

Vertical chemical gradients in a single grain of magnetite from the Bushveld Complex, South Africa

R. GRANT CAWTHORN, T. S. MCCARTHY, AND G. DAVIES

Department of Geology, University of the Witwatersrand, Jan Smuts Avenue, Johannesburg 2001, South Africa

ABSTRACT. Very large crystals of magnetite, up to 2 cm, are found in pure magnetite layers in the upper zone of the Bushveld Complex. Detailed electron microprobe analysis of one of these indicates a vertical compositional zoning of Cr (a highly compatible element in magnetite) quite different from the concentric zonation often found, for example, in feldspars in intrusive rocks. It is shown that these crystals could not have grown to their present size in suspension in the magma chamber. Annealing of many small crystals into a single grain could occur either by the Ostwald ripening process at temperatures close to the liquidus or by subsolidus recrystallization. Alternatively, these grains could have formed *directly* from the magma by upward growth from the floor of the magma chamber, by a process analogous to crescumulate or heteradcumulate growth but in the absence of other crystallizing phases. All of these models require the observed Cr gradient to be produced during the initial crystallization event and not as a secondary effect.

HIGHLY compatible trace elements are the most sensitive indicators of fractionation in magmas and variation in abundances of such trace elements in volcanic suites or in cumulate minerals from layered complexes may be used to place constraints on fractionation mechanisms. A potential area of application of these concepts in layered complex formation is in the use of Cr abundances in magnetite. The exact value for the partitioning of Cr between magnetite and silicate liquid is unknown (it is probably quite dependent on oxygen fugacity) but is almost certainly in excess of 100 (Lindstrom, 1976; Leeman *et al.*, 1978). In the upper zone of the Bushveld Complex there exist virtually pure, monomineralic layers of magnetite (Willemse, 1969; Molyneux, 1974; von Gruenewaldt, 1973), one of which (the 'Main Seam') ranges from 1.5 to 2.5 m in thickness (Willemse, 1969). Such a layer provides an excellent opportunity for geochemically testing fractionation hypotheses and also for determining mechanisms of formation of layering.

Elsewhere we have determined the Cr content of

pure magnetite separates as a function of height in several massive and disseminated sequences rich in magnetite from the Bushveld Complex (Cawthorn and McCarthy, 1980 and 1981). As a result of these studies, we have questioned the applicability of the Rayleigh Law equation as applied to fractionation processes in layered complexes. This is because the Rayleigh Law demands that the magma remains homogeneous during fractionation, which seems implausible for many reasons discussed by Jackson (1961), Campbell (1978), McBirney and Noyes (1979), Morse (1979), Irvine (1980), and Cawthorn and McCarthy (1980 and 1981).

One of the features noted by Cawthorn and McCarthy (1980) is that there is a large vertical concentration gradient for Cr in magnetite which, near the base of the main magnetite layer, reaches several hundred ppm Cr cm⁻¹. That study involved taking thin (1-2 cm) slices of rock, parallel to the layering, preparing mineral separates and analysing them by X-ray fluorescence. Willemse (1969, Fig. 18) showed that some grains of magnetite reach 2 cm in size in the almost pure magnetites. In view of this observation, we considered it would be of interest to investigate the possibility of compositional gradients existing within individual large grains, which, if comparable to those previously described, should be in the order of 1000 ppm Cr over 2 cm. In this communication we present analytical data on these megacrysts of magnetite from the base of a massive magnetite layer.

Samples and analytical procedure

The material we have analysed is taken from very close to the bottom of the main magnetite layer in the upper zone of the Bushveld Complex in the western Transvaal, from the farm Uitvalgrond 431 JQ in the Brits district, 40 km west of Pretoria. Borehole core for this, and a previous study (Cawthorn and McCarthy, 1981) was very generously provided by Union Carbide Corporation. Analytical data for Cr in magnetite separates through

the entire 2 m of the magnetite layers have been presented elsewhere (Cawthorn and McCarthy, 1981).

There is extremely fine exsolution of ilmenite within this sample, and a photomicrograph of this texture of material from the same area has been presented by Willemse (1969, Fig. 10).

