Sediment Melts at Sub-arc Depths: an Experimental Study

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The phase and melting relations in subducted pelites have been investigated experimentally at conditions relevant for slabs at sub-arc depths (T = 600–1050°C, P = 2.5–4.5 GPa). The fluid-present experiments produced a dominant paragenesis consisting of garnet–phengite–clinopyroxene–coesite–kyanite that coexists with a fluid phase at run conditions. Garnet contains detectable amounts of Na2O (up to 0.15 wt%), P2O5 (up to 0.356 wt%), and TiO2 (up to 0.19 wt%) in all experiments. Phengite is stable up to 1000°C at 4.5 GPa and is characterized by high TiO2 contents of up to 2 wt%. The solidus has been determined at 700°C, 2.5 GPa and is situated between 700 and 750°C at 3.5–4.5 GPa. At 800°C, 4.5 GPa glass was present in the experiments, indicating that at such conditions a hydrous melt is stable. In contrast, at 700°C, 3.5 and 4.5 GPa, a solute-rich, non-quenchable aqueous fluid was present. This indicates that the solidus is steeply sloping in P–T space. Fluid-present (vapour undersaturated) partial melting of the pelites occurs according to a generalized reaction phengite + omphacite + coesite + fluid = melt + garnet. The H2O content of the produced melt decreases with increasing temperature. The K2O content of the melt is buffered by phengite and increases with increasing temperature from 2.5 to 10 wt%, whereas Na2O decreases from 7 to 2.3 wt%. Hence, the melt compositions change from trondhjemitic to granitic with increasing temperature. The K2O/H2O increases strongly as a function of temperature and nature of the fluid phase. It is 0.0004–0.002 in the aqueous fluid, and then increases gradually from about 0.1 at 750–800°C to about 1 at 1000°C in the hydrous melt. This provides evidence that hydrous melts are needed for efficient extraction of K and other large ion lithophile elements from subducted sediments. Primitive subduction-related magmas typically have K2O/H2O of ~0.1–0.4, indicating that hydrous melts rather than aqueous fluids are responsible for large ion lithophile element transfer in subduction zones and that top-slab temperatures at sub-arc depths are likely to be 700–900°C.

KEY WORDS: experimental petrology; pelite; subduction; UHP metamorphism; fluid; LILE

INTRODUCTION

Subducted sediments play a key role in the recycling of incompatible elements in subduction zones. The comparison of primitive arc lavas with mid-ocean ridge basalts (MORB) provides evidence that arc lavas are enriched in H2O, large-ion lithophile elements (LILE) and, to a lesser extent, light rare earth elements (LREE) (Tatsumi & Eggins, 1995). The enrichment of these components is interpreted to be related to the addition of a ‘slab component’ to the locus of partial melting in the mantle wedge (Hawkesworth et al., 1993). Detailed chemical analyses of oceanic crustal material have revealed that subducted sediments are the dominant host of LILE in the slab (Plank & Langmuir, 1998; Thordarson & Hermann, 2004). The fundamental role of sediments in the recycling of LILE has also been demonstrated by the matching of trace element ratios of sediment input and arc output in several subduction zones (e.g. Plank & Langmuir, 1993; Peate et al., 1997). Therefore, the systematic study of subducted sediments is crucial for understanding the LILE transfer. The pressure range where this transfer occurs is constrained by the depth (70–170 km) of the subducted slab below the volcanic arc (Tatsumi, 1986; Syracuse & Abers, 2006). Hence, it is important to study phase and melting relations...
in subducted sediments that experienced pressures in the range of 2.5–5 GPa.

One approach to study such phase relations is through investigation of ultrahigh-pressure (UHP) metamorphic rocks (Hermann et al., 2006). Subducted continental crust occasionally contains relics of coesite and diamond, providing evidence that these rocks were metamorphosed at 100–150 km depth (Chopin, 1984; Sobolev & Shatsky, 1990). Metapelites, metagranites and metacarbonates in such terrains can be used as natural laboratories to study phase and melting relations in subducted sediments (Philippot et al., 1995; Stockhert et al., 2001; Hermann et al., 2006). Bulk-rock and mineral trace element analyses of such rocks have shown that phengite plays a key role as a repository for LILE (Sorenson et al., 1997; Spandler et al., 2003). However, one major problem with the interpretation of such data is that deeply subducted rocks cool relatively slowly during exhumation and hence it is not clear whether the original chemical signature of phases is preserved. Moreover, in these rocks the record of the fluid phase is, at best, only fragmentarily preserved, and so little information on the composition and nature of the fluid phase present at UHP conditions can be obtained.

High-pressure experiments on sedimentary bulk compositions provide a second way of investigating element recycling in subduction zones. Experimental studies are important for understanding mineral relations in subducted sediments and for directly constraining the composition and nature of the fluid phase. Experimental studies have confirmed that phengite is the stable K-phase in subducted sediments at sub-arc depths (Domanik & Holloway, 1996; Schmidt, 1996; Ono, 1998; Hermann, 2002b; Auzanneau et al., 2006). Consequently, an understanding of phengite melting relations is crucial for understanding the recycling of LILE. One of the problems with experimental studies is that piston cylinder techniques are used at pressures \( \leq 5 \) GPa, whereas multi-anvil experiments are used at pressures \( \geq 5 \) GPa (Schmidt et al., 2004). This might introduce some systematic errors exactly in the critical pressure range where the subduction-zone fluids leave the slab.

There are contrasting views on the nature and composition of the fluid phase that transports the key elements from the slab to the mantle wedge. Geochemical studies of arc magmas have attempted to constrain the nature of the fluid phase on the basis of element ratios. Two end-members have been proposed corresponding to a sediment fluid component and a sediment melt component (Class et al., 2000; Elliott, 2003). However, it must be stressed that the actual phase relations and buffering phases in the slab are often ignored. A second approach to constrain the nature and composition of the fluid phase involves detailed solubility studies of minerals in fluids and calculation of fluid compositions in equilibrium with the determined high-pressure phases (Manning, 1998, 2004). Such an approach has provided excellent results for major element concentrations in the aqueous fluid. To establish whether an aqueous fluid or a hydrous melt is leaving the subducted slab, it is necessary to combine expected top-slab temperatures with experimental studies on the solidus of sedimentary rocks (Nichols et al., 1994; Hermann et al., 2006). To date, this approach has been inconclusive because there exists a large variation in predicted top-slab temperatures according to different models, as well as discrepancies in the position of the wet solidus for typical subducted sediments. A further complication arises as a consequence of the potential presence of the second critical endpoint (Kessel et al., 2005b). In the pelitic system the termination of the wet solidus at the second critical endpoint might be reached at pressure and temperature conditions relevant for subducted sediments at sub-arc depth, and hence transitional supercritical fluids could be the transporting agent (Manning, 2004; Kessel et al., 2005a; Hermann et al., 2006).

In this paper we present the results of an experimental study on the phase and melting relations in a pelite composition. We used piston cylinder experiments for the entire dataset covering a \( P-T \) range of 2.5–4.5 GPa and 600–1050 °C, appropriate for sub-arc conditions. This eliminates any potential systematic errors involved in using two different experimental techniques. We systematically investigated the stability and melting behaviour of phengite to constrain the recycling of \( K_2O \) from subducted sediments. Fluid-present melting is explored and special emphasis is placed on constraining the position of the wet solidus. We show that the compositions of aqueous fluids and hydrous melts vary as a function of temperature, and we use this information to postulate that sediment melts provide the simplest way to explain the \( K_2O \) and \( H_2O \) systematics of primitive arc lavas. We also report how the common UHP phases garnet, omphacite and phengite change their composition as a function of pressure and temperature and how this information can be used as a guide to evaluate how well UHP rocks preserve original phase compositions.

**EXPERIMENTAL METHODS**

**Starting material**

A starting material has been synthesized with a major-element composition similar to average global subducting sediment (GLOSS; Plank & Langmuir, 1998) and the average upper continental crust (Fig. 1; Taylor & McLennan, 1985). The starting material was produced using a sol–gel method to eliminate problems of sluggish reaction of refractory minerals during experiments. Most major elements and some trace elements (Spandler et al., 2007b) were combined as nitrate solutions and mixed with tetraethyl orthosilicate \([Si(C_2H_5O)_4]\) and slowly dried.
to a gel. From this basic gel, two starting materials were prepared that differ only in their H2O content. For the anhydrous starting material, the gel was combined with appropriate amounts of Al2O3, TiO2 and MnO powders, finely milled and then fused at 1500°C and quenched to glass. Multiple analyses of the glass for major elements (by energy-dispersive spectrometry; EDS) and trace elements (by laser ablation inductively coupled plasma mass spectrometry; LA-ICP-MS) indicate homogeneity within analytical precision. Iron was then added to the glass in the form of synthetic fayalite. The fayalite and glass mixture was ground for 30 min to form a fine powder. For the hydrous starting material, no Al2O3 was added prior to melting. Instead, Al(OH)3, in a quantity sufficient to produce the same amount of Al2O3 as in the anhydrous starting material, was added together with fayalite at the end. This second starting material contains 6–8 wt% H2O. Blending of the hydrous and anhydrous starting materials permitted us to obtain precise but variable H2O contents in the experiments, which provide the basis for determination of melt H2O contents using mass balance. The water content of high-pressure melts increases with decreasing temperature (Hermann, 2003). To maintain 15–25% of hydrous melt in the experiments, which facilitates accurate analysis, it is, therefore, necessary to increase the amount of H2O in the starting material with decreasing temperature (Tables 1 and 2). The final hydrous and anhydrous starting material compositions are presented in Table 2.

