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EFFECTS OF P_2O_5 AND TiO_2 ON THE PARTIAL MELTING OF SPINEL LHERZOLITE IN THE SYSTEM $CaO–MgO–Al_2O_3–SiO_2$ AT 1.1 GPa

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Abstract

The effects of small amounts of P_2O_5 on the partial melting of model spinel lherzolite in the system $CaO–MgO–Al_2O_3–SiO_2$ + P_2O_5 have been investigated at 1.1 GPa in piston–cylinder experiments, in order to constrain the influence of this minor component on mantle melting. A concentration of 1 wt% P_2O_5 in the melt depresses the solidus of spinel lherzolite by only 2°C, reduces SiO_2 in melts by 1 wt% and Al_2O_3 by 0.44 wt%, but increases CaO by 0.3 wt% and MgO by 0.14 wt%. A preliminary investigation of the effect of TiO_2 in the system $CaO–MgO–Al_2O_3–SiO_2$ + TiO_2 shows that it decreases the solidus by ~1°C/wt%, and its effect on the melt composition is small, being mainly one of dilution.

Keywords: CMAS + P_2O_5, CMAS + TiO_2, partial melting, solidus, spinel lherzolite.

Sommaire

Nous avons étudié l'influence de petites quantités de P_2O_5 sur la fusion partielle d'une lherzolite à spinelle idéalisée dans le système $CaO–MgO–Al_2O_3–SiO_2$ + P_2O_5 à 1.1 GPa au moyen d'expériences avec un appareil à piston–cylindre, afin de controller le rôle de ce composant mineur sur la fusion dans le manteau. Une concentration de 1% P_2O_5 (poids) dans le bain fondu cause une baisse du solidus de la lherzolite à spinelle de 2°C seulement, réduit la teneur en SiO_2 dans le bain fondu de 1% et celle de Al_2O_3 de 0.44%, mais augmente la teneur en CaO de 0.3% et celle de MgO, de 0.14%. Une étude préliminaire des effets de la présence de TiO_2 dans le système $CaO–MgO–Al_2O_3–SiO_2$ + TiO_2 montre que ce composant abaisse le solidus d'environ 1°C par pourcent de TiO_2, son effet sur la composition du liquide demeurant faible, et surtout un de dilution.

(Traduit par la Rédaction)

Mots-clés: CMAS + P_2O_5, CMAS + TiO_2, fusion partielle, solidus, lherzolite à spinelle.

Introduction

The simplest chemical system that contains all the major phases of the lherzolitic upper mantle [olivine (Ol), orthopyroxene (Opx), clinopyroxene (Cpx), and an aluminous phase, one of plagioclase (Pl), spinel (Spl) or garnet (Grt), depending on pressure] is the system $CaO–MgO–Al_2O_3–SiO_2$ (CMAS). To a first approximation, the important features of the partial melting of the lherzolitic upper mantle are well described by this system, which has accordingly been extensively studied experimentally over a wide range of pressures (*e.g.*, Presnall *et al*. 1978, 1979, Longhi 1987, Liu & Presnall 1990, 2000, Gudfinnsson & Presnall 1996, Milholland & Presnall 1998, Herzberg & Zhang 1998, Liu & O'Neill 2004a). But other components, namely FeO, Na_2O, K_2O, Cr_2O_3, P_2O_5, TiO_2, and the volatiles H_2O and CO_2, are expected to control many of the petrologically significant aspects of the melting of realistic mantle compositions. For example, the minor incompatible components will be strongly concentrated in low-melt-fraction melts, and their presence must surely affect the temperature of the solidus (Hirschmann 2000), although to what extent remains mostly unquantified.

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Here we present results of new experiments that constrain the effects of small amounts, appropriate to the melting of the Earth's upper mantle, of P_2O_5, together with some exploratory data for TiO_2. The concentration of P_2O_5 in alkali basalts is commonly 0.5 to 1 wt%, reaching ~2 wt% in some basanites, but the effect of such concentrations on melting temperatures and phase relations is poorly known. If the experiments of Wyllie & Tuttle (1964) on the effect of P_2O_5 on depressing the vapor-saturated melting point of albite are any guide, it could be significant.

