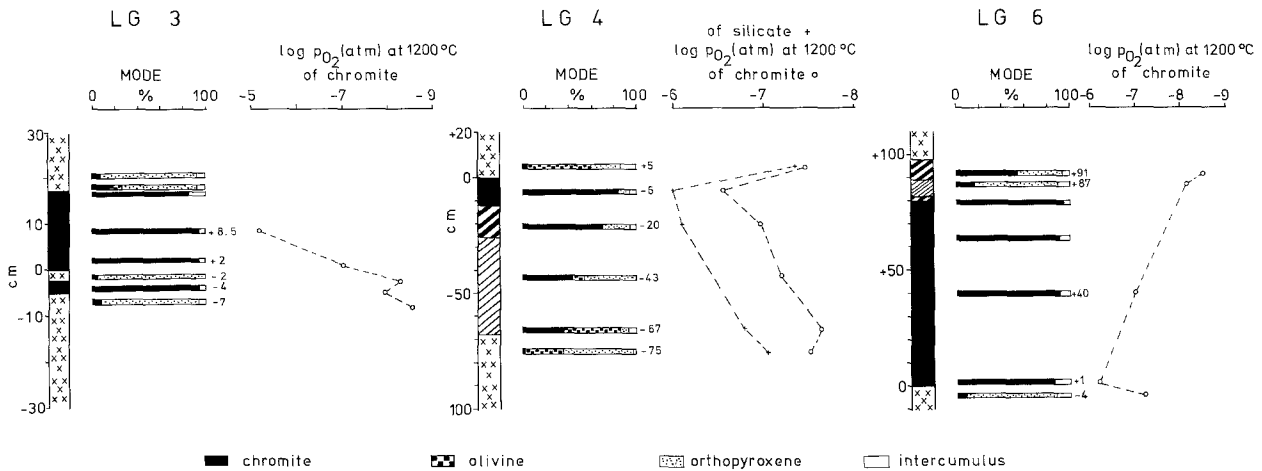


Fig. 3. Petrographic description and modal analyses of the chromitite layers LG 3, LG 4, and LG 6 from the Zwartkop Chrome Mine, western Bushveld Complex. The sample numbers are given in cm, and correspond to those in Figure 6. For all layers the  $p_{O_2}$ -profile at 1200°C shows an increase of the oxygen fugacity in the massive parts of the layer. In the case of the layers LG 3 and LG 6 there is a sudden increase of the  $p_{O_2}$  at the sharp basal contact, whereas the  $p_{O_2}$  increases continually at the gradational basal contact of LG 4 (see also LII, Fig. 4)

and 6), an isothermal profile over the chromite curves of every particular layer should reflect the relative  $p_{O_2}$ -variation during its formation.

Investigations on the liquidus phase relations of basalts (Hill and Roeder, 1974) show that under certain  $p_{O_2}$ - $T$  conditions which correspond to those of line A-B in Figures 5a and 6a there is a maximum of chromite crystallization. These  $p_{O_2}$ - $T$ -conditions can be assumed to correspond to the conditions of the formation of massive chromitite layers.

Consequently the intersections of the  $p_{O_2}$ - $T$  curves of the chromites from massive layers with the line A-B can be interpreted as the  $p_{O_2}$  and  $T$  conditions during the formation of the massive layers. Furthermore it can be seen, that in the temperature interval, which is fixed by the given intersections, the curves of the host rock chromites plot below the massive chromites. These results support Ulmer's hypotheses as well as the conclusion that an isothermal profile over the chromite curves of every particular layer reflects the  $p_{O_2}$ -variation during its formation. Therefore the investigations of Hill and Roeder, 1974 are very valuable for the interpretation of oxygen fugacity measurements on natural chromites.

(b) *Layer LXI.* The four specimens come from the underlying host rock (LXI,1) from the gradational contact zone on the basis (LXI,2) and on the hanging wall (LXI,4) and from the massive central part (LXI,3—Fig. 4).

To reduce the number of figures in this paper, the  $p_{O_2}$ - $T$  curves of all chromites are only shown as curves without the measured points in Figures 5 and 6. The measured curves of every particular

chromite specimen, however, are listed in detail in Snelthage (1976) and Snelthage and Klemm (1977).

