LETTERS

Trace element signature of subduction-zone fluids, melts and supercritical liquids at 120–180 km depth

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Fluids and melts liberated from subducting oceanic crust recycle lithophile elements back into the mantle wedge, facilitate melting and ultimately lead to prolific subduction-zone arc volcanism[3,2]. The nature and composition of the mobile phases generated in the subducting slab at high pressures have, however, remained largely unknown[1–7]. Here we report direct LA-ICPMS measurements of the composition of fluids and melts equilibrated with a basaltic eclogite at pressures equivalent to depths in the Earth of 120–180 km and temperatures of 700–1,200 °C. The resultant liquid/mineral partition coefficients constrain the recycling rates of key elements. The dichotomy of dehydration versus melting at 120 km depth is expressed through contrasting behaviour of many trace elements (U/Th, Sr, Ba, Be and the light rare-earth elements). At pressures equivalent to 180 km depth, however, a supercritical liquid with melt-like solubilities for the investigated trace elements is observed, even at low temperatures. This mobilizes most of the key trace elements (except the heavy rare-earth elements, Y and Sc) and thus limits fluid-phase transfer of geochemical signatures in subduction zones to pressures less than 6 GPa.

Trace elements and isotope ratios of arc magmas are frequently deployed to decipher their complex magmatic history and identify source components. It is well established that a slab component, identified by B, [10]Be, U and Th abundances[5–10], combines with a mantle melting component with high Mg# and high Ni and Cr contents[11], to form primitive basaltic magmas that give rise to most arc suites. Whether at high pressures the slab component, which transfers such elements to the mantle, is a fluid, melt or supercritical liquid, has remained unknown. Most thermal models of mature subduction zones[12] suggest that temperature conditions for the subducting crust are far below its solidus at subarc depths. Nevertheless, it has become increasingly popular to attribute estimated Be and Th transfer rates to slab melting[5], implying that most thermal models are in error. The missing link in this controversy is the composition and nature of the fluids or melts departing from the slab, which in turn allow conditions of their formation to be constrained. A critical petrological parameter in this debate is the closure of the immiscibility gap between an aqueous fluid and a hydrous silicate melt[13,14].

At typical crustal pressures, aqueous fluids contain a few per cent of solute while partial melts have <15 wt% H₂O. At higher pressures, the amount of solutes in the fluid and the solubility of H₂O in silicate melts both dramatically increase, and the compositions of fluid and melt converge along a miscibility gap, which eventually disappears[15]. The intersection of the miscibility gap's critical curve with the solidus then defines the end point of the solidus[14–16], and we term any fluid or melt beyond this point 'supercritical liquid'. The pressure of the critical end point of the solidus is strongly dependent on bulk

composition, and varies from 1.6 GPa in feldspatic systems[16] to >10 GPa in mantle systems[15]. In potassium- and mica-rich lithologies of the subducted crust, this endpoint is situated between 5 and 6 GPa (ref. 14), corresponding to depths of 150–180 km of the subducting slab beneath volcanic arcs. It has been proposed[3] that supercritical liquids have high trace element solubilities at relatively low temperatures. The scope of our experimental study is to quantify partitioning between the residual slab mineralogy and all three mobile phases of interest—that is, high pressure aqueous fluids, hydrous melts and supercritical liquids.

To determine fluid and melt compositions equilibrated with an eclogitic residue, we have employed two novel techniques. We performed standard diamond-trap experiments[17,18] (see Methods) on an average mid-ocean-ridge basalt (MORB), but used a 'rocking' multi-anvil apparatus[19]. In this device, the entire multi-anvil is turned upside-down regularly, such that the fluid in the capsule is constantly homogenized by induced convection. The turning has been shown to be critical for maintaining a homogeneous fluid[19] over the entire duration of the experiment (12–72 h), thus maintaining equilibrium between the fluid and all minerals. The fluid-saturated K-free MORB was doped with 26 trace elements, and equilibrated at pressures of 4–6 GPa and temperatures of 700–1,200 °C. After quenching of the experiments, the recovered capsule was placed in a freezing device. The frozen capsule was then cut open, and transferred to the laser-ablation cell for immediate laser-ablation inductive-coupled-plasma mass spectrometry (LA–ICPMS) analysis of the ice in the diamond trap, keeping it frozen for the whole duration of the analysis. This technique overcomes the hitherto unavoidable loss of some solute and precipitates upon exsolution of the high pressure fluids/liquids/melts when the fluid is released from the capsule (see Methods). Thus, for the first time, we accurately determine major and trace element concentrations and H₂O contents of high pressure fluids and unquenchable melts[16]. After analysis of the trapped ice, capsules were defrosted, mounted, and polished sections of each run were examined using scanning electron microscopy. The major element compositions of the eclogitic minerals were determined by electron microprobe, and trace element concentrations by conventional LA–ICPMS.

