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**INCOMPATIBLE TRACE-ELEMENT ABUNDANCES IN
PLAGIOCLASE AND PYROXENES IN THE
MERENSKY REEF OF THE BUSHVELD COMPLEX -
EVIDENCE FOR METASOMATISM?**

R. GRANT CAWTHORN

INFORMATION CIRCULAR No. 287

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R. GRANT CAWTHORN

*(Department of Geology, University of the Witwatersrand,
P/Bag 3, WITS 2050, Johannesburg, South Africa)*

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ABSTRACT

The ability of trapped residual liquid to reset the major element composition of minerals in layered intrusions has been quantitatively explored by Barnes (1986). This principle can be extended to model the behaviour of incompatible trace elements in minerals during crystallization of trapped interstitial liquid. It is shown here that extreme enrichment can result, especially in minerals present in low abundance, even to levels in excess of that of the parent liquid, despite the fact that the partition coefficient may be considerably less than unity.

The effects of variation in primary mineral proportions, trapped liquid content, partition coefficients, and accessory minerals crystallizing from the trapped liquid are explored mathematically. It is also shown that the assumption that the content of an incompatible element in a magma is equal to the concentration in a mineral divided by its partition coefficient is totally unjustified.

These principles are applied to published analyses of Rb in plagioclase and REE in pyroxene from the Bushveld Complex. Observed Rb values in plagioclase of 1 - 4 ppm can be produced from a parent magma with only 5 ppm Rb. Similarly, extremely high REE contents in clinopyroxene can be formed from a magma with low REE content. Infiltration metasomatism is not required to produce these high concentrations; crystallization from a trapped liquid can be equally effective.

These calculations also show that the parental magma to the Bushveld Complex was typical of continental tholeiite in terms of its incompatible trace-element content.

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INTRODUCTION

The origin of platinum mineralization in the Merensky Reef has been attributed to several processes. One of these envisages secondary enrichment by the fluxing of residual liquid, which becomes focused at the level of the Merensky Reef (Nicholson and Mathez, 1991). Very high REE contents in pyroxenes in the Merensky Reef relative to its footwall have recently been reported (Mathez, 1994) as support for this model.

The concept that primary minerals reflect the composition of the magma from which they formed was challenged by Irvine (1980) who suggested that major-element composition could be changed by reaction with migrating residual liquid. Barnes (1986) showed that such changes could also occur even if the interstitial magma was effectively trapped between the crystals which had formed from it. This was referred to as the "trapped liquid shift effect". There is no difference in the chemical principle of these two models. However, in the "trapped liquid shift" model the effect should be quantifiable, whereas if magma is capable of migration, there are too many variables to constrain the final mineral composition with any precision.

Irvine's (1980) and Barnes' (1986) models were discussed purely in terms of major oxides, specifically the $Mg/(Mg+Fe)$ ratio of olivine and pyroxene. Exactly the same principles can be applied to incompatible elements. It is the purpose of this contribution firstly to demonstrate the basic principles of trapped liquid re-equilibration with primary minerals, using Rb and REE in plagioclase and pyroxene respectively, and then to re-evaluate the significance of various published mineral analyses from the Bushveld Complex in terms of this model.

Note that in this paper the term "primary" rather than "cumulus" mineral is used. This is to distinguish between the actual composition of the mineral which initially forms from the magma, as distinct from the mineral which is observed now in the rock. As will be shown later they may be chemically very different. The term "final" composition refers to the composition of the mineral actually present in the rock and potentially amenable to analysis.

DERIVATION OF GEOCHEMICAL EQUATIONS

The calculation principle is based on the assumption that a certain proportion of liquid remains trapped within a crystalline framework and that its entire chemistry must then be accommodated within the existing minerals or new minerals crystallizing from that trapped liquid. In the present case this can be described in terms of the minerals orthopyroxene,

clinopyroxene and plagioclase, and trapped liquid. The bulk composition in each rock when the magma becomes trapped is defined by:

$$a.Opx + b.Cpx + c.Plag + (1-a-b-c).Magma \quad 1$$

where a, b and c are the weight fractions of orthopyroxene, clinopyroxene and plagioclase.

In these calculations it will be assumed in almost all examples that the trapped magma totally solidifies in the proportions 50% plagioclase and 25% of each pyroxene. Thus, after total crystallization the rock will consist of:

$$\frac{(a + \{1-a-b-c\})}{4}.Opx + \frac{(b + \{1-a-b-c\})}{4}.Cpx + \frac{(c + \{1-a-b-c\})}{2}.Plag \quad 2$$

The denominators would change if different proportions of minerals were assumed to crystallize from the trapped liquid. The effect of formation of small amounts of other phases is discussed below.

If the magma remains truly trapped, the bulk content of any element must be the same in both these formulae. Hence, formula 1 equals formula 2. In order to solve such an equation it is necessary to know or to make predictions about the values of:

- the composition of the magma;
- the partition coefficients for the element in all the minerals;
- the proportion of primary phases in the rock; and
- the proportion of trapped liquid.

It is also necessary to assume that equilibrium is attained during crystallization of the residual magma. Deviations from this latter assumption are discussed below.

To produce a general solution to this equation the magma is assumed to contain P ppm of an incompatible trace element, and the partition coefficients are taken as D_o , D_c and D_p for orthopyroxene, clinopyroxene and plagioclase respectively.