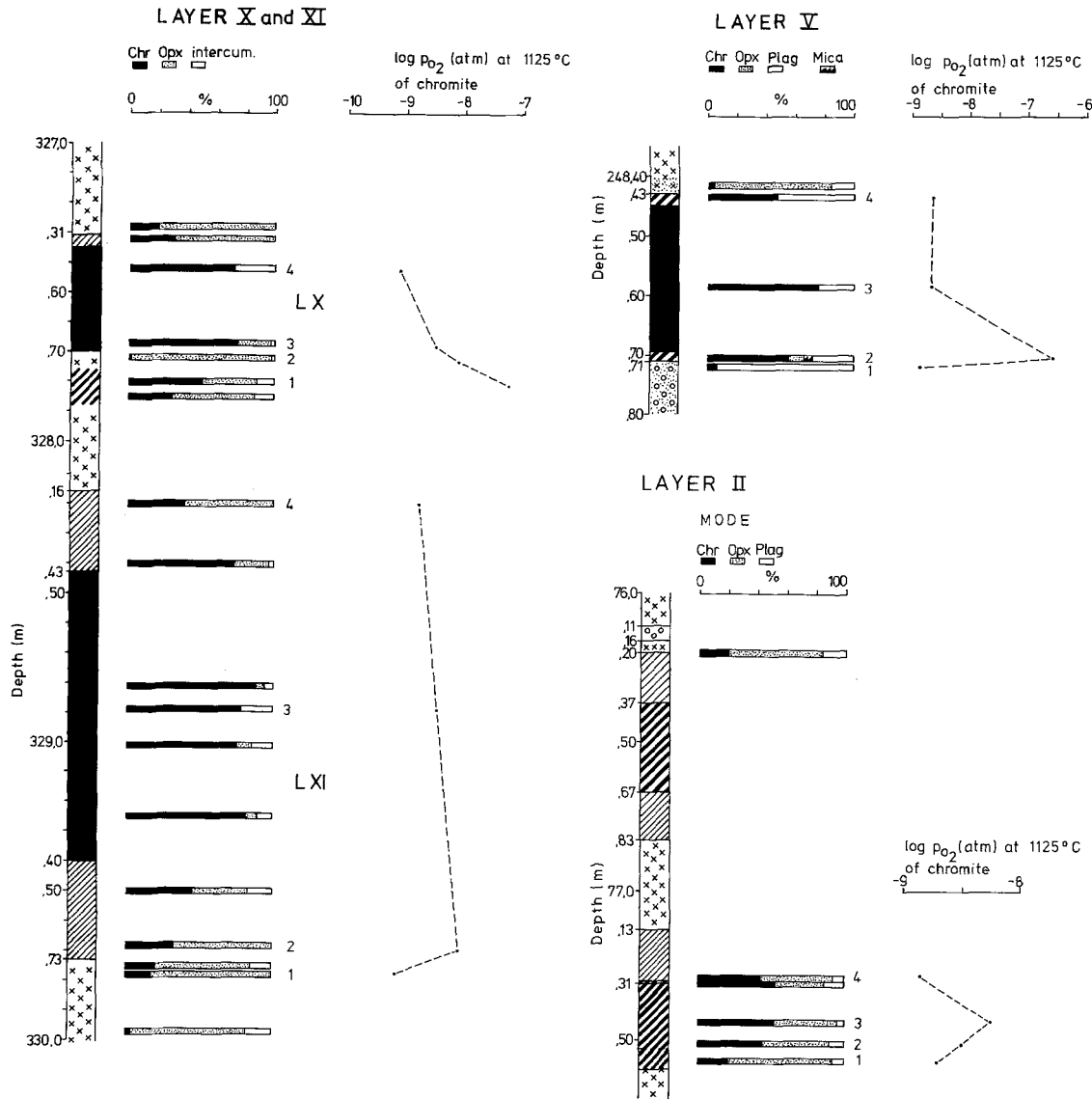
The three chromite curves No. 2, 3, 4 intersect the line A-B in the hatched area of Figure 5. From this the conditions of formation can be estimated as 1115–1150°C and  $10^{-7.8} - 10^{-8.8}$  atm  $p_{O_2}$ . The curve of chromite specimen 1 from the underlying host rock lies below the other curves in a range of inferior tendency for chromite crystallization in this temperature range (see Hill and Roeder, 1974). If 1125°C is considered as a reasonable magma temperature during the formation of Layer XI, it can be seen, that an increase of the oxygen fugacity between specimen 1, and the specimen 2, 3, and 4 must have taken place which would have been responsible for the formation of this layer. The oxygen fugacities at this temperature (1125°C) were plotted into Figure 4. It can be seen, that at the footwall contact there is a sudden increase of the  $p_{O_2}$ , followed by a continual decrease along the layer.

(c) *Layer LX.* The specimens were taken from the massive part (3,4) and from the chromite enriched zone of the pyroxenite, 10–15 cm below the sharp footwall contact of LX (specimen 1). Sufficient chromite could not be separated from the pyroxenite directly underlying LX, because of the extremely low chromite concentration of only 0.2%. Therefore LX2 is a whole rock specimen.

Only the curve of LX,3 intersects the line A-B on Hill and Roeder's diagram. From this intersection the conditions 1125°C and  $10^{-8.35}$  atm  $p_{O_2}$  can be deduced, which correspond very well to the interval of LXI. Surprisingly, the oxygen fugacities of LX,1 (below the layer) are higher than those of LX,3 and 4 (Fig. 4). This behaviour can be explained in the following way: Regarding the chemism the chromites of LX,1 have a composition as the massive chromites (comp. Table 1). Also with respect to the grain size the chromites of LX,1 belong to the massive chromites, because as the chromites from the base of LXI (LXI,2), they have the maximum size of the LX-chromites. Therefore, it seems to be justified to interpret the chromites LX,1 as the base of LX, which were separated by fractional settling or