Combining these two methods, we have determined compositions of the mobile phases and partition coefficients between the mobile phase and eclogite minerals, thus facilitating modelling of element mobilities in the subducting slab. The experimental results show that at 4 GPa, fluid saturated melting takes place, in which a fluid that increases its solute content from 13 to 22 wt% between 700 and 900 °C (Table 1) is replaced by a silicate melt with ≤56 wt% H₂O at ≥1,000 °C (ref. 20). At 5 GPa, this transition occurs at 1,000–1,050 °C, but at 6 GPa, the behaviour is different. A gradual decrease in H₂O concentrations in the mobile phase from 72 to 31 wt% H₂O

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Table 1 | Bulk average MORB (starting material), fluid, melt and supercritical liquid compositions

Conc. (wt%)	Bulk	4/800	4/1,000	6/800	6/1,000
SiO₂	52.84	12.0(1.2)‡	31.4(3.5)	19.8(6.5)	29.8(6.6)
TiO₂	1.43	0.04(1)	0.50(3)	0.11(3)	0.71(16)
Al₂O₃	17.05	1.45(49)	4.24(30)	1.41(40)	2.89(68)
FeO†	8.41	0.22(8)	1.27(21)	0.63(49)	1.12(30)
MgO	5.87	0.56(27)	0.78(6)	0.68(36)	0.85(21)
CaO	10.11	0.84(45)	2.05(12)	1.93(88)	3.25(74)
Na₂O	3.20	0.96(25)	2.80(35)	1.46(60)	2.64(3.62)
H₂O	–	83.1(2.5)	56.1(3.8)	72.6(8.7)	57.6(9.3)

*x/y: experiment at pressure x (in GPa) and temperature y (in °C).
† All Fe is presented as FeO.
‡ Numbers enclosed in parentheses indicate the absolute value of one standard deviation of the distribution of average compositions reported in terms of the least digits cited; that is, 12.0(1.2) indicates 12.0 ± 1.2.

between 800 and 1,300 °C is observed[20]. These results demonstrate a chemical continuum between fluid and melt at 6 GPa, and hence conditions beyond the critical endpoint of the solidus. The supercritical liquid replaces the classic dichotomy of fluid and melt at lower pressures.

Our results on the partitioning of trace elements (Fig. 1) show a distinct change in pattern when moving from fluid and melt at 4 GPa to a supercritical liquid at 6 GPa. A fluid at 4 GPa still behaves similarly to fluids from lower pressures[4,21,22], but with most bulk partition coefficients $D^{\mathrm{fluid/solid}}$ increased, thus increasing the mobility for most elements. Aqueous fluids resulting from dehydration of an eclogite at 4 GPa/700–800 °C are characterized by $D^{\mathrm{fluid/solid}}$ of Rb, Cs, Ba and Pb of 10 or higher, by $D^{\mathrm{fluid/solid}}_{\mathrm{U}} \geq D^{\mathrm{fluid/solid}}_{\mathrm{Th}}$ (Fig. 2), by $D^{\mathrm{fluid/solid}}_{\mathrm{REE}}$ and $D^{\mathrm{fluid/solid}}_{\mathrm{HFSE}}$ between 0.01 and 0.5, and a limited mobility of Li (here REE indicates rare-earth elements, and HFSE high field strength elements). In contrast, the hydrous melt at 4 GPa/1,000 °C has $D^{\mathrm{melt/solid}}_{\mathrm{U}} < D^{\mathrm{melt/solid}}_{\mathrm{Th}}$ and a steep REE pattern characteristic for garnet in the residue. There is no principal difference in the partitioning trends of these elements from partial melts of eclogite at lower

pressure[4,23,24]. At 4 GPa, the partition coefficients $D^{\mathrm{fluid\ or\ melt/solid}}$ of three key elements—Be, Sr and Th—display a very strong temperature dependence, but without a conspicuous jump at the solidus (Fig. 1a). The mobility of these elements (see Supplementary Tables) in the experiments is <15% at 700 °C and gradually increases to 60–90% at 1,000 °C.

