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



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A R T I C L E I N F O

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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 K₂O 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 ($T \approx 1240$ °C). Important variations of liquid compositions are observed with decreasing temperature, including strong increases in SiO₂, Na₂O, K₂O, and Al₂O₃ concentrations, and decreases in MgO, FeO, and CaO concentrations. The most extreme liquid compositions are phonolites with 57% SiO_2 , 20-22% Al_2O_3 , $Na_2O + K_2O$ 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 K₂O to 3% in a source with 2000 ppm K₂O. 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^{4+} in our experiments and, by analogy with Ti⁴⁺, 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 alkalienrichment. 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 K₂O according to Workman and Hart, 2005) and thus used starting peridotites either K₂O-free (e.g., Falloon et al., 1999, 2008; Robinson et al., 1998; Presnall et al., 2002) or very poor in K₂O (e.g., Baker and Stolper, 1994). Estimates of K₂O 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 K₂O 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, K₂O-rich peridotites: composition MBK (410 ppm K₂O) 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 K₂O). 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 Fdown to 0.9%. Our low-degree melts are rich in $Na_2O + K_2O$ (up to 14 %), SiO₂ (up to 57%), Al₂O₃ (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 K₂O (up to 2000 ppm) on melt compositions and melt fractions. Lherzolites relatively rich in potassium (HK-66, 0.07% K₂O; PHN1611, 0.14% K₂O) were studied by Kushiro and coworkers (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 to-tal 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 µm (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 °C to 4.1% at 1270 °C in MBK, and from 1.6% at 1150 °C to 5% at 1250 °C in MBK+ (Table 1). Thus, at a given temperature, *F* is higher in the composition with the larger K₂O content. The absence of microdikes in sample MBK+7 (T = 1130 °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 Krich 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 SiO₂, Na₂O, K₂O, and Al₂O₃, and decreases in MgO, FeO, and CaO (the case of TiO₂ 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% SiO₂, 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 SiO₂ 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 °C to 22.8% at 1310 °C; the sample run at 1180 °C shows

Table 1		
Compositions of starting materials and experimental	partial melts,	and phase proportions.

	P (GPa)	T (°C)	Na ₂ O	MgO	K ₂ O	CaO	TiO ₂	FeO	MnO	Cr ₂ O ₃	SiO ₂	Al ₂ O ₃	Total ^e	mg# ^f	Liq ^g	Olg	Opx ^g	Cpx ^g	Sp ^g	Felds ^g	Neph ⁱ	NBO/T ^j	D _{TiO2} ^k
MBK ^a			0.35	38.63	0.041	3.26	0.14	8.01	0.13	0.48	44.88	4.08	100.00	89.6							0.0		
MBK+ ^a			0.38	37.91	0.093	3.48	0.15	7.96	0.13	0.47	44.99	4.44	100.00	89.5							0.0		
BRI3			0.33	39.05	0.01	3.13	0.13	8.04	0.13	0.49	44.82	3.87	98.71	89.6		55.8	26.7	14.3	3.0		0.0		
gel B2			1.50	9.75	2.14	12.10	0.50	5.94	0.12	0.04	49.28	18.63	99.14	74.5							0.9		
gel +6			8.12	2.65	6.28	2.95	0.51	2.10	0.04	0.03	56.11	21.21	99.44	69.2							27.0		
MM3 ^b			0.31	38.30	0.008	3.57	0.11	7.18	0.13	0.68	45.50	3.98	100.00	90.5		50.0	30.0	17.0	3.0		0.0		
MPY ^b			0.40	38.60		3.38	0.17	7.55		0.45	44.70	4.37	99.62	90.1							0.0		
Heldburg ^c			10.17	1.16	4.64	1.42	0.33	1.92	0.12		56.04	20.61	99.41	51.8									
MBK⊥7 ^d	13	1130	no liqui	d detecte	d										0.0	54.8	22.7	19.9	2.6	0.0			
MBK+6	1.5	1150	7 27	2 72	6 25	2.88	0.60	2 10	0.04	0.02	56.89	21 23	94 57	69.7	1.6	56.6	22.7	18.0	2.0	0.0	20.5	0 183	0.80(21)
MBK+5	13	1180	6.58	4 33	4 68	4 54	0.00	3 16	0.08	0.02	54 97	20.94	95 77	70.9	2.2	55.3	22.1	18.4	2.5	0.0	16.9	0.105	0.66(21)
MBK+4	13	1200	6 35	4 90	4 11	5.06	0.78	3 52	0.07	0.02	54 66	20.52	96.29	71.3	2.6	57.4	19.7	18.1	2.3	0.0	14.9	0.316	0.54(8)
MBK+3	1.3	1220	5.95	6.05	3.44	6.22	0.87	4.22	0.08	0.04	53.12	20.01	96.25	71.9	3.1	56.6	21.5	16.7	2.2	0.0	14.8	0.404	0.43(6)
MBK+2	1.3	1240	5.31	6.55	2.95	6.89	0.91	4.79	0.11	0.02	52.74	19.73	97.50	70.9	3.7	57.6	20.2	16.5	2.0	0.0	11.1	0.439	0.43(6)
MBK+1	1.3	1250	4.74	8.01	2.18	8.16	0.89	5.43	0.09	0.04	51.51	18.94	97.33	72.5	5.0	57.1	20.8	15.3	1.8	0.0	9.5	0.546	0.41(6)
MBK+14	13	1180	7 50	2 17	6 78	1 99	0.61	1 79	0.06	0.00	57 50	21 59	98 94	68.3	14 9	51.2	86	15.4	17	82	21.2	0 140	1.06(13)
MBK+11 MBK+13	1.3	1200	7.46	2.43	6.19	2.32	0.53	2.00	0.02	0.03	57.53	21.35	99.17	68.5	21.7	47.3	12.9	16.7	1.4	traces ^h	19.4	0.153	1.12(14)
Cause Dile a D	1.0	1150	0 57	1.00	C 77	1.70	0.52	1.07	0.05	0.00	56.20	22.20	100.00	CO 2	02.2	0.1	0.0	6.9	0.0	0.0	28.0	0 122	1 41(20)
CIYSPIIOZ	1.0	1150	6.57	1.00	0.77	1.70	0.52	1.97	0.05	0.00	50.29	22.59	100.09	00.5	95.2	0.1	0.0	0.0	0.0	0.0	26.9	0.155	1.41(50)
MBK4	1.3	1180	8.04	3.50	4.75	3.41	0.67	2.70	0.05	0.02	55.70	21.15	90.08	69.8	0.9	58.3	20.4	18.1	2.4	0.0	22.5	0.237	0.71(15)
MBK3	1.3	1200	7.16	5.54	2.63	5.38	0.86	3.97	0.07	0.04	54.03	20.33	96.71	71.3	1.7	59.3	20.2	16.5	2.3	0.0	15.9	0.361	0.50(7)
MBK2	1.3	1250	5.18	8.23	1.36	8.40	0.93	5.51	0.12	0.04	51.50	18.74	97.45	72.7	3.5	59.2	20.5	15.2	1.6	0.0	9.5	0.567	0.37(6)
MBK1	1.3	1270	4.74	8.75	1.15	8.97	1.02	5.90	0.12	0.04	50.65	18.66	98.51	72.6	4.1	59.3	20.0	15.1	1.5	0.0	8.5	0.608	0.34(5)
MBK15	1.0	1180	0 very low melt fraction, not analyzed																				
MBK14	1.0	1190	5.93	4.96	3.16	5.71	1.02	3.73	0.05	0.05	55.73	19.66	92.15	70.3	0.9	61.3	19.4	13.6	2.1	2.8	8.0	0.328	0.32(9)
MBK19	1.0	1200	6.08	5.82	2.23	6.87	1.04	4.10	0.06	0.01	54.14	19.66	95.50	71.7	1.5	60.3	20.2	13.9	2.2	1.9	10.1	0.395	0.40(7)
MBK16	1.0	1220	5.59	6.81	1.24	7.74	0.91	4.67	0.13	0.02	53.39	19.50	98.27	72.2	3.0	61.4	18.5	13.8	1.7	1.6	6.7	0.451	0.44(6)
MBK18	1.0	1240	4.23	8.63	0.83	9.81	0.88	5.72	0.13	0.03	51.08	18.66	97.17	72.9	5.4	60.3	19.5	13.1	1.8	0.0	5.0	0.601	0.41(6)
MBK20	1.0	1260	2.49	10.94	0.37	11.61	0.73	6.57	0.17	0.16	49.86	17.09	98.50	74.8	12.7	60.5	18.8	7.4	0.6	0.0	0.0	0.776	0.25(8)
Dun2	1.0	1290	2.00	11.30	0.27	11.79	0.69	7.01	0.15	0.17	50.07	16.54	94.73	74.2	16.8	61.6	17.0	4.2	0.4	0.0	0.0	0.806	0.26(6)
MBK21	1.0	1310	1.52	13.36	0.19	11.28	0.47	7.42	0.16	0.37	50.64	14.60	98.84	76.2	22.8	62.2	14.7	0.0	0.1	0.0	0.0	0.937	

