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The Fluid Mobilities of K and Zr in Subduction Zones: Thermodynamic Constraints

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Abstract: A subduction zone plays a critical role in forging continental crust via formation of arc magmas, which are characteristically enriched in large ion lithophile elements (LILEs) and depleted in high field strength elements (HFSEs). This trace element pattern results from the different mobilities of LILEs and HFSEs during slab-to-wedge mass transfer, but the mechanisms of trace element transfer from subducting crusts are not fully understood. In this study, thermodynamic simulations are carried out to evaluate the mobilities of K and Zr, as representative cases of LILE and HFSE, respectively, in slab fluids. The fluids buffered by basaltic eclogite can dissolve > 0.1 molal of K at sub-arc depths (~3 to 5.5 GPa). However, only minor amounts of K can be liberated by direct devolatilization of altered oceanic basalt, because sub-arc dehydration mainly takes place at temperatures < 600 °C (talc-out), wherein the fluid solubility of K is very limited (<0.01 molal). Therefore, serpentinite-derived fluids are required to flush K from the eclogite. The solubility of K can be enhanced by the addition of NaCl to the fluid, because fluid Na⁺ can unlock phengite-bonded K via a complex ion exchange. Finally, it is further confirmed that Zr and other HFSEs are immobile in slab fluids.

Keywords: subduction zone; slab fluid; LILE; HFSE; DEW model

1. Introduction

A subduction zone, as a unique tectonic setting of planet Earth, plays critical roles in transferring water and other crustal materials into deep earth, or recycling them back to shallow earth via arc magmatism [1,2]. The mass transfer from down-going oceanic crust to the supra-subduction mantle governs the formation of continental crusts and geochemical heterogeneities of the mantle [3–6]. The geochemical features of arc volcanic rocks, compared to ridge basalts, reflect the enrichment or depletion of chemical components during the slab-to-wedge transfer. A prominent geochemical characteristics of arc magmatic rocks is their enrichment in large ion lithophile elements (LILEs; K, Rb, Cs, Sr and Ba) and depletion in high field strength elements (HFSEs; Ti, Zr, Hf, Nb and Ta) [3,4,7]. Both the former and the latter are incompatible during partial melting of the mantle peridotite, and therefore, their decoupling should be sourced from selective mass transfer from the subducting slab. Conventionally, it is interpreted as signatures of the fluid-assisted mass transfer, because the slab-derived aqueous solutions can effectively transport the fluid mobile components (e.g., LILEs) but not the immobile HFSEs [8].

However, as pointed out by Spandler and Pirard [4], most of the "fluid mobile" elements in the subducted oceanic crust (sedimentary or basaltic protoliths) do not show systematic depletion with progressive metamorphism, and therefore, they are not directly released by metamorphic fluids that are internally generated from the crustal rocks, i.e., metamorphic devolatilization. A plausible model for solving this paradox considers the involvement of metamorphic fluids liberated from underlying serpentinite in the subducting lithospheric mantle, which will infiltrate the eclogitic crustal rocks and interact with metamorphic minerals to liberate the fluid mobile elements [9].



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Copyright: © 2021 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). The role of aqueous fluids in slab-to-wedge mass transfer is also questioned because of their low concentrations of solutes and, thus, limited ability in transporting crustal matters [10]. The slab-derived fluids typically have contents of dissolved solute of ~5–15 wt.%, which are mainly aqueous species of dissolved silicates [4]. However, in some cases, the ability of slab fluid in transferring trace elements can be significantly enhanced. For example, the addition of several wt.% of chlorine to the fluid can increase the solubility of LILEs by tens of times [11].

In addition to aqueous fluids, hydrous silicate melts are believed to be another candidate that transport slab materials to the mantle wedge. They can be formed by partial melting of the eclogitic rocks with the influx of serpentinite-derived fluids at temperatures higher than water-saturated solidus [12].

An alternative model suggests that buoyant mélange diapir, a mechanical mixture of eclogites and mantle rocks formed at the slab-wedge interface, will melt at the hot core of mantle wedge and contribute the geochemical signature of arc magmas [13]. Hydrous melts have greater solubility of LILEs, as well as Th and light rare earth elements (LREEs), than slab fluids and, thus, can account for trace element enrichment in arc magmas [14].