**Experimental technique**

Arc-welded gold capsules of 2.3 mm outer diameter containing the starting material were placed in an end-loaded, 127 cm piston-cylinder apparatus using a ‘low-friction’ and ‘dry’ furnace assembly, assembled from Teflon foil, a salt outer sleeve, Pyrex glass, a graphite heater and MgO inserts. Some experiments were also run without the Pyrex glass to test if the glass introduces some friction at low-T, high-P conditions. No systematic difference was observed, indicating that friction was fully released during the long duration of the experiments. In some experiments (labelled ‘a’ in Table 1), two gold capsules with different compositions (one carbonate-bearing) were run in one assembly. Temperature was controlled using type-B thermocouples (Pt94Rh6/Pt70Rh30) and is accurate to ±10°C. Pressure is converted from load and is accurate to 0.1 GPa. For the 4.5 GPa experiments, the assembly was initially held at 700°C, 3.5 GPa, for 2 h to allow the vessels and assembly to compact. In the 4.5 GPa experiments piston travel was monitored throughout the duration of the experiments. Minimal piston travel after 30–40 h indicates that friction has been released. The use of the ‘dry’ furnace assembly, gold capsules and the relatively low temperatures of the runs produces conditions close to the Ni–NiO transition (W. O. Hibberson, personal communication). Hydrogen loss from the glass or alloying of Fe with the gold capsule would potentially yield more oxidized mineral assemblages containing acmite and andradite components in pyroxene and garnet, respectively. Normalization of the experimental run products (see the Electronic Appendix, available for downloading from http://www.petrology.oxfordjournals.org) did not provide evidence for any significant acmite and andradite component, which suggests that no significant hydrogen loss occurred.

**Diamond traps**

For experiments with diamond traps we used 3.5 mm diameter gold capsules that were filled first with 18 mg of 40–60 μm diamonds as a fluid trap, followed by 65 mg of the hydrous starting material containing 6.8 wt% H2O.
The length of the fully loaded capsule was about 7 mm; this was placed in the hotspot of a 30 mm long MgO–graphite–Pyrex–NaCl assembly with the diamond trap located close to the thermocouple. Following each experiment, the gold capsule was pierced and dried to precipitate the remaining solutes in the fluid. In the experiments of Spandler et al. (2007b) performed with an identical starting material, the fluid was analysed for major and trace elements after the experiment. The fluid contained <0.3 wt% Na₂O and <0.05 wt% K₂O. It is expected that the vapour coexisting with such a fluid contained considerably less of these elements. Hence, the major and trace element content of the escaping vapour is at least an order of magnitude lower than that of the fluid phase at the P and T conditions of the experiments and therefore is considered to be negligible. The capsule was then opened at the end containing the diamond trap and the diamond aggregate was extracted. The diamond trap was either powdery (Fig. 2a) or cements together (Fig. 2b). The diamonds and accompanying quench material were subdivided into three fractions taken at different distances from the residue (Tenthorey & Hermann, 2004). Fraction 1 was sampled from the uppermost section of the diamond trap, fraction 2 from the intermediate part and fraction 3 from the part of the diamond trap that was in contact with the petle residue. A small sample of each fraction was mounted on a glass slide and covered by immersion oils. Optical inspection of these samples with a polarized light microscope allowed distinction between isotropic amorphous quench material and anisotropic hydrothermal minerals that formed by solution precipitation reactions during the relatively long experimental runs. Fraction 3 always contained significant amounts of minerals, whereas fraction 2 was dominated by amorphous quench and contained less than 5 vol.% of minerals. Only in the experiment at 2.5 GPa, 600°C, was the overall amount of minerals higher in all fractions. Interestingly, fraction 3 generally contained more precipitated minerals than

Table 1: Experimental conditions and run products

<table>
<thead>
<tr>
<th>Run no.</th>
<th>P (GPa)</th>
<th>T (°C)</th>
<th>hours</th>
<th>wt% H₂O</th>
<th>Phases</th>
</tr>
</thead>
<tbody>
<tr>
<td>C-2098D</td>
<td>2.5</td>
<td>600</td>
<td>168</td>
<td>6.8</td>
<td>Am, Phe, Qtz, Rt, All, Ap</td>
</tr>
<tr>
<td>C-1866a</td>
<td>2.5</td>
<td>700</td>
<td>183</td>
<td>6.6</td>
<td>Am, Phe, Qtz, Rt, All, Ap, Gl?</td>
</tr>
<tr>
<td>C-2099D</td>
<td>2.5</td>
<td>700</td>
<td>168</td>
<td>6.8</td>
<td>Am, Phe, Qtz, Gl, Rt, All, Ap</td>
</tr>
<tr>
<td>C-2246</td>
<td>2.5</td>
<td>750</td>
<td>168</td>
<td>6.8</td>
<td>Am, Phe, Qtz, Phe, Gl, Rt, All, Zir, Ap</td>
</tr>
<tr>
<td>C-1928a</td>
<td>2.5</td>
<td>800</td>
<td>166</td>
<td>6.8</td>
<td>Grt, Am, Qtz, Phe, Gl, Rt, All, Zir, Ap</td>
</tr>
<tr>
<td>C-1857a</td>
<td>3.0</td>
<td>900</td>
<td>190</td>
<td>2.0</td>
<td>Grt, Cpx, Qtz, Kfs, Gl, Rt, Ky, Mon, Zir</td>
</tr>
<tr>
<td>D-48</td>
<td>3.0</td>
<td>850</td>
<td>284</td>
<td>3.4</td>
<td>Cpx, Cae, Phe, Gl, Ap, Rt, Mon</td>
</tr>
<tr>
<td>C-2082D</td>
<td>3.5</td>
<td>600</td>
<td>144</td>
<td>6.8</td>
<td>Ctd, Cpx, Cae, Phe, Q, Ap, Rt, All, graph</td>
</tr>
<tr>
<td>C-1857a</td>
<td>3.5</td>
<td>700</td>
<td>163</td>
<td>6.6</td>
<td>Cpx, Cae, Phe, Q, Ky, Rt, All, Ap</td>
</tr>
<tr>
<td>C-2083D</td>
<td>3.5</td>
<td>700</td>
<td>144</td>
<td>6.8</td>
<td>Ctx, Cpx, Cae, Phe, Q, Ap, Rt, All, Zir</td>
</tr>
<tr>
<td>C-2247a</td>
<td>3.5</td>
<td>750</td>
<td>168</td>
<td>6.8</td>
<td>Cpx, Cae, Phe, Gl, Ap, Rt, All, Mon, Zir</td>
</tr>
<tr>
<td>C-1848a</td>
<td>3.5</td>
<td>800</td>
<td>168</td>
<td>6.8</td>
<td>Cpx, Cae, Phe, Gl, Phe, Ky, Ap, Rt, Mon, Zir</td>
</tr>
<tr>
<td>C-1872a</td>
<td>3.5</td>
<td>900</td>
<td>164</td>
<td>6.1</td>
<td>Cpx, Cae, Gl, Phe, Ky, Ap, Rt, Mon, Zir</td>
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<tr>
<td>C-1699a</td>
<td>3.5</td>
<td>900</td>
<td>260</td>
<td>3.1</td>
<td>Cpx, Cae, Gl, Phe, Ky, Ap, Rt, Mon</td>
</tr>
<tr>
<td>C-1867a</td>
<td>3.5</td>
<td>950</td>
<td>170</td>
<td>2.0</td>
<td>Cpx, Cae, Gl, Phe, Ky, Ap, Rt, Mon</td>
</tr>
<tr>
<td>C-2077D</td>
<td>4.5</td>
<td>700</td>
<td>168</td>
<td>6.8</td>
<td>Cpx, Cae, Phe, Q, Ky, Ap, Rt, All</td>
</tr>
<tr>
<td>C-2500a</td>
<td>4.5</td>
<td>750</td>
<td>144</td>
<td>6.8</td>
<td>Cpx, Cae, Phe, Q, Rt, All, Ap</td>
</tr>
<tr>
<td>C-2506a</td>
<td>4.5</td>
<td>800</td>
<td>120</td>
<td>6.8</td>
<td>Cpx, Cae, Phe, Q, Ap, Rt, Mon, Zir</td>
</tr>
<tr>
<td>C-1872a</td>
<td>4.5</td>
<td>800</td>
<td>162</td>
<td>6.8</td>
<td>Cpx, Cae, Phe, Gl, Ky, Ap, Rt, Mon, Zir</td>
</tr>
<tr>
<td>C-1614a</td>
<td>4.5</td>
<td>900</td>
<td>75</td>
<td>6.8</td>
<td>Cpx, Cae, Phe, Gl, Ky, Ap, Rt, Mon, Zir</td>
</tr>
<tr>
<td>C-1563a</td>
<td>4.5</td>
<td>1000</td>
<td>138</td>
<td>2.8</td>
<td>Cpx, Cae, Gl, Phe, Ky, Rt, Mon, Zir</td>
</tr>
<tr>
<td>C-1868a</td>
<td>4.5</td>
<td>1050</td>
<td>120</td>
<td>2.0</td>
<td>Cpx, Cae, Gl, Ky, Rt, Ap</td>
</tr>
</tbody>
</table>

Phases in bold have a modal abundance of >5%, phases in regular font have a modal abundance between 5 and 1%, and phases in italics are accessory phases. Experiments with suffix ‘a’ were run in assemblies containing two capsules; suffix ‘D’ indicates experiments with a diamond trap. Am, amphibole; Phe, phengite; Qtz, quartz; Coe, coesite; Grt, garnet; Bt, biotite; Gl, glass; graph, graphite; Kfs, K-feldspar; Ctd, chloritoid; Cpx, clinopyroxene; Ky, kyanite; Rt, rutile; All, allanite; Ap, apatite; Mon, monazite; Q, quench material from fluid; Zir, zircon.

Experiments where no Pyrex sleeve was used.
fraction 2, indicating that the fluid in the diamond trap was circulating through the pelite residue to some extent. This observation also shows that special care needs to be taken to obtain meaningful data from diamond traps. The three fractions of the diamond trap were then mounted on sticky carbon tape and the residue was sectioned longitudinally and mounted in epoxy. Both the sectioned residue and the diamond trap material were then examined in detail with a JEOL 6400 scanning electron microscope (SEM) equipped with EDS. The main minerals precipitated in the trap were quartz and phengite although minor amounts of omphacite were also observed. All analytical results presented in this paper derive from fraction 2, which contained nearly pure amorphous quench.