The whole-rock content (W) of the trace element in the crystal mush (equation 1) is given by:

$$W = a.D_o.P + b.D_c.P + c.D_p.P + (1-a-b-c).P \quad 3$$

$$\text{or } W = P.(a.D_o + b.D_c + c.D_p + \{1-a-b-c\}) \quad 4$$

and after solidification (equation 2):

$$W = \frac{(a + \{1-a-b-c\})}{4}.X_o + \frac{(b + \{1-a-b-c\})}{4}.X_c + \frac{(c + \{1-a-b-c\})}{2}.X_p \quad 5$$

where X_o , X_c and X_p are the concentrations in the minerals in the solidified rock (i.e. physically amenable to analysis).

Note that the assumption which is normally made in modelling trace element behaviour is that:

$$X = D.P \quad 6$$

This is only valid if the primary composition (P) of the mineral is known. It becomes totally invalid if the final composition of the mineral is used.

Given an analysis of the whole rock (W), and if a, b and c can be estimated petrographically (or various models assumed), and if the values for the partition coefficients are known, equation 4 can be solved for P (the concentration in the liquid). This was the principle used by Cawthorn *et al.* (1991) to estimate incompatible and REE concentrations in parental magma to the Main Zone of the Bushveld Complex. In the present situation it is the concentration in different minerals which is of interest and requires reorganisation of equations 4 and 5.

In the first example to be considered it is the concentration of Rb in plagioclase, or (X_p), which is of concern. If the final minerals are in equilibrium with each other in terms of their trace-element content, then their concentrations can each be expressed in terms of the concentration in plagioclase and partition coefficients. Thus:

$$X_o = X_p.D_o/D_p \quad 7a$$

$$\text{and } X_c = X_p.D_c/D_p \quad 7b$$

Substituting these into equation 5 gives:

$$W = X_p \left[\frac{(a + \{1-a-b-c\}).D_o/D_p}{4} + \frac{(b + \{1-a-b-c\}).D_c/D_p}{4} + \frac{(c + \{1-a-b-c\})}{2} \right] \quad 8$$

Equation 8 is then set equal to equation 4.

$$\begin{aligned} X_p \left[\frac{(a + \{1-a-b-c\}).D_o/D_p}{4} + \frac{(b + \{1-a-b-c\}).D_c/D_p}{4} + \frac{(c + \{1-a-b-c\})}{2} \right] = \\ P.(a.D_o + b.D_c + c.D_p + \{1-a-b-c\}) \end{aligned} \quad 9$$

Rearranging 9 gives:

$$P = \frac{\frac{[(a + \{1-a-b-c\}).D_o/D_p + (b + \{1-a-b-c\}).D_c/D_p + (c + \{1-a-b-c\})]}{4}}{X_p.(a.D_o + b.D_c + c.D_p + \{1-a-b-c\})} \quad 10$$

Knowing the concentration of the element in plagioclase, the modal proportions (a, b and c), and partition coefficients, the composition of the original magma can be determined. Alternatively, equation 10 may be rewritten:

$$X_p = \frac{P.(a.D_o + b.D_c + c.D_p + \{1-a-b-c\})}{\frac{[(a + \{1-a-b-c\}).D_o/D_p + (b + \{1-a-b-c\}).D_c/D_p + (c + \{1-a-b-c\})]}{4}} \quad 11$$

From a knowledge of the magma composition (P), modal proportions, and partition coefficients, equation 11 will predict the composition of the plagioclase. Once X_p has been determined, values for X_o and X_c can be obtained from equations 7a and 7b.

Before some worked examples are presented another parameter needs to be discussed. This relates to the total quantity of any element in the rock which was provided by the trapped liquid, relative to that provided by the primary minerals. This is here referred to as the trapped liquid contribution (TLC), and is defined as the ratio of the contribution by the trapped liquid divided by the total content in the rock. From equation 3, TLC can be calculated as:

$$TLC = \frac{P.(1-a-b-c)}{P.(a.D_o + b.D_c + c.D_p + \{1-a-b-c\})} \quad 12a$$

or

$$TLC = \frac{1-a-b-c}{a.D_o + b.D_c + c.D_p + (1-a-b-c)} \quad 12b$$

For an element which is incompatible in all primary minerals TLC may be very close to unity even when there is only a small proportion of trapped magma. Values close to unity for this parameter have the ability to cause substantial increase in the concentration of an element into the phase in which it is least incompatible during crystallization of the trapped liquid.

Rb AND Sr IN PLAGIOCLASE

Analyses of plagioclase separates from the Bushveld Complex yield values in the range 1 - 4 ppm Rb (Hamilton, 1977; Kruger and Marsh, 1982; Quadling and Cawthorn,

1994). Using an accepted partition coefficient value of 0.05, and equation 6, leads to the implication that the magma from which the plagioclase formed contained 20 - 80 ppm Rb. This is extremely high even for a continental tholeiite and led Hamilton (1977) to conclude that the magma was highly enriched in incompatible elements. A re-examination of these data using the above equations and principles leads to an alternative interpretation.

For the following calculation the Rb content of the magma is taken as 5 ppm (i.e. that of a normal continental tholeiite). Three model rock types are examined in Table 1. Firstly, a pyroxenite, typical of the Upper Critical Zone, is considered (see Table 1, model 1). This is assumed to contain 80% primary orthopyroxene and 20% trapped liquid which crystallizes to produce a further 5% orthopyroxene, 10% plagioclase and 5% clinopyroxene. Partition coefficients for Rb into ortho- and clinopyroxene and plagioclase are taken as 0.001, 0.004 and 0.05. The primary orthopyroxene therefore contains 0.005 ppm Rb. The proportion of Rb in the whole rock contributed by the trapped liquid (TLC) can be calculated from equation 12b:

$$\begin{aligned}\text{TLC} &= 0.2 / (0.8 * 0.001 + 0.2) \\ &= 0.996.\end{aligned}$$

In other words, 99.6% of all the Rb in the solid rock has been provided by the trapped liquid. During crystallization of the trapped liquid this is divided between the pyroxenes and the plagioclase which form interstitially and also re-equilibrates with the primary orthopyroxene. However, as the partition coefficient for orthopyroxene is small a negligible amount of additional Rb from the interstitial liquid enters the original orthopyroxene. Instead it is concentrated into the plagioclase in which it is the least incompatible. As a result, the interstitial plagioclase contains 8.8 ppm Rb, determined from equation 11. The final orthopyroxene contains 0.17 ppm Rb, and so has been enriched by a factor of 33 compared to its primary composition.

