

Volatiles in Kimberlite: Volume Relationships and Implications for Conduit and Eruption Dynamics

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Introduction

The unique aspect of kimberlite magmas is their potential for having high dissolved contents of primary volatiles (e.g., H₂O + CO₂ > 15 wt. %) coupled to a high ascent rate. The high ascent rates help couple the exsolved fluid to the magma as it rises to the point of eruption. During ascent the system evolves from a system featuring 30-40% suspended solids in a silicate melt to a system that is volumetrically dominated by the exsolved fluids (due to exsolution and expansion). Here, we explore the properties of the kimberlite melt phase and the associated CO₂-H₂O fluids, and relate these to kimberlite emplacement and eruption.

Model Melt Compositions

Chemical compositions of kimberlite melt are difficult to isolate because kimberlite is a hybrid rock representing a mixture of mantle and crustal xenoliths, macrocrysts, and subordinate amounts of cognate phenocrysts and groundmass material (Mitchell, 1986). Kimberlites are also enriched in volatiles, which can have post-eruption consequences. Even where kimberlite melt is quenched, post-eruption circulation of fluids can cause changes in bulk chemistry, replacement of primary minerals, and obliteration of primary textures and structures.

Sparks et al. (2006) compiled kimberlite melt compositions deriving from fine-grained aphanitic samples of kimberlite from the margins of dykes, melt compositions corrected for olivine accumulation, and reconstructed melt compositions from pyroclasts. There is a fair degree of agreement between estimates; on a normalized anhydrous basis they contain 30-36 wt. % SiO₂, 25-36 wt. % MgO, 12-22 wt. % CaO, 8-14 wt. % FeO, and 1-2.5 wt. % K₂O. CaO shows the greatest variation. For our calculations we adopt the reconstructed compositions from Kopylova et al (2007) (Table 1). Kimberlite melts are expected to contain both CO₂ and H₂O. Their exact amounts remain largely uncertain because kimberlite glass does not exist and kimberlite rocks are nearly always affected by late-stage fluid infiltration and reaction. We have added 5 wt.% H₂O and 10 wt.% CO₂ to our base anhydrous composition which is equivalent to ~10 mol.% of each volatile component (Table 1).

Calculated Melt Properties

The physical-chemical properties of kimberlite melt govern the transport and eruption behaviour of kimberlite magmas. Here we use computational models calibrated on experimental data

for multicomponent melts to explore the physical properties of kimberlite.

Table 1. Model volatile-free and volatile-rich kimberlite melt compositions based on compositional estimates reported by Kopylova et al. (2007) and transport properties of the melts computed at 1250°C and 1.0 GPa.

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Oxide (Wt. %)	Volatile-free	H ₂ O (5 wt. %)	CO ₂ (10 Wt. %)	H ₂ O + CO ₂
SiO ₂	33.08	31.51	30.07	28.77
TiO ₂	1.71	1.63	1.56	1.49
Al ₂ O ₃	2.15	2.05	1.95	1.87
Cr ₂ O ₃	0.35	0.33	0.32	0.30
FeO(T)	8.44	8.04	7.68	7.34
MnO	0.21	0.20	0.19	0.18
MgO	32.41	30.87	29.46	28.18
CaO	18.73	17.83	17.02	16.28
Na ₂ O	0.15	0.14	0.14	0.13
K ₂ O	1.78	1.69	1.61	1.54
P ₂ O ₅	0.99	0.95	0.90	0.86
CO ₂	0.00	0.00	9.09	8.70
H ₂ O	0.00	4.76	0.00	4.35
Total	100.00	100.00	100.00	100.00
Computed Physical Properties ^{1,2}				
Density (gm/cm ³)	3.05	2.74	3.36	3.01
Volume (cm ³ mo ⁻¹)	32.74	36.42	29.77	33.25
Cp (J K ⁻¹ mol ⁻¹)	171.7	175.6	156.1	160.3
A-VFT	-4.55	-4.55	--	--
B-VFT	4038	4713	--	--
C-VFT	715	586	--	--
Log η (Pas)	0.44	0.48	--	--
Tg (°C) [10 ¹² Pa]	686	598	686	598
M	65.0	50.6	--	--

¹ Density, volume, and heat capacity computed with MELTS (Ghiorso and Sack 1995).