### Analytical techniques

The phase relations were obtained from detailed studies of backscattered electron (BSE) images. Mineral compositions were mainly determined using a JEOL 6400 SEM (Electron Microscopy Unit, ANU) with EDS operating at 15 kV and a focused beam of 1 nA. At such low beam current, no alkali loss occurs in phengite (Hermann & Green, 2001). Also, because of the high resolution, mixed analyses can be avoided. Garnets were also analysed by wavelength-dispersive spectrometry (WDS) for major elements and, in particular, for accurate determination of the minor elements P, Na, Ti and Mn. The WDS analyses were conducted using a Cameca SX-100 electron microprobe at the RSES, ANU, operating at 15 kV and a beam current of 20 nA. The comparison of major element concentrations between the SEM EDS and the electron microprobe WDS analyses showed excellent agreement. Major-element melt compositions were also analysed by EDS by scanning glass pools over an area of 5 µm × 10 µm. The scanning and the low beam current prevent destruction of the volatile-rich glass and permit accurate determination of the alkali elements (Hermann & Green, 2001).

Material from the diamond trap, mounted on carbon tape, was analysed for major and trace elements by
LA-ICP-MS at the Research School of Earth Sciences (ANU) using a pulsed 193 nm ArF Excimer laser with 100 mJ output energy at a repetition rate of 5 Hz (Eggins et al., 1998) coupled to an Agilent 7500 quadrupole ICP-MS system. Laser sampling was performed in a He–Ar atmosphere. Data acquisition was performed by peak hopping in pulse counting mode, acquiring intensity data for each element during each mass spectrometer sweep. The sample stage was driven by a step motor, allowing continuous analysis along scans through the mounted material. Four scans per fraction were run using a spot size of 112 μm diameter with 25 sweeps of background followed by 80–100 sweeps of data collection. A synthetic glass (NIST 612) was used as external standard; reference values were taken from Pearce et al. (1997). Experiments were also doped with Cs in the hope of using this element as an internal standard as previously done in ultramafic (Tenthorey & Hermann, 2004) and K-free mafic systems (Kessel et al., 2005b). However, the residual phengite in the experiments retained the great majority of the Cs and thus this technique did not provide satisfactory results. Because no reliable internal standard is available for the aqueous fluids absolute solubilities could not be directly determined. However, element ratios can be accurately determined with this method.

RESULTS
Phase relations
Phase relations were examined in detail by SEM (Fig. 2) and results are summarized in Table 1 and Fig. 3. In runs where glass is present experimental mineral phases are
well crystallized and euhedral. The mineral grain sizes are in the range 20–100 μm for garnet and some coesite, 10–20 μm for other major and minor phases, and <10 μm for accessory phases. In experiments where hydrous quench was present, the phases had significantly smaller grain sizes and were more difficult to analyse.

**Solid phases**

At 2.5 GPa phase relations are complex with the phase assemblage changing over small temperature intervals. The assemblage is dominated by hydrous phases. At 600°C amphibole, phengite and quartz are the major phases and they coexist up to at least 800°C. Biotite and garnet appear at 750°C (Fig. 2c). At 900°C K-feldspar and clinopyroxene appear at the expense of phengite and amphibole, respectively, whereas biotite is still stable (Fig. 3). At the higher investigated pressures, phase relations are simpler. The assemblage garnet, clinopyroxene, coesite, phengite and minor kyanite is stable over nearly the entire range of investigated $P$–$T$ conditions (Fig. 2f, h and i). Only at 700°C, 3.5 GPa, is chloritoid present instead of garnet. Phengite is stable up to 950°C at 3.5 GPa (Fig. 2f) and breaks down between 1000°C and 1050°C at 4.5 GPa (Fig. 2i). Kyanite is a minor phase in almost all experiments.

Rutile is the stable accessory Ti phase over the entire investigated $P$–$T$ range. Apatite is also found in all experimental charges. Allanite is present at 2.5 GPa up to 800°C (Fig. 2c), and at 3.5 and 4.5 GPa up to 750°C. At higher temperatures monazite is stable up to 1000°C. Only at the highest conditions of 4.5 GPa, 1050°C was monazite not found. Zircon grains are very small and difficult to detect, but zircon has been observed in nearly all experiments. It is definitely present up to 900°C at 2.5 and 3.5 GPa and up to 1000°C, 4.5 GPa (Fig. 2i).

**Fluid phases**

The water added to the experiments always exceeded the capacity of the hydrous phases to store $H_2O$, resulting in the presence of a fluid phase in all experiments. At the higher investigated temperatures this fluid phase quenched to a hydrous glass, which indicates that a hydrous melt was present. The added water content was always lower than that required to obtain vapour-saturated melting for the given pressure range (Huang & Wyllie, 1981), and thus the experiments constrain fluid-present, vapour undersaturated melting in subducted sediments. No mineral quench phases have been observed within experimentally produced glass.

At 2.5 GPa, clean bubble-free glass was observed down to temperatures of 750°C (Fig. 2c). In experiment C-1866 at 700°C, 2.5 GPa no glass pools were observed. However, the experimental phases were well cemented together, as was generally observed in charges where glass is present.

In a repeat experiment, a diamond trap was added to the starting material (C-2099D) to facilitate separation of fluid from solid phases. After opening the capsule, the diamond trap could be extracted as a coherent block. Inspection of the diamond trap under the SEM revealed that the diamonds were cemented together by a hydrous glass (Fig. 2b). In contrast, at 600°C, 2.5 GPa, the diamond trap after the experiment was powdery and appeared very different under the SEM (Fig. 2a). A very fine hydrous quench powder, which is not stable under the electron beam, was found. These observations indicate that at 600°C a solute-rich aqueous fluid was present, whereas at 700°C there was a hydrous melt.

At 3.5 GPa hydrous glass is present in experiments down to temperatures of 750°C (Fig. 2d). At 900 and 950°C the glass is bubble free, whereas at 800 and 750°C bubbles are abundant in the glass (Fig. 2c). At 700°C (C-1857) fine-grained minerals were observed, the grains were loose and significant porosity was present in the charge, indicative of an aqueous fluid during the run. To further test this hypothesis, a diamond trap experiment was run at the same conditions (C-2083D). The diamond trap showed the same characteristics as observed at 600°C, 2.5 GPa, indicating the presence of an aqueous fluid. At 600°C, 3.5 GPa the diamond trap again contained fine-grained, amorphous hydrous quench material.

At 4.5 GPa a hydrous glass was observed from 1050°C down to 800°C. The glass in the 1050 and 1000°C runs is bubble free. A small amount of bubbles appears in the 900°C experiment and a significant amount of bubbles
is present in the 800°C experiment (Fig. 2h). This suggests that some aqueous fluid exsolved during quenching from a melt that contained high water contents. In a second experiment at 800°C (C-2596), no glass pools were found. This might be related to the fact that the first experiment was run with two capsules, which produced a slight hot-spot, in which the melt pooled. At 750°C the run products were fine-grained and the charge was not well cemented. A Si-rich hydrous quench was observed in pores between mineral phases. The experiment at 700°C contained a diamond trap and the residual minerals were generally fine grained and not well cemented (Fig. 2g). Examination of the trap after the experiment revealed the presence of a powdery, amorphous quench material, similar to runs 2099D and C-2083D. From all these observations we suggest that the transition from quenchable hydrous glass to non-quenchable solute-rich fluid occurs at ~800°C at 4-5 GPa.

**Phase compositions**

The average composition of all analysed phases in the experiments is given in the Electronic Appendix (http://www.petrology.oxfordjournals.org).

**Garnet**

Large idiomorphic garnet is generally slightly zoned. The cores are characterized by high TiO₂ contents (often ≥1 wt%) and by slightly higher MnO and CaO contents, whereas the MgO content is generally lower than in the rim. The following discussion is based on rim compositions, which are interpreted to be in textural equilibrium with the other phases. The most prominent feature in garnet is the increase of pyrope content with increasing temperature (Fig. 4a). Grossular contents decrease slightly with increasing pressure (C-25 and 3 GPa; C-3.5 GPa; C-4.5 GPa). (b) Variation of Na and P (in cations per formula unit) in garnet from all experiments. At low temperature (700-800°C) the data plot on a 1:1 line. At higher temperatures there is more Na than P. Error bars refer to 1σ standard deviation of multiple analyses.

**Clinopyroxene**

Clinopyroxene generally forms small grains that are difficult to analyse. It often exhibits zoning in FeO, with higher contents in the core than in the rim. Because of the small grain size it has not always been possible to analyse...
The average analyses presented in the Electronic Appendix are based preferentially on rim compositions. Clinopyroxene is omphacitic in composition in all experiments. The jadeite component strongly increases with increasing pressure and reaches a maximum of 74% at 700°C, 4.5 GPa (Fig. 5a). At 3.5 GPa the jadeite content is nearly constant over the entire investigated temperature range. In contrast, at 4.5 GPa the jadeite content decreases significantly from 700 to 1050°C (Fig. 5a). TiO₂ content ranges from 0.1 to 0.6 wt% and generally increases with increasing temperature and decreases with increasing pressure. In some omphacite grains K₂O was detected when analysed by WDS; however, the rather large variation indicated that the analyses were affected by contamination from neighbouring phengite. In fact, when omphacite was analysed by SEM using a finer beam and a lower beam current, K₂O was always below the detection limit of ~0.2 wt%. All omphacite analyses exhibit Al > Na (p.f.u.). Therefore, no ferric iron is required to charge balance Na. The excess Al, which is not bound in a jadeite (NaAlSi₂O₆) or a Ca-Tschermak’s (CaAl₂SiO₆) component, provides evidence for the presence of a Ca-eskolaite component (CaO·Al₂SiO₅(OH)₂) in the omphacite. Because Ca-eskolaite contains a vacancy, it is expected that the sum of the cations should decrease with increasing Ca-eskolaite component. Figure 5b displays the correlation between excess Al and the sum of cations in relation to the theoretically expected line. The good agreement provides evidence that the experimentally produced omphacite contained up to 15% eskolaite component. The Ca-eskolaite component increases mainly as function of increasing temperature and does not change systematically with pressure. This is in good agreement with a recent comprehensive experimental study of Konzett et al. (2007), who reported that the Ca-eskolaite component in the assemblage clinopyroxene–garnet–coesite–rutile increases with increasing temperature, but that no significant increase with pressure can be observed.