The second example shows how this same principle affects the plagioclase composition in a norite which is also typical of the Upper Critical Zone. Here the primary mineralogy is taken to be 40% of both plagioclase and orthopyroxene, with 20% trapped liquid (Table 1, model 2). The primary pyroxene again contains 0.005 ppm Rb, and the plagioclase 0.25 ppm Rb. With this situation, the trapped liquid contribution is only 91%. However, the Rb in the trapped liquid again concentrates in the plagioclase and the composition of the final plagioclase is 2.1 ppm. There is therefore an eight-fold enrichment of Rb in the plagioclase which is finally formed compared to the primary composition due to this effect. In fact, all minerals show this eight-fold enrichment, and so the abundances in ortho- and clinopyroxene are 0.04 and 0.17 ppm Rb respectively. The solidified rock contains 50% plagioclase, but 97% of all the Rb in the rock is present in the plagioclase. This example is shown schematically in Figure 1.

Table 1: Models for Rb and Sr contents of plagioclase

Model No.	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17
1	Rb	80	0	0	20	.001	.004	.050	5	.005	.020	.250	.17	.66	8.30	33.20	.99
2	Rb	40	0	40	20	.001	.004	.050	5	.005	.020	.250	.04	.17	2.15	8.60	.91
3	Rb	0	0	80	20	.001	.004	.050	5	.005	.020	.250	.03	.11	1.33	5.30	.83
4	Rb	70	0	0	30	.001	.004	.050	5	.005	.020	.250	.18	.70	8.77	35.10	.99
5	Rb	35	0	35	30	.001	.004	.050	5	.005	.020	.250	.06	.25	3.10	12.40	.94
6	Rb	0	0	70	30	.001	.004	.050	5	.005	.020	.250	.04	.16	1.95	7.80	.90
7	Rb	40	0	40	20	.005	.010	.050	5	.025	.050	.250	.20	.40	2	8	.90
8	Rb	40	0	40	20	.001	.004	.100	5	.005	.020	.500	.02	.10	2.40	4.70	.83
9	Rb	40	0	40	20	.005	.010	.100	5	.025	.050	.500	.12	.23	2.30	4.60	.83
10	Rb	80	0	0	20*	.001	.004	.050	5	.005	.020	.250	.05	.18	2.25	9.00	.99
11	Rb	40	0	40	20*	.001	.004	.050	5	.005	.020	.250	.03	.11	1.32	5.30	.91
12	Rb	0	0	80	20*	.001	.004	.050	5	.005	.020	.250	.02	.08	.97	3.90	.83
13	Rb	0	0	0	100	.001	.004	.050	5				.19	.76	9.50	38	
14	Sr	80	0	0	20	.010	.050	2	200	2	10	400	1.97	9.80	394	.99	.96
15	Sr	40	0	40	20	.010	.050	2	200	2	10	400	1.99	9.97	399	1.00	.20
16	Sr	0	0	80	20	.010	.050	2	200	2	10	400	2	10.00	399	1.00	.11

Column explanation:

- 1 Element
- 2 Wt % primary orthopyroxene
- 3 Wt % primary clinopyroxene
- 4 Wt % primary plagioclase
- 5 Wt % trapped liquid
- 6 Partition coefficient - orthopyroxene
- 7 Partition coefficient - clinopyroxene
- 8 Partition coefficient - plagioclase
- 9 Concentration of element in liquid (P)
- 10 Composition of primary orthopyroxene
- 11 Composition of primary clinopyroxene
- 12 Composition of primary plagioclase
- 13 Composition of final orthopyroxene
- 14 Composition of final clinopyroxene
- 15 Composition of final plagioclase
- 16 Enrichment factor between final and primary phases
- 17 Trapped liquid contribution (TLC)