^a Fertile mantle compositions MBK and MBK+ were produced by mixing a powdered spinel peridotite from Mont Briançon, French Massif Central (Bri3), with basalt gel B2 (Laporte et al., 2004); the weight percentages of Bri3 and B2 are 98.58:1.42 and 96.13:3.87 in MBK and MBK+, respectively. The compositions of peridotite Bri3 and gel B2 were analyzed by ICP-AES at the Service d'Analyses des Roches et Minéraux (CRPG, Nancy; http://helium.crpg.cnrs-nancy.fr/SARM/pages/roches.html); K₂O in Bri3 was analyzed by atomic absorption spectroscopy (relative error: ±20%). Phonolite gel +6 was analyzed by ICP-AES at Laboratoire Magmas et Volcans.

^b MM3 and MPY are the fertile mantle compositions of Baker and Stolper (1994) and Robinson and Wood (1998), respectively. For MM3, the total includes 0.23% NiO and the K₂O content is from Table 5 of Wasylenki et al. (2003).

^c Composition of a phonolite carrying xenoliths of spinel lherzolite from Heldburg, Germany (Irving and Price, 1981). The analytical total also includes 2.12% H₂O⁺, 0.57% H₂O⁻, 0.09% CO₂ and 0.22% SO₃.

^d Runs MBK+1 to MBK+7 are partial melting experiments of bulk composition MBK+. Runs MBK1 to MBK4, MBK14 to MBK21, and Dun2 are partial melting experiments of bulk composition MBK+. Runs MBK+13 and MBK+14 are reversal experiments of run MBK+6. Run Cryspho2 is a crystallization experiment of phonolite gel +6, which was run at 1 GPa and 1150°C. The mean composition of all phases and the uncertainties are given in the Supplementary Table S1.

^e Original analytical totals (all compositions except MPY and Heldburg phonolite in the table have been recalculated to 100%).

^f $mg\# = Mg^{2+}/(Mg^{2+} + Fe^{2+})$, where Mg^{2+} and Fe^{2+} are cation fractions and all iron is as Fe^{2+} .

^g The weight percentages of phases in the run products were calculated using a mass balance program modified from Albarède and Provost (1977).

^h Only one feldspar grain was found in sample MBK+13.

ⁱ CIPW normative nepheline content (wt.%).

^j Ti is not taken into account in the calculation of NBO/T, the number of non-bridging oxygens per tetrahedrally coordinated cation (the values of NBO/T obtained by considering Ti either as a network former or as network breaker are just slightly different).

^k D_{TiO}, is the partition coefficient of TiO₂ between cpx and melt. The errors (in parentheses) are given in terms of the least unit cited and are based on the 1 – σ uncertainties in Supplementary Table S1.



Fig. 1. (a) SEM-Backscattered electron microphotograph of sample MBK3 (1.3 GPa-1200 °C) showing a microdike filled with quenched melt ("glass") into the graphite container (black). (b) Texture and paragenesis of partially molten peridotite MBK3; solid phases are as follows: Ol is grey, Opx is slightly darker than Ol, Cpx is light grey, and Spl is white. (c) Texture and paragenesis of partially molten peridotite MBK14 (1 GPa-1190 °C): pl (dark grey) is present in addition to ol, opx, cpx, and spl. The interstitial glass is barely visible in **b** and **c** due to its low fraction (1.7% in **b**; 0.9% in **c**); the dark voids correspond to grains plucked off during sample preparation. Scale bars: 60 μ m in **a**; 20 μ m in **b** and **c**.

traces of liquid, but we could not get reproducible glass analyses in this case. In a plot of *F* vs. *T*, the experiments run at $T \le 1220$ °C define a linear trend that intersects the solidus (F = 0%) at T =1178 °C. The main difference with the experiments at 1.3 GPa is the presence of up to 3% plagioclase (pl) at low F (Fig. 1c), in addition to ol, opx, cpx, spl, and liquid. The pl composition ranges from An₅₄Ab₄₃Or₃ at 1180-1190 °C to An₅₇Ab₄₁Or₂ at 1220 °C. Plagioclase disappears slightly below 1240 °C, at $F \approx 5\%$. Accordingly, despite its low fraction in the subsolidus state (3%), pl is stable up to ≈ 60 °C above the solidus. From 1240 to 1290 °C, the liquid is in equilibrium with ol + opx + cpx + spl. Over that T range, cpx is the main reactant and ol is on the product side of the melting reaction: 0.78 cpx + 0.21 opx + 0.12 spl \rightarrow 1.0 liq + 0.11 ol (see Section 2 of the Supplementary material). Clinopyroxene disappears between 1290 and 1310 °C, at $F \approx 22\%$. At 1310 °C, the liquid is in equilibrium with ol, opx, and traces of Cr-rich spl.