Phengite

Phengite grains are relatively large and easy to analyse. We preferred to analyse phengite by EDS using a low beam current and, where possible, a rastered beam. Under such analytical conditions, no K loss during the analysis occurred. Phengite displays a systematic change in the celadonite component [KAlMgSi₄O₁₀(OH)₂] with changing conditions. The Si content (p.f.u) increases with increasing pressure and decreasing temperature (Fig. 6a). An interesting feature is the systematic change in TiO₂ content. The highest TiO₂ content of 2 wt% has been measured at 1000°C, 4.5 GPa. Overall, TiO₂ increases strongly with increasing temperature and decreases slightly with increasing pressure (Fig. 6b). Na₂O was detected in all phengites and the paragonite component reaches 19% at the lowest pressure investigated. At higher pressure the paragonite component is typically between 4 and 8%. All phengites contain Mg + Fe > Si – 3, indicating that there is a biotite component present, as previously observed by Green & Hellman (1982). This biotite component is highest when phengite coexists with biotite (i.e. at 2.5 GPa) and at this pressure it increases with increasing temperature to reach more than 30% at 800°C, 2.5 GPa. Incorporation of Ti presumably on the octahedral site of phengite could either be charge balanced by substitution of Al for Si on the tetrahedral site or by a coupled substitution M²⁺TiAl⁻₂ on the octahedral site. The first

Fig. 5. (a) Na per formula unit in clinopyroxene as a function of temperature and pressure. (b) Excess Al (Al neither bound in a jadeite nor Ca-tschermakite component) vs cation sum indicates the presence of a Ca-eskolaite component in clinopyroxene. Error bars refer to 1σ standard deviation of multiple analyses. Symbols as in Fig. 4.
substitution produces phengite with a higher Al content, whereas the second substitution produces phengite with an Al content that is lower than would be expected for the celadonite and biotite substitution alone. We observe an Al deficit in all Ti-rich phengites, which indicates that Ti is dominantly incorporated by the M2TiAl/C02 substitution.

Other minerals

Only three runs at 2.5 GPa contained biotite. The TiO2 content of biotite increases from 2 wt% at 750°C to 4 wt% at 900°C, whereas the FeO content significantly decreases over the same temperature interval. All biotites contain about 0.5 wt% Na2O and are characterized by high Si content (p.f.u.) of 3.0. Four runs at 2.5 GPa contained sodic–calcic amphibole. With increasing temperature from 600 to 800°C, the Na2O, SiO2 and FeO contents decrease, whereas the TiO2, K2O and Al2O3 contents increase. The NaM4 (when normalized to 23 oxygens) decreases from 0.98 p.f.u. (600°C) to 0.56 p.f.u. (800°C), the NaA is approximately constant at 0.33 p.f.u., whereas the Al[T] increases from 1 to 1.5 p.f.u. Only one run at 900°C, 2.5 GPa contained K-feldspar with the composition Or58Ab39An3. The K-feldspar also contains detectable amounts of FeO (0.25 wt%).

Hydrous glass (quenched melt compositions)

Table 2 presents the glass analyses normalized to 100% on an anhydrous basis, whereas the Electronic Appendix contains the originally measured element concentration data. All normalized melt compositions are broadly granitic with SiO2 contents between 69 and 75 wt% and Al2O3 contents from 12 to 17 wt%. K2O and Na2O vary strongly as a function of temperature. Na2O decreases from about 7 wt% to 2.3 wt% from 750 to 1050°C. K2O is buffered in the melt by coexisting phengite up to temperatures of 1000°C at 4.5 GPa and increases from 2.6 wt% at 750°C to 10 wt% at 1050°C (Fig. 7a). Consequently, the K2O/Na2O ratio varies over about an order of magnitude (Fig. 7b). Melt compositions have low anorthite components and trend from trondhjemitic to granitic compositions with increasing temperature (Fig. 7c). Low-temperature melts are typically peralkaline (Table 2), whereas only one melt composition determined at 900°C, 2.5 GPa is clearly peraluminous. The low totals of the glass provide evidence that there is a significant amount of H2O dissolved in the melt, in agreement with the occurrence of bubbles in the glass. Mass-balance calculations using the known starting material composition and the compositions of all phases in the runs (Electronic Appendix) allowed determination of the amount of melt in each experiment (Table 2). From the known amount of water in the starting material of each experiment (Table 1) and the amount of OH stored in hydrous phases (determined by mass balance), the H2O content of the melt could also be calculated. The principal source of error in this approach derives from the amount of melt determined from mass balance, and this error can be significant, especially at very low melt fractions. Our experiments were designed to produce relatively high amounts (>20%) of melt in each experiment, which results in estimated uncertainties in the H2O content of the melt of 10–15% relative at the lower melt fractions and of 5–10% relative at the higher melt fractions. Figure 7d shows the H2O content of the melt as a function of pressure and temperature. The resulting H2O isopleths are characterized by
Fig. 7. (a) The $K_2O$ content of melt is buffered by phengite in most experiments and increases systematically with increasing temperature. Pressure has no significant influence on the $K_2O$ of the melt. (b) The ratio of $K_2O$ to $Na_2O$ increases over an order of magnitude from 600 to 850°C. The significant difference between hydrous melts and aqueous fluids should be noted. (c) The aqueous fluid and the low-temperature melts are albite-rich, whereas the high-temperature melts are orthoclase-rich. All fluids are poor in anorthite component. Classification of silicic melts after Barker (1979). (d) Estimated water contents of hydrous melts in the experimental runs as a function of $P$ and $T$ and schematic contours of wt% $H_2O$ in the melt. The numbers in parentheses represent rough estimates of the wt% $H_2O$ of the aqueous fluid. The wet solidus is defined up to 3.5 GPa. Aqueous fluid and hydrous melt display distinctly different $SiO_2/Al_2O_3$ (e) and $Na_2O/Al_2O_3$ ratios (f).
Table 3: Composition of quench material in fraction 2 of the diamond traps determined by LA-ICP-MS

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<th>2082</th>
<th>2083</th>
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</table>

Analyses are normalized to 100% anhydrous. The water content of experiment 2099 has been determined by mass balance. Other water contents are rough estimates based on published total solubilities in similar systems (see text for discussion). Other entities are as defined in Table 2.

a modest positive slope of 8°C/kbar. The highest amount of ~30 wt% H₂O was determined for the experiment at 800°C, 4.5 GPa. Fluids with higher amount of H₂O were not quenchable.

Diamond traps
To constrain the composition of the non-quenchable fluid phase, some experiments were run with diamond traps. Fraction 2 of the diamond traps contained more than 95% precipitates formed from the fluid during quenching. Therefore, this fraction was analysed by LA-ICP-MS to provide major element ratios in the quench material. The total sum of the major elements was then normalized to 100% (Table 3). Experiment 2099 provides a good test for the applied method. Detailed textural investigations showed that this trap contains hydrous melt rather than an aqueous fluid (Fig. 2b). The normalized values display all the characteristics of hydrous melts similar to the compositions reported in Table 2 and the data obtained plot along the trends established from where the melt pools have been directly measured. The quench materials in the other four low-temperature experiments have a significantly different major element composition from the hydrous melts, and are interpreted to represent quench from aqueous fluids. Whereas the SiO₂/Al₂O₃ value varies in a very limited range (4–6) in the hydrous melt, the aqueous fluids are characterized by much higher values (7–34; Fig. 7c). The aqueous fluid is also characterized by very high Na₂O and low K₂O contents, resulting in K₂O/Na₂O values that are much lower than those of the hydrous melts, but still consistent with the general temperature trend of this ratio (Fig. 7b). The relatively high Na₂O in conjunction with low Al₂O₃ makes the aqueous fluids strongly peralkaline. Therefore, Na₂O/Al₂O₃ is another effective ratio for distinguishing between aqueous and hydrous melt compositions (Fig. 7f). Similar element ratios were reported for hydrous fluids trapped as synthetic fluid inclusions equilibrated at 2.2 GPa and 600–650°C by Spandler et al. (2007b); these results further support the validity of using these chemical criteria for distinguishing aqueous fluids from hydrous melt.

Element partitioning
The compositions of solid and fluid phases (Electronic Appendix) permit determination of the partitioning of major and minor elements among the phases present. Omphacite always contains higher Na than coexisting hydrous melts at all conditions investigated. The D⁹⁸Na corresponds with pressure as well as with temperature from ~1.5 at 750°C, 3.5 GPa to ~4.5 at 1050°C, 4.5 GPa (Fig. 8a). Interestingly, in the two experiments where amphibole is present, Na is close to unity at 1000°C, 4.5 GPa. Ti is a minor element that can be detected in all major phases. The general affinity for Na incorporation is omphacite > melt > amphibole > phengite > biotite > garnet. Because Na in garnet increases and Na in phengite decreases with increasing pressure and temperature, D⁹⁸Na is close to unity at 1000°C, 4.5 GPa. Ti is a minor element that can be detected in all major phases. The general affinity for TiO₂ incorporation is biotite > phengite > amphibole > garnet > melt > omphacite. The Fe and Mg partitioning of coexisting minerals is best illustrated using X_Mg = Mg/(Mg + Fe), which decreases in the following way: biotite > phengite > amphibole > melt > garnet. Amphibole and omphacite have not been observed in the same run and the relative position is inferred from phengite–omphacite–melt and from phengite–amphibole–melt partitioning. An interesting observation concerns the X_Mg in coexisting garnet and melt. Generally the X_Mg in the melt is higher than in garnet. However, at 950°C, 3.5 GPa and at 1000°C, 1050°C at 4.5 GPa, X_Mg of garnet is higher than in the melt. Such an inversion in the X_Mg is in excellent agreement with previous studies. Rubber & Hermann (2007) found in an experimental study at 2 GPa that garnet has a lower X_Mg than the melt up to 950°C, at 950°C it is identical, and at 1000°C garnet has a higher X_Mg than the melt. Moreover, previous experiments by Green (1977) and Ellis (1986) showed that melts have a higher X_Mg than garnet below 1000°C at 3.0 GPa.
MELTING OF SUBDUCTED PELITES

It has long been known that the $K_D$ of the Fe–Mg exchange in minerals is very sensitive to temperature (Ellis & Green, 1979; Green & Hellman, 1982). Figure 8b shows the variation of the Fe–Mg partitioning between garnet and phengite as a function of inverse temperature at 4.5 GPa. Data from lower pressure experiments have larger errors, so for simplicity these data are not plotted in the figure. Three important observations can be made from examination of the plot: (1) there is a clear trend in $\ln K_D$ with inverse temperature; (2) this trend is in very good agreement with the formulated thermometer of Green & Hellman (1982); (3) the propagated errors of the variability in analyses are rather large. Although there is also a general trend in garnet–clinopyroxene partitioning with inverse temperature, the large error in determining the FeO content in clinopyroxene because of zoning prevents a sensible test of garnet–clinopyroxene thermometers with the existing dataset.

