Status report on stability of K-rich phases at mantle conditions

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Abstract

Experimental research on K-rich phases and observations from diamond inclusions, UHP metamorphic rocks, and xenoliths provide insights about the hosts for potassium at mantle conditions. K-rich clinopyroxene ($Kcpx–KM^{3+}Si_2O_6$) can be an important component in clinopyroxenes at $P > 4$ GPa, dependent upon coexisting K-bearing phases (solid or liquid) but not, apparently, upon temperature. Maximum Kcpx content can reach ~ 25 mol%, with 17 mol% the highest reported in nature. Partitioning $^{(K)}D_{(cpx/liquid)}$ above 7 GPa $= 0.1–0.2$ require ultrapotassic liquids to form highly potassic cpx or critical solid reactions, e.g., between Kspar and Di. Phlogopite can be stable to about 8 GPa at 1250 °C where either amphibole or liquid forms. When fluorine is present, it generally increases in Phl upon increasing P (and probably T) to about 6 GPa, but reactions forming amphibole and/or $KMgF_3$ limit F content between 6 and 8 GPa. The perovskite $KMgF_3$ is stable up to 10 GPa and 1400 °C as subsolidus breakdown products of phlogopite upon increasing P. $^{(M4)}$K-substituted potassic richterite (ideally $K(KCa)Mg_5Si_8O_{22}(OH,F)_2$) is produced in K-rich peridotites above 6 GPa and in Di + Phl from 6 to ~ 13 GPa. K content of amphibole is positively correlated with P; Al and F content decrease with P. In the system $1Kspar + 1H_2O$ K-cymrite (hydrous hexasanidine–$KAlSi_3O_8 \cdot nH_2O$–Kcym) is stable from 2.5 GPa at 400 to 1200 °C and 9 GPa; Kcym can be a supersolidus phase. Formation of Kcym is sensitive to water content, not forming within experiments with $H_2O < Kspar$, and melt + aluminous phases forming with $H_2O > Kspar$. Phase X, a potassium di-magnesium acid disilicate ($(K_{1-x-n})_2(Mg_{1-n}M_n^{3+})_2Si_2O_7H_{2x}$), forms in mafic compositions at $T = 1150–1400$ °C and $P = 9–17$ GPa and is a potential host for K and H_2O at mantle conditions with a low-T geotherm or in subducting slabs. The composition of phase-X is not fixed but actually represents a solid solution in the stoichiometries $\square_2Mg_2Si_2O_7H_2–(K\square)Mg_2Si_2O_7H–K_2Mg_2Si_2O_7$ ($\square$ = vacancy), apparently stable only near the central composition. K-hollandite, $KAlSi_3O_8$, is possibly the most important K-rich phase at very high pressure, as it appears to be stable to conditions near the core–mantle boundary, 95 GPa and 2300 °C. Other K-rich phases are considered.
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1. Introduction

Potassium is an important element in Earth, because as a large-ion lithophile element, it is an "incompatible" element that has been strongly parti-

tioned into the crust from the mantle by differentiation, it is important to many important mineral families (feldspars, micas, amphiboles) and, in the form of ^{40}K, it contributes to Earth's heat budget. How potassium can be retained in the mantle, whether via recycling of the crust or by inherent stabilities that prevented thorough differentiation into the crust, can only be addressed by understanding mineral reservoirs

at mantle conditions. Much experimental research has been carried out on K-rich phases at high pressure in recent years. Combined with observations from diamond inclusions, UHP metamorphic rocks, and xenoliths and enclaves from extrusives, these provide an expanding understanding of the hosts for potassium at mantle conditions. An update of the extant data is presented here.

2. K-rich phases

2.1. Sanidine

In a "dry" environment this feldspar is stable to 6.5 GPa at 1000 °C (see Table 1), breaking down to $K_2Si_4O_9 + Al_2SiO_5 + SiO_2$ (Yagi et al., 1994; Urakawa et al., 1994) and has been found as inclusions in diamonds and kyanite eclogites (always in eclogite association). Experiments in alkali basalt by Tsuruta and Takahashi (1998) found sanidine as a minor subsolidus phase up to 6 GPa. Abundant fluid inclusions (Smyth and Hatton, 1977) or strong H_2O IR-signature in sanidine, in certain cases, makes K-cymrite a logical precursor phase (see below).