Liquid compositions in MBK at 1 GPa show strong increases in SiO₂, Na₂O, K₂O, and Al₂O₃, and decreases in MgO, FeO, and CaO with decreasing *F* (Fig. 2; Table 1). Only the liquids produced at high *F* (13 to 23%) plot in the basalt field in Fig. 4: the liquids produced at $F \le 5.4\%$ are nepheline normative and plot in the trachybasalt to trachyandesite fields. In detail, comparison of melt compositions from MBK at 1 and 1.3 GPa indicates that the presence of pl has a distinct effect on Na₂O (buffered at $\approx 6\%$; Fig. 2), Al₂O₃ (buffered at 19.5%), and K₂O. At a given *F*, K₂O is smaller at 1 GPa because it is less incompatible in the presence of pl, and CaO is slightly larger. As a consequence of the effect of pl, experiments MBK4 and MBK14, which have the same melt fraction (*F* = 0.9%), have very different values of Na₂O + K₂O: 9.1% in MBK14 (1 GPa) vs. 12.8% in MBK4 (1.3 GPa).

The trend of liquid compositions from MBK14 to MBK21 is close to that reported for fertile peridotite MM3 at 1 GPa by Baker and Stolper (1994), Baker et al. (1995) and Hirschmann et al. (1998), except for the effects of pl (not found in these studies). In particular, both trends culminate at 55.7% silica close to the solidus (Fig. 2), and our lowest degree melt (F = 0.9%) is just slightly more depleted in MgO, FeO, and CaO than their lowest degree melt (F = 2.3%). Differences between the two groups of studies can readily be explained by differences in bulk compositions: for instance, the lower maximum CaO content of MBK melts (at the cpx-out temperature; Figs. 2–3) is related to the lower modal abundance of cpx in MBK (Table 1), and the lower $Na_2O + K_2O$ totals in MM3 melts (Fig. 4) are due to the lower bulk K_2O content of MM3 (<100 ppm; Table 1).

3.3. Reversal experiments

We made a series of runs to reverse partial melting experiment MBK+6 at 1.3 GPa-1150 °C. This experiment was chosen because it has the most extreme liquid composition: the aim was to verify that a phonolite composition can be at chemical equilibrium with a lherzolite. The starting material in the reversal experiments was made of peridotite MBK+ and phonolite gel +6, which is equivalent to the glass in run MBK+6 (except that it is $\approx 10\%$ richer in Na₂O; Table 1). We first used a sandwich configuration with separate layers of phonolite and peridotite, but then we switched to a homogeneous mixture of peridotite and phonolite because the initial chemical heterogeneity in the sandwich configuration may impede the approach to equilibrium. So we equilibrated a mixture of 80.2% MBK+ and 19.8% gel +6 at P = 1.3 GPa and T = 1180and 1200 °C (MBK+14 and MBK+13, respectively; Table 1), and we used the microdike technique to analyze glass compositions. Experiments MBK+14 and MBK+13 were run 30 to 50°C above the temperature of MBK+6 (1150 °C) because the liquid phase was expected to contain less dissolved water in experiments with $F \approx 20\%$ than in a low-degree melting experiment with F = 1.6%(see also Laporte et al., 2004). For instance, partial melts in runs MBK3 (F = 1.7%) and MBK20 (F = 12.7%) contain 1.09% and 0.14% H₂O, respectively. This is due to the highly incompatible behavior of water: for a given degree of water contamination in the sample capsule, the higher the melt fraction, the lower the amount of water dissolved in melt. The higher temperature in reversals MBK+13 and MBK+14 in comparison to MBK+6 is aimed at balancing the lower water content in the melts and its impact on the extent of melting.

In the reversal experiment at 1180 °C, the melt fraction (\approx 15%) is lower than the percentage of gel +6 in the starting mixture



Fig. 2. Plots of major oxide concentrations in experimental partial melts as a function of the degree of melting (F, wt.%) for fertile peridotites MBK and MBK+ at 1 to 1.3 GPa. Symbols are as follows: open green squares for MBK at 1 GPa; solid red circles for MBK at 1.3 GPa; and open red circles for MBK+ at 1.3 GPa (colors on the Web only). The results of program pMELTS are shown by the blue curves: the dark blue curve is for MBK+ at 1.3 GPa (for $F \le 5\%$ as in the experimental series); the light blue curve is for MBK at 1 GPa (for $F \ge 5\%$, that is, out of the experimental pl stability field). The small black crosses are the data for fertile peridotite MM3 at 1 GPa (Baker and Stolper, 1994; Hirschmann et al., 1998). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)



Fig. 3. Composition of partial melts of fertile peridotites between 1 and 1.5 GPa plotted in the CaO-MgO diagram. Our partial melting experiments at 1.3 GPa are shown by the red circles (colors on the WEB only); open circles for lherzolite MBK+; solid circles for lherzolite MBK. The open green squares are for the experiments with MBK at 1 GPa. The open red circle with a central dot is reversal experiment MBK+13: partial melting experiment MBK+6 and its reversal MBK+13 are surrounded by the red dashed line. The small black crosses correspond to fertile peridotite MM3 at 1 GPa (Baker and Stolper, 1994; Hirschmann et al., 1998). The other near-solidus melts from the literature are plotted for comparison: the diamonds correspond to a K₂O-free analogue of MM3 at 1 and 1.5 GPa (open and solid diamonds, respectively; Falloon et al., 2008); the solid triangle is the nearsolidus melt of MORB-pyrolite MPY at 1.5 GPa (Robinson et al., 1998). The blue symbols correspond to a phonolite carrying spinel lherzolite xenoliths (Heldburg phonolite; Irving and Price, 1981) and to the glass analyzed in the crystallization experiment CrysPho2 (crystallization of a composition equivalent to partial melt MBK+6 at 1 GPa-1150°C; Table 1). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

(19.8%), and \approx 8% of plagioclase (K-oligoclase) is present in addition to ol, opx, cpx, and spl (Supplementary Fig. S1a). Accordingly, the degree of crystallization of gel +6 is relatively large at 1180 °C. At 1200 °C (MBK+13), the melt fraction is equal to 21.7% and we found only one plagioclase left in a microdike (Fig. S1b-c). Subtracting a percentage of melt equal to the percentage of gel +6and normalizing to 100%, we obtain a mode composed of 59.0% ol, 16.1% opx, 20.8% cpx, 1.7% spl, and 2.3% liq. Accordingly the degree of melting of peridotite MBK+ in MBK+13 is equal within error to the degree of melting in MBK+6 (1.6%). The persistence of traces of plagioclase (K-andesine) in MBK+13 is presumably due to the fact that gel +6 is 10% richer in Na₂O than MBK+6 liquid, thus favoring plagioclase stability at slightly higher temperatures or degrees of melting. As in all our reversal experiments, the opx percentage in MBK+13 (16.1% after subtraction of gel +6) is lower than in MBK+6 (21.4%), and this goes along with a higher ol percentage: 59.0 vs. 56.6%. These observations are qualitatively in agreement with a reaction relation between opx and liq to produce pl + ol, which is the reaction expected upon cooling of plagioclase + spinel lherzolite (Walter et al., 1995).