A single, vertically orientated polished thin section was prepared from borehole core and examined by an automated ARL-SEMQ wavelength-dispersive electron microprobe using the following standards; chromite (for MgO, Al₂O₃, and Cr₂O₃), ilmenite (for TiO₂ and FeO), and rhodonite (for MnO and SiO₂). Operating conditions were 15 kV (excitation voltage), 0.05 mA (sample current on brass), with a focused beam, counting times were 20 seconds on peaks and 10 seconds on backgrounds, and data were reduced using the method of Bence and Albee (1968). Replicate consecutive analyses of the same point indicated the following coefficients of variance; SiO₂ ± 0.4%; TiO₂ ± 0.03%; Cr₂O₃ ± 0.04%; FeO ± 0.10%; MgO ± 0.02%; Al₂O₃ ± 0.02%; and MnO ± 0.01%. Due to the extreme inhomogeneity of the grain, resulting from minute exsolution lamellae, it was not possible to return to the identical spot during the analyses to determine longer-term drift. However, in order to avoid any systematic variations in analysis due to machine drift, points were analysed at random, rather than in stepwise traverses across the grain. Any analysis with a TiO₂ content more than two standard deviations higher than the entire average was rejected as possibly indicating that the beam was overlapping or causing excitation of ilmenite or ulvöspinel exsolution lamellae. Analyses totalling less than 92% and greater than 95% (with all iron reported as FeO) were also rejected. Totals given in Table I even with Fe₂O₃ contents calculated according to stoichiometry are slightly low because V₂O₅ contents are not determined, but are significant (Willemse, 1969).

Results

Composition of the Magnetite. Some of the fifty-eight analyses are presented in Table I. The overall variation for most of the elements is quite small.

TABLE I. *Representative magnetite analyses*

FeO _T	88.56	88.79	89.36	89.78	89.97	89.20
Cr ₂ O ₃	2.04	1.96	1.91	1.87	1.81	1.76
TiO ₂	0.79	1.07	1.35	1.18	1.02	1.31
Al ₂ O ₃	0.47	0.25	0.35	0.26	0.35	0.49
MgO	0.05	0.01	0.04	0.07	0.11	0.03
MnO	0.03	0.02	0.04	0.01	0.01	0.04
SiO ₂	0.17	0.07	0.10	0.11	0.08	0.04
Total	92.11	92.17	93.15	93.28	93.35	92.87
FeO*	31.53	31.71	32.26	32.15	31.95	32.10
Fe ₂ O ₃ *	63.38	63.43	63.45	64.05	64.48	63.46
Total	98.46	98.52	99.50	99.70	99.81	99.25

Analyst: G. Davies. *Fe₂O₃ calculated assuming a stoichiometry of twenty-four cations per thirty-two oxygen anions. Recalculated totals are low as vanadium content was not determined.

The variations are FeO (total), 88.56–92.08%; MgO, 0.00–0.36%; Al₂O₃, 0.18–0.82%; TiO₂, 0.62–1.50%; SiO₂, 0.04–1.20%; MnO, 0.00–0.05%, and Cr₂O₃, 1.74–2.15%.

Willemse (1969) reviewed much of the available geochemical data on magnetite from the Bushveld Complex and concluded that the main magnetite layer contained approximately 12% TiO₂. However, this value is based on whole rock analyses and includes the abundant ulvöspinel and ilmenite exsolution lamellae. The analyses we present are of the host magnetite between the exsolution lamellae and so are very much lower in TiO₂ than the original, homogeneous phase. Similarly low TiO₂ contents have been reported for electron probe microanalysis of magnetite by Buchanan (1976) from the eastern Transvaal.

While the major oxide composition of the analyses remains fairly constant, the Cr₂O₃ content shows significant variations across the grain with Cr₂O₃ decreasing systematically upwards (fig. 1). The immediately adjacent portions of the two grains on either side of the central grain also show comparable compositions and compositional gradients.

Discussion

There are two problems which we wish to discuss and which we believe are interrelated; namely, the reason the magnetite grains are so big, and the mechanism for the origin of the Cr compositional gradient.

Coarse grain size of magnetite. In terms of the crystal-sinking hypotheses, the rate of sinking ought to be proportional to the density contrast between mineral and liquid and to the square of the size of the grain. When compared with the size and density contrast of the silicate minerals in the Bushveld Complex, the high density contrast (± 2.0 g cm⁻³) and the extremely large size (± 2 cm) of the magnetite grains make it unlikely that these grains could have grown in suspension in the magma chamber.

In most layers of the upper zone in which magnetite is present, magnetite is not commonly enclosed in euhedral silicate grains (which contrasts markedly with the behaviour of chromite in the critical zone). However, when magnetite enclosed in silicate does occur, crystals are typically in the order of 0.2 mm in size. It could be argued that these are the true cumulus grains accumulating on the floor of the complex. The crystal-settling hypothesis would envisage such grains as being fairly homogeneous, and reaching the floor in a random crystallographic orientation. If there were subsequent growth to fill all interstitial space (at most

50% of the rock) each grain might become doubled in volume, or increase from 0.2 mm to 0.26 mm in cross-section. Obviously, to produce the grain size observed in fig. 1 of 2×1.5 cm, requires some additional process.