2.2. K-rich clinopyroxene

K-rich clinopyroxene ($Kcpx – KM^{3+}Si_2O_6$): Experiments show that Kcpx can become an important component in clinopyroxenes at pressures above 4–5 GPa, depending upon coexisting K-bearing phases (or the lack thereof) but not, apparently, upon temperature (Luth, 1997; Harlow, 1997; Schmidt and Poli, 1998; Tsuruta and Takahashi, 1998; Perchuk et al., 2002). Maximum Kcpx content can reach ~ 25 mol% with 17 mol% the highest reported from a natural (UHP) sample (see Perchuk et al., 2002), other K-rich clinopyroxene being found as inclusions in diamonds (e.g., Harlow and Veblen, 1991; see Perchuk et al., 2002). The partition coefficient for calcic clinopyroxene (cpx) and melt, $^KD_{cpx/liquid}$, above 7 GPa $\cong 0.1–0.2$ and requires either ultrapotassic liquids (inferred to require carbonatitic melt or a fluid rather than a silicate melt; e.g., Konzett and Fei, 2000; Perchuk et al., 2002) to form highly potassic cpx (>1.5 wt.% K_2O) or a "critical" cpx solid-solution reaction with a liquid (Safonov et al., 2003). In studying melt parti-

tioning for diopside–jadeite solid solutions, Chamorro et al. (2002) have confirmed $^KD_{cpx/liquid}$ values ≥ 0.2 for diopsidic cpx and lower values, ~ 0.01, for jadeitic cpx. As cpx can be a liquidus-to-subsolidus product, the only critical requirements in the formation of K-rich cpx is calcic cpx stability and K content in the phase assemblage, however, coexisting more K-rich solids (e.g., sanidine, K-rich amphibole) can reduce the K-content of the cpx coexisting with a melt relative to that in a cpx–melt pair where no K-rich solids are present (e.g., Konzett and Fei, 2000; Mitchell, 1995). Reporting on experiments with a K-spiked, water-saturated MORB composition (0.49 wt.% K_2O in their KMB-7), Schmidt and Poli (1998) found that above 4 GPa K-content of cpx increases upon increasing T up to the solidus but then decreases dramatically at supersolidus conditions. Some, thus, interpret high Kcpx contents (>1 wt.% K_2O) in natural cpx to be the result of growth in the absence of another coexisting K-rich phase and melt or, alternatively, growth from a very K-rich fluid/melt that, in all cases, was followed by encapsulation–preservation to avoid reequilibration/unmixing that would reduce the Kcpx content. A review of experimental results is provided by Perchuk et al. (2002). Oxidized iron-rich assemblages (e.g., some lamproites/lamprophyres/etc.; Plá Cid et al., 2003; Mitchell, 1995; Mellini and Cundari, 1989) may enable a ferric Kcpx at somewhat lower pressures than 5 GPa and is being investigated by the authors.

2.3. Phlogopite

In peridotites, phlogopite is stable to >6 GPa at 1100 °C (Konzett et al., 1997) and to between 8 and 12 GPa at 1250–1350 °C in diopside (Di) plus phlogopite (Phl) assemblages (depending on bulk composition, see Harlow, 2002) above which P and T either amphibole or liquid is more stable. When fluorine is present, it generally increases in Phl upon increasing P (and probably T) to about 6 GPa, but reactions to form amphibole and/or $KMgF_3$ limit F content between 6 and 8 GPa (Harlow, 2002). In peralkaline KNCMASH, Phl persists to 10 GPa at ~ 1300 °C (see Konzett and Fei, 2000). In more pelitic compositions, Phl breaks down at low P and T (~ 3 GPa at 1000 °C) to phengite ± sanidine ± fluid (see Massone, 1999).