The liquid in MBK+13 matches well the partial melt composition in MBK+6 except that it is slightly depleted in MgO and CaO (Table 1; Figs. 3–4). As the concentrations of these two elements increase strongly with *T* increasing from $1180 \degree$ C to $1200 \degree$ C, a reversal experiment run just slightly above $1200 \degree$ C should yield a good match for these two elements too, as well as a pl-free run



Fig. 4. Composition of partial melts of fertile peridotites between 1 and 1.5 GPa plotted in the total alkali-silica diagram (Le Bas et al., 1986). Our partial melting experiments at 1.3 GPa are shown by the red circles (open circles: MBK+; solid circles: MBK); the open green squares are for the experiments with MBK at 1 GPa (colors on the Web only). The open red circle with a central dot is reversal experiment MBK+13: partial melting experiment MBK+6 and its reversal MBK+13 are surrounded by the red dashed line. The small black crosses correspond to fertile peridotite MM3 at 1 GPa (Baker and Stolper, 1994; Hirschmann et al., 1998); the diamonds correspond to a K₂O-free analogue of MM3 at 1 and 1.5 GPa (open and solid diamonds, respectively; Falloon et al., 2008). The solid triangle is the near-solidus melt of MORB-pyrolite MPY at 1.5 GPa (Robinson et al., 1998). The blue symbols correspond to Heldburg phonolite (Irving and Price, 1981) and to the glass analyzed in the crystallization experiment CrysPho2 (crystallization of a composition equivalent to partial melt MBK+6 at 1 GPa-1150 °C). The star labeled "DGA-40" corresponds to a trachyte melt in equilibrium with ol + opx + cpx at 1.2 GPa and 1150 °C (Draper and Green, 1999). Melt compositions computed by pMELTS for MBK+ at 1.3 GPa are shown by the blue curve (the theoretical trend is shifted to the left of the experimental data because of a slight underestimation of SiO2 by pMELTS). The grid corresponds to the chemical classification of volcanic rocks, with the main fields of interest labeled as follows: (0) Phonotephrite; (1) Tephriphonolite; (2) Phonolite; (3) Trachyte; (4) Trachyandesite; (5) Basaltic trachyandesite; (6) Trachybasalt; (7) Basalt; (8) Basaltic andesite. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

product. There is also a good correspondence between the compositions of mineral phases in experiments MBK+6 and MBK+13 (see Supplementary Table S1), specially for Mg-numbers. The correspondence is not so good for CaO in cpx, which is lower in MBK+13 compared with MBK+6, and CaO in opx, which is higher. These discrepancies are presumably a direct consequence of the higher temperature of run MBK+13. Despite some minor differences between MBK+6 and MBK+13, we conclude that phase compositions in partial melting experiment MBK+6 are very close to chemical equilibrium, and that partial melting of a fertile spinel lherzolite produces phonolitic liquids at low degrees of melting.

4. Theoretical results

4.1. The composition of low-degree melts of MBK+ at 1.3 GPa

We used the software pMELTS (Ghiorso et al., 2002; Smith and Asimow, 2005) to verify that phonolite melts can be produced at low degrees of melting of a fertile peridotite (see Section 3 of the Supplementary material for details). A comparison of the theoretical results with our experimental series at 1 GPa shows



Fig. 5. Evolution of the modal proportions of solid phases with increasing degree of melting in peridotite MBK at 1 GPa (**a**) and in peridotite MBK+ at 1.3 GPa (**b**). The theoretical modes (pMELTS) are shown by continuous lines (the vertical dashed lines correspond to pl disappearance in pMELTS calculations). The symbols for the experimental data are as follows: \times for ol; + for opx; circles for cpx; squares for spl (not shown in **a** for clarity); diamonds for pl. In **a**, the short, thick line in the lower left corner (intersecting the *F* axis at 0.7%) corresponds to the pl modes computed by pMELTS.

that pMELTS predicts quite accurately the oxide concentrations in liquids (Fig. 2) and the modal proportions of solid phases at degrees of melting \geq 5% (Fig. 5a). For F <5%, however, the theoretical results are not in good agreement with the experimental observations because pl seems to be strongly underestimated by pMELTS, with important consequences for pl mode at the solidus, the melt fraction at which pl disappears, and pl composition. The calculations with composition MBK+ at 1.3 GPa are also affected by this problem, but to a lesser extent: only the data at F < 1.6% are concerned.

At a given degree of melting (with $F \ge 1.6\%$), the proportions of cpx and spl computed for MBK+ at 1.3 GPa are in good agreement with the experimental values while opx is slightly overestimated and ol slightly underestimated (Fig. 5b). The trends of liquid compositions as melting progresses are very close to the experimental trends (Fig. 2). The main systematic differences are for MgO, which is overestimated by 2.1% in average, and to a lesser extent for SiO₂, which is underestimated by 1.1% in average. These discrepancies are presumably related to the overestimation of opx proportion and to the underestimation of ol proportion. Leaving aside the case of MgO, the model accurately predicts the evolution of melt compositions with increasing degree of melting of MBK+ at 1.3 GPa. In particular, the liquids calculated at the beginning of melting (F = 1.6-2%) are silica-enriched (55-56%), phonolitic (Fig. 4), and very poor in FeO and CaO (2-3%; Fig. 2), thus matching very well the compositions of our lowest degrees of melting (MBK+6, MBK+13).