Finally, at temperatures near wet solidus and pressures higher than the second supercritical point (~3.5 to 5 GPa for basaltic protoliths), silicate melt and silicate-bearing fluid are expected to show a continuous transition, and liquid with intermediate solute contents (~30–40 wt.%), known as supercritical liquid, will form [14,15]. The supercritical liquid has been suggested to be an ideal solvent for LILEs, as well as HFSEs at high temperatures and may contribute to the mass transfer to the mantle wedge [14].

Beyond experimental studies, thermodynamic modelling provides an alternative approach to investigate the geochemical processes in the deep Earth. Especially, it may help to overcome the potential bias associated with the scarcity of natural records of slab-derived fluids, which are mostly sampled from subducting continents that are more frequently exhumed and better preserved than their oceanic equivalents (e.g., Xiao et al. [16]).

In recent years, taking advantages of the better understandings in the high-pressure properties of water solvent, thermodynamic models have been updated so that it can better describe the stabilities of aqueous species at mantle pressures (up to 6 GPa). In particular, the deep Earth water (DEW) model [17] has been incorporated with the solid solution models of metamorphic minerals and the Gibbs minimization algorithms, so that the chemical equilibrium of complex fluid-rock systems can be calculated to investigate the nature of eclogite-buffered fluid at mantle depths [18,19]. Successful applications in this field have provided important insights in understanding the fluid-induced processes in subduction zones, such as the pH of slab fluids [20], and the speciation of aqueous carbon [21,22] and nitrogen [23,24]. Particularly, the speciation and solubility of major rockbuilding lithophile elements have been investigated for pelitic protoliths [18,25], and the solubility of K, as a case representing LILEs, is numerically evaluated. These simulations yield K solubilities typically in the magnitudes of 10^{-2} to 10^{-1} molal (mol/kg H₂O), in fluids buffered by pelitic eclogites at sub-arc depths (~3 to 5.5 GPa; [26]).

For slab including a sediment layer, mass transfer is expected to be controlled by hydrous melts, evidenced by the enrichment in LREEs of relevant arc magmas (high La/Sm ratios), and their MORB-like Ba/Th ratios [27], two trace elements with similar magma compatibility but different fluid solubilities. Particularly, slabs with thick sedimentary covers are prone to form buoyancy-driven mélange diapirs and melt within the mantle wedge [28]. On the contrary, subducting crusts with only basaltic rocks is more likely to be predominated by fluid mass transfer [27]. In this study, we simulated the geochemistry of fluids that are buffered by an altered oceanic basalt at eclogite facies, to investigate the fluid mobilities of K and Zr as representative cases of LILEs and HFSEs, respectively. To better understand how the thermal structure of a subduction zone can influence the mobilities of K and Zr, their solubilities were simulated over a pressure–temperature (P-T) grid of 400 to 790 °C and 3 to 5.4 GPa, which covers the conditions of sub-arc environments. In addition, the fluid halogen content will also influence the mobilities of trace elements,

especially LILEs [11]. Therefore, two fluids with different Cl contents (pure water and solution with 2 wt.% NaCl) were used as the starting compositions to equilibrate with the basaltic eclogite. Special focuses were paid on (i) the fluid mobility of slab K and the influences of fluid Cl contents; (ii) whether slab K can be liberated via devolatilization of the crust or externally sourced fluid is required (e.g., serpentinite dehydration); and (iii) whether slab fluids can account for the decoupling between LILEs and HFSEs.

2. Methods and Limitations

The thermodynamic simulation was carried out using the HighPGibbs program [19], which was developed based on the HCh software [29] and solves the fluid-rock equilibrium using the Gibbs minimization algorithm at pressures up to 5.5 GPa. The fluid-rock equilibrium was calculated in the Na-Ca-K-Fe-Mg-Al-Zr-Si-O-H-Cl system, over a P-T grid of 400 to 790 °C and 3 to 5.4 GPa at increments of 10 °C and 0.025 GPa, respectively (Figure 1). The bulk rock composition used for thermodynamic modeling is from the average of sheeted dyke samples at Pito Deep, a tectonic window near the East Pacific Rise. These samples represent the composition of altered oceanic crust at depths of ~3000 m [30] (Table 1).

