



AN EXPERIMENTAL INVESTIGATION OF PHASE RELATIONS IN KIMBERLITE MELTS

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INTRODUCTION

The composition of kimberlite magma remains enigmatic partly due to the explosive eruption style, but also contamination by xenolithic material and strong alteration post-emplacement. Various kimberlite magma compositions have been hypothesized. Experiments at the conditions prior to and during emplacement provide an important way of testing the viability of such melts in reproducing the observed phase relations seen in the rocks. The results presented in this study extend the range of previous investigations (Sparks *et al.*, 2009; Brooker *et al.*, 2011) that have concluded the original 'magma' part of a kimberlite (i.e. xeno-lith/cryst free) may have a lower SiO₂ and MgO content than the bulk rock composition measured for 'emplaced' rocks. This suggests the kimberlite melt are more 'transitional' towards a carbonatitic composition.

The composition of olivine in this series of experiments was surprising in terms of low FeO and high CaO contents. Such olivine-melt data may be useful in reconstructing the original co-existing melt composition from just the solid phase compositions in natural rocks. In particular we need to predict the partitioning of MgO and FeO between olivine and liquid ($K_{D(Fe-Mg)}$), as this mineral is a ubiquitous phase in a broad range of kimberlite rocks. It exerts a major control 'at source' where the magmas leave the upper mantle and controls the composition as magmas fractionate or accumulate this phase during their evolution on the way to the surface. The CaO

content of olivine may also provide information on the melt and through equilibrium with co-existing monticellite the temperature of kimberlite magmas.

METHODOLOGY

Starting compositions used to test the viability of more 'transitional' compositions and K_D values for olivine are based on very fresh natural kimberlitic rock compositions from Dutoitspan (Ogilvie-Harris *et al.*, 2008), Wesselton and Jericho (Sparks *et al.* 2009; Brooker *et al.* 2011). The kimberlite rock compositions were systematically moved towards carbonatite as the original compositions were found to have very high and unrealistic liquidus temperatures. Examples of the resulting starting compositions are shown in Table 1.

The experiments were conducted at 100MPa and temperatures of 1100°C to 1250°C with mixed CO₂-H₂O volatile contents to simulate the conditions of kimberlitic melts during the eruption and emplacement of the hypabyssal intrusions at shallow levels in the crust.

RESULTS

Melt compositions

The first examined composition ROK1 (13.38 wt% SiO₂) produced an abundant amount of apatite, spinel and approximately 58% melt at 1250°C. ROK2 (17.25 wt% SiO₂) crystallised a



more ‘typical’ kimberlite assemblage of olivine, monticellite, spinel, apatite but had minimal interstitial melt at 1250°C, which was difficult to analyse.

Table 1. Compositions of the starting material

Oxides	ROK1 Wt%	Vol Free basis	ROK2 Wt%	Vol Free basis
SiO ₂	13.38	15.67	17.25	20.57
TiO ₂	5.26	6.15	4.14	4.93
Al ₂ O ₃	4.88	5.72	3.85	4.59
Cr ₂ O ₃	3.49	4.08	2.75	3.28
Fe ₂ O ₃	2.25	2.64	2.11	2.52
FeO	6.91	8.09	6.48	7.73
MnO	0.17	0.20	0.16	0.19
MgO	10.18	11.93	16.09	19.19
NiO	0.12	0.14	0.11	0.13
CaO*	28.47	33.34	22.80	27.18
Na ₂ O	0.08	0.10	0.13	0.16
K ₂ O	2.76	3.23	2.17	2.58
P ₂ O ₅	5.87	6.87	4.61	5.49
BaO	0.57	0.66	0.44	0.53
SrO	1.01	1.19	0.80	0.95
Water	4.55	-	6.04	-
CO ₂	10.05	-	10.08	-
Total	100.00	100.00	100.00	100.00

Unfortunately, the residual melts for both starting compositions (Figure 1) had characteristics that are likely inconsistent with ‘residual’ kimberlite matrix/melt, being very high in CaO and SiO₂ with no evidence of calcite precipitation that is common in the groundmass of many natural kimberlites. To examine even more ‘carbonatitic’ compositions, a further carbonate component (50/50 mix of CaCO₃/MgCO₃) was added to ROK2 in varying proportions. Some of these very low SiO₂ experiments did produce calcite that may be a stable phase or formed on the quench.