² Melt viscosity, glass transition temperature (Tg) and fragility (M: steepness index) are computed using model of Giordano et al. (2008): $\log \eta = A + B/[T(K)-C]$.

Density

Magma density controls the efficacy with which kimberlites ascend and their style of eruption. Figure 1 shows values of density for the main constituents in kimberlite magmas computed at 1250°C and crustal pressures; the bulk density of the magma is a linear combination of these constituent properties. Densities of kimberlite melts are computed with MELTS (Ghiorso & Sack 1995; Fig. 1). Density decreases between 2% (dry) and 12% (volatile-rich) during ascent depending on volatile content. Anhydrous kimberlite has a density ~3 g/cc (Table 1); addition of H₂O decreases density whilst dissolved CO₂ causes an apparent increase in melt density (Note: relevant high-P compressibility data are sparse). Olivine macrocrysts have a density in excess 3.3 g/cc and can comprise ~40% of the kimberlite magma. The consequence is that, in the absence of an exsolved fluid phase, kimberlite magmas are likely to have densities in excess 3 g/cc (~3.12 g/cc).

Exsolution of a CO₂-H₂O fluid phase provides a logical and efficient means of reducing magma density and promoting the buoyancy critical for rapid ascent and eruption. Depending on fluid composition, density at the base of the crust varies between 1.1 and 0.7 g/cc. Magma density would be reduced to ~2.7 g/cc if exsolution produced 20 vol. % fluid at lower crustal

conditions. Even with no additional exsolution, the fluid phase will expand ~60% once it reaches the upper crust reducing magma density to < 2.4 g/cc.

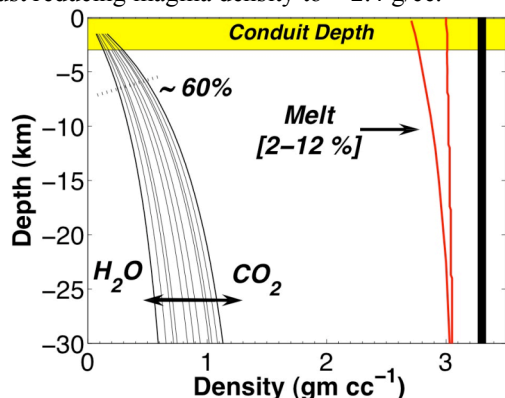


Fig. 1. Calculated densities pertinent to kimberlite ascent, including: kimberlite melt (red lines), olivine megacrysts (thick line), & CO₂-H₂O fluids plotted as a function of depth.

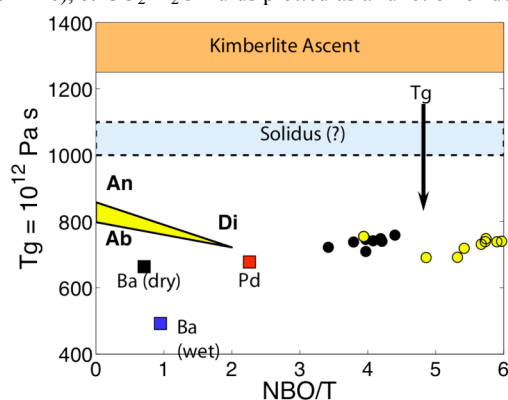


Fig. 2. T_g values for kimberlite, basalt (Ba), peridotite (Pd) and melts from system Di-Ab-An. Values are for dry (black) & volatile-rich (yellow) kimberlite (Sparks et al. 2006).

Viscosity (η) & Glass Transition Temperature (T_g)

The model of Giordano et al. (2008) allows us to compute transport properties of kimberlite melt (Table 1). The model does not account for dissolved CO₂, however, recent work by Morizet et al. (2007) shows that, relative to H₂O, the effects of CO₂ on melt transport properties are slight. Under normal conditions kimberlite melt will have values of η < 5 Pa s.