We are aware of three processes by which such large crystals may form. First, annealing processes may operate in the supersolidus region. Bowen (1928, p. 167) discussed mechanisms for the formation of monomineralic rocks. He noted 'that if a mass of discrete crystals of a soluble salt lie in the bottom of a beaker of saturated solution the mass will gradually be converted into a solid cake of salt'. Cameron (1969, p. 759) alludes to the same process regarding the formation of chromitites containing over 90% chromite. He stated that 'such rocks might result through expulsion of liquid by compaction, if this were attended by re-solution of crystals at points of contact and redeposition in interstices. The importance of this is difficult to assess, but the process has found little favor with students of magmatic sediments, for lack of evidence.' In fact, the process and the mechanism are well known to metallurgists, and is referred to as the Ostwald ripening process (Ostwald, 1900). It is caused by continuous solution-reprecipitation of crystals in a saturated solution, such that small crystals gradually are redissolved and reprecipitated on to larger crystals. Interstitial liquid is gradually eliminated by this mechanism. This is fundamentally different from the process of adcumulus growth envisaged by Wager *et al.* (1960), as no net precipitation of solid occurs from liquid percolating through the interstices. The Ostwald ripening process involves only recrystallization and compaction among existing grains.

If the cumulus pile were composed of magnetite grains, there would be a great many points of contact of grains where this solution-precipitation process may occur, resulting in relatively rapid enlargement of grains. In contrast, if there were silicate grains associated with the magnetite there would be fewer points of mutual contact of magnetite grains, and the intervening silicate crystals will impede growth. Consequently, from the Ostwald ripening process, it can be concluded that, given equal time for recrystallization, in pure monomineralic layers the grain size may be larger than in polymineralic rocks. In support of this suggestion, it can be seen in Willems's diagram (1969, Fig. 18) that the coarsest grains of magnetite often occur in pure magnetite, and magnetite grain size tends to decrease as plagioclase content increases.

Secondly, subsolidus annealing and recrystallization has been documented extensively with reference to metamorphic rocks and especially so

for sulphides (Stanton, 1972). This may be accompanied by an increase in grain size. Such a process could have operated in the present instance only if the rock was originally essentially a monomineralic magnetite adcumulate.

Thirdly, several studies have cast doubts upon the hypothesis of crystal sinking and sorting in the production of mineral layering (e.g. Campbell, 1978; McBirney and Noyes, 1979; Campbell *et al.*, 1978; Cawthorn and McCarthy, 1980; Irvine, 1980). In particular, Campbell *et al.* (1978) showed that the feldspar crystals would float, not sink, in a ferrogabbroic liquid, comparable to that which produced the upper zone of the Bushveld Complex. Possibly the only mechanisms by which plagioclase grains could have accumulated in layers in the upper zone is for them either to have grown there or to have been carried there by magmatic currents (Irvine, 1978) which counteracted their buoyancy. This may also apply to the other phases. As the coolest layers of liquid would be at the very top and bottom of the magma column (Irvine, 1970), this is where most nuclei and pre-existing grains, suitable for initiating subsequent growth, would occur. Thus, nucleation and crystal growth on existing grains (as heterogeneous nucleation) as observed by Kirkpatrick (1977) is plausible at the base of the magma chamber. If the degree of supersaturation is small, spontaneous nucleation rates would be extremely slow and there would be few nuclei competing during growth. Given the very slow cooling rates in the Bushveld Complex, large crystals could be produced despite the slow growth rate under these conditions. The commercial production of large crystals of semiconductors would be a close analogy. Hence, variations in the degree of supercooling with its consequent effect on growth and nucleation rates may be reflected in variations in grain size in the magnetite layers. Jackson (1961, p. 97) discussed in general terms how such variations in crystal growth rate could result. Convective overturn brings variably supersaturated liquid into the zone of crystallization. The liquid would gradually heat up due to release of latent heat, causing a decrease in crystallization rate. Another way of producing erratic variations in the growth rate has been discussed by Cawthorn (1982) whereby fluctuations in pressure (as envisaged by Cameron, 1978 and 1980) change the liquidus temperature of the magma. This causes undercooling or superheating in the system, which will affect the crystallization rate. A slow cooling rate will permit large crystals to form, and it would also allow for a greater degree of adcumulus, as opposed to orthocumulus growth, producing a rock with a greater proportion of the cumulus mineral. Thus the relation between grain size