At 6 GPa, supercritical liquids are characterized by a high mobility of almost all of the investigated elements except heavy rare-earth elements (HREE), Y and Sc, whose $D^{\mathrm{liquid/solid}}$ remain in the range 0.01–0.5 (Fig. 1b). In the supercritical liquids, $D^{\mathrm{liquid/solid}}_{\mathrm{Li}}$ is $< D^{\mathrm{liquid/solid}}_{\mathrm{Cs}}$, and $D^{\mathrm{liquid/solid}}_{\mathrm{Sr}}$ ranges from 6 to 22. In conjunction with the extreme fractionation of REE (for example, $D^{\mathrm{liquid/solid}}_{\mathrm{La}}/D^{\mathrm{liquid/solid}}_{\mathrm{Lu}} \approx 10^3$) and the highly mobile Sr (Figs 1b and 2a), a trace element pattern similar to lower pressure silicate melts emerges, although this pattern is produced by a supercritical liquid with 72–56 wt% H₂O (ref. 20) over the entire investigated temperature range (800–1,200 °C). In particular, the mobility of Be increases dramatically with pressure. Although fairly insoluble at 2 GPa/900 °C ($D^{\mathrm{liquid/eclogite\ solid}}_{\mathrm{Be}} < 0.5$; ref. 25), $D^{\mathrm{fluid/solid}}_{\mathrm{Be}}$ increases to 1–3 at 4 GPa/800–900 °C, and to 6–8 at 6 GPa/800–900 °C, leading to >60% of the Be being dissolved in the supercritical liquid of our experiments at temperatures of 800 °C. Fluids are clearly distinguished from melts and supercritical liquids (for example, U/Th, Th/Rb, La/Lu), but none of the ratios of the investigated trace elements can be used unequivocally to discriminate between trace element transfer through hydrous melts or supercritical liquids. The supercritical liquids exhibit in fact an 'adakite-type pattern'[26] with high LREE/HREE, Sr/HREE and Sr/Y, and with excess Th (ref. 8) through a petrological process different from the melting of metabasaltic or metasedimentary eclogites at moderate pressures. This adds further evidence that high bulk Mg#, Ni and Cr for a given SiO₂ content of an arc lava are the only reliable indicators of andesitic to dacitic melts passing through the mantle wedge[3].

In our experiments, the solubilities of Nb, Ta, Zr and Hf in garnet decrease strongly with temperature. While garnet retains >70% of Nb, Ta, Zr and Hf at 700–800 °C, these elements become
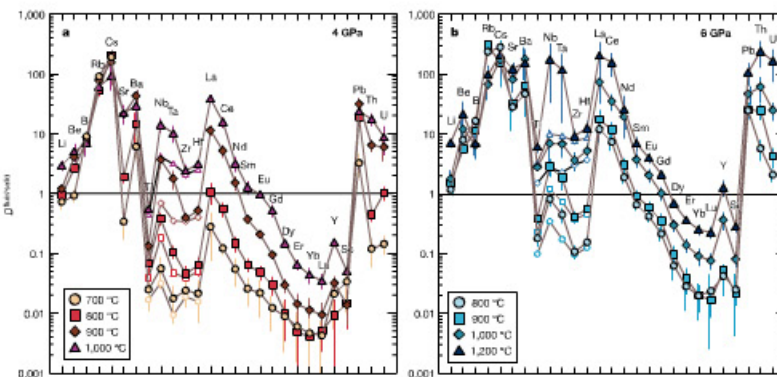