Table 1
Potential K-rich mantle minerals

Mineral	Composition	Stability	Citations
Sanidine	$KAlSi_3O_8$	to ~ 6 GPa, 1200 °C	Yagi et al. (1994), Urakawa et al. (1994)
Phengitic muscovite	$KAl_{2-x}Mg_xAl_{1-x}Si_{3+x}O_{10}(OH)_2$	to 9.5–10, 750–1050 °C	Schmidt (1996), Schmidt and Poli (1998)
		to 8–11 GPa, 750–1050 °C	Domanik and Holloway (2000)
Phlogopite	$KMg_3AlSi_3O_{10}(OH)_2$	to ~ 9 GPa, 1400 °C	Luth (1997)
	$KMg_3AlSi_3O_{10}(F)_2$	to ~ 10 GPa, 1400 °C	Harlow (2002)
KK-richterite	$KKCaMg_5Si_8O_{22}(OH)_2$	from 6 GPa at 1000 °C to >15 GPa at 1400 °C	Inoue et al. (1998), Luth (1997), Sudo and Tatsumi (1990),
		from 8 GPa at 1100 °C to 14 GPa at 1400 °C	Harlow (2002) Konzett and Fei (2000)
	$K(Ca,K,Na)_2Mg_5(Si,Al)_8O_{22}(F,OH)_2$	Konzett et al. (1997) to 13 GPa at 1400 °C	Konzett and Ulmer (1999) Konzett and Fei (2000)
Phase X	$(K□)Mg_2Si_2O_7H$	9–23 GPa at 1150–1700 °C	Luth (1997), Harlow (1997), Inoue et al. (1998), Konzett and Ulmer (1999), Konzett and Fei (2000)
(21)-MHP	$KNa_2Ca_2Mg_6AlSi_{12}O_{34}(OH)_2$	Konzett and Fei (2000) 5–18 GPa at 1100–1600 °C	Konzett and Japel (2003)
K-clinopyroxene	$K(Al,Cr)Si_2O_6-Cpx_{ss}$	5–15 GPa at 1000–1500 °C Kcpx1 to Kcpx20	Harlow (1997), Wang and Takahashi (1999), Safonov et al. (2003)
Si-wadeite (or K-wadeite)	$K_2Si_4O_9$	from 6 GPa at 1000 °C to ~ 16 GPa at 1400 °C to 12 GPa at 1500 °C	Yagi et al. (1994), Kanzaki et al. (1998) Harlow (1997)
Wadeite	$K_2ZrSi_3O_9$	from 1 atm at 800 to >3 GPa at 1200 °C	Arima and Edgar (1980) Orlando et al. (2000)
K-cymrite (or sanidine hydrate)	$KAlSi_3O_8•nH_2O$ ($n ≤ 1$)	from 2.5 GPa at 400 °C to 9 GPa at 1200 °C	Massone (1995), Fasshauer et al. (1997), Thompson et al. (1998) This work
$KMgF_3$-perovskite $KMgF_3$		to ≥ 8 GPa at 1400 °C	Harlow (2002), Thibault (1993)
Al-rich phase	$[K,Na]_{0.9}[Mg,Fe]_2[Mg,Fe,Al,Si]_6O_{12}$	≥ 24 GPa at 1700–1800 °C	Gasparik and Litvin (2002)
K-phase 1	$(K,Na)_2FeMg_4Si_5O_{16}$ or	15 GPa at 1400 °C	Wang and Takahashi (2000),
	$(K,Na)_2Mg_4Si_4O_{13}$	to 20 GPa at <1900 °C	Gasparik and Litvin (2002)
K-hollandite	$KAlSi_3O_8$	from ~ 9 GPa at >1000 °C to >25 GPa at >1600 °C to 95 GPa at 2300 °C	Yagi et al. (1994), Urakawa et al. (1994), Wang and Takahashi (1999) Tutti et al. (2001)
K-Ti silicates	$K_2TiSi_3O_9$	from 1 to 3 GPa at 1100 °C	Gulliver et al. (1998)
	$K_4Ti_2Si_7O_{20}$ to $K_4TiSi_8O_{20}$	from ~ 4 to >6 GPa at 1100–1400 °C	Mitchell (1995)
Priderite	$(K,Ba,□)_2(Ti,Fe^{3+},Fe^{2+})_8O_{16}$	1200–1500 °C, 3.5–5 GPa	Foley et al. (1994)
Mathiasite	$K(Ti_{13}Cr_4FeZrMg_2)O_{38}$	1300 °C, 5 GPa	Foley et al. (1994)
LIMA	$(Ba_{0.5}K_{0.5})(Ti_{13}Cr_{3.5}FeZrMg_{2.5})O_{38}$	1200–1300 °C, 3.5–5 GPa	Foley et al. (1994)
Yimengite	$K(Ti_3Cr_5Fe_2Mg_2)O_{19}$	1200 °C, 5 GPa	Foley et al. (1994)
HAWYIM	$(Ba_{0.5}K_{0.5})(Ti_3Cr_{4.5}Fe_2Mg_{2.5})O_{19}$	1150–1350 °C, 4.3–5 GPa	Foley et al. (1994)