Table 1. Bulk rock compositions used in the modelling (in wt.%, H₂O in access).

Altered Oceanic Basalt			
SiO ₂	51.23		
Al_2O_3	14.80		
MgO	8.36		
FeO	9.28		
Fe ₂ O ₃	1.98		
CaO	11.38		
Na ₂ O	2.75		
K ₂ O	0.10		
ZrO_2	0.12		

At each P-T point, the composition of eclogite-buffered fluid was calculated using the "two-step" mode of HighPGibbs [19]: (i) At the first step, the equilibrium of a solute-free system was calculated with a bulk composition of 100 kg of dry basalt (Table 1) and excess pure water. The aim of this step is to obtain the water amount required to stabilize the hydrous minerals (e.g., lawsonite or talc) at the given P-T; (ii) At the second step, minor amounts (1 kg) of free water or H₂O-NaCl solution (2 wt.% of dissolved NaCl) were added to the bulk composition of eclogite obtained from the last step. The fluid-rock equilibrium of these systems is characterized by low fluid/rock ratios (1/100), so that the geochemistry of the eclogite-buffered fluids is obtained. Two fluids with or without dissolved NaCl were used to evaluate the influence of Cl in trace element migration. The NaCl concentration (2 wt.%) was selected for two reasons: (i) slab fluids at sub-arc depths typically have halogen concentrations lower than 5 wt.% NaCl equivalent [4]; (ii) fluids with higher NaCl contents would have too high ionic strengths, beyond the limitations of activity coefficient models for the aqueous species [19].

The aqueous species involved in the simulation are listed in Table 2, and most of their thermodynamic properties are from the database provided by Huang and Sverjensky [31], which was extended from the original DEW database [17] with additions of newly calibrated aqueous species of rock-building elements (Ca, Fe, Mg, Al, etc.). In addition, aqueous Zr species (Zr^{4+} , $ZrOH^{3+}$, ZrO^{2+} , $HZrO_2^+$, $ZrO_2(aq)$ and $HZrO_3^-$) are also included in our simulation. Their thermodynamic properties are from Sverjensky et al. [32], with volumetric properties (pressure dependence) recalculated using the extrapolations proposed by Sverjensky et al. [17], for high-pressure simulations. The rock-building silicates and oxides used in this simulation are from the database of Holland and Powell [33], and the metamorphic minerals and the relevant mixing parameters of solid solutions are listed in Tables 3 and 4.

Aqueous Species				
H ₂ O	Mg ²⁺	FeCl ⁺		
H ⁺	MgOH ⁺	FeCl ₂ (aq)		
OH-	MgCl ⁺	Fe ³⁺		
$H_2(aq)$	Mg(HSiO ₃) ⁺	FeOH ²⁺		
O ₂ (aq)	Ca ²⁺	FeCl ²⁺		
$SiO_2(aq)$	CaOH ⁺	FeO (aq)		
Cl	CaCl ⁺	FeO ⁺		
HCl(aq)	CaCl ₂ (aq)	HFeO ₂ (aq)		
Na ⁺	Al ³⁺	FeO ₂ ⁻		
NaOH(aq)	AlOH ²⁺	Zr^{4+}		
NaCl(aq)	Al(OH) ₂ ⁺	ZrOH ³⁺		
$Na(HSiO_3)$	AlO_2^-	ZrO^{2+}		
K ⁺	HAlO ₂ (aq)	HZrO ₂ +		
KOH(aq)	Fe ²⁺	$ZrO_2(aq)$		
KCl(aq)	FeOH ⁺	HZrO ₃ ⁻		

Table 2. Aqueous species included in the modelling.

Table 3. Pure minerals considered in the modelling. The thermodynamic properties are from Holland and Powell [33].