BACKGROUND INFORMATION

In principle, the effects of minor components on the partial melting process could be derived from the data collected in high-temperature – high-pressure experiments with multicomponent compositions. But in reality, the incompatible minor components are generally highly correlated in all the bulk compositions selected for partial melting experiments, as they are in nature, hindering the discrimination of the effects of individual components (Hirschmann 2000, Wasylenki *et al.* 2003). A solution to this conundrum is to study individually the effects of each minor component on the partial melting in CMAS. In the last decade, the effects of Na_2O, FeO, K_2O, Cr_2O_3, and small amounts of H_2O and CO_2 have been experimentally evaluated (Walter & Presnall 1994, Gudfinnsson & Presnall 2000, Liu & O'Neill 2004a, b, Liu *et al.* 2006). However, the influences of P_2O_5 and TiO_2 have not been experimentally evaluated in the appropriate systems.

EXPERIMENTAL DETAILS

Two types of starting materials (Table 1) were prepared for this investigation; lherzolitic crystalline mixtures LJ01 and LJ03 were made by crystallizing the decarbonated oxide mixes at 1280°C, 1.1 GPa and 48 hours in Pt capsules in a 15.9 mm piston–cylinder press, and basaltic glasses LJ02 and LJ04 were melted in an one-atmosphere furnace at 1400°C for 20 minutes, and then quenched to glass. High-purity oxides (SiO_2, Al_2O_3, MgO, TiO_2), carbonate ($CaCO_3$) and ammonium dihydrogen phosphate ($NH_4H_2PO_4$) were used to prepare these starting materials. These starting materials were packed in Pt capsule as layers in a sandwich geometry (LJ01 with LJ02, or LJ03 with LJ04), with the glass material in the middle and the crystalline material at both ends. In order to produce large quench-free pools of melt, the proportions of the glass material and the crystalline material were regulated according to the targeted experimental temperatures.

All experiments were made in a conventional 12.7 mm piston–cylinder apparatus (Boyd & England 1960) with the "piston-out" method (Johannes *et al.* 1971), using a salt–pyrex pressure assembly with a Fe_2O_3 sleeve surrounding the Pt capsule, as described previously in Liu & O'Neill (2004a); see also Figure 1 of Liu *et al.* (2006). The salt–pyrex assembly has a low friction, and no pressure correction is required (Green *et al.* 1966, Bose & Ganguly 1995, Klemme & O'Neill 1997). The Fe_2O_3 sleeve was used as an H_2-getter to achieve an almost completely anhydrous experimental environment (Robinson *et al.* 1998, Liu *et al.* 2006). Temperature was measured and controlled with a $Pt_{94}Rh_6$–$Pt_{70}Rh_{30}$ thermocouple, with any possible effect of pressure on its e.m.f. ignored. As Liu & O'Neill (2004a) argued, the temperature uncertainties of the experiments reported here are ~5°C.

The experimental product was sectioned longitudinally, mounted in epoxy, polished with diamond paste, carbon-coated and then analyzed with a JEOL 6400 scanning electron microprobe in energy-dispersion mode at the Electron Microprobe Unit, Australian National University, with a beam current of 1 nA and an accelerating voltage of 15 keV. The ZAF correction procedure was applied to all analyses (Ware 1991). A beam-spot size of 1 μm was used for the crystalline phases, whereas both 1 and 10 μm beam-spot sizes were used for glass analyses. Analytical accuracy and precision are expected to be similar to those reported in Liu & O'Neill (2004a).

Previous experience on similar experiments in the system CMAS, with or without minor components, suggests that equilibrium should be achieved closely. The literature data in the system CMAS (*e.g.*, Presnall *et al.* 1978, Sen & Presnall 1984, Liu & Presnall 1990) indicate that a period of several hours is adequate to establish reversals of phase boundaries at liquidus temperatures. Experiments in the systems CMAS + Na_2O (Walter & Presnall 1994), CMAS + FeO (Gudfinnsson & Presnall 2000), CMAS + K_2O (Liu & O'Neill 2004a), CMAS + Cr_2O_3 (Liu & O'Neill 2004b), CMAS ± H_2O ± CO_2 ± Na_2O (Liu *et al.* 2006) show that a period of 48 hours is long enough for the attainment of equilibrium at temperatures just above the solidi. All experiments reported here ran for longer times at similar pressure–temperature conditions.