## CHROMITITE LAYERS at FARM MAANDAGSHOEK

## EASTERN BUSHVELD COMPLEX

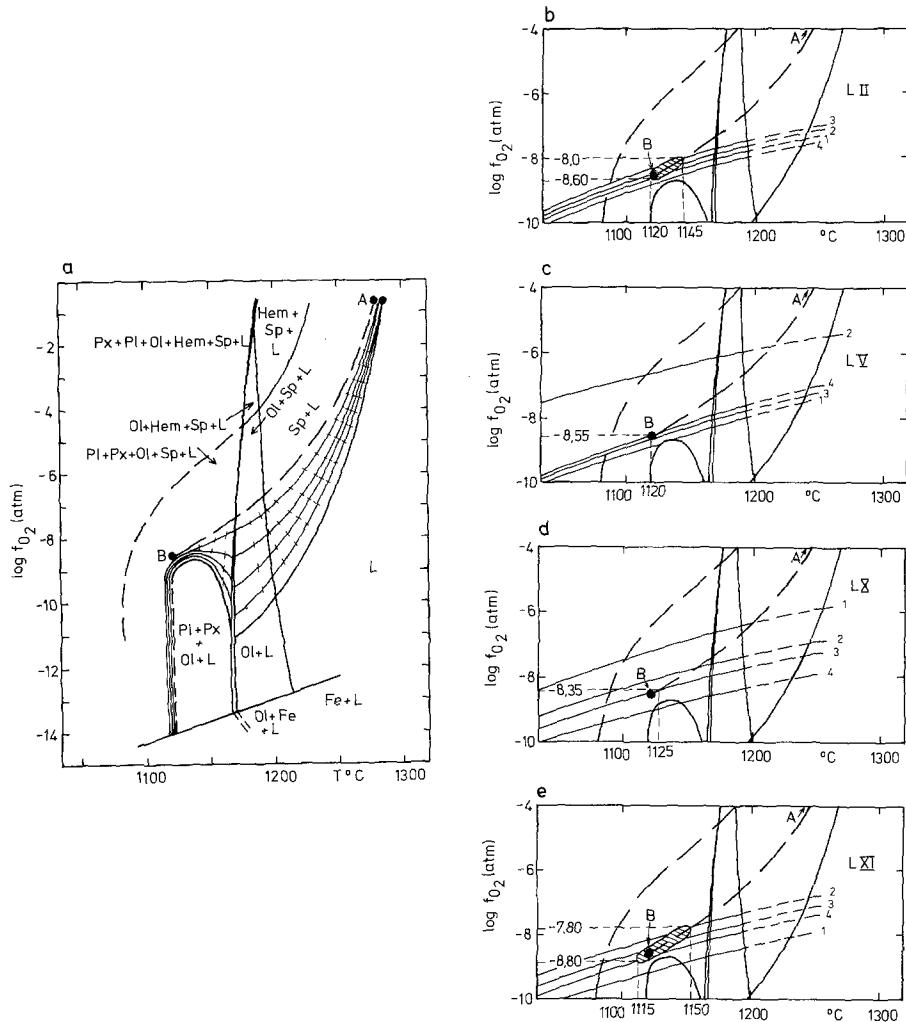


**Fig. 4.** Petrographic description and modal analyses of the layers LII, LV, LX and LXI (Steelpoort Seam), farm Maandagshoek, eastern Bushveld Complex (legend the same as for Fig. 2). The  $p_{O_2}$ -profiles of LII, LV and LXI at 1125°C (compare Fig. 5) show an increase of the oxygen fugacity towards the massive parts of the layers. The chemical composition of LX,1 (Table 1) gives an indication that this chromite is the basis of LX and was separated from this layer by gravitational settling or similar processes. The  $p_{O_2}$  of LX,2 is a  $p_{O_2}$ -value of the whole rock, because sufficient chromite could not be separated from this sample. The very high oxygen fugacity of LV, 1 may be explained by the fact that mica occurs in considerable amounts at the base of LV. For further explanations see the text

magma turbulences from the massive part of the layer. Following this interpretation it can be concluded, that the formation of LX was caused by an increase of the oxygen fugacity, presumably from the level of LXI,4 up to the level LX,1. From the intersection of the specimen LX,3 with the line A-B (see Fig. 5) 1125°C can be regarded as reasonable for all chromites of this layer so that the range of formation of LX,1 and LX,2 lies in the

area above the line A-B. The anomalous behaviour of LX,4 can not be explained sufficiently with the present knowledge even if a contamination of these chromites in a post-cumulus stage seems very likely.

(d) *Layer LV.* The investigated samples are the underlying host rock (LV, 1), from the lower and the upper contact zone (LV,2



**Fig. 5 a-e.** Conditions of formation of the chromite layers LXI, LX, LV and LII from farm Maandagshoek, eastern Bushveld Complex.

a simplified diagram of the liquidus phase relations of an olivine tholeiite G1-1921, after Hill and Roeder (1974). The line A-B shows the  $f_{O_2}$ - $T$ -conditions, under which Hill and Roeder found enhanced chromite crystallization (Line A-B is not a phase boundary). **b-e** sections through Hill and Roeder's diagram, showing the experimentally determined  $f_{O_2}$ - $T$  curves of chromites. The sample numbers correspond to those in Figure 4. The intersections between the chromite curves and the line A-B determine the conditions of formation of the layers. Further explanations are given in the text

and LV,4) and from the central part of the layer (LV,3). The underlying host rock is anorthosite, the hanging, like in the other layers, is pyroxenite (Fig. 4).