* Models 10-12 contain 20% trapped liquid, which crystallizes 2.5% mica

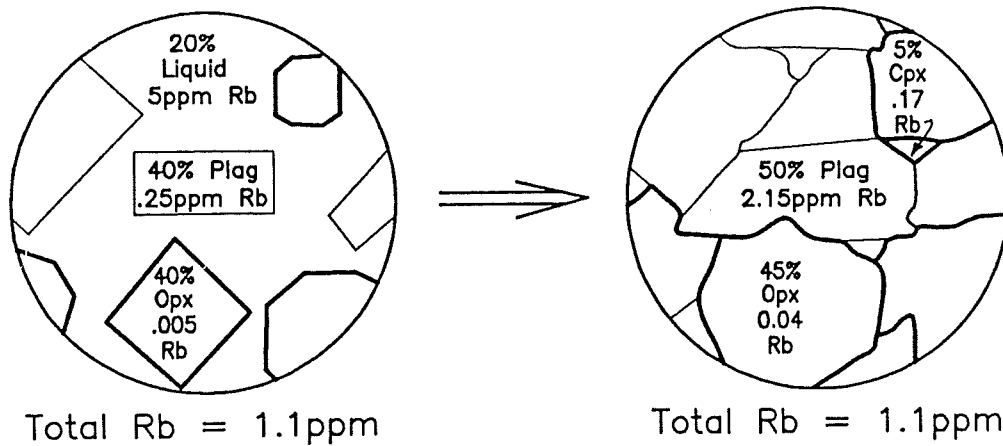


Figure 1: Schematic micrograph showing the sequence of events depicted by Model 2 in Table 1. The system initially contains 40% plagioclase, 40% orthopyroxene and 20% trapped liquid with Rb contents as shown. The total Rb content is 1.1 ppm. After total solidification the rock consists of 50% plagioclase, 45% orthopyroxene and 5% clinopyroxene with Rb contents as shown. The total Rb content of the whole rock remains unchanged at 1.1 ppm.

The final example is that of an anorthosite (Table 1, model 3), again common in the Upper Critical Zone, which initially contains 80% primary plagioclase. Now only 83% of all the Rb in the rock is contained in the trapped liquid, and it has to re-equilibrate with a substantial proportion of plagioclase with only 0.25 ppm Rb, which buffers the enrichment process. Nevertheless, there is still an enrichment by a factor of five in the final plagioclase, which contains 1.3 ppm.

Changing the proportion of trapped liquid has a significant effect on these calculations (models 4, 5 and 6). If the trapped liquid content is 30% in these examples, the enrichment factor would increase from 33 to 35 for the pyroxenite model (model 1); from 9 to 12 for the norite and from 5 to 8 for the anorthosite. The use of alternative partition coefficients will also affect these calculations, as shown in models 7, 8 and 9, which all relate to the norite. In model 7 the partition coefficient for both pyroxenes has been increased considerably, but for plagioclase it has been kept the same. Comparing these results with model 2 shows a negligible decrease in the Rb content in final plagioclase and enrichment factor. In model 8 the partition coefficient for plagioclase is increased, but not for pyroxenes. A marginal increase in Rb in plagioclase and in the enrichment factor is seen. In model 9 the partition coefficients for all the minerals is increased, which produces only minor increases in Rb and enrichment factor.

The crystallization of new minerals from the interstitial liquid will also affect these

calculations. To test this effect the interstitial liquid is assumed to form 2.5% mica, the only mineral present at this level in the Bushveld Complex to contain significant Rb. As there is 20% trapped liquid, this leads to the presence of 0.5% of mica in the final rock, which is a reasonable approximation to its observed abundance. A partition coefficient of 3 is used for Rb in mica. In the pyroxenite model (model 10), this would result in a reduction of the Rb content of the plagioclase from 8.3 to 2.3 ppm, while for the norite model (model 11) the decrease would be from 2.1 to 1.3 ppm Rb in plagioclase, and for the anorthosite model (model 12) the decrease is from 1.3 to 1.0 ppm. However, there is still at least a four-fold enrichment in Rb in plagioclase compared to the primary compositions in all these models.

The last variation which is considered, is that of disequilibrium. All the previous calculations assume that equilibrium is achieved between and within all minerals as the trapped liquid crystallizes. It is not possible to quantitatively evaluate disequilibrium. However, end-models can be discussed. Complete equilibrium is one end-model. The other extreme is to assume that no re-equilibration of the primary phase occurs. In this case, a rim of highly enriched material would be present around primary minerals, and the composition of interstitial minerals would not be buffered by the diffusion of trace element into the primary grains. This can be modelled by assuming that there are no primary minerals present, but only 100% trapped liquid. Model 13 shows that the plagioclase forming in this way would contain up to 9.5 ppm Rb (i.e an enrichment of a factor of 38 relative to the putative primary plagioclase). This could either be present as an interstitial phase in a pyroxenite, or as a rim around a primary plagioclase grain. In the anorthosite model, this would result in the presence of 80% primary plagioclase with 0.25 ppm Rb surrounded by 10% plagioclase with 9.5 ppm Rb, leading to a bulk plagioclase with 1.27 ppm Rb. This compares with a figure of 1.33 for the equilibrium model (model 3). Thus, if the bulk minerals were analyzed, the difference between equilibrium and disequilibrium crystallization would be insignificant, but if ion probe analyses were undertaken extreme zoning would be observed in the latter case.

The use of equation 6 to determine the concentration of Rb in the magma would lead to an error by a factor of four in the prediction (for model 12). In fact, this model yields a plagioclase which actually contains more Rb than the magma from which it formed, even though Rb is incompatible in that mineral. In the most extreme case (model 4), there could be an error of a factor of 35 between actual and calculated magma composition.

For plagioclase, Sr is a compatible element and so the effect of re-equilibration with trapped liquid is far less. This can be shown by the calculations in Table 1 (models 14-16). Given a magma composition of 200 ppm Sr and a partition coefficient into plagioclase of 2, the effect of reaction with trapped liquid is trivial.

REE IN PYROXENES

The high concentration of REE in clinopyroxene (for example, Ce contents of up to 48 ppm) from the Merensky Reef led Mathez (1994) to infer that there was a high concentration of REE in the magma. However, analyses of rocks parental to the Upper Critical Zone and Main Zone of the Bushveld do not suggest anomalous REE content. For example, Harmer and Sharpe (1985) suggested that the $(Ce)_N$ content of such magmas was between 15 and 40, and for $(Yb)_N$ 6 to 10. Values of 15 to 8 for $(Ce)_N$ and $(Yb)_N$ respectively, i.e. at the lower end of the range of Harmer and Sharpe (1985), will be used in the following calculations. These concentrations are typical of continental tholeiitic magmas.