Figure 1 | Experimental fluid–solid partition coefficients for average MORB. a, Aqueous fluids (700–900 °C) and hydrous melt (1,000 °C) at 4 GPa; **b**, supercritical liquid (800–1,200 °C) at 6 GPa. The solid residue is calculated from the element concentrations in the solids multiplied by their abundance in the residue. Filled symbols refer to a garnet–clinopyroxene residue, open symbols to a garnet–clinopyroxene–rutile residue (see also Supplementary Information). Uncertainties are given as 1σ and were calculated by propagating uncertainties of elemental concentrations. 1σ error bars are sometimes shifted off the symbol centre for clarity.

incompatible and enter the silicate melt or supercritical liquid at $\geq 1,000\,^\circ C$. However, as at lower pressures, Nb, Ta and Ti may be held back by residual rutile[21]. In the investigated pressure range, TiO_2 solubilities in the liquid are mostly temperature dependent, and significant amounts of rutile (for average MORB decreasing from 0.5 wt% at $900\,^\circ C$ to respectively 0.3 and 0.2 wt% at 1,000 and $1,200\,^\circ C$) will produce Ti, Nb and Ta anomalies typical for most arc magmas. We suggest that the extent of this anomaly, combined with the abundances of Be and Th in primary arc magmas, are probably the best constraints on the temperature during release of the mobile slab component.

Beryllium, Th, U, and radiogenic Pb and Sr are enriched in pelitic sediments and greywackes[4], thus dominating the budget and transfer rates of these elements. These sediments have the same eclogitic mineralogy (but different mineral proportions) as basaltic rocks at depths >100 km (ref. 14): in particular, they have up to 25 wt%
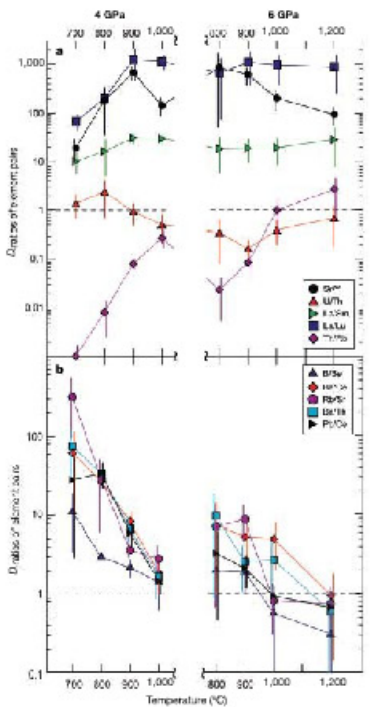

Figure 2 | Key trace element distribution coefficients characterizing the geochemical signature of the mobile phase during subduction processes. Uncertainties are given as 1σ and were calculated by propagating uncertainties of elemental concentrations. 1σ error bars are sometimes shifted off the symbol centre for clarity.

phengite owing to much higher bulk K_2O contents. The high solubility of K_2O in hydrous liquids has the result that a few per cent of H_2O entirely dissociate phengite[34], with all K_2O dissolved in the mobile phase. Thus, any significant mass transfer process will remove phengite from the residue and our data can thus be equally applied to pelitic and clastic metasediments. Fluid/rock ratios in the metasediments located on top of the subducting lithosphere are intrinsically high, as any fluid liberated below must pass through the comparatively thin sediment pile. Although fewer H_2O sources are available in hydrated metabasites at 4–6 GPa than at ≤ 3 GPa (ref. 27), a major H_2O reservoir at these depths is the partially hydrated peridotite underlying the oceanic crust. Serpentine and chlorite[25] therein may reach their stability limits, dehydrate, and flush the oceanic crust. Geochemically effective H_2O/sediment ratios are a result of the relative masses of the major H_2O reservoirs (MORB, serpentinite) and the fluid flow mechanism (pervasive versus channelled flow). Both dehydration and flushing are incremental processes significantly increasing mobilities for all elements with $D^{fluid/solid}$ greater than unity. It is thus safe to conclude that a large fraction of Be, B, Rb, Cs, Sr, Ba, LREE, Pb, Th and U will be removed effectively from the sediments by supercritical liquids.