The curve of the sample LV,4 intersects the line A-B close to B (Fig. 5) and the derived conditions of  $1120^{\circ}\text{C}$  and  $10^{-8.55}$  atm  $p_{O_2}$  are in good agreement with the values derived from LX and LXI. Although the curve of sample LV,3 does not intersect the line A-B, it plots so close to LV,4, that it confirms the derived values.

The high oxygen fugacity of the sample LV,2 can be explained by the occurrence of remarkable amounts of mica in the footwall of that layer. Thus also LV is an example, that an increase of the oxygen fugacity leads to the formation of massive chromite layers, even though the relations are not so clear as in the other layers.

(e) *Layer LII.* Samples were investigated from the basal contact zone (LII,1) and from parts of different chromite concentrations of the layer (LII,2,3,4). The contacts of this layer are gradational, so that the chromite concentrations increase and decrease continually. The intersections of the curves with the line A-B (see Fig. 5) yield the conditions of formation  $1120$ - $1145^{\circ}\text{C}$  and  $10^{-8.0}$ - $10^{-8.60}$  atm  $p_{O_2}$ . Curves 1 and 4 belong to specimens with lower chromite concentrations and consequently they do not intersect the line A-B, but seeing that they plot very close to the other curves, they can be enclosed into the above derived conditions. If the temperature of formation is  $1125^{\circ}\text{C}$ , a  $p_{O_2}$ -profile as shown in

Figure 4 can be drawn. From this it can be seen that an increase of the oxygen fugacity is reflected in an increase in the chromite concentration. The  $p_{O_2}$  of the sample LII,4 from the upper contact zone is lower than that of LII,1 from the lower contact zone. This could again be due to contamination of these chromites after settling.

(f) *Chromite Layers LG3, LG4, LG6.* The specimens for the  $p_{O_2}$ -measurements were chosen according to the modal analysis (see Fig. 3). Because the petrography and the geochemistry of these layers is discussed in detail in other papers (Sneathlge and v. Gruenewaldt, 1978 and v. Gruenewaldt, in preparation), only the most important results are briefly reported here. The following conditions of formation can be deduced from Figure 6: LG3:  $1160$ - $1237^{\circ}\text{C}$ ,  $10^{-5}$ - $10^{-7.6}$  atm  $p_{O_2}$ ; LG4:  $1175$ - $1200^{\circ}\text{C}$ ,  $10^{-6.35}$ - $10^{-7.5}$  atm  $p_{O_2}$ ; LG6:  $1162$ - $1207^{\circ}\text{C}$ ,  $10^{-6.20}$ - $10^{-7.50}$  atm  $p_{O_2}$ . All three intervals overlap widely, so that  $1200^{\circ}\text{C}$  and  $10^{-6.0}$ - $10^{-7.0}$  can be considered as reasonable conditions of formation for all three layers (see also Sneathlge and v. Gruenewaldt, 1978).

As Figure 3 shows there is a correlation between the increase of the  $p_{O_2}$ -values and the mode. The layers LG3 and LG6, which have sharp footwall contacts show a sudden increase (see also LXI, farm Maandagshoek); Layer LG4, however, shows a continual increase at the footwall contact in accordance with the gradational increase of the modal percent of chromite (see also LII, farm Maandagshoek), whereas at the hanging wall there is a sudden decrease of  $p_{O_2}$  according to the sharp contact.

## E. Discussion

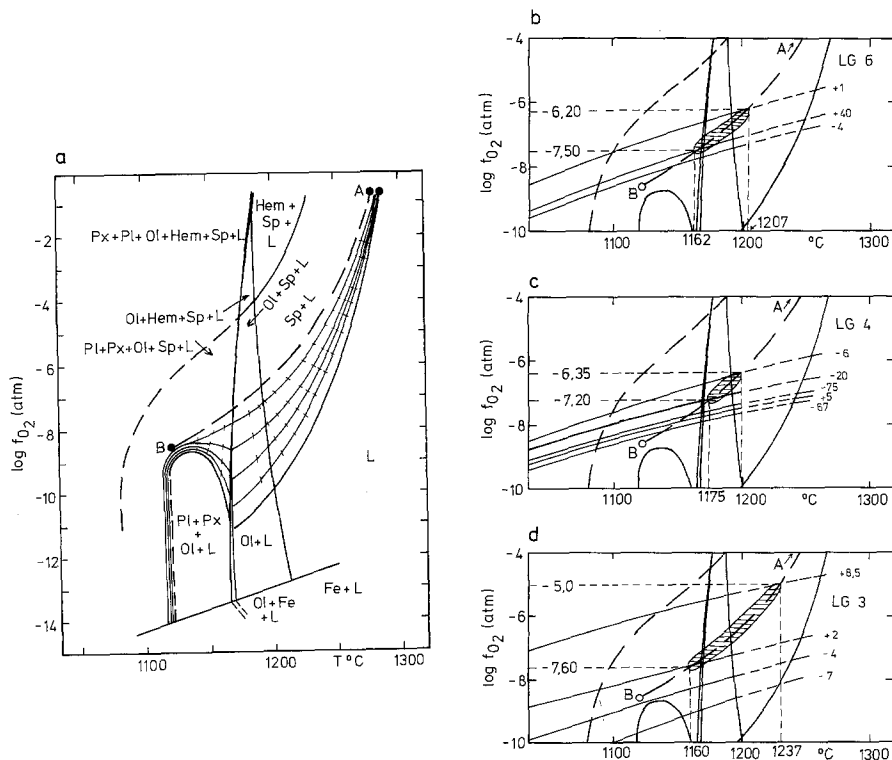
Generally can be found, that the chromites from the massive parts of the layers are in equilibrium with higher oxygen fugacities than the chromites from the host rocks. Consequently they have a higher MgO/MgO+FeO-ratio, which is, in agreement with the experimentally investigated systems, a result of high oxygen fugacities (Ulmer, 1969).