Natural silicate glasses form under a variety of geological conditions and commonly form in silicic lava and in rapidly cooled mafic rocks. There are no occurrences of kimberlitic glass, which raises the question of whether glass forms in kimberlite eruption. Glass formation is a boundary between changing environmental states and the model for melt viscosity provides a means of predicting that boundary: T_g (the temperature where $\eta \sim 10^{12}$ Pa s). Above T_g, rates of nucleation, crystallization and vesiculation are sufficiently fast to operate. Conversely, where the magma temperature intersects the melt's T_g, glass forms and these magmatic processes effectively cease. Glass formation, therefore, depends on the gap between T_{Liq} and T_g and rates of melt cooling (Fig. 2).

The depression of T_g by increased H₂O content provides a simple vehicle for production of glass during an eruption. Ascent and eruption causes

volatile loss and a concomitant increase in T_g, to the point that, T_g intersects magma temperature causing the melt to quench to glass. Kimberlite melts do not show the same depression in T_g (Fig. 2; Table 1) and thus lack this means of aiding glass formation. Furthermore, the ΔT between kimberlite formation temperature and T_g is higher than in most magmas.

Volatile Phase

Ascent of kimberlite causes exsolution of a CO₂-H₂O fluid; the fluid composition depends on the total dissolved fluid content of the melt and the T-P ascent path (e.g., Holloway & Blank 1994). Under conditions of equilibrium degassing (e.g., closed system), the original dissolved fluid content limits the range of fluid compositions produced during ascent. Under perfect fractional degassing (open system), increments of equilibrium fluid are released and "fractionated". Such situations arise when 2-phase flow (melt and gas) develops and the gas phase decouples from the host magma. Separated two-phase flow is likely to develop in kimberlite and allows for highly transient fluid compositions beginning with fluids extremely enriched in CO₂, and ending with H₂O-dominated fluid. The physical properties and behaviour of the fluids during ascent are, thus, constantly changing in response to the evolving fluid composition.

The CO₂-H₂O Equation of State

The exsolved magmatic fluid is modelled as mixtures of CO₂ and H₂O. No speciation calculations were attempted. The thermodynamic properties were retrieved using program REFPROP (Lemmon et al. 2007) that employs the GERG-2004 equation of state and mixing models (Kunz et al. 2007). The upper pressure limit for computations is restricted by the CO₂ to pressures below 800 MPa. The lower pressure and temperature limits were chosen at 50 MPa, 320 °C to ensure all compositions could be represented by a single fluid phase. Below we compute how the properties (V, H, S) of the expanding fluid change as a function of ascent path. Subsequent plots of entropy and enthalpy and the isentropic and isenthalpic paths are based on "intrinsic" thermodynamic properties (Dodson, 1971). They do not include energy associated with motion or position in the gravitational field.

Ascent Paths: Reversible vs. Irreversible

The heat content of the magma is reduced by loss to wall rocks, by interactions with xenoliths, and by other endothermic reactions (e.g., vesiculation), or is increased by crystallization or viscous heating during flow (e.g., Spera 1984; Sparks et al 2006). However, as the magma decompresses, the fluid phase increases in mass and volume, and the thermal consequences of adiabatic expansion begin to dominate. There are two-end-members to adiabatic expansion processes (e.g., Spera 1984; Mastin & Ghiorso 2003) in ascending magma (Fig. 3). The adiabatic expansion can proceed as a reversible isentropic process in which the expanding system does work on the environment. This process applies best to the final expansion of CO₂-H₂O

fluids during eruption of kimberlite where the system vents at high velocity into the atmosphere (Mastin & Ghiorso 2003, Sparks et al 2006). The work released to the environment is balanced by cooling of the system and entropy is conserved. Efficient cooling of the fluid phase can help cool and quench the melt to form glass.