**DISCUSSION**

The results of this experimental study provide information on two main aspects of research on the behaviour of deeply subducted sediments. The first part of the discussion addresses issues related to the use of ultrahigh-pressure (UHP) rocks as a natural laboratory for subduction processes. The second part focuses on the phase and melting relations in subducted sediments and how the nature and composition of the fluid phase determines the way these elements are recycled in the subduction factory.

**UHP indicators in mineral compositions**

It is not always easy to distinguish between minerals that formed at UHP conditions and minerals that formed or equilibrated during retrograde evolution. Most UHP rocks occur within subducted continental crust. Hence, detailed phase compositions in a pelitic starting material are useful to evaluate whether or not there are clear compositional signatures that can indicate a UHP origin of crustal rocks. Generally UHP conditions are deduced from the presence of coesite and/or diamond. In this section we compare the major and minor element composition of the main phases garnet and phengite in the experiments with data from UHP rocks as well as from deep-seated xenoliths to provide some constraints on possible UHP indicators in rock-forming minerals.

**Garnet**

The experimental garnets are characterized by high Na, Ti and P. At temperatures of 700–800°C the exchange NaPM$^{2+}$Si$^{-1}$ seems dominant for the incorporation of P and Na. This exchange has been experimentally confirmed and a complete solid solution series has been documented at very high pressures (15–17 GPa) and high temperatures (Brunet et al., 2006). In our experiments at temperatures higher than 800°C, a second substitution linked to Ti such as NaTi$^{4+}$M$^{2+}$Al$^{-1}$ is proposed to accommodate Na in excess of P. This substitution was first documented experimentally by Ringwood & Major (1971) at 5 GPa. Those workers also produced experimental garnets at 3.5 GPa and 1200°C with significant amounts of Na and Ti. Our results are in agreement with the conclusion of
Ringwood & Major (1971) that, in the presence of Ti, Na can enter garnet at relatively modest pressures. Previous experiments in the pressure range of 2.0–3.5 GPa in natural compositions suggested that Na, P and Ti are incorporated into garnet. Thompson (1975) conducted anhydrous melting experiments in basaltic compositions and found up to 0.4 wt% Na2O, 0.6 wt% P2O5 and up to 3 wt% of TiO2 in garnet. Auzanneau et al. (2006) investigated phase relations in a hydrous metagreywacke and reported garnet compositions with significant amounts of TiO2 (~1 wt%) and 0.1–0.3 wt% of Na2O in runs at 2.2–2.4 GPa, 800–900°C. In experiments on a natural tonalite composition, Patinœ o Douce (2005) found garnets with Na2O ~0.1 wt% and TiO2 >1 wt%, even at 15 GPa, 950°C.

Garnet grains in UHP rocks occasionally display exsolution of Ti-, Na- and P-rich phases, indicating that there was a P- and Ti-rich garnet precursor. Ye et al. (2000) found such garnets in the Sulu UHP belts of China, and Mposkos & Kostopoulos (2001) described similar garnet from the Rhodope UHP belt in Greece. By integrating the inclusions in garnet Ye et al. (2000) obtained 0.34 wt% Na2O, 0.28 wt% P2O5 and 147 wt% TiO2, and Mposkos & Kostopoulos (2001) obtained similar values of 0.6 wt% Na2O, 0.33 wt% P2O5 and 1.03 wt% TiO2. These values were used by both groups to postulate that the rocks originated from more than 200 km depth. However, the concentrations of these elements are very similar to what we find in garnet at 3.5–4.5 GPa (300–150 km equivalent depth), indicating that such compositions are not unequivocal proof of an ultra-deep origin of subducted crust.

According to our experiments and literature data, garnets with high Ti, Na and P should be the rule and not the exception in UHP terrains. However, it is interesting to note that most reported garnet analyses from UHP rocks display rather low concentrations of these minor elements. For example, garnet from diamond-bearing meta-granitic to meta-pelitic rocks from the Kokchetav massif and the Erzgebirge generally has TiO2 <0.25 wt% and Na2O <0.1 wt% (Zhang et al., 1997; Massonne, 2003; Massonne & Nasdala, 2003). Only in some rare garnets from eclogites did Zhang et al. (1997) find some elevated TiO2 contents of 0.34 wt% and Na2O of 0.14 wt%. However, all these values are significantly lower than what is expected based on our experiments, given the diamond-facies metamorphic conditions of these rocks (T = 950–1000°C, P ≥4.5 GPa). This inconsistency between garnet compositions from experiments and natural UHP garnet compositions provides evidence that element re-equilibration occurred during exhumation. Such re-equilibration for P and Ti has been documented in UHP mafic rocks from the Northern Dabie Complex (Malaspina et al., 2005). It is expected that garnet grains in crustal xenoliths are less affected by such retrograde modification. Although available literature data are restricted to mafic UHP xenoliths in which the buffering of P and Ti is not always clear, there is convincing evidence that garnet from such rocks contains much higher Na, P and Ti than is generally observed in UHP rocks of similar composition and metamorphic grade. For example, Sobolev & Lavren’ev (1971) observed that Na2O contents of 0.1–0.22 wt% are common in eclogitic garnet from diamond-bearing rocks, whereas 0.01–0.02 wt% Na2O is generally present in garnet from UHP eclogite-facies rocks. Bishop et al. (1978) reported garnet compositions from eclogite xenoliths with up to 0.1 wt% P2O5, 0.14 wt% Na2O and 0.8 wt% TiO2.

In summary, there is clear evidence that garnet formed in subducted metapelitic rocks contains significant amounts of Na2O, P2O5 and TiO2. The much lower content of these elements in garnet from UHP felsic rocks indicates that, in most cases, garnet is not able to retain its original UHP chemical signature in such slowly cooling rocks. Garnet is one of the most important phases for thermobarometry. Therefore, the application of thermobarometers using garnet in relatively slowly cooled UHP rocks should be done with care, as in some cases these thermobarometers may be unable to provide meaningful constraints on peak metamorphic conditions.

**Phengite**

The Si content of phengite increases strongly with increasing pressure but depends also on the buffering mineral paragenesis, as has been demonstrated in several earlier studies (Massonne & Schreyer, 1987; Massonne & Szpurzka, 1997; Hermann, 2002). The Si content of phengite must therefore be used in conjunction with the compositions of coexisting phases to estimate pressure. The most interesting observation on experimental phengite is the systematic change in TiO2 content when buffered with rutile and quartz-coesite, a feature that has not been described before. The TiO2 content increases strongly with increasing temperature and decreases moderately with increasing pressure (Fig. 6b), and provides a useful semi-quantitative tool to evaluate whether or not phengite compositions record peak conditions or equilibrated during exhumation. For example, Meyre et al. (1999) reported phengite containing 0.5–6 wt% TiO2 from high-pressure pelites that experienced peak conditions of T ~650°C, P ~2.5 GPa. This is in very good agreement with the experimental values of 0.59 wt% TiO2 (600°C, 2.5 GPa) and 0.63 wt% TiO2 (700°C, 2.5 GPa). Phengite in metapelites of the Dora-Maira massif (peak conditions T ~730°C, P ~4 GPa) have ~0.4 wt% TiO2 (Hermann, 2003), in good agreement with the measured 0.42 wt% TiO2 in the experiment at 750°C, 4.5 GPa. Phengite-bearing eclogites of the Erzgebirge equilibrated at significantly higher temperatures of ~850°C with less precise pressure estimates of ~3.5 GPa (Schmadicke &
These phengites contain 14–15 wt% TiO$_2$, which again is consistent with our experimental results (Fig. 6b). Even higher TiO$_2$ contents in phengite of 175–204 wt% have been described from UHP metapelites of the Greenland Caledonides, for which peak metamorphic conditions of ~970°C and 3-6 GPa have been proposed (Lang & Gilotti, 2007). This is in very good agreement with the TiO$_2$ content of 19 wt% determined in an experiment at 950°C, 3-5 GPa. Because phengite breaks down at significantly lower temperatures of 700–750°C at crustal pressure (Vielzeuf & Holloway, 1988) than at UHP conditions (Fig. 3), phengite with such very high TiO$_2$ contents might be used as an indicator for UHP conditions. For phengites that do not contain a major biotite component (<20%), TiO$_2$ contents of >2 wt% seem to be stable only at pressures >3 GPa (i.e. at UHP conditions). In fact, such phengite has been observed as inclusions in zircon from the diamond-bearing gneisses of the Kokchetav massif (2-7 wt% TiO$_2$; Hermann et al., 2001) and as inclusions in garnet from the Erzgebirge (3-3 wt% TiO$_2$; Massonne & Nasdala, 2003). These first results are promising; however, clearly more experimental data are needed to fully understand and quantify the TiO$_2$ incorporation in phengite as a function of pressure, temperature, bulk-rock composition and buffer paragenesis.