2.4. Phengitic muscovite

Phengite stability has been examined in "wet" graywacke and K-rich basalt compositions (Schmidt, 1996; Schmidt and Poli, 1998), a bulk composition approximating something between mica and a pelitic sediment (Domanik and Holloway, 1996), and calcareous metapelite (Domanik and Holloway, 2000) over the general range of 7–11 GPa and 750 to 1100 °C (see Table 1). Upon increasing pressure phengite

yields to K-hollandite stability between 8 and 11 GPa and 750–900 °C (the reaction has a slightly negative P/T slope), with the transition pressure depending perhaps on bulk composition, such as alumina content. Melt breakdown of the mica occurs above 900 °C at low bulk Al content and above 1075–1150 °C at 7–8 GPa and high Al content. Phengite is the most significant host for potassium in the subducting oceanic crust (sediments + basaltic components) and, in that role, also carries water to pressures from 2 to perhaps 10 GPa, as pointed out by Schmidt and Poli (1998).

2.5. Amphibole–^{M4}K-substituted potassic richterite

This amphibole, sometimes called KK-richterite (ideally K[KCa]Mg$_5$Si$_8$O$_{22}$[OH,F]$_2$), must be differentiated from K-richterite (ideally K[NaCa]Mg$_5$Si$_8$O$_{22}$[OH,F]$_2$) that is a moderate to high-pressure (~ 2 to < 6 GPa) amphibole found in xenoliths, such as from the Kimberley (RSA) pipes (e.g., Erlank et al., 1987), and in lamproites (e.g., Mitchell and Bergman, 1991; Mitchell, 1995). The substitution of K into the M4 site, analogous to K in M2 in cpx, is the defining high-pressure feature of this K-rich amphibole (Yang et al., 1999). It has been produced from of Di + Phl and K-rich peridotitic compositions at P>6 to 15 GPa (Trønnes, 1990; Sudo and Tatsumi, 1990; Luth, 1997; Konzett et al., 1997; Inoue et al., 1998; Konzett and Ulmer, 1999; Konzett and Fei, 2000; Harlow, 2002; see Table 1), above which it breaks down to phase X, Si-wadeite, and/or liquid. Various experimental studies have shown that K content is positively correlated with P; Al and F content decrease with P; and F content is positively correlated with T but lowered by coexisting KMgF$_3$ (Harlow, 2002). In less K-rich bulk compositions, such as natural KLB-1, amphibole breaks down at 12–13 GPa and 1200 °C (see Konzett and Fei, 2000). Amphibole is a major potential reservoir in the upper mantle at depths exceeding ~ 200 km and may be important in fertilized mantle wedge during subduction (e.g., Schmidt and Poli, 1998).

