

## Kimberlites: High H<sub>2</sub>O/CO<sub>2</sub>, MgO-rich, Al- and K-Poor, Silica Undersaturated Magmas

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### Introduction and Data Set

Kimberlite magmas are typically considered to be silica undersaturated, alkaline, potassic, CO<sub>2</sub>-rich melts. Analyses of 387 hypabyssal kimberlite samples from worldwide localities (ALL) have been compiled from the literature and unpublished sources, excluding samples that exhibit obvious crustal contamination.

We consider only archetypal kimberlites (usually referred to as Group I kimberlites) in the database and the following discussion. The data set is dominated by examples from southern Africa (SA; n=166) and a new large data set from North America (NA; n = 166) that is dominated by examples from Lac de Gras, plus 55 additional analyses from other localities worldwide. The Lac de Gras suite was prepared by selecting samples with the lowest visible crustal fragments and in most cases by additional post-coarse crushing hand picking to remove any obvious additional crust. Of fundamental importance in interpreting the data is understanding that whole-rock geochemical data is a proxy for mineralogy (mineral species, composition, and modes). Combined use of kimberlite whole-rock geochemical and mineralogical data can be applied to provide constraints or brackets on kimberlite magma composition. A significant issue with whole-rock analyses of hypabyssal kimberlite is the degree of lithospheric mantle and/or crustal contamination. Application of major element screens (e.g. Clement's Contamination Index, C.I.) are problematic in that while entrainment or digestion of mantle lithosphere lowers C.I., the addition of crust has the opposite effect and increases C.I. (Dowall, 2004). Thus, it may be extremely difficult to focus on minimally crustally contaminated hypabyssal kimberlite that contains significant amounts of entrained lithospheric peridotite, even utilizing trace element screens. Application of more robust trace element-based screens for crustal contamination (e.g. Sm/Yb ratio) have been applied to the data set, and while this reduces the number of analyses available for interpretation, it does not materially change the results presented below.

### Alkalis, alumina, and peralkalinity

Graphical analysis of the hypabyssal kimberlite data set using relative probability plots reveals geochemical systematics that are inconsistent with many of the purported

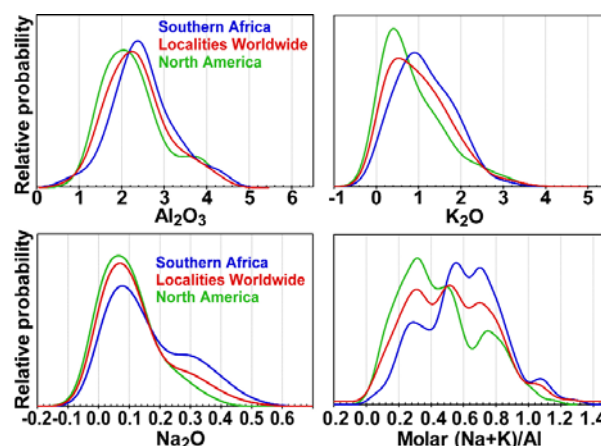


Fig. 1. Relative probability plots for a) alumina as wt.% Al<sub>2</sub>O<sub>3</sub>; b) potassium as wt.% K<sub>2</sub>O; c) sodium as wt.% Na<sub>2</sub>O; d) peralkalinity, [molar (Na + K)/Al].

hallmarks of kimberlite magma, i.e., alkaline, potassic, CO<sub>2</sub>-rich melts. For silica undersaturated rocks, alkalinity is defined on the basis of molar (Na+K)/Al. Kimberlites have low alumina contents (modes of 2.4, 2.0, and 2.2 wt.% Al<sub>2</sub>O<sub>3</sub> for SA, NA, and ALL, respectively; Fig. 1a), potassium contents are very low (modes of 0.9, 0.4, and 0.5 wt.% K<sub>2</sub>O for SA, NA, and ALL, respectively; Fig. 1b), and sodium contents are exceptionally low (modes of 0.08, 0.06, and 0.07 wt.% Na<sub>2</sub>O for SA, NA, and ALL, respectively; Fig. 1c). Combined, this leads to (Na+K)/Al being <1 (~0.25-0.75; Fig. 1d), i.e., by definition, kimberlite is not an alkaline rock. The absence of feldspathoids in kimberlite is consistent with the observed (Na+K)/Al < 1. Kimberlites that are contaminated by four-phase peridotite will not have their Na-K-Al systematics affected significantly, due to lower concentration levels in the entrained/digested mantle xenoliths than in the kimberlite magma. Al and K will be diluted slightly by this process, e.g., average cratonic peridotite has ~1.1 wt.% Al<sub>2</sub>O<sub>3</sub> (Pearson and Wittig, in press). Since kimberlites are not alkaline (as defined by (Na+K)/Al < 1), this precludes further refining these rocks as being of a 'sodic' or 'potassic' lineage. Although many kimberlites have molar K/Na > 1 (often with values of 3–30) this is largely a manifestation of their extremely low levels of Na<sub>2</sub>O. This means that kimberlites may appear to be nominally ultrapotassic, but bulk rocks rarely have >3 wt.% K<sub>2</sub>O (Fig. 1b) and average much lower (0.5%).