### Implications for garnet–clinopyroxene–phengite barometry

Although the composition of single minerals, as discussed above, can give some insights into the conditions of potential UHP metamorphism, the most complete approach is to obtain pressure information by combining the composition of garnet, clinopyroxene and phengite. The compositions of these three phases are related through the fluid-absent, pressure-sensitive equilibrium

\[
6 \text{ diopside}_{cpx} + 3 \text{ muscovite}_{phe} = 2 \text{ grossular}_{grt} + 1 \text{ pyrope}_{grt} + 3 \text{ celadonite}_{phe}. \tag{1}
\]

The large stability field of garnet–phengite–clinopyroxene in a great variety of subducted crustal rocks makes this assemblage ideal for determination of pressure in UHP terrains (Carswell et al., 1997; Krogh Ravna & Terry, 2004). In the following discussion we compare the calculated pressure at the nominal run temperature from phase compositions in experiments using the recently formulated garnet–phengite–clinopyroxene barometer of Krogh Ravna & Terry (2004) with the nominal pressure of the experimental runs (Fig. 8c). This barometer has been calibrated empirically and has so far not been tested by experiments. The calibration uncertainty at 3.5–4.5 GPa is ~10%, as indicated by the grey band in Fig. 8c. For most of the runs the pressure obtained from the barometer is within this grey band, indicating that it can be successfully used to identify UHP rocks. However, there is a clear trend in the data at 3.5 and 4.5 GPa, showing that the barometer is probably underestimating pressures at the low-temperature end (i.e. 700°C) and overestimating the pressures at the high-temperature end (i.e. T ≥950°C).

### Pelite phase relations at sub-arc depths

The experiments of this study on a pelitic starting material document an important change in phase relations from fore-arc to sub-arc depth. There are complex phase relations in subducted sediments that involve a variety of hydrous phases at P <2.7 GPa (Patino Douce & McCarthy, 1998; Hermann, 2002b; Poli & Schmidt, 2002; Auzanneau et al., 2006). In our experiment this is manifested by the presence of amphibole, phengite and biotite at 2.5 GPa. Amphibole is stable only in runs at 2.5 GPa and below 900°C, as has also been found in experimental studies on mafic hydrous systems (e.g. Liu et al., 1996; Poli & Schmidt, 2002). In contrast, the lack of garnet at 600 and 700°C, 2.5 GPa and at 600°C, 3.5-GPa is not consistent with natural phase assemblages or thermodynamic grids of high-pressure, low-temperature metapelites (Yardley, 1989; Powell & Holland, 1990) or other experimental studies. Experiments on pelitic compositions at 2–3 GPa by Nichols et al. (1994) produced garnet as part of the solid assemblage at temperatures down to 600°C. Spandler et al. (2007b), using the same starting compositions as used here, formed garnet in runs down to 600°C at 2.2 GPa. It should be noted, however, that in the experiments of Spandler et al. (2007b), garnet growth at subsolidus run conditions was achieved only by adding pyrope seeds to circumvent the sluggish nucleation of new garnet grains. Therefore, we expect that the lack of garnet in the lowest temperature experiments reported here is an artefact of sluggish nucleation of garnet at these conditions.

With increasing pressure from 2.5 GPa amphibole transforms to clinopyroxene and biotite reacts to form phengite. The transition from biotite-bearing to phengite-bearing parageneses has been investigated in detail by Auzanneau et al. (2006) in a greywacke bulk composition. They found that biotite disappears at 2–3–2.5 GPa at 800–900°C. At higher pressure, the paragenesis garnet + clinopyroxene + phengite + coesite ± kyanite is stable over a large P–T range (Fig. 9). Interestingly, this paragenesis is stable not only in metapelites but also in greywacke and K-bearing MORB (Schmidt et al., 2004). This confirms that at sub-arc depths phengite will be the stable K phase in subducted crust. Within this dominant sub-arc paragenesis, a fluid-present melting reaction can be postulated based on the observed proportions and compositions of phases. Especially useful are those experiments in which the P–T conditions are constant, but the added water content changes. At 900°C, 3–5 GPa we performed two experiments with 6–8 and 3–1 wt% H$_2$O added. Based on mass balance using the compositions given in the Electronic Appendix,
a significant decrease in the abundance of clinopyroxene, phengite and, to a lesser extent, coesite has been observed in the experiment with the higher water content, whereas there is a strong increase in the amount of melt and a smaller increase in the amount of garnet. These observations suggest the following melting reaction:

\[
\text{Cpx} + \text{Phe} + \text{Coe} + \text{Fluid} \rightarrow \text{Grt} + \text{Melt} \tag{2}
\]

Such a melting reaction has been proposed previously (Schmidt, 1996; Schmidt et al., 2004) but is different from that of Auzanneau et al. (2006), who suggested that garnet is on the reactant side and not on the product side, which creates considerable problems in balancing Fe and Mg.

Phengite is stable to surprisingly high temperatures at sub-arc depths. At 3.5 GPa, it was still stable at 950°C, whereas at 4.5 GPa phengite disappeared between 1000 and 1500°C. Our experiments provide information on the minimum stability of phengite because we did not perform fluid-absent melting experiments. In fact, it has been observed in a natural tonalite composition (no fluid added, \(\sim 1\) wt% H\(_2\)O) that phengite was stable up to 100°C at 3 GPa and up to 1500°C at 3.2 GPa (Patino Douce, 2005).

The new data in combination with literature data provide evidence for the key role of phengite as a K (and other LILE) carrier at sub-arc depths. Other trace elements are likely to be controlled by accessory phases such as apatite, zircon, rutile, allanite and monazite, which are stable to high temperatures and pressures (Table 1). The influence of accessory phases on the trace element contents of the liberated liquids will be presented elsewhere. The new data support previous suggestions that significant liberation of a range of trace elements is most probably related to fluid-present metamorphic conditions in the subducted sediments (Domanik & Holloway, 1996; Hermann & Green, 2001).

The position of the wet solidus

Experimental determination of the position of the wet solidus at low pressures (\(P < 2.5 \text{ GPa}\)) in felsic systems is relatively straightforward, as a clear transition from glass-absent to glass-present runs can be observed (Huang & Wyllie, 1981). For example, Spandler et al. (2007b) determined that the wet solidus for the same chemical system as investigated here is at 675°C at 2.2 GPa. However, at higher pressures, experimental determination of the solidus becomes more complex, as the amount of dissolved...
H₂O in the hydrous melts at the solidus increases with increasing pressure (Huang & Wyllie, 1981). In this experimental set we found that the melt produced is quenchable to a glass only if the H₂O content is <30 wt% (Fig. 6a). Thus we are confident that we were able to track the wet solidus up to pressures of 3.5 GPa, where it is situated between 700 and 750°C. This is in very good agreement with the study of Nichols et al. (1994), who determined the wet solidus in subducted red clay sediments up to pressures of 3 GPa (Fig. 9). However, the wet solidus determined is very different from that in other studies. For example, Johnson & Plank (1999) reported a wet solidus in the red clay system that is more than 100°C higher than our results. This might be related to a difference in the starting material, because the red clay they used has significantly lower SiO₂ and higher FeO + MgO contents than the starting material used in the present study (Fig. 1), or to sluggish reaction in the lower temperature runs of their experiments because of the use of an already crystalline starting material. The locus of fluid-present melting for a metagreywacke composition (Auzanneau et al., 2006), which is very similar in composition to our starting material identical to that in this study. They found that total dissolved solutes range from ~4 to 5.5 wt%. This value is likely to be representative also for our run at 600°C, 2.5 GPa (Table 3). Solubilities tend to increase with increasing pressure and temperature (Manning, 2004), and guided by the general topology of the solubility isopleths (Hack et al., 2007) we have estimated that the total dissolved solutes are ~6 and 11 wt% at 3.5 GPa at 600 and 700°C, respectively. This seems reasonable considering that Kessel et al. (2005b) reported total solute contents of ~12 wt% at 4-0 GPa, 700°C in the MORB + H₂O system. This system produced a mineral assemblage (apart from phengite) similar to that in the pelite system and, considering that the main solutes are SiO₂, Al₂O₃ and Na₂O (Table 3), total solute contents are likely to be comparable. For the run at 4.5 GPa, 700°C we estimated a total amount of solutes of 15% based on the findings of Kessel et al. (2005b) in the MORB + H₂O system; those workers reported aqueous fluids with total dissolved solutes of 7–17 wt% in the range 4.0–5.0 GPa and 700–800°C.

As solute contents increase along the solidus for the aqueous fluid and the H₂O increases in the hydrous melt, the two compositions merge together until they are the same at the second critical endpoint where the solidus terminates. The solubility isopleths obtained in this study indicate that at 3.5 GPa the second critical point has not been reached for the pelite bulk composition. However, it must be noted that the design of our and the Schmidt et al. (2004) experiments is not suitable to detect any closure of the miscibility gap between aqueous fluid and hydrous melt. The position of the second critical endpoint cannot be determined with such experiments because the melts are no longer quenchable along the solidus above 3.5 GPa. It is necessary to conduct experiments at high and variable water contents to locate the second critical endpoint.