Values used for the partition coefficients in the following calculations are essentially those also used by Mathez (1994). Typically they are 0.003, 0.20 and 0.06; and 0.04, 0.40 and 0.01 for Ce and Yb into orthopyroxene, clinopyroxene and plagioclase respectively. All values used are listed in the calculations in Table 2. The effect of variations in these values is also explored in that table.

The behaviour of REE will be discussed in terms of the two rock types which were the subject of the study by Mathez (1994); one is the pyroxenitic Merensky Reef and the other is a gabbro norite some metres into the footwall. The exact mineralogy of the samples studied is not quoted, but general information is presented. The Merensky Reef is described as a rock with 80-85% primary orthopyroxene. The gabbro norite is not documented in detail, and hence an estimated mode of 50% plagioclase and equal proportions of both pyroxenes is assumed. These figures are used as they match the proportions used in the crystallization of the magma, and approximate to cotectic proportions.

Numerous calculations are presented in Table 2 demonstrating how primary and final phase compositions may vary depending upon the various parameters discussed above for Rb in plagioclase. In the first calculation (model 1) it is assumed that there is 80% primary orthopyroxene and 20% of trapped magma. The magma has a $(Ce)_N$ content of 15. D_o , D_c and D_p are 0.003, 0.20 and 0.06. The primary orthopyroxene therefore contains 0.045 $(Ce)_N$. The TLC is 0.99, which means that virtually all of the Ce in the final rock was supplied by the interstitial magma with the primary minerals contributing almost nothing.

The final clinopyroxene composition, as determined from equation 10, has a $(Ce)_N$ content of 32.7. The final orthopyroxene contains 0.5 $(Ce)_N$, and the plagioclase 9.8. Hence, during re-equilibration with the trapped liquid the orthopyroxene has become enriched in Ce by a factor of 10.9 compared to its primary composition. If there had been any primary clinopyroxene and plagioclase in the rock their compositions would have been 3 and 0.9 $(Ce)_N$ respectively.

Table 2: Models for REE content of pyroxene and plagioclase

Model No.	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17
1 Ce	80	0	0	0	20	.003	.200	.06	15	.05	3.00	.90	.50	32.7	9.8	10.9	.99
2 Ce	70	0	0	0	30	.003	.200	.06	15	.05	3.00	.90	.50	34.4	10.3	11.4	.99
3 Ce	60	0	0	0	40	.003	.200	.06	15	.05	3.00	.90	.53	35.3	10.6	11.8	.99
4 Ce	80	0	0	0	20	.003	.100	.06	15	.05	1.50	.90	.67	22.4	13.4	3.0	.99
5 Ce	80	0	0	0	20	.002	.200	.03	15	.02	3.00	.45	.32	42.3	6.3	14.1	.99
6 Ce	20	20	20	40	20	.003	.200	.06	15	.05	3.00	.90	.15	9.8	2.9	3.3	.76
7 Ce	80	0	0	0	20*	.003	.200	.06	15	.05	3.00	.90	.67	22.3	6.0	7.4	.99
7b Ce	80	0	0	0	20*	.003	.200	.06	15	.05	3.00	.90	.59	39.2	11.8	13.1	.99
8 Nd	80	0	0	0	20	.006	.300	.04	13	.08	3.90	.52	.66	33.1	4.4	8.5	.98
9 Nd	20	20	20	40	20	.006	.300	.04	13	.08	3.90	.52	.22	11.2	1.5	2.9	.72
10 Sm	80	0	0	0	20	.010	.350	.02	12	.12	4.20	.24	.90	31.2	1.8	7.4	.96
11 Sm	20	20	20	40	20	.010	.350	.02	12	.12	4.20	.24	.30	11.8	.7	2.8	.71
12 Eu	80	0	0	0	20	.010	.350	1.00	11	.11	3.90	11.00	.18	6.4	18.1	1.7	.96
13 Eu	20	20	20	40	20	.010	.350	1.00	11	.11	3.90	11.00	.13	4.4	12.5	1.1	.30
14 Yb	80	0	0	0	20	.040	.400	.01	8	.32	3.20	.08	1.40	13.5	.3	4.2	.86
15 Yb	20	20	20	40	20	.040	.400	.01	8	.32	3.20	.08	.81	8.1	.2	2.5	.69
16 Yb	80	0	0	0	20*	.040	.400	.01	8	.32	3.20	.08	1.23	12.3	.1	3.9	.86

Column explanation:

- 1 Element
- 2 Wt % primary orthopyroxene
- 3 Wt % primary clinopyroxene
- 4 Wt % primary plagioclase
- 5 Wt % trapped liquid
- 6 Partition coefficient - orthopyroxene
- 7 Partition coefficient - clinopyroxene
- 8 Partition coefficient - plagioclase
- 9 Concentration of element in liquid (P)
- 10 Composition of primary orthopyroxene
- 11 Composition of primary clinopyroxene
- 12 Composition of primary plagioclase
- 13 Composition of final orthopyroxene
- 14 Composition of final clinopyroxene
- 15 Composition of final plagioclase
- 16 Enrichment factor between final and primary phases
- 17 Trapped liquid contribution (TLC)

* Models 7 and 16 contain 20% trapped liquid which crystallizes 0.25% apatite,

for which D_{ce} and D_{xb} are 25 and 12.5.