4.2. Effect of bulk K_2O on the mass fraction and composition of low-degree melts

We used pMELTS to evaluate the effect of the K_2O content of a lherzolite source on the production of silica- and alkali-enriched low-degree melts. The calculations were made on a series of bulk compositions (based on Bri3 in Table 1) and containing from 0 to 2000 ppm K_2O (see the spreadsheet "Effect of K_2O " in Supplementary Table S2). We did not take into consideration the results at very low *F* due to the difficulties related to pl stabilization in pMELTS as detailed in the Supplementary material. Thus the discussion hereafter is restricted to liquids with Na₂O + $K_2O \le 14\%$, but our general conclusions are not sensitive to the exact limit chosen. The calculations were made at 1.2 GPa and are representative of the melting behavior at moderate pressures (1–1.5 GPa). At P = 1 GPa and below, Na₂O and K₂O become less incompatible due to the abundance of pl, and the enrichment in alkalis at low *F* is less marked. With *P* increasing above 1.5 GPa, the effect of alkalis on the structure and silica content of mantle melts decreases (Hirschmann et al., 1998). Calculations for a lherzolite with 1000 ppm K₂O confirm that the silica content of low-degree melts (with $F \approx 1.6\%$ and Na₂O + K₂O = 14%) decreases rapidly with increasing pressure: from 56.8% at 1.2 GPa, to 54.4% at 1.5 GPa, and to 50.5% at 2 GPa (Supplementary Fig. S2a).

The K₂O content of the lherzolite source has a strong effect on the SiO₂ content in melt at a given melt fraction (Fig. 6): at F = 3%, for instance, SiO₂ in melt increases from 49.3% to 53.8%, and to 57.0% for bulk K₂O contents of 0, 1000, and 2000 ppm, respectively. The SiO₂ increase is accompanied by an increase of the K₂O content in melt (at nearly constant Na₂O) and by strong decreases in MgO, FeO, and CaO. A major effect of increasing the K₂O content of the source is to multiply the amount of phonolite liquid generated: considering liquids with a total alkali of 14% as a basis for comparison, the amount of phonolitic liquid produced increases from 0.27% in a source with 100 ppm K₂O to 2.58% in a source with 2000 ppm K₂O (Fig. 6). This increase of the fraction of phonolite melt goes along with an increase of its SiO₂ content (from 55.1% to 57.7%) and a strong increase of the ratio K₂O/Na₂O (from 0.36 to 1.23; Supplementary Table S2).

5. Discussion

5.1. Composition of low-degree mantle melts at $P \le 1.5$ GPa

Our main result is that low-degree melts of a fertile lherzolite are strongly enriched in alkalis and silica, reaching the fields of trachyandesites, tephriphonolites or even phonolites in the TAS diagram (Fig. 4). The best example is provided by our series with composition MBK+ (930 ppm K₂O) at 1.3 GPa, but the production of phonolites is not restricted to mantle sources so enriched in K₂O: a phonolite liquid was produced in our series with composition MBK (410 ppm K₂O) at 1.3 GPa, and phonolite compositions are found by pMELTS for a source with 100 ppm K₂O. The main difference is that a source with 100 ppm K₂O will produce only 0.3% of phonolite melt and \approx 1% of tephriphonolite melt as compared to more than 3% of phonolite melt and up to 5.2% of tra-



Fig. 6. SiO₂ in melts as a function of melt fraction, *F*, for a lherzolite source with K_2O equal to 0, 100, 300, 500, 1000, 1500, and 2000 ppm (thick continuous lines) at 1.2 GPa; the calculations were made with the software pMELTS. For a given value of bulk K_2O , the total of alkalis in the melt increases from right to left (that is, with decreasing *F*). Each curve is terminated on the left by a small solid circle that corresponds to the point where $Na_2O + K_2O$ in the melt reaches 14%: the theoretical results were not taken into consideration beyond this limit due to the difficulties related to pl stabilization in pMELTS; the shape of the curve beyond this limit is shown by thick dashed line for the source with 2000 ppm K_2O . The open circles are the experimental data for composition MBK+ (930 ppm K_2O) at 1.3 GPa. The thin dashed lines subdivide the melt compositions into the following fields: (II) phonolites; (IV) trachybasalts; and (V) basalts (see Fig. 4 for the nomenclature of volcanic rocks).

chyandesite melt for a source with 2000 ppm K₂O (Fig. 6). Basalts *sensu stricto* only appear at F = 4.3% for a K₂O-free source and F = 9.5% for a source with 2000 ppm K₂O.

Silica enrichment in low-degree melts of lherzolites has been observed in the experimental studies of Baker and Stolper (1994), Baker et al. (1995), Hirschmann et al. (1998), and Robinson et al. (1998), as illustrated in Fig. 4. The liquid in equilibrium with an albite-bearing harzburgite residue at 1 GPa is also strongly enriched in silica, with $\approx 64\%$ SiO₂ and 12% Na₂O (Falloon et al., 1997). Silica-rich liquids in equilibrium with ol + opx (\pm cpx, spl, pl) have been reported in partial melting experiments of Na₂Orich starting materials at 0.75 GPa (Chalot-Prat et al., 2010). In these systems, the enrichment in silica at low F is mainly a consequence of high concentrations in alkalis, which depolymerize the liquid and lower the activity coefficient of SiO₂. As the silica activity in peridotite melt is buffered by the equilibrium with magnesian ol + opx, the decrease of the activity coefficient of SiO₂ must be compensated by an increase of the SiO₂ concentration of the melt (Ryerson, 1985). This effect is supposed to be maximum at $P \le 1.5$ GPa (Hirschmann et al., 1998), but Davis and Hirschmann (2013) recently documented it to be significant at 3 GPa as well.

In addition to a strong enrichment in silica and alkalis, our lowdegree melts are also characterized by high Al₂O₃ contents (up to 21%) and extreme depletions in MgO, FeO, and CaO (down to 2.7, 2.9, and 2.1%, respectively; Fig. 3). The partial melt at the lowest degree of melting of fertile peridotite MM3 at 1 GPa ($F \approx 2\%$) is a trachyandesite with a silica enrichment close to the maximum value reached in this study (see Fig. 4; Baker et al., 1995; Hirschmann et al., 1998), but it is less enriched in Al₂O₃ and alkalis, and still relatively rich in MgO, FeO, and CaO (5.7, 4.1, and 6.5%, respectively). To our knowledge, degrees of depletion in MgO, FeO, and CaO as strong as in our study have not yet been observed in experimental partial melts of a fertile peridotite at 1–1.5 GPa: near-solidus melts from the literature contain \approx 6% of MgO and CaO, and 5% of FeO (Hirschmann et al., 1998; Robinson et al., 1998) or more (Falloon et al., 2008). Note that all the liquids in our study, even the most depleted in MgO, are in equilibrium with a spl (±pl) lherzolite paragenesis with typical mantle mg# values (e.g. olivine with mg# \approx 90).