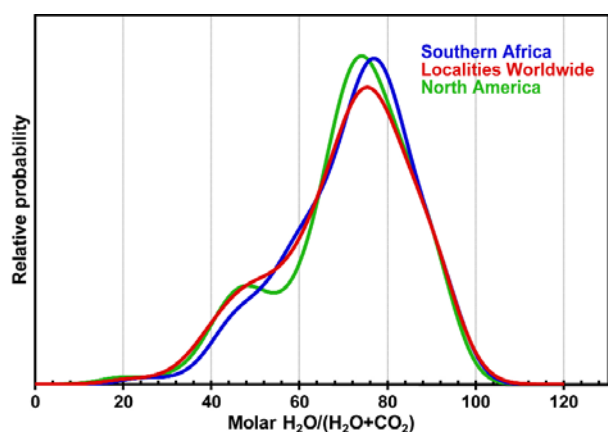


Fig. 2 Relative probability plot for molar  $\text{H}_2\text{O}/(\text{CO}_2+\text{H}_2\text{O}) \times 100$ .

Thus, kimberlite cannot be considered an ultrapotassic rock, as defined by Foley et al. (1987). Kimberlites have similar potassium contents to those in MORB and OIB, and lower levels than more common alkaline rocks such as basanite. In contrast, major element data from aillikite sills and dykes (data from Tappe et al., 2004, 2007, 2008, and unpublished) have significantly higher average levels of  $\text{K}_2\text{O}$  (1.5 wt.%) and  $\text{Na}_2\text{O}$  (0.2 wt.%), and slightly higher  $\text{Al}_2\text{O}_3$  (2.7 wt.%) and  $(\text{Na}+\text{K})/\text{Al}$  ( $\sim 0.5$ – $1.2$ ) compared to the whole-rock hypabyssal kimberlite data. These geochemical attributes are consistent with aillikite having either different mineral phase assemblages, or similar mineral assemblages with different mineral chemistry, than kimberlites (Mitchell, 1999; Tappe et al., 2005). A manifestation of the low potassium concentrations in kimberlite is the substitution of Ba for K in phenocrystal and groundmass phlogopite (e.g. Mitchell, 1995).

### Water and carbon dioxide

While kimberlites are usually considered to be  $\text{CO}_2$ -rich or volatile-rich ( $\text{CO}_2$  and  $\text{H}_2\text{O}$ ), whole-rock  $\text{H}_2\text{O}$  and  $\text{CO}_2$  analyses from hypabyssal kimberlites suggest this is not the case. Measured  $\text{H}_2\text{O}$  contents (mode  $\sim 7.2$  wt.%) are greater than  $\text{CO}_2$  contents (mode  $\sim 4.8$  wt.%), suggesting that kimberlites are better termed volatile-rich ( $\text{H}_2\text{O}$  and  $\text{CO}_2$ ) rocks, emphasizing their water-rich nature. Examination of the  $\text{H}_2\text{O}$  and  $\text{CO}_2$  data on a molar basis [ $\text{H}_2\text{O}/(\text{CO}_2+\text{H}_2\text{O})$ ] clearly demarcates the  $\text{H}_2\text{O}$ -rich nature of kimberlite (modes of 0.77, 0.74, and 0.75 for SA, NA, and ALL, respectively; Fig. 2). Aillikite whole-rock data exhibit lower  $\text{H}_2\text{O}$  and higher  $\text{CO}_2$  contents with molar [ $\text{H}_2\text{O}/(\text{CO}_2+\text{H}_2\text{O})$ ] of approximately 0.5, significantly lower than kimberlites (data from Tappe et al., 2004, 2007, 2008, and unpublished). This is another indication of the difference between this magma type and kimberlites. The measured high water content and molar  $\text{H}_2\text{O}/(\text{CO}_2+\text{H}_2\text{O})$  of hypabyssal kimberlite are thought to reflect volatile speciation and volatile contents of the kimberlite melt on the basis of a number of observations. For example, the presence of serpentine (and not talc) in