Minerals	Formula
Magnetite (Mt)	Fe ₃ O ₄
Hematite (Hm)	Fe ₂ O ₃
Coesite (Coe)	SiO ₂
Quartz (Qt)	SiO ₂
Sillimanite (Sil)	Al_2SiO_5
Kyanite (Ky)	Al_2SiO_5
Lawsonite (Law)	$CaAl_2Si_2O_{10}H_4$
Zircon (Zrn)	$ZrSiO_4$

Limitations of the simulation are noted here: (i) Due to the lack of available thermodynamic properties, the possible complexations between Cl and Zr are neglected, and aqueous Zr is assumed to be in the forms of aqua or hydroxide complexes (see Table 2). This simplification should be reasonable, because there is no evidence showing the formation of Zr-chloride complexes in Cl-bearing solutions at elevated P-T [34]. The experiment conducted by Rustioni et al. [11] also shows that the fluid mobilities of HFSEs (Hf, Nb and Ta) are generally independent of fluid Cl concentration under subduction P-T conditions; (ii) in P-T regimes with elevated ionic strengths, the accuracy of the simulation cannot be guaranteed, as limited by the HighPGibbs built-in activity coefficients model, i.e., the Davies extension of the Debye–Hückel law [35]. The limitation is believed to be <~0.5 molal [36] or <~0.7 molal (a manual introducing models used for GEM-Selector, available now at http://gems.web.psi.ch/TSolMod/doc/pdf/Activity-Coeffs.pdf-(accessed 6 April 2021)), according to different researchers. Under most P-T conditions, the simulated ionic strength ranges from 0.1 to 0.5 for the Cl-absent fluid, and 0.4 to 0.7 for the Cl-bearing, within the valid range of the Davies extension. Ionic strengths beyond the Davies limitations will be faced under the low-temperature and high-pressure conditions, and the ionic strength contours of 0.5 and 0.7 molal are shown in Figures 2 and 3, i.e., simulation results to the upper left of the contours are of low accuracies.

Mineral	End Member	Formula	Activity Model
Clinopyroxene (Cpx)	diopside	CaMgSi ₂ O ₆	Symmetrical $W_{diopside} - W_{hedenbergite} = 4$ $W_{diopside} - W_{jadeite} = 26$ $W_{diopside} - W_{acmite} = 15$ $W_{iadeite} - W_{bedenbergite} = 24$
	jadeite acmite	NaAlSi ₂ O ₆ NaFeSi ₂ O ₆	$W_{acmite} - W_{hedenbergite} = 14$ $W_{jadeite} - W_{acmite} = 5$
Garnet (Gr)	almandine	Fe ₃ Al ₂ Si ₃ O ₁₂	Symmetrical $W_{almandine} - W_{pyrope} = 2.5$ $W_{almandine} - W_{grossular} = 10$ $W_{almandine} - W_{andradite} = 75$
	pyrope grossular andradite	$\begin{array}{l} Mg_{3}Al_{2}Si_{3}O_{12}\\ Ca_{3}Al_{2}Si_{3}O_{12}\\ Ca_{3}Fe_{2}Si_{3}O_{12} \end{array}$	$W_{pyrope} - W_{grossular} = 45$ $W_{pyrope} - W_{andratite} = 90$ $W_{grossular} - W_{andratite} = 0$
Chlorite (Chl)	daphnite Al-free chlorite amesite	$\begin{array}{c} Fe_{5}Al_{2}Si_{3}O_{10}(OH)_{4} \\ Mg_{6}Si_{4}O_{10}(OH)_{4} \\ Mg_{4}Al_{4}Si_{2}O_{10}(OH)_{4} \end{array}$	Symmetrical $W_{daphnite} - W_{Al-free chlorite} = 14.5$ $W_{daphnite} - W_{amesite} = 13.5$
	clinochlore	$Mg_5Al_2Si_3O_{10}(OH)_4$	$W_{daphnite} - W_{clinochlore} = 2.5$ $W_{Al-free chlorite} - W_{amesite} = 20$ $W_{Al-free chlorite} - W_{clinochlore} = 18$ $W_{amesite} - W_{clinochlore} = 18$
Talc (Tc)	talc Fe-talc	$\begin{array}{c} Mg_{3}Si_{4}O_{10}(OH)_{2} \\ Fe_{3}Si_{4}O_{10}(OH)_{2} \end{array}$	Ideal
Epidote (Ep)	clinozoisite epidote Fe-epidote	Ca ₂ Al ₃ Si ₃ O ₁₂ (OH) Ca ₂ FeAl ₂ Si ₃ O ₁₂ (OH) Ca ₂ Fe ₂ AlSi ₃ O ₁₂ (OH)	$\begin{array}{l} Symmetrical \\ W_{clinozoisite} - W_{epidote} = 0 \\ W_{clinozoisite} - W_{Fe-epidote} = 15.4 \\ W_{epidote} - W_{Fe-epidote} = 3 \end{array}$
Phengite (Phg)	muscovite celadonite	KAl ₃ Si ₃ O ₁₀ (OH) ₂ KMgAlSi ₄ O ₁₀ (OH) ₂	Ideal

