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 $CaO–MgO–Al_2O_3–SiO_2 + P_2O_5$ au moyen d’expériences avec un appareil à piston–cylindre, afin de contrôler 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.

(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 (Op), clinopyroxene (Cp), and an aluminous phase, one of plagioclase (Pl), spinel (Sp) 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 $\sim$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$_2$O, FeO, K$_2$O, Cr$_2$O$_3$, and small amounts of H$_2$O 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$_2$O$_3$, MgO, TiO$_2$), carbonate (CaCO$_3$) and ammonium dihydrogen phosphate (NH$_4$H$_2$PO$_4$) 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$_2$O$_3$ 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$_2$O$_3$ 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$_{79}$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 $\sim$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$_2$O (Walter & Presnall 1994), CMAS + FeO (Gudfinnsson & Presnall 2000), CMAS + K$_2$O (Liu & O’Neill 2004a), CMAS + Cr$_2$O$_3$ (Liu & O’Neill 2004b), CMAS ± H$_2$O ± CO$_2$ ± Na$_2$O (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 $\sim$2°C (Fig. 1), which is somewhat less than that inferred by Wasylenki et al. (2003) from the regression of partial melting experiments on multicomponent compositions ($\sim$5°C/wt% $P_2O_5$). The effect of $P_2O_5$ on the multiply-saturated melt compositions is to
reduce SiO$_2$ by 1.0 wt% and Al$_2$O$_3$ by 0.44 wt%, but to increase CaO by 0.3 wt% and MgO by 0.14 wt% per wt% of P$_2$O$_5$ (Fig. 1).

The effects of P$_2$O$_5$ 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$_2$O$_5$ on the normative mineralogy in two ways. Firstly, we use the traditional component chosen to represent P$_2$O$_5$ on normative calculations, namely “apatite”, actually a sort of dehydroxylated version with molar stoichiometry of 3.33 CaO to 1 P$_2$O$_5$ (e.g., Cox et al. 1979, p. 407-414; empty squares in Fig. 2). Secondly, we simply use P$_2$O$_5$ (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$_2$O$_5$ causes a reduction in the Al$_2$O$_3$ 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$_2$O$_5$ to form normative “apatite”, resulting in less Di component in the melts (Fig. 2a). The decrease of Di, coupled with the effect of P$_2$O$_5$ 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$_2$O$_5$ on the normative components runs parallel to the An–Hy join (Fig. 2b). The net result
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. 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).
the partial melting of lherzolite

...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 P2O5 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 SiO2 as a network former. The appropriate way to handle P2O5 in a normative calculation thus should actually depend on the nature of the melt.

Fig. 2. The multiply-saturated (Ol + Opx + Cpx + Spl) melt composition in the system CMAS + P2O5 and run C–2169 in CMAS + TiO2 (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).
System CMAS + TiO₂

In contrast to the experiments in the system CMAS + P₂O₅, those in the system CMAS + TiO₂ did not produce the full phase-assemblage of spinel lherzolite (Table 1). However, the results bracket the isobaric invariant point at 1.1 wt% TiO₂. 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 TiO₂ 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% TiO₂. The composition of this melt (empty triangle in Fig. 2) is close to that in the pure CMAS system, indicating that the effect of TiO₂ 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 TiO₂ to the simple systems MgO–SiO₂ and K₂O–MgO–SiO₂ expands the protoenstatite or enstatite fields relative to forsterite. The effect of TiO₂ 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 1530°C, in multicomponent compositions with ~48 wt% SiO₂ when renormalized to zero TiO₂, for TiO₂ contents in the melts up to ~20%. The presence of Ol + Opx along the cotectic buffers the activities of SiO₂ and the pseudocomponent (MgO + FeO), but not CaO or Al₂O₃. Xirouchakis et al. (2001) showed that TiO₂ decreases the SiO₂ of the melt by 0.65 wt% for each 1 wt% TiO₂, in approximate agreement with the expectation from our results that the main effect of TiO₂ is one of dilution. As in the case for P₂O₅, the structural role of TiO₂ 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 P₂O₅ and TiO₂ have rather small effects on the temperature of partial melting at concentrations typical of terrestrial basalts (sensu lato): 1 wt% P₂O₅ depresses the solidus by ~2°C, whereas 1 wt% TiO₂ depresses it by ~1°C. As to the melt composition, the effect of TiO₂ is almost negligible, whereas that of P₂O₅ seems to be slightly stronger, but is still relatively minor, given that P₂O₅ is usually less than 2 wt%, even in extremely enriched alkali basalts.

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