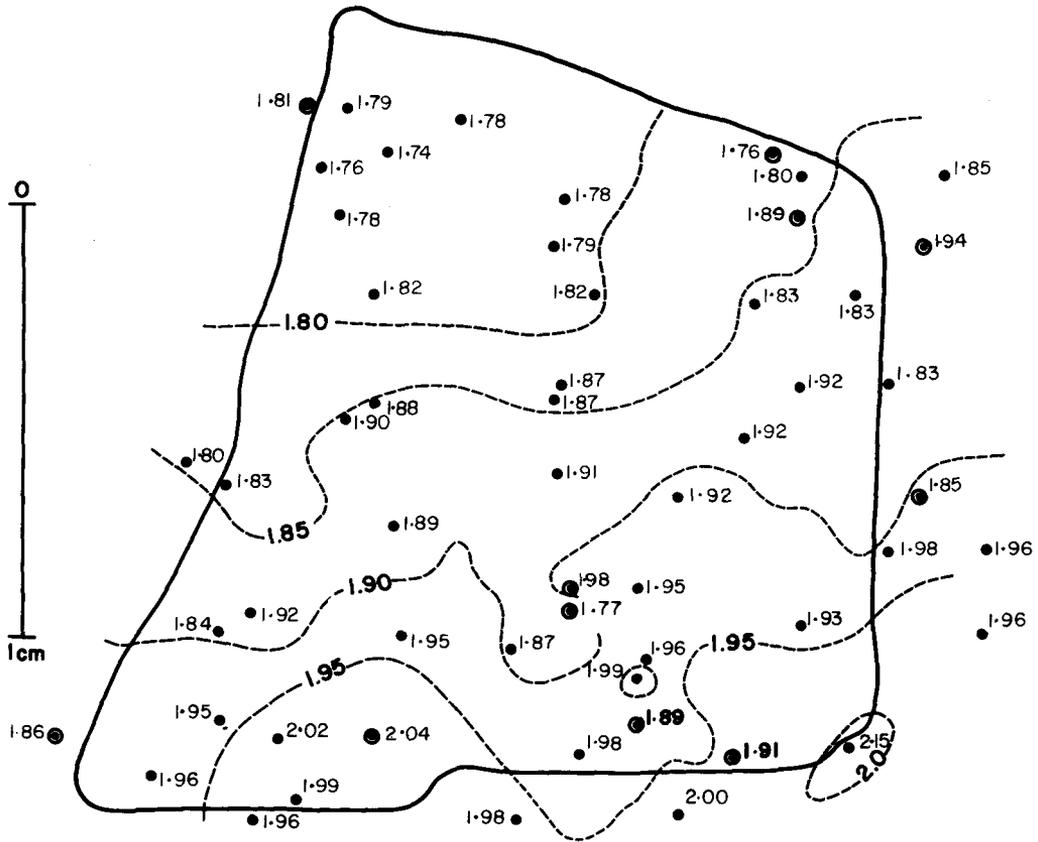


FIG. 1. Cr_2O_3 contents (wt. %) in magnetite plotted and contoured in relation to the grain boundary. The diagram is orientated vertically with respect to the layering. Ringed circles are data points which are misplaced by greater than 1σ relative to the contours.

of magnetite and proportion of silicate phases described above is also satisfied by this model.

Variation in Cr_2O_3 content of a single magnetite grain. In fig. 1 we show the variation in Cr_2O_3 from a single grain of magnetite, the base of which is less than 5 mm above the base of the magnetite layer. At the bottom of the grain the Cr_2O_3 content is very close to 2.00% while at the top of the grain, 2 cm higher, it is about 1.80%. This variation is five times greater than the standard deviation inherent in our analyses, and is also systematic. The data have been computer-contoured, as shown in fig. 1, using a standard statistical program—SURFACE II. Given a standard deviation of 0.04%, we find there are only eleven samples out of fifty-eight, which are misplaced on this contour diagram at 1σ , and only one which is misplaced at 2σ .

It is surprising that the substantial chemical gradient for Cr remains in the crystal, even though there has been equilibrium in terms of magnetite-

ilmenite bulk composition down to temperatures of less than 600 °C (Buchanan, 1976). The lower TiO_2 content of magnetite analysed in this study compared with that of Buchanan (1976) suggests even lower temperatures of final equilibration, but the compositions obtained plot outside the curves of Buddington and Lindsley (1964). We believe that the retention of the gradient in Cr content may be aided by the exsolution process. The ilmenite lamellae in the magnetite contain on average 0.1% Cr_2O_3 . The lamellae are too narrow to detect any compositional gradients across them. As a result of their low Cr content, we suggest that these rods and blades of ilmenite have acted as barriers to diffusion of Cr, and hence reduced the rate of migration of Cr during subsolidus re-equilibration (Hart and Allegre, 1980, p. 123).