* Model 7b contains 20% trapped liquid which crystallizes 5% opx, 13% plag and 2% cpx

The same calculation has been performed for Nd, Sm, Eu and Yb using the same mineral proportions but changing the magma composition and values for partition coefficients as shown in Table 2 (models 7, 9, 11 and 13). This allows the plotting of the REE profile of the primary and final orthopyroxene on Figure 2 (curves 1 and 3 respectively). There is a very significant enrichment of REE in the final phase compared to that predicted by equation 6 for the primary mineral.

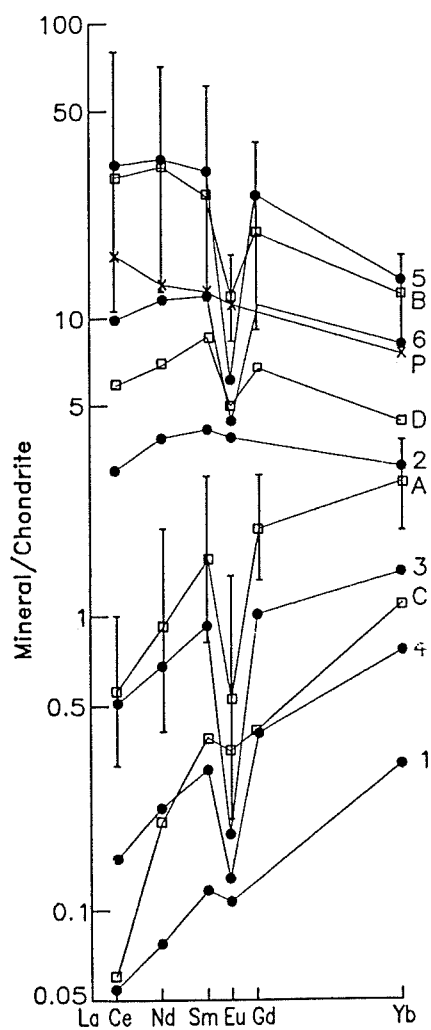


Figure 2: Plot of chondrite-normalised REE contents in pyroxenes. Some are observed compositions (shown by open squares), others are calculated in Table 2 (solid circles). Analysis P (shown by crosses) is the composition of the parent magma used in the calculations, and is taken from Harmer and Sharpe (1985). Observed compositions (from Mathez, 1994): A and B are ortho- and clinopyroxene from the Merensky Reef; C and D are ortho- and clinopyroxene from footwall gabbro-norite. For A and B vertical lines indicate the total range reported, and the squares are the median values. Calculated compositions from Table 2: 1 and 2 are primary ortho- and clinopyroxene; 3 and 5 are final ortho- and clinopyroxene in pyroxenite (models 1, 8, 10, 12 and 14), Table 2); 4 and 6 are final ortho- and clinopyroxene in gabbro-norite (models 6, 9, 11, 13 and 15).

The second example relates to the gabbro-norite. Here it is assumed that the primary mineralogy is in the ratio 50:25:25 for plagioclase and both pyroxenes. Again there is 20% trapped magma. Model 6 in Table 2 shows that the primary mineral compositions are exactly the same as in the first example. However, because Ce is less incompatible in both

clinopyroxene and plagioclase (by a factor of 67 and 20 respectively) than in orthopyroxene the trapped liquid contribution is only 0.76. After total solidification there is an enrichment by only a factor of 3.3 in $(Ce)_N$ in the final minerals compared to their primary compositions. These various compositions are also plotted on Figure 2.

As with Rb in plagioclase, various other models are presented in Table 2 to show the effect of changing the trapped liquid content, the partition coefficients, and also allowing for the formation of minor apatite, the only mineral in these rocks with a partition coefficient greater than unity for the REE.

Models 2 and 3 in Table 2 show the effect of changes in the proportion of trapped liquid. Increasing the proportion to 30% and 40% increases the $(Ce)_N$ in the final pyroxene to 34 and 35, and so does not fundamentally influence the REE pattern produced.

The effect of changing the partition coefficients is shown in models 4 and 5. In model 4 the partition coefficient for clinopyroxene is halved. The $(Ce)_N$ in the final clinopyroxene composition decreases from 33 to 22 compared to model 1. Likewise in model 5 the partition coefficients for plagioclase and orthopyroxene are halved, and this results in an increase in $(Ce)_N$ to 42 in the final clinopyroxene.

The last, and most important, consideration is that of the formation of a minor mineral into which REE will concentrate. In the case of the Upper Critical Zone there is extremely rare interstitial apatite in most samples. Typical P_2O_5 concentrations in these rocks are 0.02% (Eales *et al.*, 1990), which translates to 0.05% apatite. This is included in the calculation shown as models 7 and 16. For Ce and Yb partition coefficients into apatite of 25 and 12.5 are used. These are based on the values determined by Mathez (1994). Allowing for the formation of this apatite, $(Ce)_N$ and $(Yb)_N$ in the final clinopyroxene become 22 and 12 respectively. Thus, this parameter has a greater effect on final composition than any of the others discussed above, but there is still significant enrichment in the final compared to the primary clinopyroxene.