EXPERIMENTAL RESULTS AND DISCUSSION

System CMAS + P_2O_5

Three experiments in the system CMAS + P_2O_5 at 1.1 GPa successfully produced the five-phase assemblage Ol + Spl + Opx + Cpx + Melt (Table 1). These experiments show that 1 wt% P_2O_5 in the melt depresses the solidus of spinel lherzolite (Ol + Spl + Opx + Cpx) by ~2°C (Fig. 1), which is somewhat less than that inferred by Wasylenki *et al.* (2003) from the regression of partial melting experiments on multicomponent compositions (~5°C/wt% P_2O_5). The effect of P_2O_5 on the multiply-saturated melt compositions is to

TABLE 1. STARTING MATERIALS, EXPERIMENTAL CONDITIONS AND MELT COMPOSITIONS IN THE SYSTEMS CMAS-P_2O_5 AND CMAS-TiO_2 At 1.1 GPa

Run no.	T (°C)	t (h)	Phases observed	Composition				
				CaO	MgO	Al_2O_3	SiO_2	P_2O_5 or TiO_2
Starting materials for experiments in the system CMAS–P_2O_5								
Crystalline LJ01				7.34	30.98	17.12	44.06	0.5
Glass LJ02				15.19	15.20	19.94	48.68	1
Starting materials for experiments in the system CMAS–TiO_2								
Crystalline LJ03				7.34	30.98	17.12	44.06	0.5
Glass LJ04				15.19	15.20	19.94	48.68	1
Experiments in the system CMAS–P_2O_5								
C-2175	1318	72	Fo Spl Opx Cpx Melt	15.74(11)*	15.47(13)	19.37(15)	48.26(9)	1.15(11)
C-2155	1315	71.5	Fo Spl Opx Cpx Melt	16.21(31)	15.91(27)	18.61(24)	46.16(21)	3.11(12)
C-2144	1312	74	Fo Spl Opx Cpx Melt	16.38(20)	15.59(29)	18.91(33)	46.22(36)	2.90(23)
Experiments in the system CMAS–TiO_2								
C-2180	1325	72	Fo Spl Opx Melt	13.68(15)	16.04(11)	20.03(10)	49.20(18)	1.05(8)
C-2169	1318	72	Fo Spl Opx Melt[§]	14.81(12)	15.49(10)	19.55(13)	49.06(17)	1.09(7)
C-2159	1315	55	Spl Opx Cpx Melt[†]	15.19(15)	11.06(32)	22.91(43)	49.76(13)	1.16(4)

T refers to temperature in °C; t refers to time in hours. Compositions are expressed in wt%. Symbols: Fo: forsterite, Spl: spinel, Opx: orthopyroxene, Cpx: clinopyroxene. * 15.74(11) is the mean, followed by one standard deviation, read as 15.74 ± 0.11. The results of the analyses were normalized to 100 wt% before the means average and standard deviations were calculated. At least six sets of electron-microprobe data were collected for the melts in every experiment. [§] Clinopyroxene quench was observed, indicating this experiment was close to saturation in Cpx. [†] A few small grains of forsterite (up to ~2 μm in size) were found out in the sandwiching parts.

reduce SiO_2 by 1.0 wt% and Al_2O_3 by 0.44 wt%, but to increase CaO by 0.3 wt% and MgO by 0.14 wt% per wt% of P_2O_5 (Fig. 1).

The effects of P_2O_5 on the normative composition of the melt can be illustrated graphically in the projection from Ol onto the plane Di–JdCaTsLc–Qtz (Fig. 2a) and from Di onto the plane Ol–JdCaTsLc–Qtz (Fig. 2b). The normative components of a magma have been found to be a useful guide to its low-pressure crystallization, *e.g.*, both hypersthene- or quartz-normative compositions follow either a tholeiitic or calc-alkaline trend, whereas nepheline-normative magmas crystallize down quite different trends. Here, we represent the effect of P_2O_5 on the normative mineralogy in two ways. Firstly, we use the traditional component chosen to represent P_2O_5 in normative calculations, namely "apatite", actually a sort of dehydroxylated version with molar stoichiometry of 3.33 CaO to 1 P_2O_5 (*e.g.*, Cox *et al.* 1979, p. 407-414; empty squares in Fig. 2). Secondly, we simply use P_2O_5 (empty circles in Fig. 2). In both cases, the phosphorus-containing component is subtracted prior to calculating the other components that are plotted in the projections.