The existence of these low-Cr exsolution lamellae raises a different problem. If there were a greater proportion of exsolution of ilmenite at the base of

the crystal than at the top, in theory, this could produce an apparently higher Cr content in the magnetite host at the bottom, even though the original grain contained a uniform Cr content. In view of the extremely fine scale of the exsolution it is not possible to estimate the proportion of exsolution optically, and we have to resort to a geochemical estimate. From our unpublished analyses we know that the *bulk* TiO₂ content of the lowest sample analysed in our previous study (Cawthorn and McCarthy, 1981) is 12.2%. The exsolved ilmenite contains 51.2% TiO₂. The average TiO₂ in the magnetite host is 1.10% TiO₂. The proportion of exsolution required to produce these TiO₂ data is 22%. This 22% ilmenite contains 0.1% Cr₂O₃ and the remaining 78% of host magnetite contains on average 1.9% Cr₂O₃; and hence the bulk sample contains 1.50% Cr₂O₃, which is in good agreement with the bulk analysis from the base of this magnetite layer (Cawthorn and McCarthy, 1981).

Let us assume that the 2 cm grain was originally homogeneous, containing 1.50% Cr₂O₃ and 12.2% TiO₂. We can calculate how much exsolution of ilmenite with 0.1% Cr₂O₃ and 51.2% TiO₂ is required to produce a host magnetite with 2.00% Cr₂O₃ (at the bottom of the grain) and 1.80% Cr₂O₃ (at the top). A 26% exsolution is required at the bottom and 18% at the top to satisfy the Cr₂O₃ data. The resultant TiO₂ contents of the host magnetite, given such degrees of exsolution, are -1.50% and 3.64% TiO₂ at the bottom and top of the grain respectively. However, no systematic variation is observed in the TiO₂ content (see figs. 2 and 3) and so we do not believe that exsolution is the cause of the variation in Cr₂O₃ seen in the host magnetite (fig. 1).

Studies on cumulus plagioclase feldspars suggest that they have a fairly homogeneous, euhedral area (although sometimes they have an albite-rich nucleus), with more irregular, normally zoned margins (e.g. Maaløe, 1976). Phenocrysts of feldspar

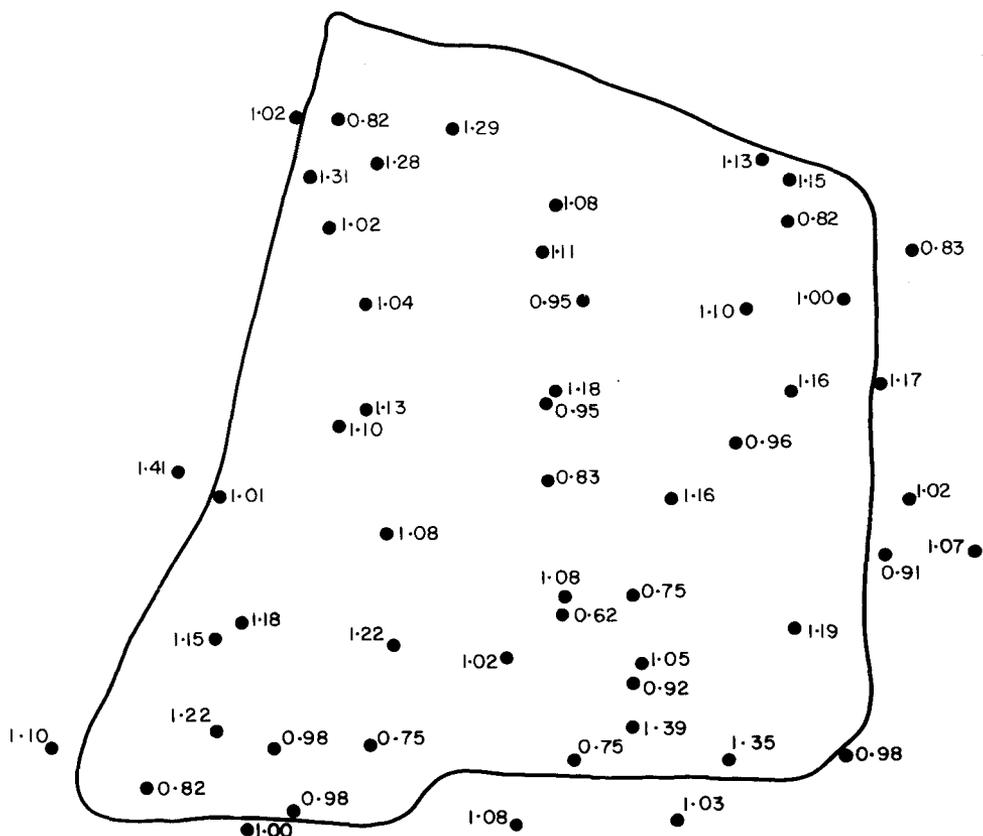


Fig. 2. TiO₂ contents (wt. %) in magnetite in relation to the grain boundary (cf. fig. 1). There is no systematic variation in these data.