**Composition of the fluid phase**

The first-order control on the composition of the fluid phase is given by the H₂O content. Where the fluid phase is able to quench to a glass we classify it as a hydrous melt (Hermann et al., 2006). For the studied pelite composition the transition from quenchable glass to non-quenchable fluid occurs at 30 wt% H₂O. With increasing temperature the H₂O content in the hydrous melt decreases in a systematic way (Fig. 9b). The liquidus determined by Nichols et al. (1994) for a red clay composition with 8 wt% H₂O is situated between the 5 and 10 wt% H₂O isopleths and thus is consistent with the isopleths determined in this study. At the low-temperature side of the solidus, the fluid phase is dominated by H₂O and thus represents an aqueous fluid (Fig. 9). In our study we were unable fully to quantify the amount of solute in the diamond traps. However, a comprehensive compilation of major element solubilities by Manning (2004) indicates that such aqueous fluids are surprisingly dilute and are likely to contain <5 wt% of total dissolved solutes at P <2.0 GPa and T ~600°C. At 2.2 GPa and 600–650°C, Spandler et al. (2007b) constrained the solubilities of elements with synthetic fluid inclusions using a starting material identical to that in this study. They found that total dissolved solutes range from ~4 to 5.5 wt%. This value is likely to be representative also for our run at 600°C, 2.5 GPa (Table 3). Solubilities tend to increase with increasing pressure and temperature (Manning, 2004), and guided by the general topology of the solubility isopleths (Hack et al., 2007) we have estimated that the total dissolved solutes are ~6 and 11 wt% at 3.5 GPa at 600 and 700°C, respectively. This seems reasonable considering that Kessel et al. (2005b) reported total solute contents of ~12 wt% at 4-0 GPa, 700°C in the MORB + H₂O system. This system produced a mineral assemblage (apart from phengite) similar to that in the pelite system and, considering that the main solutes are SiO₂, Al₂O₃ and Na₂O (Table 3), total solute contents are likely to be comparable. For the run at 4.5 GPa, 700°C we estimated a total amount of solutes of 15% based on the findings of Kessel et al. (2005b) in the MORB + H₂O system; those workers reported aqueous fluids with total dissolved solutes of 7–17 wt% in the range 4.0–5.0 GPa and 700–800°C.
As long as solubilities in the fluid phase are considered, the actual position of the second critical endpoint is not of paramount importance because there is a strong increase in solubilities over a temperature interval of \(\sim 100^\circ C\) (as observed, for example, between 700° C and 800° C, 4-5 GPa) whether or not the wet solidus is still present (e.g. Manning, 2004; Hermann et al., 2006).

The large melt pools obtained in this study permit accurate analysis of the experimental melts as a function of increasing temperature (Fig. 7). The melts are essentially granitic in composition. The most significant observed change within the granite field is the change of Na\(_2\)O and K\(_2\)O with temperature. Close to the wet solidus the melts are trondhjemitic with Na\(_2\)O > K\(_2\)O. At higher temperatures, the melts are granitic \textit{sensu stricto} with K\(_2\)O > Na\(_2\)O. It is interesting to note that a very similar trend has been observed at lower pressures by Patiño-Douce & McCarthy (1998). Fluid-present melting in a muscovite schist at 700–750°C, 0.6–1.0 GPa produced trondhjemitic melt compositions, whereas melting at higher temperatures produced granitic melt compositions. This similarity in melt composition evolution with temperature at high and low pressures is not expected, as the buffering paragenesis changes significantly from quartz–plagioclase–muscovite–biotite–garnet (low pressure) to coesite–clinopyroxene–phengite–garnet (high pressure). Because of the large stability field of phengite, most experimental melts are buffered in K\(_2\)O. In fact, there is a systematic increase in K\(_2\)O with increasing temperature, as is expected for an element that has a constant composition in the buffering phase (Fig. 7a). In conjunction with the decrease in H\(_2\)O with increasing temperature, there is a very pronounced and systematic change of K\(_2\)O/H\(_2\)O as a function of temperature (Fig. 10a).

Figure 10 can also be used to predict, in experiments with a given K\(_2\)O/H\(_2\)O, at which temperature an aqueous fluid is stable, and hence a very high fluid–rock ratio is needed to strip substantial K\(_2\)O out of subducted sediments. In contrast, at higher temperatures, much less H\(_2\)O is required to efficiently remove K\(_2\)O with a hydrous melt. Figure 10 can also be used to predict, in experiments with a given K\(_2\)O/H\(_2\)O, at which temperature it is expected that the solid K phase is completely dissolved in the produced fluid. The temperature range of phengite dissolution, used as an argument for the presence of supercritical fluids by Schmidt et al. (2004), can be readily explained in terms of this diagram. A K\(_2\)O/H\(_2\)O \(\sim 1.2\) in their starting material is reached by the hydrous melt at 1000–1100°C, in agreement with the disappearance of phengite observed by Schmidt et al. (2004).
We have already highlighted the difficulties of constraining the nature of the fluid phase based on textural observations when the amount of fluid phase is low and/or the fluid phase does not quench to a glass. However, in this study we have observed some compositional characteristics that might help researchers in future studies to constrain the nature of the fluid phase. Element ratios are particularly useful, because determination of absolute concentrations is often difficult in the hydrous quench from aqueous fluids. We found that SiO$_2$/Al$_2$O$_3$ and Na$_2$O/Al$_2$O$_3$ abruptly increase from hydrous melts to aqueous fluids (Fig. 7e and f). This is in excellent agreement with the calculated solubilities in aqueous fluids in equilibrium with eclogite, showing that Si and Na are the main cations. The Na$_2$O/Al$_2$O$_3$ of aqueous fluids in equilibrium with a high-pressure metapelite has also been determined in fluid inclusions trapped in experiments at 2.2 GPa, 600–650°C and is close to unity (Spandler et al., 2007b), in agreement with our data (Fig. 7f). Green & Adam (2003) analysed the quench material precipitated from aqueous fluids that had been equilibrated with a basaltic eclogite assemblage at 650–700°C, 3.0 GPa. The quench material was characterized by high SiO$_2$/Al$_2$O$_3$ of 12–20 and high Na$_2$O/Al$_2$O$_3$ of 0.7–0.8, providing further evidence for the distinct characteristics of these ratios in aqueous fluids.

A surprising feature is the very low K$_2$O content of the aqueous fluids, which is between 0.04 and 0.16 wt% when the H$_2$O content of the fluid is taken into account (Table 3). Such low K$_2$O contents have also been observed in the fluids present in the K-bearing basalt experiments of Green & Adam (2003). Although their starting material contained only 0.3 wt% K$_2$O and they applied a high H$_2$O/starter material ratio of unity, all experiments produced residual phengite. This provides strong evidence that the solubility of K$_2$O in the aqueous fluid must be smaller than 0.3 wt%. In fact, if the K$_2$O content of the fluid is normalized to a total solute content of 5 wt%, as suggested by Green & Adam (2003), then it reaches values of 0.07–0.11 wt%; these values are in excellent agreement with the low concentrations found in our study.

**Element recycling and top-slab temperatures**

One of the most remarkable characteristics of primitive arc lavas compared with MORB is the distinct enrichment of H$_2$O and LILE (Tatsumi & Eggins, 1995). A range of isotopic and geochemical criteria provide strong evidence that these components are derived from the subducted slab (Hawkesworth et al., 1993; Plank & Langmuir, 1993, 1996). Although the H$_2$O may be sourced from a number of lithologies in the slab (Poli & Schmidt, 2002), several studies have confirmed that subducted sediments play a key role in the LILE budget of subduction zones (Plank & Langmuir, 1993, 1998; Peate et al., 1997). In particular, pelites are regarded as the most important component of the subducted sediment for hosting most lithophile trace elements (Plank & Langmuir, 1998). It is, therefore, of prime interest to understand the nature and composition of the fluid phase that is formed at sub-arc depths in subducted pelites. To evaluate the process of LILE recycling, it is necessary to compare the position of the wet metapelite solidus (and the extension of the transition of hydrous melt to non-quenchable fluid) to thermal models of top-slab temperatures. Figure 10b shows a variety of thermal models with respect to the wet pelite solidus, the field where hydrous melts are stable and the stability of phengite. Thermal modelling has shown that temperatures at the top of the subducting slab are mainly controlled by the age of the incoming plate (the older the cooler) and the speed of subduction (the faster the cooler (Peacock et al., 1994). Recent thermal and mechanical modelling has also highlighted the importance of coupling between the slab and mantle wedge, which may dramatically influence temperatures on top of the slab (van Keken et al., 2002; Kincaid & Griffiths, 2004). The variety of controlling parameters results in vastly different model conditions at sub-arc depths that range from very cold (400–600°C) to very hot (950–1000°C). This highlights the need to obtain independent constraints on top-slab temperatures.

To characterize recycling of elements from the subducted sediments to the mantle wedge, we can consider three fundamentally different scenarios. In the first scenario, the top-slab temperature is within the aqueous fluid field at relatively low temperatures at sub-arc depths. This is the case for all but the hottest proposed geotherms of the models given by Peacock et al. (1994). Under such conditions effective extraction of K$_2$O and other LILE will be difficult. Our experiments have shown that the K$_2$O content and, more importantly, the K$_2$O/H$_2$O ratio of such fluids are very low (Fig. 10a). This means that LILE can be removed by fluids only in zones where there is a very high fluid–rock ratio. Also, the solubility of LREE, which are often enriched in arc lavas, is extremely low (Hermann, 2002a; Spandler et al., 2007b). In the second scenario, top-slab temperatures are high enough (>700°C) for fluid-present melting at sub-arc depths, but no fluid-absent melting of phengite occurs. Kincaid & Griffiths (2004) reported results from scaled analogue models that produced top-slab temperatures that fall within this scenario. K$_2$O and LILE will be efficiently removed from the sediments depending on the availability of an externally derived fluid that triggers melting. It has been suggested that the breakdown of hydrous phases in mafic and ultramafic rocks in the deeper and cooler parts of the slab might provide the fluids necessary for melting the sediments on top of the slab (Hermann & Green, 2001). Alternatively, hybrid chlorite- and talc-rich rock types that form as a result of interaction between the subducted slab and the mantle wedge might liberate significant amounts of...
fluid at 700–800°C at sub-arc depths and thus will trigger melting of the sediments (Spandler et al., 2007a). In the third scenario, very high top-slab temperatures of 950–1000°C might lead to fluid-absent melting of phengite in subducted sediments. Such high top-slab temperatures could occur where there is enhanced coupling with a hot mantle wedge (van Keken et al., 2002) or where asthenospheric inflow occurs in response to slab rollback (Kincaid & Griffiths, 2004). In such a case, nearly complete transfer of K$_2$O and LILE from the subducted sediments to the mantle wedge occurs at sub-arc depths independent of whether or not there is additional fluid fluxing.