The isobarically invariant melt produced by the spinel lherzolite assemblage in the system CMAS at 1.1 GPa is an olivine-normative tholeiite (solid square in Fig. 2; Presnall *et al.* 1979, Walter & Presnall 1994, Liu & O'Neill 2004a). Addition of P_2O_5 causes a reduction in the Al_2O_3 content of the melt (Fig. 1), so that the amount of normative anorthite (An) decreases. Whereas this leads to more CaO available to form the diopside component (Di), this is more than counteracted by the assignment of 3.33 CaO to 1 mole of P_2O_5 to form normative "apatite", resulting in less Di component in the melts (Fig. 2a). The decrease of Di, coupled with the effect of P_2O_5 in increasing the MgO content, makes more hypersthene (Hy) + olivine (Ol) or hypersthene + quartz (Qtz). The extra MgO and SiO_2 appearing from the formation of the "apatite" component are approximately in a proportion of 1:1, so that the effect of P_2O_5 on the normative components runs parallel to the An–Hy join (Fig. 2b). The net result

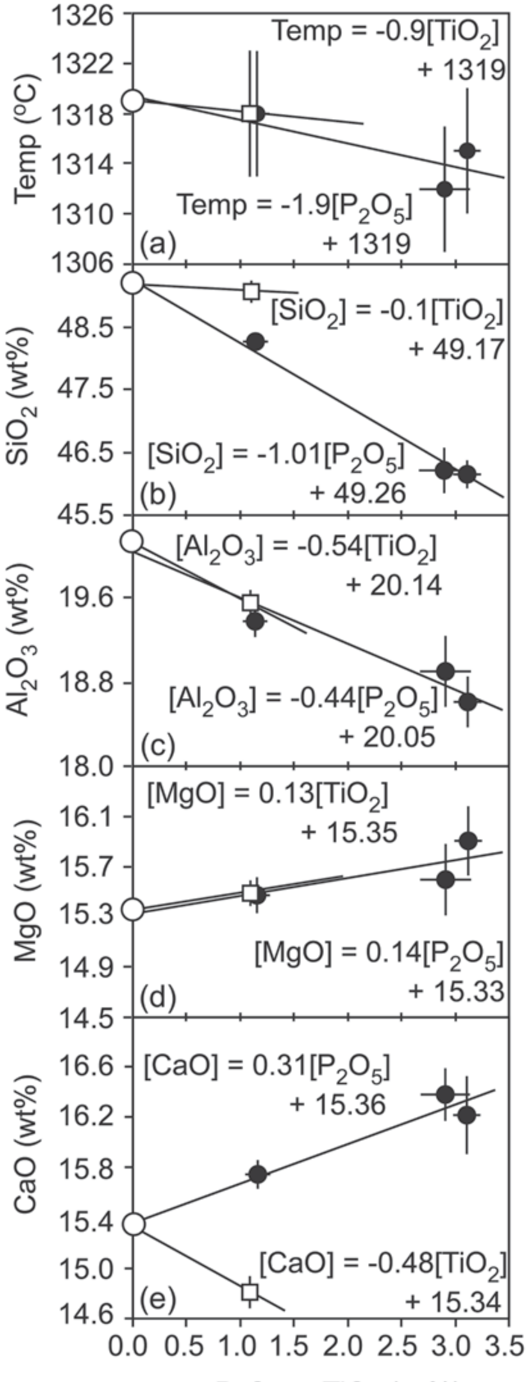

FIG. 1. Effects of P_2O_5 and TiO_2 on the partial melting of spinel lherzolite in the system CMAS at 1.1 GPa: (a) solidus temperature, (b) SiO_2 in melts, (c) Al_2O_3 in melts, (d) MgO in melts, and (e) CaO in melts. Symbols: empty circle: the isobarically invariant point in the system CMAS at 1.1 GPa (Liu & O'Neill 2004a); solid circle: experiments showing a spinel lherzolite phase-assemblage in the system CMAS + P_2O_5; empty square: run C–2169, which is considered to be close to multiple saturation, although lacking in primary Cpx (see text).

is that P_2O_5 appears to have a neutral effect on the melt's nepheline-normative *versus* quartz-normative affinities, although we emphasize that this conclusion is determined entirely by the selection of "apatite" as the appropriate constituent for the norm calculation. To illustrate the importance of different constituents in the norm calculation, we have also plotted the results from this study as normative components calculated simply by subtracting P_2O_5 from the total and renormalizing to 100% ("P_2O_5-subtraction"). This procedure produces an utterly different trend that carries the melt composition across the AbAnOr–Di join into the field of alkali basalt (Fig. 2).