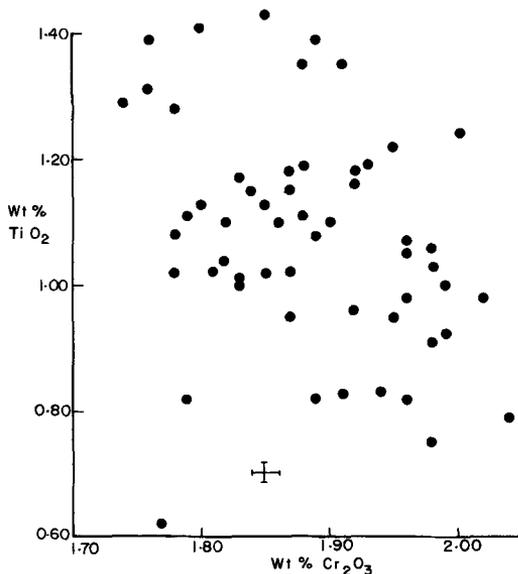


FIG. 3. Plot of TiO_2 vs. Cr_2O_3 (wt. %) for magnetite analyses. The model of Shimizu (1981) demands a positive correlation between these elements. There may, in fact, be a small negative correlation.

often have concentric, oscillatory zoning (e.g. Bottinga *et al.*, 1966). Both these examples support the hypothesis of crystals growing freely suspended with little interference from adjacent crystals. In contrast, in fig. 1 we see compositional contours running approximately horizontally and not concentrically through the crystal and its neighbours. This observation makes it impossible to envisage a single crystal with the observed concentration profile growing to 2 cm freely suspended in a magma.

Shimizu (1981) presented a geochemical study of an augite phenocryst and concluded that the primary control on the composition of crystals depended upon the charge to radius ratio of the elements concerned and not on equilibrium partition coefficients. We note that if enrichment factors were related to charge to radius ratios, elements such as Al and Ti would show a bigger variation across the grain than observed for Cr (see Shimizu, 1981, Fig. 3). This is not observed. In fact, Al_2O_3 and Cr_2O_3 show no correlation (fig. 4). Hence, the chemical controls during growth of the magnetite grain studied here differ from those of the augite phenocryst of Shimizu (1981).

We can reassess our chemical data in the light of the three models proposed to explain the abnormally large grain size of the magnetite crystals either by annealing of numerous smaller crystals,

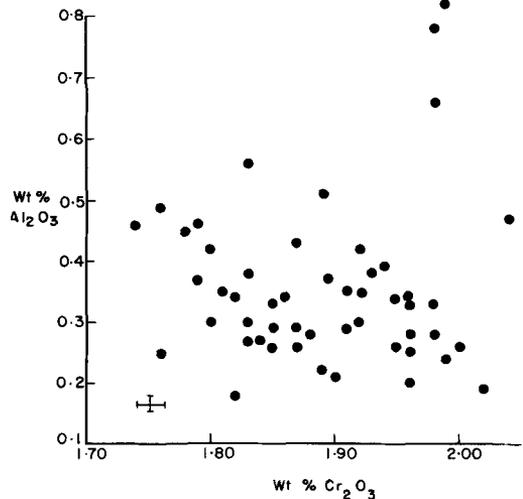


FIG. 4. Plot of Al_2O_3 vs. Cr_2O_3 (wt. %) for magnetite analyses. The model of Shimizu (1981) demands a positive correlation between these elements.

with or without interstitial melt, or by growth under conditions which favour large crystals. Let us consider the first of these possibilities. The grain studied could represent an accumulation of some 600 000 small (0.2 mm) grains. The envisaged annealing process which converted these to a single grain could not be simple adcumulus growth, as grains would need to be reorientated during annealing. Either solution and precipitation (the Ostwald ripening process; Ostwald, 1900), or subsolidus recrystallization, as is typically seen in metamorphic rocks, would be necessary.

It is clearly impossible for the Cr gradient to have been generated during, or as a result of, the annealing process. Therefore, if annealing has operated, concentration gradients must have existed in the small crystals prior to commencement of the process.