2.6. Phase X

Phase X, a potassium di-magnesium acid disilicate ([K$_{1-x-n}$]$_2$[Mg$_{1-n}$M$_n^{3+}$]$_2$Si$_2$O$_7$H$_{2x}$), was discovered

in synthesis products in various studies at T = 1150–1400 °C and P = 9–17 GPa (e.g., Luth, 1997; Harlow, 1997; Inoue et al., 1998; Konzett and Ulmer, 1999). It is the "cold" breakdown product of amphibole: < 1200 °C at P ~ 16 GPa (Inoue et al., 1998). Its maximum stability in KNCMASH and KLB-1 peridotite reaches 20–23 GPa at 1500–1700 °C where it breaks down to K-hollandite; the stability limit is reduced by a few GPa in subalkaline KNCMASH (Konzett and Fei, 2000). Thus, phase X is a potential host for K and H$_2$O in the mantle to the bottom of the transition zone. The composition of phase-X is not fixed but actually represents a solid solution in the stoichiometries □$_2$Mg$_2$Si$_2$O$_7$H$_2$—(K□)Mg$_2$Si$_2$O$_7$H—K$_2$Mg$_2$Si$_2$O$_7$, where the center part of the solid solution series appears to be the most stable portion at the conditions examined so far. There is also solid solution with a Na-version of phase X, but experiments show that K is preferred over Na at higher pressures (Konzett and Fei, 2000).

2.7. K-hollandite

KAlSi$_3$O$_8$, in which Al and Si are both 6-coordinated forming a channel for the K site, is stable from ~ 8 GPa through conditions of the lower mantle (95 GPa to 2300 °C in DAC experiments) (e.g., Yagi et al., 1994; Urakawa et al., 1994; Konzett and Fei, 2000; Tutti et al., 2001). This phase appears to be the main K-rich solid-phase reservoir for potassium through the transition zone to the lower mantle when considering silicate compositional systems, as most K–Al silicates react to yield K-hollandite upon increasing pressure (e.g., Faust and Knittle, 1994; Irifune et al., 1994; Schmidt, 1996). One inclusion in diamond (Kankan, Guinea) has been reported where K-hollandite might have been the precursor phase (Stachel et al., 2000).

2.8. KMgF$_3$ perovskite

Pure KMgF$_3$ was studied by Gulliver et al. (1998) and shown to be stable to 2.6 GPa and 1400 °C. Thibault (1993) and Edgar and Pizzolato (1995) found it as a breakdown of F-phlogopite up to 8 GPa. It (with F-bearing clinohumite and chondrodite) is stable up to at least 10 GPa and 1400 °C as subsolidus breakdown products of F-bearing phlogopite (+ Di)

upon increasing P (Harlow, 2002), thus some phlogopite (or melts) may be a reaction product of this phase upon uplift.

2.9. K-cymrite

K-cymrite (or hydrous hexasanidine–$KAlSi_3O_8 \cdot nH_2O$, $n \leq 1$) has been shown to be stable above 2.5 GPa at 400 to 1000 °C and $\sim$ 4 GPa (Massone, 1995; Fasshauer et al., 1997; Thompson et al., 1998) in the pure system $KAlSi_3O_8 + H_2O$. Producing K-cymrite (Kcym) at high pressure appears to be highly dependent upon H_2O content of the system. At low water contents ($H_2O < KAlSi_3O_8$) experiments yield the anhydrous assemblages plus vapor or melt without ever forming a hydrous crystalline phase, whereas high water content ($H_2O > KAlSi_3O_8$) produces extensive melting with coexisting aluminous crystalline phases such as muscovite, kyanite, and corundum. At conditions of $H_2O \approx KAlSi_3O_8$, Kcym is stable to at least 9 GPa at 1200 °C and 8 GPa at 1250 °C, suggesting a negative P/T slope for breakdown to K-hollandite + stishovite + fluid. Kcym can be a supersolidus phase, which may be very significant to its survival at mantle conditions. Study of K-cymrite stability conditions continues by the authors. In experiments with a mixture of Di + sanidine + Phl, Kcym was found at 6–8 GPa and 1200 °C coexisting with Cpx + Phl $\pm$ kyanite $\pm$ enstatite.

Whereas no preserved examples of K-cymrite have been identified, the existence of sanidine with an abundance of fluid inclusions from a sanidine grospydite (Smyth and Hatton, 1977) and sanidine + quartz + biotite inclusions coexisting with apparent graphite pseudomorphs of diamond in garnets from high-pressure enclaves of the Erzgebirge (Massone and Nasdala, 2003) appear to be the retrograde assemblages after K-cymrite. K-cymrite appears to be an important potential reservoir for both potassium and water at UHP and upper mantle conditions for eclogites and continental crust components.