Table 4. Solid solutions involved in the modelling. The thermodynamic properties of end members are from Holland and Powell [33] and mixing parameters are from White et al. [37].

3. Results of Modeling

Under the P-T conditions of interest, the altered basalt shows typical eclogitic mineral assemblage, including garnet, clinopyroxene and coesite, with or without kyanite and talc. In addition, accessory amounts of phengite and zircon are present as the K and Zr minerals, respectively (Figure 1a). The calculated mineral assemblage and the P-T conditions of critical phase transitions (e.g., lawsonite-out) are in good agreement with experiment results on MORB protoliths [38].

The simulations show that lawsonite is the predominant hydrous mineral in basaltic eclogite, retaining ~2 wt.% of water relative to the bulk rock mass and remaining stable at up to ~750 °C at sub-arc depths (Figure 1a). However, in most cases, lawsonite-bonded water will not be released at sub-arc environment. As shown in Figure 1a, the P-T path of slab Moho is generally parallel to that of lawsonite-out reaction and does not crosscut the isopleths of bulk rock water contents, indicating that lawsonite dehydration will not take place at sub-arc depths. Compared to slab Moho, the slab top follows a hotter P-T path during subduction, where it typically undergoes lawsonite breakdown below 3 GPa, i.e., before entering sub-arc regions (see Figure 3 of Spandler and Pirard [4]). It has been suggested that lawsonite can remain stable beyond sub-arc depths and, thus, contribute to the water-rich and arc-like signatures (e.g., LILE enrichment and crustal Sr and Nd isotopes) of back-arc magmas [4]. The simulation instead shows that water liberation from altered basaltic crusts is more likely to be governed by talc breakdown at temperatures lower than ~600 °C (Figure 1a). Talc dehydration can liberate ~1.5 wt.% of water at sub-arc depths.



Figure 1. Results of thermodynamic simulation using the NaCl-absent fluid. (**a**) P-T pseudosection showing mineral assemblages and contents of lithological bound water in eclogite metamorphosed from altered oceanic basalt. The geotherms of hot, intermediate and cold subduction zones are for slab Moho, from van Keken et al. [39]. (**b**) The acidity (Δ pH, red dashed lines with labels) and redox (Δ FMQ, blue) of the rock-buffered fluid. Δ pH is the deviation from neutral pH (pH_n) (Δ pH = pH – pH_n), and Δ FMQ is the difference in log *f*O₂(g) of the fluid relative to the fayalite-magnetite-quartz (FMQ) buffer (Δ FMQ = log *f*_{O2, fluid} – log *f*_{O2, FMQ}). The bulk rock composition is given in Table 1. Mineral abbreviations: Cpx = clinopyroxene; Gr = garnet; Coe = coesite; Law = lawsonite; Tc = talc; Ky = kyanite; Phg = phengite; Zrn = zircon.

Fluid pH and, to a lesser extent, $fO_2(g)$ can influence the solubilities and speciation of aqueous lithophile elements such as K and Zr [20], and they are shown in Figure 1b as the differences from neutral pH (defined as $\Delta pH = pH - pHn$, where pH and pHn are values of the fluid and pure water, respectively) and the fayalite-magnetite-quartz buffer (ΔFMQ), respectively (Figure 1b).