A large number of small crystals, graded vertically in their Cr content, such as those which might have given rise to one single grain, could not have formed from a thin magma layer, as envisaged by Irvine (1975) as gradients in the overall magnetite layer are very variable, and in some cases no gradients exist at all (fig. 5). The small crystals could not have formed by sinking from a relatively large volume of magma, or from a turbulent horizontal current (Wager and Brown, 1968; Irvine, 1978), as these would produce a homogeneous or randomly variable Cr distribution. Such a vertically graded accumulation of small crystals could only have originated by growth near the bottom of melt layer, in which the liquid boundary zone gradually

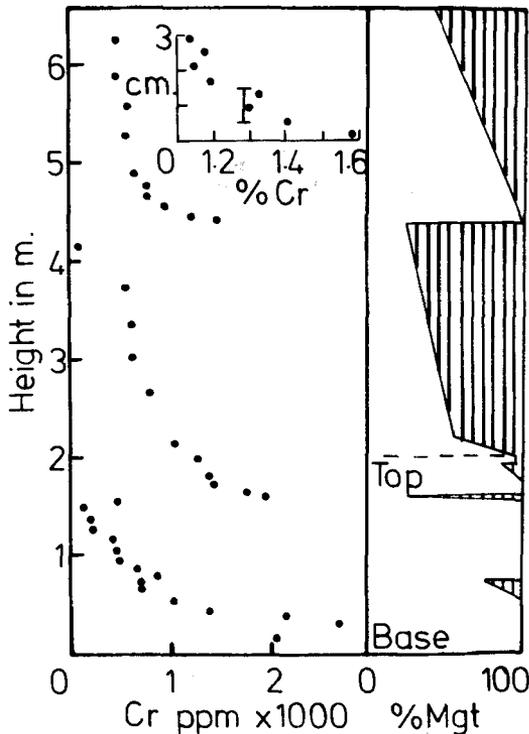


Fig. 5. Distribution of Cr in magnetite as a function of height from the section from the Brits magnetite mine. See Cawthorn and McCarthy (1981) for details and discussion. The weight proportion of magnetite in the samples is shown as the unshaded part of the column on the right, together with the top and bottom of the layer. Three mineral separate analyses from heights of 1, 5, and 7 cm containing 12 895, 6778, and 5950 ppm Cr respectively have been excluded to avoid extreme compression of the scale. The inset shows a detailed study of the bottom 3 cm of the layer. The vertical bar shows the analysis of the mineral separate from a height of 1 cm. Dots are analyses by electron microprobe. (See Cawthorn and McCarthy, 1981). The grain studied here comes from the interval between 0.5 and 2.5 cm height.

became progressively depleted in Cr as a result of magnetite crystallization.

The exact process of annealing is difficult to envisage. Variations in the size of magnetite grains in adjacent layers of pure magnetite (Willemse, 1969) would not be expected during subsolidus recrystallization. It is also difficult to envisage that dissolution of grains could occur to permit the Ostwald ripening process in a liquid that is continuously precipitating magnetite. However, it is difficult to prove that such processes have not been operative.

The alternative process, that of upward growth

of large crystals as opposed to settling of small crystals, is equally compatible with our analytical results. This model would be akin to a combination of crescumulate and adcumulate growth. In the case of crescumulate growth, first recognized on Rhum (Brown, 1956), cumulus crystals grow from the floor of the complex. They are subsequently surrounded by other minerals growing either as orthocumulus or heteradcumulus phases. However, if the liquid composition lay within the primary phase field of one mineral rather than being close to multiple saturation there is no reason why adcumulate growth could not take place. In the original definition of adcumulus growth Wager *et al.* (1960) envisaged cycling of magma through a crystal mush to cause the overgrowth. They subsequently realized that this was implausible and that adcumulus growth could only occur to any extent at the crystal pile/liquid interface (Wager and Brown, 1968; Hess, 1972). Thus adcumulus growth would not be due to later infilling but would keep pace with the solid/liquid interface. Mechanisms of adcumulus and postcumulus growth in general are not adequately understood (e.g. Irvine, 1980) and the formation of pure monomineralic rocks represents the extreme case of this complex process. Further studies of the type described by Chen and Turner (1980) are required to clarify this problem. Especially interesting would be studies on the proportion of interstitial liquid trapped behind advancing crystal fronts (cf. their Fig. 3) as a function of cooling rate.

Confirmation of the vertical zonation in composition in other grains of magnetite would be highly desirable. Unfortunately, the sample studied comes from borehole core, one thin slice of which was preserved for this study, the rest was crushed and analysed (Cawthorn and McCarthy, 1981). This sample has the highest Cr content by a factor of two of any of the bottom-most samples from layers of magnetite so far studied (Cawthorn and McCarthy, 1980 and 1981). Consequently, the absolute concentration gradient is also a maximum for this sample (Cawthorn and McCarthy, 1980, Fig. 3). For samples having a smaller concentration gradient the analytical uncertainty would become relatively large in comparison to the gradient and it would mask any systematic trend. Hence, it is not possible to duplicate these results on other material at present.