2.10. Wadeite and Si-wadeite

Wadeite, $K_2ZrSi_3O_9$, a common minor constituent in lamproites, and some other highly potassic rocks and carbonatites, is stable from 1 atm to at least 3 GPa

at 800–1200 °C (Arima and Edgar, 1980; Orlando et al., 2000). It forms a complete solid solution with $K_2TiSi_3O_9$ in binary experiments, but in the presence of melt or phlogopite or Ti content decreases, indicating the more refractory nature of wadeite. Si-wadeite ($K_2Si_4O_9$) is a common product in K-rich experiments with stability from 6 to >12 GPa, typically limited by reactions forming sanidine, K-cymrite, or K-hollandite. Pure $K_2Si_4O_9$ melts congruently to at least 12 GPa (Kanzaki et al., 1998). It was found as a breakdown product of K-rich amphibole at T>1200 °C and P from 14 to 16 GPa (Inoue et al., 1998). There are no citations of Si-wadeite in natural samples.

2.11. K–Ti-silicates

$K_2TiSi_3O_9$, a wadeite analog (see above), is stable to at least 3 GPa in the pure K–Ti-silicate system, but in nature has only been found in one lamproite (Gulliver et al., 1998). Perhaps related to $BaTi_9O_{20}$ (hollandite-like structure), a phase with apparent formula $K[Si,Ti]_9O_{20}$ was produced from sanidine–phlogopite lamproite in experiments at >4.5 GPa and $\sim$ 1400–1500 °C (Mitchell, 1995). These K–Ti silicates bear a passing resemblance to members of the crichtonite group, particularly mathiasite, $(K,Ca,Sr)(Ti,Cr,Fe,Mg)_{21}O_{38}$, which are interpreted as forming by kimberlite-related metasomatism in the upper mantle (Haggerty et al., 1983).

2.12. K–Ba–Ti–Fe-oxides

Experiments have been carried out on priderite $[(K,Ba,\square)_2(Ti,Fe^{3+})_8O_{16}$—with a hollandite-like structure] and the lindsleyite–mathiasite (LIMA—with a rhombohedral layer structure) and hawthorneite–yimengite (HAWYIM—with a magnetoplumbite structure) series, a group of K–Ba–Ti–Cr–Zr oxides (see Table 1), considered important in the origin of deep alkaline magmas such as lamproites and kimberlites. These experiments have shown that priderite and LIMA phases are stable to pressures between 3.5 and 5 GPa and HAWYIM phases between 4.3 and 5 GPa at 1200 to 1500 °C (Foley et al., 1994), which do not represent their maximum stabilities as the experiments only reached 5 GPa.

2.13. (21)-MHP

The mixed-chain (21)-hydrous clinopyribole, nominally $KNa_2Ca_2Mg_6AlSi_{12}O_{34}(OH)_2$—a combination of K-richterite plus 2 omphacite formulae, was found in experiments on a KNCMASH bulk composition by Konzett and Fei (2000). In recent work with compositions approximating its own composition, (21)-MHP has been shown to be stable from 5–18 GPa and 1100–1600 °C (Konzett and Japel, 2003) and, potassium has been shown to be necessary to produce this clinopyribole.

2.14. K-phase-1

$(K,Na)_2Mg_4Si_4O_{13}$ and related K-rich phases have been reported at high P in experiments by Wang and Takahashi (2000) and Gasparik and Litvin (2002) (see Table 1), but the low-melting temperatures (subgeotherm) make them unlikely candidates as a sink or sampleable phase in the mantle.

2.15. Al-rich phase

A phase with a composition like $[K,Na]_{0.9}[Mg, Fe]_2[Mg,Fe,Al,Si]_6O_{12}$ with up to ~ 7 wt.% K_2O has been reported in experiments (Gasparik et al., 2000; Gasparik and Litvin, 2002) at 24 GPa from the breakdown of garnet to perovskite in the presence of potassium and invoked as a partial explanation for a cpx-corundum pair from a São Luiz, Brazil diamond (Hutchison, 1997).

Acknowledgements

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