With Hill and Roeder's (1974) diagram, temperature marks can be derived which determine the temperatures of formation of the layers. Because of the small progress of differentiation during the formation of a chromitite layer and its immediate host rock, practically isothermal conditions can be assumed during their formation and it is therefore possible to compare the oxygen fugacities of the massive and of the host rock chromites at these derived temperatures. It is indicated from these isothermal  $p_{O_2}$ -profiles over the chromitite layers (Figs. 3 and 4), that an increase of  $p_{O_2}$  enhances the formation of chromite whereas the following decrease enhances the formation of silicate (see Ulmer, 1969). Moreover, it is interesting that this increase is in the range of about 0.5–1.0 log units.

Layer LX could be seen as exception from this observation; there is, however, some evidence at hand, that fractional settling might have been effective, so that the same interpretation is valid as for the other layers.

The temperature and  $p_{O_2}$  ranges of the chromite layers from the Zwartkop Chrome Mine (LG 3, 4, and 6, Western Bushveld Complex) overlap each other (Fig. 6) so that for these layers the same conditions of formation of  $10^{-6.0}$ – $10^{-7.0}$  atm  $p_{O_2}$  and  $1200^\circ\text{C}$  can be deduced. Consequently a trend from LG 3 up to LG 6 cannot be observed. From this it can be concluded that, in spite of their considerable differences with respect to petrography and chemical composition, these three layers have formed under nearly identical conditions (Sneath and v. Gruenewaldt, 1978). The same observation holds for the chromitite layers from Maandagshoek (eastern Bushveld Complex) whose conditions of formation range between  $1115$ – $1150^\circ\text{C}$  and  $10^{-7.80}$ – $10^{-8.80}$  atm  $p_{O_2}$ .

Oxygen fugacities of the same order of magnitude are reported by Ulmer (1969, p. 131) for the Leader Seam from eastern Bushveld Complex; massive chromite:  $10^{-6.30}$  atm  $p_{O_2}$  at  $1300^\circ\text{C}$  and chromite from the overlying pyroxenite:  $10^{-7.7}$  atm  $p_{O_2}$  at  $1300^\circ\text{C}$ . An extrapolation of the chromite curves reported here yields similar values. A remarkably lower oxygen fugacity ( $10^{-11.85}$  atm) at a slightly lower temperature ( $1085^\circ\text{C}$ ) is reported by Flynn (1972). These values were derived from the intersection of the  $p_{O_2}$ -curves of the cumulus minerals bronzite, chromite and anorthite of the 'F'-unit. Because the 'F'-unit lies between layers LV and LII, these values should be appropriate for a direct comparison. It must, however, be born in mind, that the 'F' unit



**Fig. 6 a-d.** Conditions of formation of the chromitite layers LG 3, LG 4 and LG 6, Zwartkop Chrome Mine, western Bushveld Complex. **a** simplified diagram of the liquidus phase relationships of an olivine tholeiite G1-1921, after Hill and Roeder (1974). The line A-B shows the  $f_{O_2}$ - $T$ -conditions under which Hill and Roeder found enhanced chromite crystallization. **b-d** sections through Hill and Roeder's diagram showing the experimentally determined  $f_{O_2}$ - $T$  curves of chromites. The sample numbers correspond to those in Figure 3. The intersections between the chromite curves and the line A-B determine the conditions of formation of the chromitite layers. Further explanations are given in the text



displays various unique features (Cameron, 1971) and that the formation of massive chromite layers must be considered as extraordinary events during fractional crystallization of the magma. Because of this, these differences should not be over-estimated.