5.2. Implications for minor and trace element partitioning

The evolution from basalts and trachybasalts to phonolites with decreasing F results in changes in melt polymerization, which may have important consequences for the partitioning of minor and trace elements. The degree of polymerization increases with decreasing F, as indicated by the variations of the ratio of non-bridging oxygens to tetrahedrally coordinated cation (NBO/T; Mysen and Richet, 2005): NBO/T decreases from 0.78-0.94 in basalts (e.g., samples MBK21 and MBK20; Table 1) to 0.33-0.36 in trachyandesites (MBK14 and MBK3), and to 0.18 in phonolites (MBK+6). We did not measure the trace elements in our run products, but the TiO₂ data can be used to discuss the interactions between melt structure and partitioning. In partial melts from composition MBK at 1 GPa, TiO₂ decreases from 1.0 to 0.5% with increasing F (Fig. 2). On the contrary, TiO₂ increases with increasing F in the two series at 1.3 GPa: from 0.7 to 1.0% for composition MBK, and from 0.6 to 0.9% for composition MBK+. Mass balance calculations and SEM observations preclude the existence of a Tirich accessory phase that would explain the different behavior of TiO₂ at 1.3 GPa.

The contrasted behavior between the series at 1 and 1.3 GPa is not due to the effect of pressure because TiO₂ is incompatible in basaltic melts both at 1 and 1.5 GPa (Baker et al., 1995; Gaetani, 2004). The contrast presumably reflects in part a crystalchemical control on element partitioning between minerals and melt (Blundy et al., 1998), in relation to the enrichment in Na⁺ and other charge-balancing cations in cpx (the primary host for Ti⁴⁺) near the solidus. We suggest, however, that the behavior of TiO₂ in our experiments is primarily controlled by major changes in melt structure and polymerization at low degrees of melting (Gaetani, 2004; Huang et al., 2006). To illustrate this point, TiO₂ in melt is plotted as a function of melt polymerization (as embodied by NBO/T) in Fig. 7a, and as a function of the degree of silica undersaturation (as embodied by the amount of normative nepheline or hyperstene) in Fig. 7b. On the right side of these two figures, TiO_2 increases with decreasing F (that is, from the right to the left) up to a maximum of about 1%; on the left side, it decreases with decreasing F. The maximum is located between NBO/T equal 0.3 and 0.6 in Fig. 7a, and at 10% nepheline in Fig. 7b. The decrease of TiO₂ at low F is mostly due to an increase of the partition coefficient of TiO₂ between cpx and melt with increasing degree of melt polymerization: $D_{Ti}^{cpx/melt}$ is >0.5 for NBO/T < 0.3, and up to 0.8–1.1 in phonolite melts (NBO/T < 0.2; Table 1), as compared to values in the range 0.25–0.41 for melts with NBO/T > 0.5. Our results are in agreement with those of Baker et al. (1995) who found an increase of $D_{Ti}^{cpx/melt}$ at low *F*, with the work of Gaetani (2004) who found an increase of the compatibility of TiO₂ and rare earth elements in cpx with increasing melt polymerization near the peridotite solidus, and with pMELTS calculations (Hirschmann et al., 1999). By analogy with Ti⁴⁺, other highly charged cations and rare earth elements, which are also primarily hosted into cpx, are expected to become more compatible near the peridotite solidus (Hirschmann et al., 1999), especially in the presence of melts strongly enriched in silica and alkalis (Huang et al., 2006). Extraction of very lowdegree mantle melts with a high degree of polymerization should leave residues with specific trace element patterns.



Fig. 7. (**a**) TiO_2 in experimental partial melts versus the ratio of non-bridging oxygens to tetrahedrally coordinated cation (NBO/T). Symbols are as follows: open squares, source MBK at 1 GPa; solid circles, same source at 1.3 GPa; open circles, source MBK+ at 1.3 GPa (reversal experiment MBK+13 included). The thin dashed line is the third order polynomial curve best fitting the whole data set. (**b**) TiO₂ concentrations in partial melts as a function of the percentage of normative nepheline or hyperstene (same symbols as in **a**).

5.3. Partial melting of fertile peridotites at 1 GPa: the role of plagioclase

At 1 GPa, the paragenesis of composition MBK is characterized by the presence of both spinel and plagioclase in addition to ol, opx, and cpx: the mass fraction of pl at the solidus temperature is \approx 3% and pl disappears at $F \approx$ 5%. We did not notice any nucleation difficulty for pl using a finely ground natural spl lherzolite (devoid of pl) as starting material. The abundance of pl at 1 GPa (Fig. 1c) and its absence at 1.3 GPa are in agreement with an upper stability limit of plagioclase at the fertile peridotite solidus close to 1.3 GPa (Falloon et al., 1999; Till et al., 2012), with the exact value depending on bulk CaO, Na₂O, K₂O, Cr₂O₃ and mg#. Comparison of our results with those of Baker et al. (1995) and Borghini et al. (2010) illustrates the importance of bulk composition on pl stability. Borghini et al. (2010) did not find pl above 0.8 GPa in a fertile peridotite containing less Na₂O than MBK (0.26 vs. 0.35%). Similarly, Baker et al. (1995) did not find pl at the 1-GPa solidus of composition MM3, which contains slightly less Na₂O and more Cr₂O₃ than MBK (Table 1). This issue is controversial, however, because Falloon et al. (2008) found pl in a composition equivalent to MM3 at 1 GPa. Kushiro (1996) observed pl in lherzolite PHN1611 at 1 GPa and 1200 °C (F = 4.4%). The pl composition in Falloon's et al. experiments (An₅₂Ab₄₈ and An₆₁Ab₃₉ in runs T-4353 and T-4377, respectively) is close to the labradorite compositions in our run products (An₅₄₋₅₇Ab₄₁₋₄₃Or₂₋₃), while pl in Kushiro's experiment is more calcic (An₇₂Ab₂₈).

The disappearance of pl is responsible for the inflexions of the compositional trends of the liquids observed for composition MBK at 1 GPa (open square symbols in Fig. 2). The curves for Na₂O and Al₂O₃ provide the best examples: they are first buffered at \approx 6% and 19.5%, respectively, in the pl stability field (the three data points at $F \leq 3$ %), then, after pl disappearance, they show a continuous decrease with increasing *F* typical of an incompatible behavior.