In the eclogite-buffered fluids, aqueous K is solely sourced from phengite dissolution and predominated by simple ion (K⁺) in both NaCl-bearing and -absent fluids. In the NaCl-absent fluid, the solubility of K ranges from ~0.01 to 0.3 molal, increasing towards higher P-T (Figure 2a). Within the P-T regime of talc dehydration (T < 600 °C), the solubility of K is significantly lower, down to 0.03 molal (Figure 2a). In the NaCl-bearing fluid, only minor amounts of K-chloride species (KCl(aq)) are formed, contributing to about 2 to 3 mol% of the total aqueous K (Figure 3a). Although the contribution from K-chloride species is basically neglectable, the solubility of K is 1.5 to 4 times higher than in Cl-absent fluid at the same P-T conditions (Figure 3b).



Figure 2. Thermodynamic simulation results of the solubilities of K and Zr in NaCl-absent fluid. (**a**) The solubility of K in the eclogite-buffered fluid shown as logarithm of molality. (**b**) The solubility of Zr as logarithm of molality. (**c**) The solubility ratio of K/Zr in fluid shown as logarithm of molar ratio. Additionally shown are the contours of ionic strengths equal to 0.5 and 0.7 molal (green dashed lines with labels).



Figure 3. The effect of fluid chlorine in the dissolution of K. (a) Molar ratio of KCl(aq)/total K in the fluid with 2 wt.% of dissolved NaCl. (b) The molar ratio between K solubility in NaCl-bearing fluids and that in NaCl-absent fluid.

In the mildly alkaline fluids ($\Delta pH = 2$; Figure 1b), nearly all of (>99.9%) the dissolved Zr is present in the form of HZrO₃⁻, with solubility increasing from 10^{-5} to 10^{-2} molal towards higher P-T (Figure 2b). Zr solubility is similar in Cl-bearing and -absent fluids (Figure A1 of Appendix A). Compared to K, the solubility of Zr shows stronger pressure dependence, with increasing solubilities toward higher pressures. As expected, the solubility of Zr, which is sourced from the dissolution of zircon, is much lower than that of K, with the molality of K typically hundreds to thousands of times higher than that of Zr in slab fluids (Figure 2c).

4. Discussion

In this study, we simulated the solubilities of K and Zr in slab fluids, which are controlled by dissolution of phengite and zircon, respectively. In addition to K, phengite is also the predominant host mineral of Rb and Cs in basaltic eclogite [4]. It is also the major host for Ba in basaltic rocks that have neglectable amounts of carbonate and sulfate minerals [4]. Therefore, the dissociation of phengite will also liberate other LILEs in addition to K. Similarly, in addition to Zr, zircon is the major host for Hf, and thus, the dissolution of Zr is coupled with that of Hf [4].

4.1. The Mobility of K and Other LILEs in Cl-Free Slab Fluids

The solubility of K in Cl-free slab fluids shows a positive correlation with slab depth and temperature, increasing from 0.01 molal to a maximum of 0.3 above 600 °C (Figure 2a). Assuming an average value of 0.1 molal K dissolved in fluids, and typical concentrations of 0.1–0.3 wt.% K₂O in altered marine basalts (Table 1) [40], simple mass balance calculation indicates that a cumulative fluid/rock mass ratio of ~0.2 to 0.6 is required to unlock all the K in the rock. Potassium loss before entering eclogite facies (e.g., devolatilization under blueschist facies) is here omitted, because of the much lower solubility of K at T < 500 °C (Figure 2a).

Simple devolatilization of the eclogite, which only contains up to 4.5 wt.% mineralogically bound H₂O (Figure 1a), cannot provide sufficient amounts of fluids to fully dissociate the LILE-bearing phengite. Furthermore, under most slab geotherms, lawsonite remains stable to sub-arc depths, and talc breakdown will be the main dehydration event (Figure 1a). Taking the Cl-absent simulation for example, talc breakdown will liberate ~1.5 wt.% of water relative to rock mass and only cumulatively release 24 ppm of K relative to rock mass, due to the low solubility of K at temperatures below 500–600 °C. Conclusively, direct devolatilization of altered marine basalt is unlikely to lead to significant LILE enrichment in the mantle wedge, and this accounts for the paradoxical decoupling between water and LILE loss in eclogite [4].