One of the problems with the results is that the temperatures needed to get reasonable amounts of

melt are considerably higher than the estimates made for natural kimberlites.

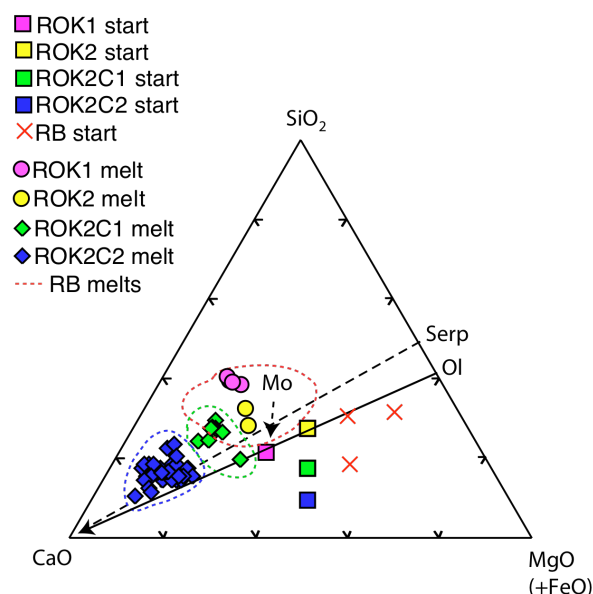


Figure 1. Ternary diagram to show the different starting compositions in a simplified CaO-MgO-SiO₂ system and the residual melts produced. RB experiments (in red) are from Sparks *et al* (2009) and Brooker *et al* (2011).

OLIVINE COMPOSITIONS

One of the surprising discoveries is the composition of olivines that have very high Fo contents giving a very low $K_{D(Fe-Mg)}$ (see Figure 2).

The K_D Problem

Roeder & Emslie (1970) were the first to pair these elements in an exchange reaction between olivine and melt for use in correlating data in both experimental and natural systems. The olivine-liquid exchange coefficient, known as K_D , is most correctly expressed as:

$$K_D^{Fe^{2+}+Mg} = (FeO/MgO)_{Ol} / (FeO/MgO)_{melt}$$

where FeO and MgO refer to concentrations (by weight). This is where the problems start as the melt can have any proportion of the Fe as either ferrous Fe²⁺ or ferric Fe³⁺ depending on the oxidation state of the system (fO_2), but also dependant on other compositional features of the melt.



In contrast, the Fe in olivine is almost exclusively Fe²⁺. As a result it becomes critical to consider the Fe²⁺/Fe³⁺ ratio in the melt when calculating K_D . Based on early studies in the 70's it became an effective 'law' of igneous petrology that K_D has a value of 0.30 ± 0.03 , and that this was independent of temperature and liquid composition (Roeder and Emslie, 1970). In general, this value considered all Fe in the melt as FeO. Eventually there was some consideration of the Fe²⁺/Fe³⁺ ratio in the melt, but analytical techniques did not allow a proper analysis of this ratio and it was generally back calculated to agree with a K_D of 0.3. Any olivine failing to meet this criterion is considered a 'xenocryst' out of equilibrium with its surroundings. For experimentalists in the laboratory, the failure to reproduce a value near 0.3 is considered a failure of the experiment (Beattie *et al.*, 1991; Toplis, 2005) and an indication of disequilibrium. Unfortunately, the 0.3 paradigm has led to a self-perpetuating myth with experiments falling outside the accepted range, filtered and eliminated from a data base that then continues to support the idea (Beattie *et al.*, 1991). Some workers have shown that liquid composition does exert a 'significant' effect on K_D (Gee and Sack, 1988; Kushiro and Walter, 1998; Toplis, 2005). However, these are minor effects compared with the variation found in this study (and Canil and Bellis, 2008).

Experimental Olivines

Figure 2 shows the olivine-melt K_D calculated for the experiments (solid symbols) plotted against a compositional parameter mainly based on the SiO₂ content and developed by Gee & Sack (1988) to fit data for a range of igneous compositions. The experiments involved rather extreme, low-silica kimberlite compositions and the K_D is plotted for an assumed Fe²⁺/Fe³⁺ values in the melt at NNO (based on the oxidation state most likely in the experiment) although values for a range of fO_2 conditions are indicated. These in turn are calculated from the equation given by

Kress and Carmichael (1988) that shows the supposed ratio as a function of fO_2 relative to a known buffer (NNO). For the experiment of this study the Fe²⁺/Fe^{tot} should be between 20% (NNO-2.5) and 60% (NNO+2).