One interesting aspect of fluid-present melting in sediments is that the amount of K$_2$O in the melt (buffered by phengite) increases systematically with increasing temperature. It was suggested previously that in many island-arc systems there exists a relationship between the K$_2$O content of primitive lavas and the depth to the top of the subducting slab beneath the volcano—the so-called ‘K–depth’ relationship (Dickinson, 1975). Consequently, it has been postulated that pressure is the primary control on K$_2$O release from the slab. Our study, however, suggests that temperature and not pressure is the controlling parameter. Because the temperature at the top of the subducting slab increases with increasing depth, the observed ‘potash–depth’ relationship still holds.

We suggest that the systematic change in the K$_2$O/H$_2$O ratio in the slab fluid as a function of temperature and, to a lesser extent, pressure, provides a useful tool to distinguish between the three scenarios outlined above. K$_2$O is buffered by residual phengite and is a good proxy for the behaviour of the LILE, which are the most important elements in the subduction component of arc lavas. The rationale behind normalizing to the water content is that the amount of water added to the mantle wedge will be a principal factor in determining how much basaltic melt is produced during wet melting of the mantle wedge peridotite, which in turn will have an influence on the final concentration of LILE in the resultant arc magmas. The K$_2$O/H$_2$O of the fluid phase leaving the subducted sediments at the top of the slab is extremely low (∼0.002) in scenario 1 (Fig. 10a). As soon as hydrous melts are present (scenario 2) the K$_2$O/H$_2$O increases drastically to 0.1–1 for the temperature range of fluid-present melting. For fluid-absent phengite melting at sub-arc depths, as outlined in scenario 3, the K$_2$O/H$_2$O is bracketed between ∼1, given by the high temperature of melting, and ∼2.3, given by the stoichiometry of phengite (10.5 wt% K$_2$O, 4.5 wt% H$_2$O).

These constraints can now be compared with the K$_2$O/H$_2$O ratio of primitive arc lavas. Primitive lavas from a range of volcanic arcs have between 0.2 and 0.8 wt% K$_2$O (Kelemen & Hanghoj, 2003) and between 2 and 4 wt% H$_2$O (Sobolev & Chaussidon, 1996; Stern, 2002), giving K$_2$O/H$_2$O ratios of between 0.05 and 0.4. An excellent dataset has been recently published on melt inclusions in olivine from the Kamchatka arc, where K$_2$O and H$_2$O have been measured in the same inclusions (Portnyagin et al., 2007). The observed K$_2$O/H$_2$O values range from 0.05 to 0.42, with the majority of data clustering at 0.23. The depleted mantle source of arc magmas is expected to contain of the order of 0.007 wt% K$_2$O and 0.01 wt% H$_2$O (Salters & Stracke, 2004) and so is unlikely to contribute significantly to the budget of these elements in arc magmas. Therefore, we can reasonably assume that the K$_2$O/H$_2$O ratio of primitive arc magmas is primarily derived from slab contributions.

To make a link between the K$_2$O/H$_2$O of arc magmas and the K$_2$O/H$_2$O of the slab-derived sediment flux, we have to consider potential alteration of this ratio in the mantle wedge according to the three different scenarios. For models predicting cool top-slab temperatures (scenario 1), aqueous fluids leaving the slab will interact with the mantle wedge and form a variety of hydrous phases such as antigorite, amphibole, talc, chloride and phlogopite (Poli & Schmidt, 2002). Talc, chloride and phlogopite, in particular, are stable up to considerable pressures and temperatures and the formation of these phases will alter the H$_2$O and K$_2$O content of the residual fluid. However, overall it is expected that the solubilities in the peridotite system are lower than in the pelite system and that the residual fluids are likely to be H$_2$O-rich, aqueous fluids with very low K$_2$O/H$_2$O. An interesting alternative model is that the fluid, which transports the slab signature to the locus of partial melting in the mantle wedge, derives from the breakdown of the hydrous chloride–talc assemblage, which will occur at ∼800°C (Spandler et al., 2007a). We can estimate the proportion of hydrous minerals from the interaction of peridotite with aqueous fluids derived from the subducted sediments. For a fluid composition such as that determined at 600°C, 3.5 GPa (Table 3), we obtain an estimated talc:chlorite:phlogopite ratio of 30:5:1. If upon dehydration of such an assemblage at 800°C all the K$_2$O hosted in phlogopite would be ~0.03. This is a maximum value as potentially some phlogopite will remain. This calculated ratio is considerably higher than in the original aqueous fluid leaving the slab, but is still significantly lower than the K$_2$O/H$_2$O ratio in arc lavas (Fig. 10). Therefore, it is very difficult to explain the K$_2$O/H$_2$O of arc lavas with scenario 1. Clearly, more experiments are needed to constrain the solubility of K$_2$O in aqueous fluids in such systems.

In the second scenario a hydrous melt is produced from the subducted sediments. This melt will most likely enter the mantle wedge at pressures above the amphibole stability field (Fumagalli & Poli, 2005) and at temperatures
that exceed the stability of antigorite, talc and chlorite (Poli & Schmidt, 2002). Hence, the only mineral phase capable of altering the K$_2$O/H$_2$O is phlogopite. Sekine & Wyllie (1982) have shown that interaction of granitic melts with peridotite will generally produce phlogopite. The extent of phlogopite formation depends on the temperature and especially on whether the melts are in contact with olivine or are shielded by the formation of new orthopyroxene. Malaspina et al. (2006) have investigated garnet-orthopyroxenites that have been interpreted as the products of interaction of peridotites with hydrous silicate melts at sub-arc pressures. They have observed that a residual fluid was trapped in the garnet that was enriched in incompatible elements. These garnet-orthopyroxenites are surrounded by layers of phlogopite, which probably formed during the interaction process (N. Malaspina, personal communication, 2007). Phlogopite has K$_2$O/H$_2$O of ~2, given by the stoichiometry. Figure 10 shows that hydrous melts released from the slab at temperatures of 700–900°C have a K$_2$O/H$_2$O of 0.1–1, which is lower than the K$_2$O/H$_2$O of phlogopite. Thus if phlogopite is formed in the mantle wedge peridotite, this will lower the K$_2$O/H$_2$O of the residual fluid that will enter the locus of wet melting. The observed K$_2$O/H$_2$O of ~0.05–0.4 of primitive arc lavas thus constrains the likely minimum K$_2$O/H$_2$O in the slab-derived fluid phase. Therefore, estimated top-slab temperatures based on the K$_2$O/H$_2$O of arc lavas would represent minimum values, and would depend on the amount of interaction of the slab-derived fluid with the mantle wedge. In the case of channel flow, such interaction would be minimal and the slab signature could be transported nearly entirely to the locus of partial melting. In such a case K$_2$O/H$_2$O temperature estimates based on this work would be accurate. On the other hand, if the fluid is transported via porous flow, extensive interaction and phlogopite formation is expected. K$_2$O/H$_2$O would then be determined by the solubility of phlogopite in aqueous fluids in the peridotite system. No experimental results are available yet to quantify this process, but it is expected that K$_2$O/H$_2$O would increase systematically with increasing temperature.

Fluid-absent melting of phengite at high temperatures (scenario 3) produces melts that have virtually the same K$_2$O/H$_2$O as phlogopite. Therefore in such a case, the K$_2$O/H$_2$O is not significantly changed by the potential formation of phlogopite in the mantle wedge. It is also worth noting that fluid-absent melting of a phlogopite-peridotite would produce melts with K$_2$O/H$_2$O of ~2. These values are significantly higher than what is observed in primitive arc lavas and consequently we do not consider this scenario to be likely.

The combination of our experimental results on the systematics of K$_2$O/H$_2$O variation in the fluid phase released from subducted sediments with considerations of the interaction of these fluids with the overlying mantle wedge suggests that the easiest way to explain the observed K$_2$O/H$_2$O in arc lavas is if fluid-present melting (scenario 2) at top-slab temperatures of 750–900°C occurs in the subducted sediments (Fig 10). Although this study clarifies the nature and composition of the fluid phase present in subducted sediments, clearly more experiments are needed to constrain the interaction of these fluids with the mantle wedge for a complete understanding of LILE recycling in subduction zones.

CONCLUSIONS

(1) Phengite is the most important host for K (and other LILE) in the subducted crust. This study shows that phengite is stable to high temperatures at sub-arc depths (950°C at 3.5 GPa; 1000°C at 4.5 GPa) and hence fluid-absent phengite breakdown is not a viable process to release K from the subducted slab in most subduction zones.

(2) The pelite solidus is steeply sloping and is located at 700°C at 2.5 GPa and between 700 and 750°C at 3.5 GPa. At higher pressures we could only determine the transition from hydrous glass to non-quenchable fluid, at 800°C, 4.5 GPa. Hence, the solute content of the fluid phase released from subducted sediments will strongly increase in the temperature interval from 700 to 800°C at sub-arc depths.

(3) The K$_2$O and H$_2$O content of the fluid phase is buffered by the phengite-bearing residue and changes drastically as a function of the nature of the fluid phase and the slab temperature. Aqueous fluids, which are stable at temperatures lower than the wet solidus, are dilute and contain K$_2$O <1 wt% and H$_2$O >80 wt%. In contrast, hydrous melts display increasing K$_2$O and decreasing H$_2$O contents, with typical K$_2$O/H$_2$O of 0.1–1. Thus, efficient extraction of LILE from the subducted sediments requires wet melting.

(4) The comparison of K$_2$O/H$_2$O produced in hydrous experiments with primitive arc basalts provides evidence that the most important process for element recycling from the slab to the mantle wedge occurs via fluid-present melting of the sediments and suggests that top-slab temperatures must be in the range of 700–900°C. Once the interaction of the fluids with the mantle wedge is understood, the K$_2$O/H$_2$O of primitive arc basalts can be used to obtain independent constraints on top-slab temperatures.

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SUPPLEMENTARY DATA
Supplementary data for this paper are available at Journal of Petrology online.

REFERENCES