Fluids with higher K concentrations (e.g., 0.1 molal and above) can be formed at higher temperatures, but they need to be sourced externally. A plausible fluid source is

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the serpentinite in subducting lithospheric mantle, and serpentinite-derived fluids can flush the overlaying eclogite when moving upward (e.g., Spandler and Pirard [4]). When the serpentinite-derived fluids infiltrate the overlying crust, it will be chemically buffered by the latter and have the relatively high solubility of K. In this process, LILE-rich fluids can be released from slab and responsible for the LILE enrichment of arc magma. We speculate that this model matches best the situations of the cold and sediment-starved subduction zones such as Mariana, Izu and Tonga. Arc magmas formed in these subduction zones are characterized by high Ba/Th ratios and depleted Sr and Nd isotopes, indicating fluid-dominated mass transfer from altered oceanic basalts [27].

Fully serpentinized peridotite can have water contents higher than 14 wt.% [41], and large amounts of the water can be transferred to depths of up to 200 km [42]. A case study on exhumed slab mantle in southern Spain shows that subducted serpentinite can retain over 5 wt.% of water when metamorphosed to 1.6–1.9 GPa and ~700 °C [42]. Serpentinization of oceanic mantle is spatially heterogeneous on sea floor, with most intensive alterations taking place along fracture zones or transform faults. Globally, it is estimated that all serpentinite in the altered mantle can make up a 500-m-thick layer in the subducting slab [43]. These figures, combined with the several-kilometer-thick oceanic crust, indicate that the amounts of serpentine-derived fluids are far from sufficient to entirely unlock K and other LILEs from the altered oceanic crusts, and large amounts of LILEs can be transferred to greater depths locked in phengite, which is stable to depths greater than 150 km [4]. Formation of slab melts or supercritical fluids may further enhance the liberations of LILEs, but they would not significantly change the budget of LILE circulation, because the solubilities of LILEs (Rb, Cs and Ba) are within the same order of magnitude in slab fluids, melts and supercritical liquids [14]. Any LILEs remaining may contribute to the crustal geochemical signatures of back-arc magmas through deep dehydration of lawsonite or infiltration by serpentinite-derived fluids, or eventually contribute to the formation of deep-sourced intraplate magmas such as plume-related basalts or kimberlites.

4.2. The Effect of NaCl in Mobilizing K and Other LILEs

The presence of NaCl in slab-derived fluids will further enhance LILE mobility. Experiments by Rustioni et al. [11] show that the solubility of LILEs (Rb, Cs, Sr and Ba) can be elevated by more than one order of magnitude with fluid Cl contents increasing from 0 to 6 wt.%. The elevation in LILE solubility is interpreted as a result of the formation of chloride complexes [11]. As the activity coefficient models implemented by HighPGibbs are limited to relatively low Cl contents [19], the effect of Cl on LILEs' mobilization was only estimated to a maximum of 2 wt.% NaCl. The simulation confirms the positive effect of Cl on LILE aqueous transport [11,44], with K solubility increasing by 1.5 to four times with the addition of 2 wt.% NaCl (Figure 3b).

Different from the previous thoughts, the simulations suggest that the enhanced solubility of K is not a direct product of K-Cl complexation, at least for the investigated composition. In the NaCl-bearing fluid, only small proportions (2–3%) of aqueous K are associated with Cl^- (as KCl(aq); Figure 3a), and this cannot account for the elevation in the solubility of K. The weak association between K⁺ and Cl⁻ is expected in slab fluids, because the cold geotherm of subduction zones favors the formation of high-density slab fluids (i.e., high pressure but relatively low temperature), which enhances dissociation of chloride complexes as revealed by studies on the speciation of NaCl [45] and HCl solutions [46].