The effects of P_2O_5 on the Ol + Opx cotectic have been studied experimentally by Kushiro (1975) in the systems Mg_2SiO_4–$CaMgSi_2O_6$–SiO_2–H_2O and Mg_2SiO_4–$NaAlSiO_4$–SiO_2–H_2O at 2 GPa with excess H_2O. Kushiro observed that the cotectics in both systems were shifted markedly away from silica (*i.e.*, contraction of the primary phase-volume of olivine) with the addition of ~3 wt% P_2O_5, which is an amount comparable to that investigated in this study. He also found a similar shift away from silica for the pseudowollastonite + silica cotectic at atmospheric pressure. Whereas the decrease of silica is in agreement with the results obtained here (Fig. 1), the inferred implication that this would lead to melts that "should tend to be critically silica-undersaturated" (Kushiro 1975), is only supported by our analysis if we calculate normative components by P_2O_5 subtraction, rather than using the "apatite" component. In fact, any conclusions regarding normative trends in multicomponent systems are likely to be artefacts of the projection procedure.

There is, however, a real difference between the effects of P_2O_5 on multiply-saturated melts and on those coexisting with Ol + Opx along a cotectic. This difference arises because the activity of CaO is buffered in multiply-saturated experiments, with the amount of CaO in the melt being free to vary (*cf.* Fig. 1); in the experiments at the Ol + Opx or pseudowollastonite + silica cotectic, however, it is not the activity but rather the amount of CaO in the melt that is kept constant. Because of the attachment of CaO to P_2O_5 to form a complex (as assumed in the assignment of 3.33 moles CaO to each mole of P_2O_5 to form the "apatite" compo-