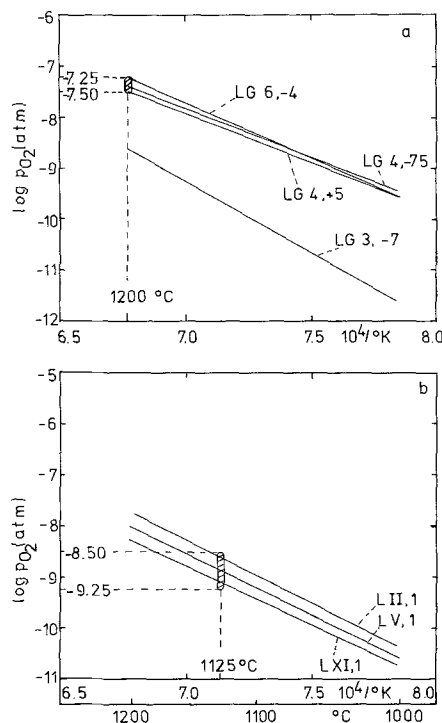
The comparison of the derived temperatures with the temperature data from synthetic systems is not satisfying. For the coexistence of orthopyroxene and spinel in the system  $MgO$ -Iron Oxide- $Cr_2O_3$ - $SiO_2$  for example Arculus and Osborn (1975) found a temperature interval from 1550/1540°C down to 1405/1380°C ( $p_{O_2} = 0.21$  atm). In the  $Cr_2O_3$ -free system this assemblage is stable to temperatures as low as 1380 to 1260°C at oxygen fugacities not lower than  $10^{-7}$  atm (Speidel and Osborn, 1967). Both temperature intervals are considerably higher than those derived here, but these differences are not surprising, since the experiments in the synthetic systems were carried out with pure reagents under dry conditions.

In addition, other experiments show that a water pressure of 1 kb, corresponding to a water content of 3%, lowers the crystallization temperatures of basalts by about 100°C (Hamilton et al., 1964). Consequently, the experiments on natural basalts, for example the experiments of Hill and Roeder (1974) as well as the estimated temperatures of crystallization of the Skaergaard Intrusion (Williams, 1971), lead to temperatures (1300 to below 1100°C) which are very close to those derived here. The temperature of 1085°C derived by Flynn (1972) for the 'F'-unit also agrees reasonably well with the temperatures obtained in this investigation.

Likewise, the  $T$ - and  $p_{O_2}$ -interval for the coexistence of pyroxene + anorthite + magnetite + liquid (1060°C at  $p_{O_2} = 10^{-10.6}$  atm; 1125–1150°C at  $p_{O_2} = 10^{-9}$  atm; 1150–1200°C at  $p_{O_2} = 10^{-7}$  atm; see Osborn, 1969 (a) shows that the  $T$ - and  $p_{O_2}$ -ranges found here can be considered as plausible for the formation of chromitite layers.

Contrary to the conditions of formation of the massive chromitite layers, which can be considered as extraordinary events, the oxygen fugacities of the host rock chromites should reflect the conditions during differentiation of the magma. Osborn (1959) has clearly proved, that the rock sequences of the layered intrusions like the Stillwater, Skaergaard, Great Dyke and Bushveld intrusions have formed by fractional crystallization under 'constant total composition of the condensed phases'. This implies, that the  $p_{O_2}$  decreases with falling temperature during crystallization. Hill and Roeder (1974) point out, that under this condition the decrease of the oxygen fugacity is in the order of 1.5 log units per 100°C.

On the basis of mineral equilibria Williams (1971) calculated the range of temperature and of the  $p_{O_2}$



**Fig. 7 a and b.** Conditions of formation of the host rocks, Zwartkop Chrome Mine, western Bushveld Complex = a, and Maandagshoek, eastern Bushveld Complex = b. The  $p_{O_2}$ - and  $T$ -values are derived from the plotted intersection areas. The temperatures correspond to the mean formation temperatures of 1200 and 1125°C which were derived from Figures 5 and 6. The narrow course of the curves and the  $p_{O_2}$ - and  $T$ -values indicate, that a progress in differentiation can not be recognized in either of the two rock sequences. The sample numbers correspond to those in Figures 3 and 4

during formation of the total Skaergaard Intrusion as being between 1300–900°C and  $10^{-9}$ – $10^{-14.5}$  atm respectively. For the total Bushveld Complex comparable ranges could be concluded. The 250–300 m vertical rock sequences from which material was investigated, are very small portions of the ca. 8 km thick rock sequence of the total Bushveld Complex. Therefore, it is not surprising if a progress in the path of differentiation is not detectable.

Figure 7 shows that except of LG 3, -7 the curves of the host rock chromites of the eastern and western Bushveld lie in very narrow  $p_{O_2}$ -ranges in the order of 0.5 log units. Regarding the eastern Bushveld Complex, the specimen L II,1 yields the highest oxygen fugacity value of the investigated disseminated chromites.

This behaviour is opposite to the trend of the crystallization path derived at by Osborn (1959). This observation, however, should not be interpreted to conclude a reverse differentiation trend, as it must be kept in mind, that on the one hand the degree of accuracy ( $\pm 0.2$  log units) is about the same as the

separation of the curves from one another and that on the other hand a noticeable progress in the magma differentiation must not be observed.