Instead, the presence of Na^+ in the fluid will favor the decomposition of phengite and release of K^+ and Mg^{2+} via reaction 1:

 $\begin{aligned} &4CaAl_2Si_2O_{10}H_4(Law) + 3CaFeSi_2O_6(hedenbergite in Cpx) + \\ &4Mg_3Si_4O_{12}H_2(talc in Tc) + 2KMgAlSi_4O_{12}H_2(celadonite in Phg) + 4Na^+ = \\ &7CaMgSi_2O_6(diopside in Cpx) + 4NaAlSi_2O_6(jadeite in Cpx) + 7SiO_2(Coe) + \\ &2Mg_3Al_2Si_3O_{12}(pyrope in Gr) + Fe_3Al_2Si_3O_{12}(almandine in Gr) + 2K^+ + Mg^{2+} + \\ &14H_2O \end{aligned}$ (1)

This reaction was obtained by checking the changes in abundances of minerals and aqueous species as fluid salinity increased from 0 to 2 wt.% NaCl at 3.5 GPa and 550 °C. It is noted that reaction 1 is only a first-order approximation of the complex fluid–rock interaction, which involves changes in the amounts of all minerals (and end members) and aqueous species.

Reaction 1 is essentially a displacement reaction, in which fluid Na replaces phengitebonded K and Mg, leading to the formation of Na-rich clinopyroxene (with elevated jadeite end member) and decomposition of phengite. With increasing salinity, the fluid K solubility is elevated and phengite-bonded LILEs are liberated. A side effect of the displacement reaction is a reduction in fluid pH with increased Cl contents, due to the release of Mg to the fluid and its association with OH⁻ (i.e., formation of MgOH⁺). Our simulation shows that the pH values of the Cl-bearing fluid are up to half a unit lower than those of the Cl-absent fluid, at the same P-T (c.f. Figures 1b and A1).

4.3. The Immobility of Zr and Other HFSEs in Slab Fluids

Our simulations on the solubility of Zr further confirms the consensus that HFSEs are generally immobile in slab fluids. The simulation shows that the solubility of Zr are tens to hundreds of times lower than that of K at the same P-T (Figures 2c and A1), and therefore, slab-to-wedge fluid transfer of HFSEs is neglectable, even with the flushing by serpentinite-derived fluids. Thus, higher degrees of HFSE mobilization must require the involvement of aqueous slab melt or supercritical liquid (e.g., Kessel et al. [14]), or melting of mélange diapirs [28].

5. Conclusions

- (1) Eclogite-buffered fluids can have K solubility greater than 0.1 molal under sub-arc P-T conditions, as products of phengite dissolution. Direct devolatilization of oceanic basalts would only mobilize trace amounts of K and other LILEs, and externally sourced, serpentinite-derived fluids should be required for LILE enrichment of the mantle wedge. Although, large amounts of LILEs could be retained in the subducting crust and recycled to deep mantle beyond sub-arc depths.
- (2) Sodium chloride can increase the solubilities of K and other LILEs in slab fluids, but the formation of LILE-chloride complexes only plays a subsidiary role in solubility elevation. Sodium ion (Na⁺) in the fluid can replace K and Mg in phengite, leading to formation of the jadeite end member, breakdown of phengite and, thus, liberation of K and other LILEs.
- (3) Under sub-arc conditions, the solubilities of Zr in slab fluids are hundreds to thousands of times lower than those of K. This further confirms the idea that HFSEs are immobile in slab fluids.

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Minerals assemblage, H2O in rock (wt.%) ΔpH (red), ΔFMO (blue) Ky Pressure (GPa) 4 4.(3.5 Temperature (°C) Temperature (°C) c Potassium (lg molal) in eclogite-buffered fluid d Zirconium (lg molal) in eclogite-buffered fluid 5.0 Pressure (GPa) 45 4.0 3.: 34 3.0 Temperature (°C) Temperature (°C) Lg molar K/Zr ratio in fluid 5.0 Pressure (GPa)

Figure A1. Thermodynamic simulation results of fluid-eclogite equilibrium using fluid with 2 wt.% of dissolved NaCl, showing the mineral assemblage and water content of eclogite (**a**), the Δ pH and Δ FMQ (**b**) and the solubilities of K (**c**) and Zr (**d**) in the eclogite-buffered fluids, as well as the logarithm of molar ratio between fluid K and Zr (**e**). The contours of ionic strength equal to 0.5 and 0.7 are shown as green dashed lines.

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