



# Experimental derivation of nepheline syenite and phonolite liquids by partial melting of upper mantle peridotites



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## ABSTRACT

Piston-cylinder experiments were performed to characterize the composition of liquids formed at very low degrees of melting of two fertile lherzolite compositions with 430 ppm and 910 ppm K<sub>2</sub>O at 1 and 1.3 GPa. We used the microdike technique (Laporte et al., 2004) to extract the liquid phase from the partially molten peridotite, allowing us to analyze liquid compositions at degrees of melting *F* down to 0.9%. At 1.3 GPa, the liquid is in equilibrium with olivine + orthopyroxene + clinopyroxene + spinel in all the experiments; at 1 GPa, plagioclase is present in addition to these four mineral phases up to about 5% of melting (*T* ≈ 1240 °C). Important variations of liquid compositions are observed with decreasing temperature, including strong increases in SiO<sub>2</sub>, Na<sub>2</sub>O, K<sub>2</sub>O, and Al<sub>2</sub>O<sub>3</sub> concentrations, and decreases in MgO, FeO, and CaO concentrations. The most extreme liquid compositions are phonolites with 57% SiO<sub>2</sub>, 20–22% Al<sub>2</sub>O<sub>3</sub>, Na<sub>2</sub>O + K<sub>2</sub>O up to 14%, and concentrations of MgO, FeO, and CaO as low as 2–3%. Reversal experiments confirm that low-degree melts of a fertile lherzolite have phonolitic compositions, and pMELTS calculations show that the amount of phonolite liquid generated at 1.2 GPa increases from 0.3% in a source with 100 ppm K<sub>2</sub>O to 3% in a source with 2000 ppm K<sub>2</sub>O. The enrichment in silica and alkalis with decreasing melt fraction is coupled with an increase of the degree of melt polymerization, which has important consequences for the partitioning of minor and trace elements. Thus Ti<sup>4+</sup> in our experiments and, by analogy with Ti<sup>4+</sup>, other highly charged cations, and rare earth elements become less incompatible near the peridotite solidus.

Our study brings a strong support to the hypothesis that phonolitic lavas or their plutonic equivalents (nepheline syenites) may be produced directly by partial melting of upper mantle rock-types at moderate pressures (1–1.5 GPa), especially where large domains of the subcontinental lithospheric mantle has been enriched in potassium by metasomatism. The circulation of low-degree partial melts of peridotites into the upper mantle may be responsible for a special kind of metasomatism characterized by Si- and alkali-enrichment. When they are unable to escape by porous flow, low-degree melts will ultimately be trapped inside neighboring olivine grains and give rise to the silica- and alkali-rich glass inclusions found in peridotite xenoliths.

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## 1. Introduction

Basaltic magmas at mid-ocean ridges, oceanic islands, intracontinental rifts and subduction zones are mainly produced by partial melting of upper mantle peridotites. Many experimental studies

were focused on partial melting of depleted mantle at mid-ocean ridges (where the mantle contains only 60 ppm K<sub>2</sub>O according to Workman and Hart, 2005) and thus used starting peridotites either K<sub>2</sub>O-free (e.g., Falloon et al., 1999, 2008; Robinson et al., 1998; Presnall et al., 2002) or very poor in K<sub>2</sub>O (e.g., Baker and Stolper, 1994). Estimates of K<sub>2</sub>O in the primitive mantle (160 to 340 ppm; Taylor and McLennan, 1985; McDonough and Sun, 1995; Arevalo et al., 2009, and references cited therein) are, however, up to 6 times higher than in the depleted MORB mantle, and there are source regions in the upper mantle that may be even more enriched (McKenzie, 1989). In particular, the lithospheric mantle

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below continental and oceanic crust may be enriched in potassium by repeated episodes of metasomatism: for instance, [Menzies et al. \(1987\)](#) describe metasomatized peridotite xenoliths in which  $K_2O$  exceeds 1%.