For these reasons, the chromitite layers in the eastern Bushveld Complex seem to have formed during isothermal increases of the oxygen fugacity from a uniform magma, which proceeded only insignificantly on its differentiation path between the layers LXI and LII. If  $1125^\circ\text{C}$  is considered as a plausible formation temperature for all chromitite layers than a  $p_{O_2}$  range of  $10^{-8.5} - 10^{-9.25}$  atm prevailed in the magma (Fig. 7).

The host rock chromites of LG 4 and LG 6 from the Zwartkop Chrome Mine, western Bushveld Complex, also lie very close together (Fig. 7), so that the existence of a uniform magma can be concluded. In this case the temperature of formation of the chromitite layers was found to be in the order of  $1200^\circ\text{C}$ , so that here the  $p_{O_2}$  range of the magma was between  $10^{-7.25} - 10^{-7.50}$  atm. These values correspond very well to the experimental results of Biggar (1974) who studied the liquidus of the chilled margin from the Bushveld at various  $p_{O_2}$  at 1 atm. The  $p_{O_2}$ - $T$ -range derived here, lies in the stability field of olivine + plagioclase + chromian spinel + liquid, found by Biggar. In spite of the absence of orthopyroxene, which Biggar ascribes to the dry experimental conditions or alternatively to the fact that the sample was not representative for the Bushveld, his  $p_{O_2}$ - and  $T$ -values agree very well with those derived at in this investigation.

The curve of the host rock chromite of LG 3 lies at much lower oxygen fugacities than those for LG 4 and LG 6. Although olivine is the only cumulus silicate associated with LG 4, whereas it is orthopyroxene for layer LG 6, the narrow range of these two curves indicates that these two layers are genetically associated and that there could be a hiatus in the development of the Critical Zone between the layers LG 3 and LG 4.

If the  $T$ - and  $p_{O_2}$ -conditions derived for the western and the eastern Bushveld Complex are compared, there is a slope from west to east of about  $75^\circ\text{C}$  and 1.5 log units. These differences fit very well to the conditions of the 'differentiation at constant total composition of the condensed phases' (see Osborn, 1959).

The chromitites and the rocks of the Zwartkop Chrome Mine therefore have formed at higher temperatures than those of the eastern Bushveld Complex, under the assumption, that they were formed from the same magma. This observation is supported by the occurrence of olivine ( $Fo=92$ ) in the LG 4, the high MgO-content and the high Cr/Fe-ratio in the LG 4 chromites (McDonald, 1967). Additionally this

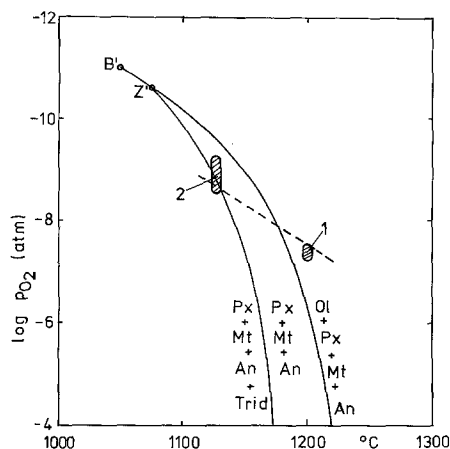


Fig. 8.  $p_{O_2}$ - and  $T$ -variation along the interior boundary curves in the anorthite saturation volume of the system  $\text{Mg}_2\text{SiO}_4 - \text{FeO} - \text{Fe}_2\text{O}_3 - \text{SiO}_2 - \text{CaAl}_2\text{Si}_2\text{O}_8$  (Osborn, 1969). The crystalline phases coexist with liquid and a gas phase with fixed  $p_{O_2}$ . The hatched areas (1 and 2) outline the  $p_{O_2}$ - and  $T$ -conditions prevailing during the formation of the host rocks in the western (1) and the eastern (2) Bushveld Complex (compare Fig. 7). The dashed line (1.5 log units  $p_{O_2}$  per  $100^\circ\text{C}$ ) corresponds to the conditions of 'differentiation under constant total composition of the condensed phases'. The position of the areas near the liquid lines shows that the temperatures derived are plausible for magmatic conditions. The position of the areas along the dashed line documents the progress in 'differentiation under constant total composition...' of the Bushveld magma between the formation of the LG-chromitite layers in the Zwartkop Chrome Mine area (western Bushveld Complex) and the formation of the chromitite layers in the eastern Bushveld Complex, farm Maandagshoek. Px pyroxene, Mt magnetite, An anorthite, Trid tridymite

result is also confirmed by the experimental results in the system  $\text{Mg}_2\text{SiO}_4 - \text{FeO} - \text{Fe}_2\text{O}_3 - \text{SiO}_2 - \text{CaAl}_2\text{Si}_2\text{O}_8$  (Osborn, 1969). In Figure 8 the conditions derived for the magma in the western Bushveld Complex (area 1) lie close to the coexistence  $\text{Ol} + \text{Px} + \text{Mt} + \text{An} + \text{L}$ , so that the occurrence of olivine (LG 4) and pyroxene (LG 6) is plausible. Under a gradient of 1.5 log units per  $100^\circ\text{C}$  the area 2 is reached (dashed line), which represents the conditions for the formation of the rock sequence of the eastern Bushveld Complex. The greater part of area 2 lies in the stability field of  $\text{Px} + \text{Mt} + \text{An} + \text{L}$ , and therefore agrees with the observed mineral associations such as the absence of olivine and the presence of cumulus pyroxene and plagioclase.