5.4. Sources and geological settings required to generate low-degree mantle melts of phonolitic affinity

A specific feature of the K₂O-enriched sources in our work is that they are either water free (in pMELTS calculations) or water poor (in the nominally anhydrous experiments). Spinel lherzolite xenoliths bearing alkali feldspar and containing 300 to 1000 ppm K₂O, as described in Siberia (Ionov et al., 1995, 1999), provide natural examples of this type of sources. Alkali feldspar-bearing upper mantle peridotites are extremely rare, however: the typical potassium carriers in peridotite xenoliths are phlogopite and/or amphibole (e.g., Menzies et al., 1987), indicating that large scale potassium enrichment of the subcontinental lithospheric mantle is almost invariably accompanied by the introduction of H₂O. Lowdegree melts in equilibrium with phlogopite (\pm amphibole) in hydrous lherzolites at 1 GPa contain 3-4% dissolved water, are enriched in silica as our low-degree melts, but not as enriched in alkalis (Condamine and Médard, 2014): as a consequence, they are quartz normative and plot in the trachyte field of the TAS diagram. Thus our study is clearly not applicable to partial melting of mica-rich peridotites, in which the liquid may be in equilibrium with phlogopite over a large temperature interval. We emphasize, however, that melts in our low-*F* experiments (F = 1-2%) contain $\approx 1\%$ H₂O (e.g., 1.1% H₂O at F = 1.7% in MBK3; see the Supplementary material) so that the bulk water content of the partially molten peridotite is 100 to 200 ppm. Accordingly, this work not only applies to dry melting of a potassium-enriched mantle, but also to the melting of lherzolites containing small quantities of mica and/or amphibole (\approx 1% or less) above the breakdown temperatures of these hydrous phases (1050-1150°C; e.g. Conceição and Green, 2004; Condamine and Médard, 2014). The conclusion that low-degree melts may be phonolitic also applies to pyroxenerich sources as long as some ol and opx are present (in addition to cpx) to maintain the silica content in the liquid at a high level. An example is given in the Supplementary material (Section 3.4).

Given an appropriate source, the generation of a phonolite melt requires that melting begins at $P \approx 1.5$ GPa or less (Supplementary Fig. S2a), and its preservation requires that the degree of melting remains low (as partial melts become basaltic at higher degrees of melting; Fig. 4). In an upwelling mantle with a potential temperature of 1280-1400 °C (Herzberg et al., 2007), melting will begin at too high pressures to produce silica-enriched low-degree melts, especially if the mantle contains traces of water (Asimow et al., 2004), and if any phonolite melt is formed somehow at lower pressures, it may get lost by mixing with non-phonolitic melts formed underneath. Comparatively minor P-T perturbations may trigger mantle melting where the lithosphere is in extension and the upper mantle has variable fertility and solidus temperature (e.g., Anderson, 2005; Foulger, 2007): such a geological setting is clearly more appropriate to the generation and preservation of phonolite melts. For instance, McKenzie (1989) proposed that a metasomatic layer enriched in K₂O formed with time into the subcontinental

lithospheric mantle by accumulation and freezing of small melt fractions from the asthenospheric mantle: remelting of this layer by adiabatic decompression related to extension of the lithosphere is a process that could yield large volumes of phonolite melt.

5.5. Direct generation of phonolites and nepheline syenites by partial melting of upper mantle rocks

Many felsic alkaline rocks (phonolites, nepheline syenites, etc.) are the products of crystal fractionation of basic precursors, such as basanites or alkali basalts, at relatively shallow depths (Kyle et al., 1992; Ablay et al., 1998; Thompson et al., 2001). There are, however, a number of occurrences where these rocks cannot be produced by low-pressure differentiation (Bailey, 1987). This is the case of phonolites and trachyandesites carrying ultramafic xenoliths of upper mantle origin (Wright, 1969; Green et al., 1974; Irving and Price, 1981; Dautria and Girod, 1983; Grant et al., 2013) and of volcanic provinces with abundant phonolites but no or little associated basic to intermediate rocks (e.g., the plateau-type flood phonolites from the Kenya rift; Hay and Wendlandt, 1995). Models for a deep origin of felsic alkaline rocks include high-pressure fractionation of a basanitic precursor at mantle depths (Irving and Price, 1981; Irving and Green, 2008), melting of alkali basalts underplated or injected into the lower crust (Hay and Wendlandt, 1995; Price et al., 2003), or low-degree melting of metasomatized mantle (Bailey, 1987; Riley et al., 1999). Dikes of silicaundersaturated felsic rocks intruding orogenic lherzolites have also been interpreted as low-degree mantle melts (Stähle et al., 1990; Pin et al., 2006).

The hypothesis that some phonolites or their plutonic equivalents (nepheline syenites) are produced directly by partial melting of upper mantle rocks is strongly supported by our experimental results. Heldburg phonolite, Germany, is one of the best examples of a phonolite carrying spinel lherzolite xenoliths (Irving and Price, 1981; Wedepohl et al., 1994; Grant et al., 2013). For many elements, there is a very good correspondence between partial melt in run MBK+6 and Heldburg phonolite (Table 1). The correspondence is not good, however, for MgO: with only 1.16% MgO, Heldburg phonolite has a mg# of 51.8, which is too low for a primary mantle melt in equilibrium with MgO-rich olivine (mg# \approx 90); for comparison, the partial melt in run MBK+6 contains 2.72% MgO and has a mg# of 69.7. Accordingly, Heldburg phonolite cannot be the direct equivalent of the high-mg# phonolite melts in our experiments. It could be produced, however, by the separation of 10-15% of ferromagnesian minerals from such high-mg# melts (at upper mantle pressures to account for the incorporation of mantle xenoliths) or by partial melting of more pyroxene-rich mantle veins with mg# <90. To test the first hypothesis, we performed a crystallization experiment of phonolite gel +6 at 1 GPa-1150 °C (CrysPho2; Table 1 and Supplementary Fig. S3): with less than 7% of crystallization (mostly cpx, plus minor ol), the MgO content of the liquid dropped to 1.7% and its mg# to 60.3, but the overall composition remains typically phonolitic and close to Heldburg phonolite (Figs. 3-4). Therefore low-degree melting of a peridotitic or more pyroxene-rich source (containing some water to account for the presence of phlogopite and amphibole phenocrysts) at $P \leq 1.5$ GPa is a plausible model for the formation of Heldburg phonolite and other phonolites carrying peridotite xenoliths. Reevaluation of the geochemical data available on these rocks and acquisition of new isotopic data are required to establish unambiguously a direct derivation by partial melting of a mantle source.

We used the compaction model of McKenzie (1989) to estimate how fast a phonolite melt could be extracted from a lherzolite source by buoyancy (see Section 4 of the Supplementary material for details of the model). The lherzolite source is assumed to be a layer of thickness h with an interconnected melt network and

an initially uniform melt fraction. As the polycrystalline matrix is denser than the liquid, it compacts with time and the liquid expelled by compaction forms a layer at the top of the system. For given values of h and melt fraction, the melt viscosity, the density contrast between melt and matrix, and the permeability of the matrix are the three major parameters controlling the efficiency of melt extraction. In our calculations, we considered melt viscosities of the order of 10^2 Pa \cdot s (Giordano et al., 2008), a melt density of 2500 kg/m³ (Seifert et al., 2013) and a matrix density of 3200 kg/m³. Maumus et al. (2004) measured a dihedral angle $\theta \approx 50^{\circ}$ for SiO₂- and alkali-rich liquids close to phonolites in contact with ol. In a partially molten rock with a dihedral angle $\theta < 60^{\circ}$, the melt is interconnected at all melt fractions and the permeability k at low melt fraction is proportional to the square of melt fraction per unit volume, F_V (von Bargen and Waff, 1986; McKenzie, 1989):

$$k = \frac{a^2 \cdot F_V^2}{3000}$$

where *a* is the grain size in the matrix ($a \approx 10^{-3}$ m).