Further complications in the production of a mobile phase may arise from carbonate saturated sedimentary or altered mafic crust compositions[29,30]. Characteristically, at high pressure/low temperature conditions, these have dolomite or magnesite in addition to the eclogitic garnet ± clinopyroxene ± coesite ± kyanite ± phengite assembly[30,31]. Most important, the only significant carbonaceous species at these conditions is CO_2, and the molar fraction of CO_2 in a carbonate saturated aqueous fluid is low (≤ 0.10) at subsolidus conditions[29], resulting in a minor shift of the fluid saturated solidus of carbonated basaltic eclogite[31] of less than $50\,^\circ C$. Likewise, the addition of carbonates is expected to have a small effect on the pressure of the critical endpoint of the solidus and on trace element partition coefficients in the fluid or supercritical liquid.

The transport properties of supercritical liquids at moderate temperatures result in high Be and Th transfer rates similar to those observed in many arcs[5] that so far have been attributed to melting of the sediment layer of the subducting crust[4]. Similarly, excess Th over U was thought to be a unique characteristic of slab melting. We have demonstrated here that such melt-like characteristics can be produced by supercritical high-pressure liquids at any temperature. We argue that the slab component in these arc magmas may result from supercritical liquids rather than from relatively shallow melts from a sediment source, thus relaxing the apparent temperature discrepancy between geochemical arguments and geophysical models. Finally, the chemical properties of supercritical liquids liberated at depths exceeding ~160 km removes the dichotomy of fluids versus melts. As a consequence, fluid-type geochemical signatures from the oceanic crust are limited to depths ≤ 160 km: at higher pressures, the mobile phase will inevitably add a melt-like trace element pattern to the mantle wedge.

METHODS

Experimental. A K-free average MORB composition[32] was synthesized as a glass at an oxygen fugacity close to fayalite–magnetite–quartz (FMQ) at the experimental conditions. The glass was doped with 860 p.p.m. Cs, which is necessary as an internal standard for LA–ICPMS analyses. 26 trace elements were fused into a second glass of diopside composition, and about 2% of the diopside glass was mixed with the basalt powder such that individual bulk trace element concentrations were 100–250 p.p.m. Water (17–26 wt% H_2O) was first pipetted into the 2.3 mm Au capsule followed by ~3–5 mg basalt powder, overlain by a thin layer of synthetic diamond aggregates (15–25 μm diameter grains), and another layer of doped basalt powder. Capsules were welded shut while cooled with liquid nitrogen to avoid H_2O loss.

Experiments were conducted in a Walker-type multi-anvil apparatus employing a 19 mm MgO octahedron and WC cubes with a 12 mm truncation (each experiment used a different MgO octahedron). The Au capsule was placed in a BN cylinder inside a stepped graphite furnace, filled with MgO spacers and Mo caps. To avoid compositional zoning, the multi-anvil apparatus was mounted on a rocking device enabling the apparatus to be turned 180° while maintaining pressure and temperature[19]. Frequent inversion (every 15 min) of the charge in the gravitational field leads to convection in the fluid and thus to re-homogenization and migration of the fluid phase in the capsule. The re-homogenization of the fluid counteracts Soret diffusion, which otherwise would automatically lead to zonation and disequilibrium between the fluid and one or several of the solids which would segregate into growth zones. This method allows for chemical equilibrium between all solids and the fluid and as a side effect enhances reaction rates.

Analytical. After the experiment, we analyse the diamond trap and the minerals as described above. The decisive advantage of the freezing method[32] is that it allows us to determine directly the composition of unquenchable liquids. Such liquids constitute a mud of quench phases and water that maintains considerable amounts of trace elements (for example, of Cs, Rb, K) in solution. The traditional method of piercing the capsule releases a milky fluid that contains all of the solute and part of the quench crystals. Any further preparation step results in additional losses of quench material. We thus avoid all of these steps by maintaining the fluid in the capsule in its solid state during the LA–ICPMS analyses, to allow ablation of the complete fraction of the then unmixed liquid. The largest suitable ablation spot (60–110 μm diameter) is used to analyse the diamond trap in order to obtain the best averaging during sampling of the experimental product interstitial to the ~20 μm diameter diamonds. A highly incompatible element (Cs), fractionating completely into the fluid or melt phase, is used as an internal standard for LA–ICPMS signal; at a known Cs:H ratio of the starting material, we can quantify the H_2O content of the unquenchable liquid that has within the error the same Cs:H ratio, which in turn enables us to determine absolute concentrations of major and trace elements in the unquenchable liquid. Details of the LA–ICPMS analytics are found in ref. 32.

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