Conclusions

Strong, vertical Cr concentration gradients appear to be the norm in the main magnetite layer of the Bushveld Complex. Study of an individual 2 cm magnetite crystal has revealed that concentra-

tion gradients exist even on this scale. These result either from the annealing of many very small crystals which possess a vertical concentration gradient or from diffusion-controlled growth of large crystals on the bottom of the magma chamber. At present, we know of no diagnostic test to distinguish these different processes, but both demand that the observed Cr gradients are primary, magmatic phenomena.

Acknowledgements. The material for this study was provided by Union Carbide Corporation, and the staff at the Brits magnetite mine are very gratefully acknowledged for their assistance. The CSIR (South Africa) provided financial support for this research as part of the National Geoscience Programme on the evolution of earth resource systems.

REFERENCES

- Bence, A. E., and Albee, A. L. (1968) *J. Geol.* **76**, 382–403.
- Bottinga, Y., Kudo, A., and Weill, D. (1966) *Am. Mineral.* **51**, 792–806.
- Bowen, N. L. (1928) *The Evolution of the Igneous Rocks*. Princeton University Press, Princeton, New Jersey.
- Brown, G. M. (1956) *Phil. Trans. R. Soc. Lond.* **B240**, 1–53.
- Buchanan, D. L. (1976) *Trans. geol. Soc. S. Afr.* **79**, 76–80.
- Buddington, A. F., and Lindsley, D. H. (1964) *J. Petrol.* **5**, 310–57.
- Cameron, E. N. (1969) *Am. Mineral.* **54**, 754–79.
- (1978) *J. Petrol.* **19**, 437–62.
- (1980) *Econ. Geol.* **75**, 845–71.
- Campbell, I. H. (1978) *Lithos*, **11**, 311–23.
- Roeder, P. L., and Dixon, J. M. (1978) *Contrib. Mineral. Petrol.* **67**, 369–77.
- Cawthorn, R. G. (1982) *Chem. Geol.* **36**, 227–36.
- and McCarthy, T. S. (1980) *Earth Planet. Sci. Lett.* **46**, 335–43.
- (1981) *Trans. geol. Soc. S. Afr.* **84**, 41–50.
- Chen, C. F., and Turner, J. S. (1980) *J. Geophys. Res.* **85**, 2573–93.
- Hart, S. R., and Allegre, C. J. (1980) In *Physics of Magmatic Processes*, Hargraves, R. B. (ed.). Princeton University Press, Princeton, New Jersey, 121–59.
- Hess, G. B. (1972) In *Studies in Earth and Space Sciences*, Shagan *et al.* (eds.). Geol. Soc. Am., Mem. 132, 503–20.
- Irvine, T. N. (1970) *Can. J. Earth Sci.* **7**, 1031–61.
- (1975) *Geochim. Cosmochim. Acta*, **39**, 991–1020.
- (1978) *Carnegie Inst. Washington, Yearb.* **77**, 717–25.
- (1980) In *Physics of Magmatic Processes*, Hargraves, R. B. (ed.). Princeton University Press, Princeton, New Jersey, 325–83.
- Jackson, E. D. (1961) *U.S. Geol. Surv., Prof. Pap.* 358.
- Kirkpatrick, R. J. (1977) *Geol. Soc. Am. Bull.* **88**, 78–84.
- Leeman, W. P., Ma, M.-S., Murali, A. V., and Schmitt, R. A. (1978) *Contrib. Mineral. Petrol.* **65**, 269–72.
- Lindstrom, D. J. (1976) Ph.D. thesis, University Oregon, Eugene.
- Maaløe, S. (1976) *J. Petrol.* **17**, 398–419.
- McBirney, A. R., and Noyes, R. M. (1979) *Ibid.* **20**, 487–554.
- Molyneux, T. G. (1974) *Trans. geol. Soc. S. Afr.* **77**, 329–38.
- Morse, S. A. (1979) *J. Petrol.* **20**, 591–624.
- Ostwald, W. (1900) *Z. Phys. Chem.* **34**, 495–503.
- Shimizu, N. (1981) *Nature*, **289**, 575–7.
- Stanton, R. L. (1972) *Ore Petrology*. McGraw-Hill, New York.
- von Gruenewaldt, G. (1973) *Trans. geol. Soc. S. Afr.* **76**, 207–27.
- Wager, L. R., and Brown, G. M. (1968) *Layered Igneous Rocks*. Oliver and Boyd, Edinburgh.
- and Wadsworth, W. J. (1960) *J. Petrol.* **1**, 73–85.
- Willemse, J. (1969) In *Magmatic Ore Deposits*, Wilson, H. D. B. (ed.), Econ. Geol. Monograph 4, 187–208.

[Manuscript received 6 April 1982;
revised 28 June 1982]