As  $K_2O$  is highly incompatible with respect to most minerals during mantle melting, and as the incorporation of alkalis strongly affects the degree of polymerization of silicate liquids ([Ryerson, 1985](#); [Hirschmann et al., 1998](#)), even a moderate increase of  $K_2O$  in the mantle source may have a dramatic effect on the major element composition and on the structure of partial melts, specially at low degrees of melting ( $\leq 5\%$ ; all percentages are wt.% except when specified otherwise). These changes in melt structure may in turn have important consequences for the partitioning of minor and trace elements ([Gaetani, 2004](#); [Huang et al., 2006](#)).

Here we present the results of melting experiments on two fertile,  $K_2O$ -rich peridotites: composition MBK (410 ppm  $K_2O$ ) is within the range of the primitive mantle as estimated by [Arevalo et al. \(2009\)](#):  $340 \pm 140$  ppm  $K_2O$ ; composition MBK+ is significantly more enriched (930 ppm  $K_2O$ ). Three series of experiments were performed: two with MBK at 1 and 1.3 GPa, and one with MBK+ at 1.3 GPa. The pressures of 1 and 1.3 GPa were chosen because the effect of alkalis on the structure of mantle melts is more important below 1.5 GPa ([Hirschmann et al., 1998](#)). In addition, this range of pressure straddles the transition from plagioclase + spinel lherzolite (at 1 GPa) to spinel lherzolite (at 1.3 GPa), allowing to study the effect of plagioclase on low-degree melt compositions. We used the microdike technique ([Laporte et al., 2004](#)) to extract and analyze liquids at degrees of melting  $F$  down to 0.9%. Our low-degree melts are rich in  $Na_2O + K_2O$  (up to 14%),  $SiO_2$  (up to 57%),  $Al_2O_3$  (20–22%), poor in MgO, FeO, CaO (down to 2–3%), and classify as trachyandesites, tephriphonolites and phonolites in the total alkali–silica (TAS) diagram ([Le Bas et al., 1986](#)). Calculations with the pMELTS software ([Ghiorso et al., 2002](#)) confirm the experimental findings and document the effect of bulk  $K_2O$  (up to 2000 ppm) on melt compositions and melt fractions. Lherzolites relatively rich in potassium (HK-66, 0.07%  $K_2O$ ; PHN1611, 0.14%  $K_2O$ ) were studied by Kushiro and co-workers ([Takahashi and Kushiro, 1983](#); [Hirose and Kushiro, 1993](#); [Kushiro, 1996](#)), but most of their experiments were at high degrees of melting and none produced a partial melt as enriched in alkalis as in our work.

## 2. Experimental and analytical techniques

Techniques are described in detail in Section 1 of the Supplementary material. The starting material used to prepare compositions MBK (410 ppm  $K_2O$ ) and MBK+ (930 ppm  $K_2O$ ) was a spinel lherzolite xenolith (Bri3) from Mont Briançon volcano, French Massif Central. As Bri3 contains only 100 ppm  $K_2O$ , small amounts of synthetic basalt B2 were mixed to Bri3 to produce MBK and MBK+ (compositions Bri3, B2, MBK and MBK+ are given in [Table 1](#)). Except for their larger  $K_2O$  contents, MBK and MBK+ are broadly similar to fertile peridotites studied in the past (MM3, [Baker and Stolper, 1994](#); MPY, [Robinson and Wood, 1998](#); [Table 1](#)).

The experiments were made in a piston-cylinder apparatus, using double containers made of a graphite crucible fitted into a platinum capsule. Despite the fast quench rate of this apparatus ( $\approx 100^\circ C/s$ ), quench crystals grow at the end of the experiments and modify substantially the composition of interstitial liquid in partially molten peridotites (e.g., [Baker and Stolper, 1994](#)). In this study, we used the microdike technique ([Laporte et al., 2004](#); [Lambart et al., 2009, 2013](#)) to separate small volumes of liquid in equilibrium with mineral phases into fractures of the graphite container ([Fig. 1a](#)). Microfractures develop into the graphite container at the beginning of the experiment and pump small volumes of partial melt out of the neighboring peridotite: as most of the liquid

in the microdike is not in close contact with peridotite minerals, it is not modified by the growth of quench crystals at the end of the experiment. In all our runs except MBK+7 and MBK15, we observed a few microdikes varying from tens to hundreds of microns in length and from a few microns to a few tens of microns in width, and yielding consistent glass compositions ([Table 1](#)). The length of the microdikes is short compared with the thickness of the graphite walls (0.7 to 0.9 mm) so that the partial melt is not in contact with the outer platinum container. This technique is perfectly suited to the study of low degrees of melting because the volume of the microdikes is very small in comparison with the total volume of partial melt in the sample.