APPLICATION TO MINERALS IN THE BUSHVELD COMPLEX

Plagioclase

There are few analyses for Rb in plagioclase from the Bushveld Complex. Hamilton (1977) quoted one value of 1.75 ppm and, based on this, inferred (using equation 6) that the magma from which it formed contained 60 ppm Rb. Kruger and Marsh (1982) presented data for 17 mineral separates from the Merensky Reef and obtained an average of 2.2 ppm. Model 2 in Table 1 shows that a magma with 5 ppm Rb can produce a final plagioclase with 2.15 ppm Rb in a noritic rock, and hence it is not necessary to appeal to a magma anomalously enriched in Rb to explain these observations. Furthermore, Kruger and Marsh (1982) showed that the two plagioclase separates from the pyroxenite facies of the Merensky

Reef contained 4.4 and 4.9 ppm Rb. These extremely high values are predicted by the effect discussed above and shown in Table 1, model 1, where values up to 8 ppm are possible. Conversely, the anorthositic rocks of the Merensky Reef contain plagioclase with 1.4 to 2.9 ppm Rb (Kruger and Marsh, 1982), these lower values again being predicted as a result of the higher modal plagioclase content of the rocks (compare models 1, 2 and 3 in Table 1). It can be concluded that the Rb data for plagioclase from the Merensky Reef are entirely consistent with crystallization from trapped liquid containing a mere 5 ppm Rb, and no anomalous liquid or infiltration metasomatism is required.

Quadling and Cawthorn (1994) presented analyses of eight plagioclase separates from the Main Zone of the Bushveld Complex and obtained Rb contents between 2 and 4 ppm. There is therefore no difference between plagioclase from the Merensky Reef and the Main Zone to suggest that any atypical process has influenced the final chemistry of Merensky Reef samples.

Pyroxenes

Hamilton (1977) and Mathez (1994) analyzed pyroxenes from the Critical Zone, especially the Merensky Reef, for their REE content, and concluded that they were extremely enriched in REE. One exception was a sample just below the Merensky Reef which was a gabbro-norite, and had significant primary clinopyroxene. The concentrations obtained by Mathez (1994) are shown in Figure 2, where they are compared with the values calculated in Table 2. Mathez (1994) argued that the clinopyroxene in the Merensky Reef had formed from a liquid with $(Ce)_N$ values of 120 to 900, and $(Nd)_N$ values of 25 to 40. The calculations in Table 2 use values of only 15 and 8 for these two elements, but predict final clinopyroxene compositions consistent with the observed values. The REE of the clinopyroxene from the Merensky Reef (B in Fig. 2), where it is interstitial, and the clinopyroxene from the gabbro-norite (D in Fig. 2), where it is primary, differ by a factor of approximately five. However, the hypothetical curves for models with interstitial and primary clinopyroxene (curves 5 and 6 in Fig. 2 respectively) also differ by a factor of four. The agreement between curves B and 5, and between D and 6 in Figure 2 is good, suggesting that the proposed model of reaction with trapped liquid is consistent with the observations. A comparison of the orthopyroxene compositions of the two rock types may also be made. The observed orthopyroxene in the Merensky Reef is shown as curve A and the calculation as curve 3. For Ce agreement is good, but the calculated curve is slightly depleted in heavy REE. The observed orthopyroxene in the gabbro-norite is shown as curve C and the calculated composition as curve 4. Curve C has a slightly steeper slope, but otherwise agreement is good.

These two examples demonstrate that what are traditionally called cumulus and intercumulus clinopyroxene can vary enormously in incompatible element abundances even though they may have formed from exactly the same magma composition, and solidified with

exactly the same proportion of trapped liquid. The difference is due to the variation in mode and in the trapped liquid contribution (TLC) - the greater its contribution, the greater the enrichment in the final minerals. Furthermore, it can be seen that use of equation 6 for incompatible element abundance in single minerals can yield to very misleading inferences about parent magma composition.

There are several features highlighted by Mathez (1994) which deserve further mention. The analyzed pyroxenes in the pyroxenite have a significant negative Eu anomaly. This demonstrates that they have equilibrated with plagioclase. The present models show that because of the large partition coefficient for Eu into plagioclase, the formation of only 10% interstitial plagioclase in the rock is sufficient to produce this substantial Eu anomaly in the coexisting pyroxenes. This occurs even though the parent magma does not have an Eu anomaly.

Analyses of the coexisting *primary* clino- and orthopyroxene yield a smaller partition coefficient (cpx/opx) compared to analyses where the clinopyroxene is *interstitial* (Mathez, 1994). This can be attributed to incomplete re-equilibration of the primary orthopyroxene with the interstitial liquid, as seen from the data in Table 2. Model 6 shows that $(Ce)_N$ values for primary clino- and orthopyroxene are 3 and 0.045, giving a partition coefficient of 67, in agreement with the observed values (Mathez, 1994). Similarly, if the final $(Ce)_N$ of clino- and orthopyroxene are compared in any of the models, the same partition coefficient is obtained. However, if the composition of the *final* clinopyroxene is compared with that of the *primary* orthopyroxene in model 1, $(Ce)_N$ values of 32.7 and 0.045, and an apparent partition coefficient of 700, are obtained. This is far higher than the value observed (120) for these pairs by Mathez (1994). The difference between the partition coefficients for primary clino- and orthopyroxene, and interstitial clinopyroxene to primary orthopyroxene does not indicate formation from two different magmas as suggested by Mathez (1994), merely that there has been incomplete re-equilibration during crystallization of the trapped liquid.

There appears to be a decoupling of major and trace element behaviour in the pyroxenes, in that the $mg\#$ ($100 \cdot Mg / (Mg + Fe)$) ratio of the pyroxenes suggests a relatively primitive magma, while the REE content indicates a highly evolved or enriched magma. The reason for the great abundance of REE has been explained above. The reason the major element composition remains fairly magnesian is explained in the trapped liquid shift model of Barnes (1986). As there is approximately 80-85% orthopyroxene in the Merensky Reef, the effect of 20% trapped liquid is minimal. This is shown in Figure 3, which illustrates the variation in whole-rock $mg\#$ as a function of the proportion of primary orthopyroxene, plagioclase and trapped liquid. The primary orthopyroxene is taken to have $mg\#$ of 82, and that of the liquid 47. The changes in whole-rock $mg\#$ as a function of the three components is shown by the solid lines which radiate from the plagioclase apex. The effect of changing plagioclase to orthopyroxene ratio at constant trapped liquid content is shown in the lower diagram. Provided there is more than 30% pyroxene, the effect of the trapped liquid on $mg\#$

is trivial, and only becomes significant in anorthosite. Hence, in the case of the Merensky pyroxenite, the pyroxene retains a near-primary major-element composition, while the incompatible trace-elements are enriched.