From this it seems a reasonable conclusion that the rocks of Zwartkop Chrome Mine were formed in an earlier stage of the magma differentiation. On the other hand, it is indicated by petrographic data that the chromitite layers LG 6 and LXI (Steelpoort) are the same layer, and there is no indication that LG 6 was formed before LXI (v. Gruenewaldt, pers. comm.). This would imply that there is a temperature gradient of  $75^\circ\text{C}$  between these two Bushveld areas.

This, however, seems not to be realistic because the temperature difference is very great related to the total liquidus range of olivine tholeiitic magmas. Obviously there is a discrepancy between the experimental and the petrographic results, which can not be cleared up with the present knowledge.

If the conditions for the formation of the rocks and the conditions for the formation of the chromitite layers are compared, the results confirm that an increase of the oxygen fugacity in the order of magnitude of 0.5–1.0 log units is enough to cause the formation of chromitite layers. This can be considered as a further support of Ulmer's thesis, because the quantities of  $CO_2$  and  $H_2O$  necessary for the  $p_{O_2}$ -increase can be explained more easily. The course of the magma in this stage of differentiation indeed seems to go along or near cotectical lines or border areas so that the increase of the oxygen fugacity is enough to shift the magma into the phase volume of chromite.

The discussion has shown that interesting conclusions are possible on the basis of the combination of  $p_{O_2}$ -measurements and petrographic investigations. However, it has to be kept in mind, that the interpretation is complicated by processes like convection, fractional settling and periodic influences of fresh, undifferentiated magma, which were surely effective, but which are not discussed here as they were briefly reviewed by Sneathlge and v. Gruenewaldt (1978). However, mechanisms must be found, which are able to cause a cyclic increase and decrease of the oxygen fugacity of the magma. Processes of this kind were reviewed by Ulmer (1969), among which the periodic assimilation of  $CO_2$  and  $H_2O$  from the country rocks or a periodic variation of the total and of the water pressure seem to have been the most effective. Furthermore, because only the homogeneous distribution of a gas phase in the magma must be postulated, mechanisms of this kind seem to be the most appropriate to explain the immense lateral continuity and uniformity of many chromitite layers such as the Steelpoort Seam (LXI). In addition Cameron and Desborough (1969) provide some evidence that the assimilation of host rocks in the eastern Bushveld Complex could have resulted in increases of the  $p_{H_2O}$  and  $p_{CO_2}$ , and that the formation of the 'F'-unit was conceivably caused by such a process (Cameron, 1971).

It can be easily envisaged, that assimilation and/or variations of the total pressure were effective especially during the periods of tectonic readjustment of the magma chamber. In the western flank of the eastern Bushveld Complex these tectonic processes reached such an extent during crystallization of the layered sequence that rocks of updomed Critical

Zone are seemingly directly overlain by rocks of the Upper Zone (Marlow and Van der Merwe, 1977).

Very recent gravimetric measurements on the Bushveld Complex (v. Gruenewaldt, pers. comm.) shall still be discussed, although they conflict with the discussion up to now, which was based on the existence of a homogeneous Bushveld Complex. The existence of several gravimetric centres can be interpreted in that way that the whole complex is composed by distinct intrusions. It must be emphasized, therefore, that this interpretation is fully consistent with the results reported here, because the conditions of formation of the western and the eastern Bushveld Complex differ significantly.

In summarizing, also on the basis of several 'small Bushveld Complexes' there is the central problem that the models which can be responsible for the increase of the oxygen fugacity are not fully satisfying for example with respect to the immense quantities of contaminating species or with respect to the lateral continuity of the chromitite layers. This is not only a problem of the chromitite layers of the Bushveld Complex, but also of those of other ultrabasic intrusions. Under this aspect it could be successful to research for mechanisms of a  $f_{O_2}$ -increase which is caused by the differentiation trend of the intrusions itself, so that some questions can be solved which can not be explained sufficiently by the contamination models.

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#### Note Added in Proof

After going to print of the manuscript we received further critical remarks from Professor G.C. Ulmer, Temple Univ., Philadelphia, USA. These remarks point out the discrepancy between comparable data from the eastern Bushveld Complex (R.T. Flynn, G.C. Ulmer, and C.F. Sutphen, 1978): Petrogenesis of the Eastern Bushveld Complex: Crystallization of the Middle Critical Zone. – *J. Petrol.*

**19**, 136–152 with the above published ones. In the temperature range of 1100°C the  $f_{O_2}$ -data from Flynn et al. are about three orders of magnitude lower than ours. The causes of these differences can not be sufficiently explained at the present stage. We have decided, however, to publish our results, because our data agree very well with the experimental investigations of Hill and Roeder (1974) and Osborn (1969) and therefore allow far-reaching geological interpretations.