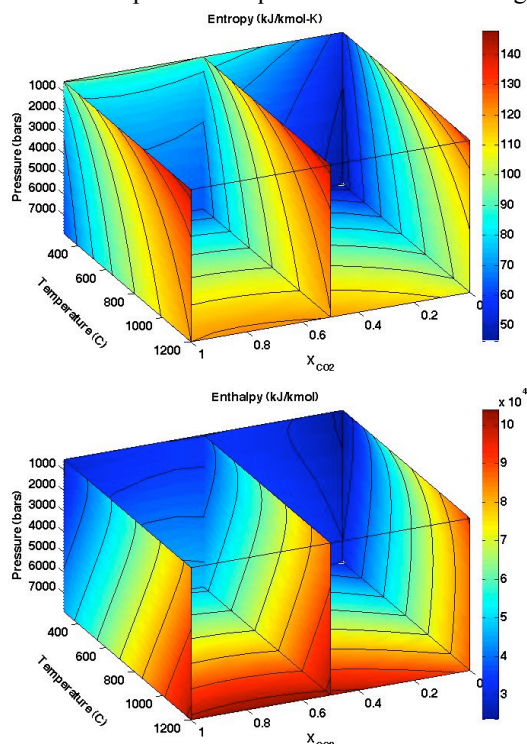


Fig. 3. Adiabatic expansion paths of CO_2 - H_2O fluids as a function P , & T . Upper: reversible adiabatic expansion paths of fluid as iso-entropy contours; isentropic depressurization from depth can cause 400-500°C cooling of the fluid. Lower: irreversible isenthalpic expansion paths for CO_2 - H_2O fluids. Isenthalpic expansive cooling of H_2O -fluids is slight until <3 Kb; CO_2 -rich fluids heat until during ascent until <400 bars.

Alternatively, during adiabatic isenthalpic expansion entropy is not. Isenthalpic expansion of a real fluid can cause either heating or cooling of the fluid depending on its composition (Fig. 3). This condition is best met during upward flow of kimberlite along established dykes where the magma loses negligible heat to the wall rocks. In this case, CO_2 fluid-bearing kimberlite will heat during ascent until the point of eruption (Fig. 3) where adiabatic isentropic expansion into the atmosphere will cause substantial cooling of pyroclasts.

Volcanological Implications

High CO_2 - H_2O contents promote explosive eruption of kimberlite characterized by high eruption velocities and high volume fluxes. There are several possible consequences of a collapsing volcanic plume at the end of the eruption. Depending on column height and the depth of the final fragmentation surface, the excavated portion conduit may be filled by a combination of: i) fragmented magma that did not erupt, ii) fall back material from the eruption column, and iii) material shed from inside flanks of the volcanic edifice. If the infill is above T_g (Fig. 4) we predict low

porosity deposits due to welding or hot pressing; the loss of porosity and permeability ultimately facilitates deuteric alteration processes. Alternatively, we can envision a situation where highly efficient adiabatic cooling of the pyroclastic material resulting in conduits filled with cooler ($< T_g$) deposits (Fig. 4). Porosity and permeability are preserved and passive-degassing proceeds along preferred pathways within the conduit. Alteration is expected to be patchy and to be localized around fluid escape channels. The nature of this late stage alteration is a direct indication of fluid composition in the waning stages of the eruption. In many cases these fluids are dominated by H_2O .

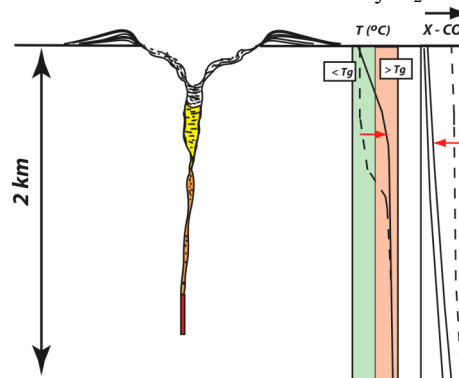


Fig 4. Post-eruption configuration of kimberlite pipe (left). Right side shows fluid composition and $T(^{\circ}\text{C})$ in pipe-infill. Dashed lines are for small-volume, eruptions dominated by CO_2 with high gas:melt ratios and resulting in cool conduit fill. Welding limited by the T -profile in conduit (see text). Solid lines denote large volume, eruptions featuring evolving fluid compositions. Final phase is H_2O -rich, has low gas:melt ratios and results in hot conduit fill (see text).

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