Relationship between $mg\#$ and ratio of Opx:Plag

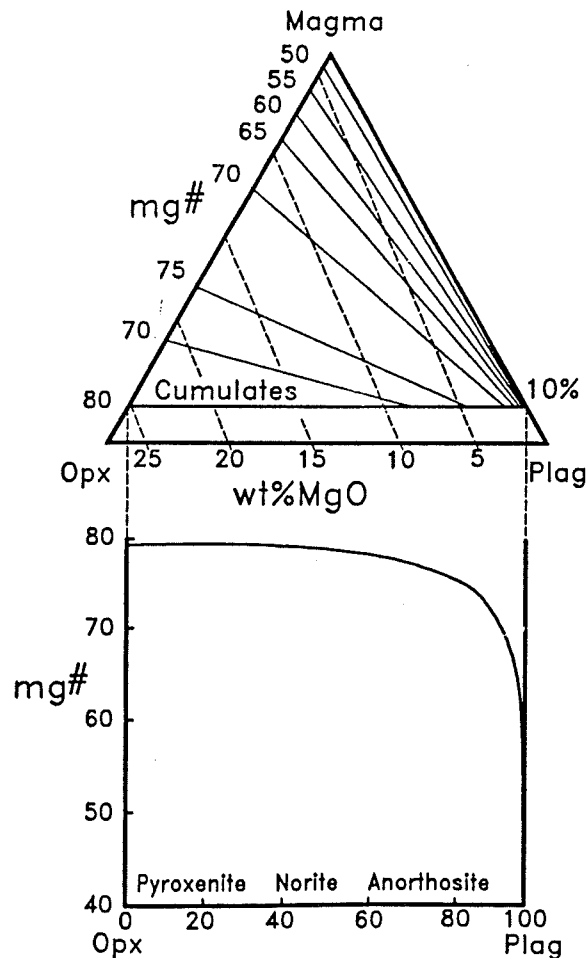


Figure 3: Relationship between $mg\#$ and proportion of orthopyroxene, plagioclase and trapped liquid in whole-rock samples. The solid lines show constant $mg\#$ values for the re-equilibrated pyroxene, and are enumerated on the left side. Dashed lines show the whole-rock MgO content, enumerated along the base. The horizontal line, denoted "cumulates", shows a plausible range of whole-rock compositions formed with differing proportions of primary pyroxene to plagioclase. The variation in $mg\#$ values along this line is shown in the lower diagram. Note that it is only in extremely leucocratic rocks that there is a significant decrease in $mg\#$ for the whole-rock and pyroxene compositions.

INFILTRATION VERSUS TRAPPING OF LIQUID

The model presented above indicates that it is perfectly possible to produce all the observed incompatible trace element data for minerals from the Bushveld Complex by trapping of interstitial liquid. However, this does not prove that this must have occurred, any more than the modelling of Mathez (1994) proves that infiltration must have occurred. Both models can be made consistent with the data. Other criteria must be sought. Mathez (1994) showed that the minerals in the gabbronorite, a few metres below the Merensky Reef, had apparently normal (fairly low) abundances of REE. If there had been infiltration of liquid derived from greater depth, its passage through this gabbronorite layer should have enriched the minerals in REE. The fact that they are not enriched argues against pervasive and reactive residual liquid migration through this interval of the Bushveld Complex. In the present model the low abundance of REE in minerals in the gabbronorite is the result of buffering by the abundant primary clinopyroxene, which reduced the trapped liquid contribution in the whole rock.

CONCLUSIONS

A mathematical model is derived for studying the variation in incompatible trace-element abundances in minerals in layered intrusions, as a result of crystallization of a *trapped* liquid. This is complementary to the model developed by Barnes (1986) for major elements, which were referred to as the trapped liquid shift. Various assumptions need to be made about the proportion of primary phases and interstitial liquid, the chemistry and mineralogy produced by that interstitial liquid, and the value of partition coefficients, in order that a mineral composition may be predicted from a magma composition, or so that a magma composition may be inferred from an analysis of an individual phase.

These calculations show that extreme enrichment of incompatible elements in all phases in a rock is possible, but mainly in the mineral into which the element in question is least incompatible. It is perfectly plausible for a minor mineral to contain higher abundances of an element than the magma from which it formed, even though the partition coefficient is considerably less than unity.

These models are applied to examples from the Bushveld Complex. It is shown that Rb contents in plagioclase from 1-4 ppm from the Merensky Reef and other horizons can form from a magma with only 5 ppm Rb. Similarly, clinopyroxene may contain up to three times the abundance of REE than the magma from which it formed, even though the partition coefficients range from 0.2 to 0.4. Specifically, high concentrations of REE from samples from the Merensky Reef can be produced from a magma with low REE abundances, typical of continental tholeiite, by trapping and crystallization of interstitial liquid. There is no need to appeal to anomalously high incompatible element contents in the magma or to metasomatic

events to produce any of the previously published trace element data for minerals from the Bushveld Complex.

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