A drawback of the experiments at low degrees of melting is that any trace of water in the capsule will partition preferentially into the partial melt, yielding significant amounts of dissolved water even under nominally anhydrous conditions. Dissolved water contents in some experimental glasses were measured using an ion microprobe with a beam diameter of 5  $\mu m$  (see Section 1 of the Supplementary material; [Ottolini and Hawthorne, 2001](#); [Ottolini et al., 1995, 2002](#); [Scordari et al., 2010](#)). The water contents are relatively low and decrease with increasing melt fraction  $F$ : from 1.1% at our lowest degrees of melting ( $F \approx 1\%$ ) to 0.1% at  $F = 12.7\%$ .

## 3. Experimental results

### 3.1. Experiments at 1.3 GPa

Run information ( $P$ – $T$  conditions, run products, modes, liquid compositions, etc.) is summarized in [Table 1](#); compositions of solid phases are given in Supplementary Table S1. Liquid is in equilibrium with olivine (ol) + orthopyroxene (opx) + clinopyroxene (cpx) + spinel (spl) in all the experiments at 1.3 GPa ([Fig. 1b](#)). The melt fraction  $F$  increases from 0.9% at  $1180^\circ C$  to 4.1% at  $1270^\circ C$  in MBK, and from 1.6% at  $1150^\circ C$  to 5% at  $1250^\circ C$  in MBK+ ([Table 1](#)). Thus, at a given temperature,  $F$  is higher in the composition with the larger  $K_2O$  content. The absence of microdikes in sample MBK+7 ( $T = 1130^\circ C$ ) and its lower degree of textural equilibration suggest that it could be subsolidus. In this case, a K-bearing solid phase, such as feldspar, must be present even if we did not find it despite careful examination. Alternatively, a quantity of K-rich glass (a few 0.1%) too small to be detected with the scanning electron microscope may be present in MBK+7.

Oxide concentrations in liquids are plotted as a function of the degree of melting in [Fig. 2](#). In both MBK and MBK+, important variations of liquid compositions are observed with decreasing  $F$ , including increases in  $SiO_2$ ,  $Na_2O$ ,  $K_2O$ , and  $Al_2O_3$ , and decreases in MgO, FeO, and CaO (the case of  $TiO_2$  is discussed later; [Table 1](#)). These compositional trends are qualitatively similar to those previously described in the literature ([Baker and Stolper, 1994](#); [Kushiro, 1996](#); [Pickering-Witter and Johnston, 2000](#)), but the degrees of enrichment or depletion are more pronounced: for instance, near-solidus melts from the literature at 1 to 1.5 GPa contain  $\approx 6\%$  of MgO and CaO ([Hirschmann et al., 1998](#); [Robinson et al., 1998](#)) or more ([Falloon et al., 2008](#)) while our near-solidus melts at 1.3 GPa contain only  $\approx 3\%$  of these oxides ([Fig. 3](#)). Our most extreme liquid composition (MBK+6) has  $\approx 57\%$   $SiO_2$ , 21%  $Al_2O_3$ ,  $Na_2O + K_2O \approx 13.5\%$ , MgO, FeO, and CaO concentrations as low as 2–3%, and plots in the phonolite field in the TAS classification diagram ([Fig. 4](#)). Despite the enrichment in  $SiO_2$  and the strong depletions in MgO and FeO, it coexists with typical mantle olivine and pyroxenes (mg#  $\approx 89$ –90), and it is strongly nepheline normative (20.5%; [Table 1](#)).

### 3.2. Experiments at 1 GPa

In the experiments with MBK at 1 GPa,  $F$  increases from 0.9% at  $1190^\circ C$  to 22.8% at  $1310^\circ C$ ; the sample run at  $1180^\circ C$  shows

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