In a lherzolite source with 100 ppm K₂O, the fraction of phonolite melt is very small (0.27 wt.%, that is $F_V = 0.0035$; Fig. 6), and so the permeability is only 4.0×10^{-15} m². Assuming h = 1000 m, it would take 3×10^5 years to extract a melt layer only 2.2 m thick (see the Supplementary material for calculation details). By contrast, a source with 2000 ppm K₂O yields almost 10 times more phonolite melt (2.6 wt.%, that is $F_V = 0.033$), and thus its permeability is two orders of magnitude larger: 3.6×10^{-13} m². As a result, for the same source thickness, the time scale of compaction drops to 8×10^4 years and the layer of extracted melt is ten times thicker: 21 m. Accordingly, a moderate increase of the K₂O content of mantle sources has a major effect both on the amount of phonolite melts produced and on the efficiency of melt separation (through the effect of melt fraction on permeability): the extraction of a body of primary mantle phonolite or nepheline syenite sufficiently large to reach the upper crust or the Earth's surface presumably requires a large volume of K₂O-enriched mantle.

5.6. Implications for mantle metasomatism

Metasomatism of the lithospheric mantle by the percolation of small fractions of Si- and K-rich melts has been reported by Bodinier et al. (1996) in spinel peridotites from the Ronda massif, Spain, and the East African Rift, Ethiopia, and by Pilet et al. (2002) in the source of Cenozoic alkali basalts of the Cantal massif, France. The migration of silica- and alkali-enriched liquids produced by low-degree melting of fertile peridotites, as in this study, could be responsible for this type of metasomatism. The suites of megacrysts observed in many alkaline basalt provinces (alkali feldspar, clinopyroxene, etc.; Wright, 1969; Green et al., 1974; Bailey, 1987) and sometimes associated with syenite xenoliths (e.g., Upton et al., 1999) may be another manifestation of the circulation and crystallization of Si- and K-rich melts in the lithospheric mantle.

Detailed studies of mantle xenoliths worldwide have revealed the presence of alkali-rich glasses with $SiO_2 \ge 55\%$ either as intergranular patches, films and reaction rims (Draper and Green, 1997; Neumann and Wulff-Pedersen, 1997; Coltorti et al., 1999) or as inclusions in primary minerals, notably olivines (e.g., Schiano and Clochiatti, 1994). One interpretation of the intergranular glasses is that they result from the reaction between a metasomatizing agent and primary mantle minerals (but this issue is still controversial; see Shaw et al., 2006, for a discussion). In particular, Coltorti et al. (2000) identified a Na- and a K-alkali silicate metasomatism that they ascribed to the infiltration of basic melts, but the infiltration of low-degree phonolitic melts of fertile peridotites may be an alternative explanation.

5.7. Implications for the origin of glass inclusions in peridotite xenolith minerals

Silica- and alkali-rich glass inclusions showing similarities to our experimental melts have been described in magnesian olivines in spinel peridotite xenoliths from the sub-continental and suboceanic lithosphere (e.g., Schiano and Clocchiatti, 1994). They were interpreted as low-degree melts of spinel lherzolites formed at pressures around 1 GPa (Schiano et al., 1998) and acting as metasomatic agents, in good agreement with this study. We did not find olivine-hosted phonolitic glass inclusions in the literature data, but trachyandesitic to tephriphonolitic glass inclusions (54-57% SiO₂; 9-11% Na₂O + K₂O) are common. They presumably correspond to melt fractions too small to escape by buoyancy-driven porous flow as discussed above, and that were ultimately trapped inside olivine grains as a result of grain boundary migration (Renner et al., 2002) or thermally driven transcrystalline melt migration (Schiano et al., 2006). The software pMELTS could be used to compute the pressure and degree of melting from the composition of such glass inclusions provided that the bulk xenolith composition is known.

Some olivine-hosted glass inclusions in peridotite xenoliths contain SiO₂ in excess of 60% and are trachytic in compositions (60-63% SiO₂; 9-11% Na₂O + K₂O; Schiano et al., 1998; Schiano and Bourdon, 1999). Draper and Green (1997, 1999) also found a class of mantle-xenolith glasses with broadly trachytic compositions (Fig. 4), and they performed multiple saturation experiments that yielded melts with SiO₂ \approx 61% and Na₂O + K₂O \approx 13% in equilibrium with a lherzolitic mineral assemblage at 1.2 GPa-1150 °C. On the basis of these observations, it was one of our initial objectives to produce trachytic compositions at low degrees of melting of a fertile peridotite. Our experiments and calculations show instead that low-degree melts of a dry lherzolite at 1–1.3 GPa are phonolitic, with up to 14% Na₂O + K₂O but SiO₂ \leq 58%. We infer that the trachytic melt compositions in peridotite xenoliths must be produced at pressures <1 GPa and/or under hydrous conditions. The association of a trachytic liquid with an ol + opx + cpx assemblage at 1.2 GPa in Draper and Green's (1999) study is presumably due to the effect of water. According to pMELTS, it is indeed necessary to add several hundred ppm of H₂O into the source (\approx 2.5% H₂O in the liquid) in order to keep opx stable in addition to ol and cpx in their experimental conditions.

6. Conclusions

Partial melts produced just above the solidus of fertile peridotites at 1-1.5 GPa have compositions very far from basalts and classify as trachyandesites, tephriphonolites and even phonolites. These silica- and alkali-rich melts have a high potential as metasomatic agents of the lithospheric mantle. Because their high degree of polymerization has important consequences for the partitioning of minor and trace elements, as demonstrated here for Ti⁴⁺, they may lead to specific chemical and isotopic changes of the upper mantle. When a large volume of the upper mantle is enriched in potassium, the silica- and alkali-rich melts generated just above the peridotite solidus due to lithospheric extension could be extracted and yield bodies of phonolite or nepheline syenite sufficiently large to reach the upper crust or the Earth's surface. Production of phonolite liquids from a mantle source is presumably restricted to a narrow range of pressures (between \approx 1.5 and 1 GPa): strong SiO₂ enrichment of low-degree melts is not expected above \approx 1.5 GPa, and at 1 GPa or less, Na₂O and K₂O become less incompatible due to the abundance of pl, preventing a strong enrichment of those two elements in the liquid.

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Appendix A. Supplementary material

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