hypabyssal kimberlite requires a high  $\text{H}_2\text{O}/(\text{CO}_2+\text{H}_2\text{O})$  in the fluid phase (Chernovsky et al., 1988). Wilson et al. (2007) utilized comprehensive C,O isotopic studies on fresh Lac de Gras hypabyssal kimberlite and mineral separates, combined with isotopic modelling, to conclude that the kimberlite melt (and fluid) had high  $\text{H}_2\text{O}/(\text{CO}_2+\text{H}_2\text{O})$ . The paucity of orthopyroxene xenocrysts in kimberlite requires high  $\text{H}_2\text{O}/(\text{CO}_2+\text{H}_2\text{O})$  in the melt in order to efficiently resorb orthopyroxene from entrained lithospheric peridotite xenoliths, based on the experimental work of Eggler (1973) on enstatite–olivine–liquid relationships. The experiments of Edgar et al. (1988), with loaded volatiles having molar  $\text{CO}_2 > \text{H}_2\text{O}$ , importantly show a significantly increased stability field for clinopyroxene at 2.0 to 3.0 GPa as compared to experiments with loaded volatiles with  $\text{H}_2\text{O} > \text{CO}_2$ . Based on results from these experiments, coupled with the absence of clinopyroxene phenocrysts in kimberlite, implies that kimberlite melts cannot be as  $\text{CO}_2$ -rich as some studies have suggested. Although water solubility in kimberlite melt has not been determined, the Wesselton aphanitic experiments of Edgar et al. (1988) show that on the liquidus at 1.0 GPa, the melt is undersaturated in loaded volatiles and contains 6.2 wt.%  $\text{H}_2\text{O}$  and 4.77 wt.%  $\text{CO}_2$ . This experiment clearly shows that high water solubilities are certainly possible in kimberlite melts at crustal pressures.

### A comparison of calculated ‘primary’ or ‘parental’ kimberlite magma compositions with high-pressure experimental kimberlitic melts – the nature of kimberlite source regions

A variety of research groups over the past decade have utilized a diverse set of techniques and sample suites to calculate a ‘primary’ or ‘parental’ kimberlite magma composition (e.g. Le Roex et al., 2003; Kopylova et al., 2008). It is worthwhile to carefully compare these calculated magma compositions with liquid compositions determined by high-pressure experiments, within the context of proposed source region bulk major element geochemistry (including volatiles) and inferred depth of melting. It should be noted that for most experimental studies, only very general matches to “calculated primary kimberlite melt compositions” can be made, with a number of key chemical components being significantly different. Comparing the liquid composition determined by Brey et al. (2008) for fertile magnesite peridotite SC-1 at 10 GPa and 1600°C to the calculated kimberlite melt composition of Kopylova et al. (2008) or Le Roex et al. (2003) indicates the experimental melts are silica- and calcium-poor and iron- and magnesium-rich. Brey et al. (2008) concluded that primitive kimberlite melts cannot be formed by partial melting of carbonate-bearing fertile asthenosphere. Importantly, high-pressure (11 GPa) near-solidus (1100°C) partial melting experiments on fertile peridotite KLB-1 with  $\text{H}_2\text{O}$  by Kawamoto and Holloway (1997), produced kimberlite melts that are much more similar to calculated kimberlite primary magma compo-

sitions than the Brey et al. (2008) melt compositions, but these H<sub>2</sub>O-rich experiments also produced liquids that were too iron-rich. The results of this study on hydrous melting appear to have been ignored by the kimberlite community, perhaps because of the common belief that CO<sub>2</sub> is much more important than water in the volatile budget of kimberlite. However, it is clear that for most parameters, the compositions of the liquids produced by high-pressure H<sub>2</sub>O-rich melting appear to more closely match primary kimberlite magma compositions than the melts produced experimentally in peridotite-CO<sub>2</sub> systems at high pressure. Nonetheless, even partial melting with H<sub>2</sub>O of fertile asthenospheric mantle does not produce melts that are exact analogues of kimberlite, suggesting a more depleted source is required. Currently we know of no experiments on H<sub>2</sub>O-rich harzburgite at high pressure (>10 GPa). Using a different approach, mixed volatile experiments by Ringwood et al. (1993) and Kesson et al. (1994) led these authors to suggest that the source region (at 10–16 GPa) was a depleted garnet harzburgite (10 GPa), or majorite -  $\beta$ -olivine (16 GPa). Based on 5 to 12 GPa experiments on an aphanitic kimberlite, Mitchell (2004) concluded the source region could not be a simple carbonate-bearing garnet lherzolite. Melts from a depleted source, however, will be Ca-poor, which requires a second component that must be Ca- and incompatible element-rich. The experiments of Edgar and Charbonneau (1993) indicate that at high-pressure (10 GPa), Ca-rich kimberlite melt can be produced by partial melting of an “eclogitic” (olivine websterite – websterite source) source with mixed (H<sub>2</sub>O+CO<sub>2</sub>) volatiles. We suggest that from a major element perspective, the key to kimberlite petrogenesis may lie in the transition zone (~400 km depth) via partial melting of foundered “eclogitic” oceanic slabs, which then invade and crystallize as veins in depleted harzburgite, that subsequently are vein-wall rock flux melted. The trace element and isotopic implications of this model, a refinement of that of Ringwood and coworkers, are explored by Pearson et al. (this volume).

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