It is clear that the data do not give the traditional K_D value of 0.3 and some petrologists would claim that equilibrium has not been achieved. However, the euhedral shape of the olivines and the lack of any zoning of Fe and Mg (or Al, Ca or P) suggest equilibrium has been achieved. In addition, an independent dataset from Canil and Bellis (2008) shows a similar range for K_D . An alternative possibility is that the melt composition has a much stronger control and in particular, that there is significantly more Fe³⁺ in the melts than calculated from models such as Kress & Carmichael, 1988. However, Ardnt *et al.*, (2010) suggest that a much higher K_D of 0.5 is more applicable olivines found in kimberlite.

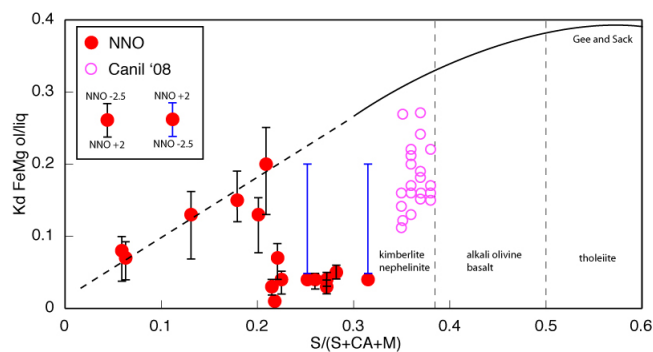


Figure 2. Olivine-liquid K_D for kimberlite liquids in this study plotted against their degree of silica saturation given in terms of molar S, CA, and M components (where $S = \text{SiO}_2 - 4\text{Na}_2\text{O} - 4\text{K}_2\text{O}$; $\text{CA} = \text{CaO} + \text{Al}_2\text{O}_3 + 3\text{Na}_2\text{O} + \text{K}_2\text{O} - 0.33\text{P}_2\text{O}_5$; $\text{M} = \text{FeO} + \text{MnO} + \text{MgO}$, after Gee and Sack, (1988)). The Fe³⁺ contents for liquid compositions in equilibrium with olivine were calculated using the algorithm of Kress and Carmichael (1988). Canil '08 data is for a 'silica-rich' kimberlite from Canil & Bellis, (2008).

Another feature of the experimental olivines is the high CaO content, which has a range from 0.38 to 3.98 wt%, but is usually between 1.5 and 3 wt%. We consider the systematics of Ca partitioning between the olivine and melt, but also the role of the olivine-monticellite solvus. This may give complementary data on the temperature



of equilibration as shown in Figure 3. The lower CaO content observed in natural kimberlites (< 1.0 wt%), indicating much lower equilibration temperature than our experiments.

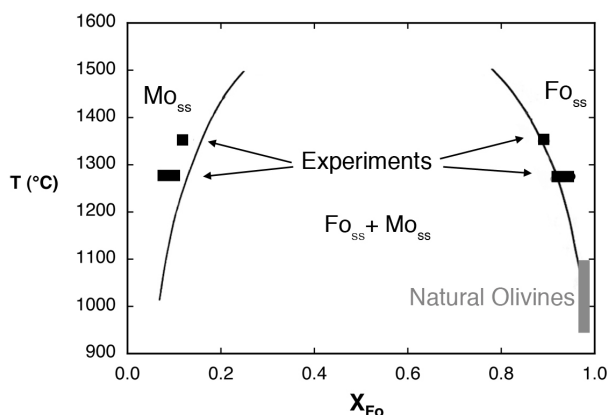


Figure 3. Olivine-monticellite solvus as a function of temperature (from Adams and Bishop, 1985). Experiments at 1275 and 1350°C have compositions close to the solvus. Natural olivine phenocrysts suggest lower temperatures.

As well as providing information on the melt composition and temperature, the understanding of olivine compositions will help to unravel the confusion that results from a variety of olivine populations (xenoliths, xenocrysts, macrocrysts, phenocrysts and groundmass) that may have re-equilibrated (or not) during the evolution and ascent of the kimberlite magma.

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