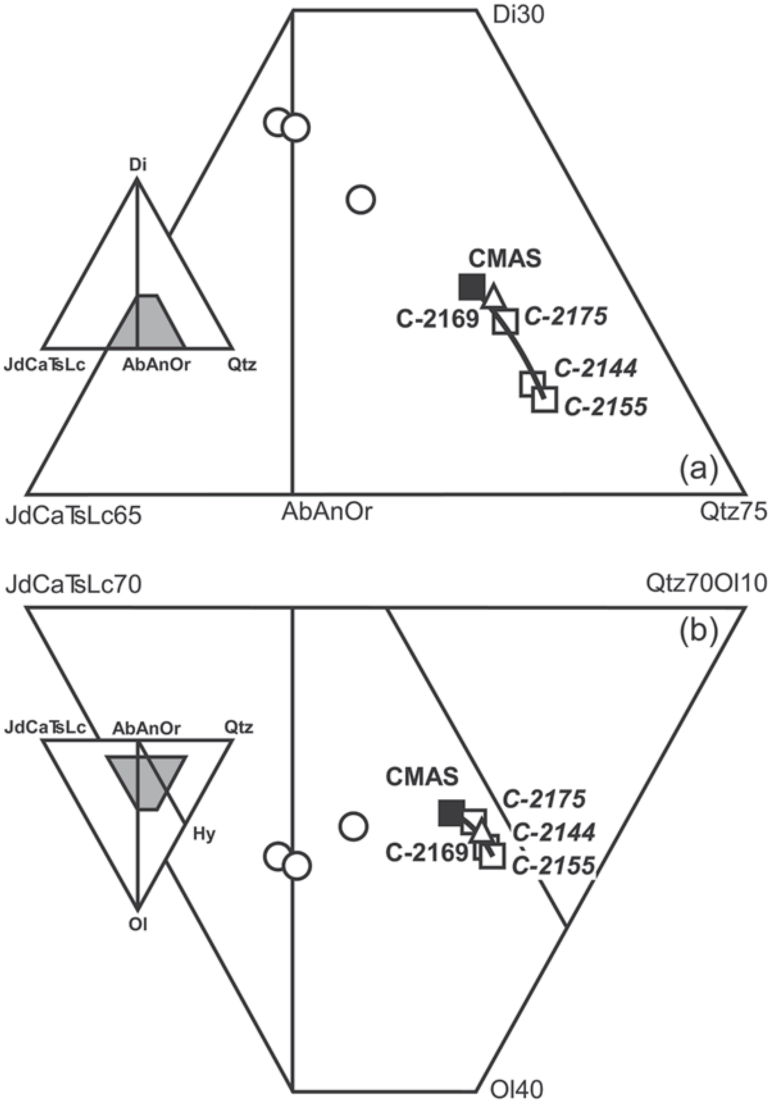

FIG. 2. The multiply-saturated (Ol + Opx + Cpx + Spl) melt composition in the system CMAS + P_2O_5 and run C–2169 in CMAS + TiO_2 (a) projected from Ol onto the plane Di–JdCaTsLc–Qtz, and (b) projected from Di onto the plane JdCaTsLc–Qtz–Ol. The projection procedure of Falloon & Green (1988) is used. The CMAS composition is from Liu & O'Neill (2004a).

nent), the increase in CaO seen in our experiments counteracts any tendency for the multiply-saturated pseudo-invariant point to move away from silica in the normative projections. At fixed CaO content in the cotectic experiments, this compensatory behavior is not an option.

As demonstrated by Ryerson & Hess (1978), Mysen *et al*. (1981a, b) and Ryerson (1985), the structural role of P_2O_5 in basaltic or relatively unpolymerized melts is to form discrete anion complexes, such as that implied by the normative "apatite" component; in more polymerized melts, its role is quite different, because it joins with SiO_2 as a network former. The appropriate way to handle P_2O_5 in a normative calculation thus should actually depend on the nature of the melt.

System CMAS + TiO_2

In contrast to the experiments in the system CMAS + P_2O_5, those in the system CMAS + TiO_2 did not produce the full phase-assemblage of spinel lherzolite (Table 1). However, the results bracket the isobaric invariant point at 1.1 wt% TiO_2. Both C–2180 and C–2169 display the phase assemblage Ol + Spl + Opx + Melt, whereas C–2159 shows the phase assemblage Spl + Opx + Cpx + Melt. The TiO_2 contents in these three experiments are similar, ~1.1 wt%. The melt composition in run C–2180 differs from that in C–2169 by having less normative Di and CaTs, the two components that make up Cpx in the CMAS system. Thus, C–2169 should be the closer to Cpx saturation, and indeed quench clinopyroxene was observed in this experiment. We therefore believe that the melt composition of C–2169 is a close approximation to the multiply-saturated melt with 1.1 wt% TiO_2. The composition of this melt (empty triangle in Fig. 2) is close to that in the pure CMAS system, indicating that the effect of TiO_2 is predominantly one of simple dilution, with a hint that it should lead to a slight increase of normative hyperthene (Fig. 2b). This is opposite to the observation of Kushiro (1975), that addition of TiO_2 to the simple systems MgO–SiO_2 and K_2O–MgO–SiO_2 expands the protoenstatite or enstatite fields relative to forsterite. The effect of TiO_2 on the Ol + Opx cotectic has also been studied by Xirouchakis *et al.* (2001), at 1.2 GPa and 1360°C and at 2.8 GPa and 1530ºC, in multicomponent compositions with ~48 wt% SiO_2 when renormalized to zero TiO_2, for TiO_2 contents in the melts up to ~20%. The presence of Ol + Opx along the cotectic buffers the activities of SiO_2 and the pseudocomponent (MgO + FeO), but not CaO or Al_2O_3. Xirouchakis *et al.* (2001) showed that TiO_2 decreases the SiO_2 of the melt by 0.65 wt% for each 1 wt% TiO_2, in approximate agreement with the expectation from our results that the main effect of TiO_2 is one of dilution. As in the case for P_2O_5, the structural role of TiO_2 changes with the degree of polymerization of the melt (Mysen *et al.* 1980, 1981b); hence the inferences from studies of basaltic systems should not be extrapolated to more highly polymerized melts.

In conclusion, both P_2O_5 and TiO_2 have rather small effects on the temperature of partial melting at concentrations typical of terrestrial basalts (*sensu lato*): 1 wt% P_2O_5 depresses the solidus by ~2°C, whereas 1 wt% TiO_2 depresses it by ~1°C. As to the melt composition, the effect of TiO_2 is almost negligible, whereas that of P_2O_5 seems to be slightly stronger, but is still relatively minor, given that P_2O_5 is usually less than 2 wt%, even in extremely enriched alkali basalts.

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