

# STATUS REPORT ON STABILITY OF K-RICH PHASES AT UPPER-MANTLE CONDITIONS

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## INTRODUCTION

Experimental research on K-rich phases and observations from diamond inclusions, UHP metamorphic rocks, and xenoliths and enclaves from extrusives provide an expanding understanding of the hosts for potassium (and water and fluorine) at mantle conditions. An update is presented:

## K-RICH PHASES

### SANIDINE

In a “dry” environment this feldspar is stable to 6.5 GPa at 1000 °C (see Table 1), breaking down to  $K_2Si_4O_9 + Al_2SiO_5 + SiO_2$ , and has been found as inclusions in diamonds and kyanite eclogites (always in eclogite association). Abundant fluid inclusions or strong  $H_2O$  signature in IR, in certain cases, makes K-cymrite a logical precursor (see below).

### 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; Perchuk, 2002). Maximum Kcpx content can reach ~25 mol% with 17 mol% the highest reported from a natural (UHP) sample (see Perchuk, 2002), other K-rich clinopyroxene (cpx) being found as inclusions in diamonds (e.g., Harlow and Veblen, 1991; see Perchuk, 2002). The partition coefficient for calcic cpx and melt,  $^KD_{cpx/liquid}$ , above 7 GPa  $\cong 0.1 - 0.2$  and requires 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 or requires a “critical” cpx solid-solution reaction with a liquid (Safonov, personal communication). Chamorro et al. (2002) have confirmed  $^KD_{cpx/liquid}$  values  $\geq 0.2$  for diopsidic cpx (Di-Jd<sub>ss</sub>) and lower values,  $\sim 10^{-2}$ , 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 K-rich solids (e.g., sanidine, K-rich amphibole) 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). Some, thus, interpret high Kcpx contents ( $>1$  wt%  $K_2O$ ) to be the result of cpx growth in the absence of another coexisting K-rich phase (or growth from a K-rich fluid/melt) 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. – Mitchell, 1995; Mellini and Cundari, 1989) may enable a ferric Kcpx at somewhat lower pressures than 5 GPa and is being investigated.

### PHLOGOPITE

In peridotites, phlogopite is stable to  $> 6$  GPa at 1100 °C 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, 2002). In more pelitic compositions, Phl breaks down at low P and T (~3 GPa at 1000 °C) to phengite  $\pm$  sanidine  $\pm$  fluid (see Massone, 1999).

### PHENGITIC MUSCOVITE

Phengite stability has been examined in “wet” graywacke and K-rich basalt compositions (Schmidt, 1996), 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 transition pressure perhaps depending 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.

**Table 1: Potential K-rich Mantle Minerals**

Mineral	Composition	Stability	Citations
Sanidine	$\text{KAlSi}_3\text{O}_8$	to ~6 GPa, 1200 °C	Yagi et al. (1994), Urakawa et al. (1994)
Phengitic muscovite	$\text{KAl}_{2-x}\text{Mg}_x\text{Al}_{1-x}\text{Si}_{3+x}\text{O}_{10}(\text{OH})_2$	to 9.5–10, 750-1050 °C to 8-11 GPa, 750-1050 °C	Schmidt (1996) Domanik and Holloway (2000)
Phlogopite	$\text{KMg}_3\text{AlSi}_3\text{O}_{10}(\text{OH})_2$ $\text{KMg}_3\text{AlSi}_3\text{O}_{10}(\text{F})_2$	to ~9 GPa, 1400 °C to ~10 GPa, 1400 °C	Luth (1997) Harlow (2002)
KK-richterite	$\text{KKCaMg}_5\text{Si}_8\text{O}_{22}(\text{OH})_2$  $\text{K}(\text{Ca},\text{K},\text{Na})_2\text{Mg}_5(\text{Si},\text{Al})_8\text{O}_{22}(\text{F},\text{OH})_2$	from ~7 GPa @ 1000 °C to >15 GPa @ 1400 °C from 8 GPa @ 1100 °C to 14 GPa @ 1400 °C  to 13 GPa @ 1400 °C	Luth (1997), Sudo & Tatsumi (1991), Harlow (2002) Konzett & Fei (2000)  Konzett & Ulmer (1999) Konzett & Fei (2000)
(21)-MHP	$\text{KNa}_2\text{Ca}_2\text{Mg}_6\text{AlSi}_{12}\text{O}_{34}(\text{OH})_2$	5-18 GPa and 1100-1600 °C	Konzett & Fei (2000) Konzett & Japel (in press)
K-clinopyroxene	$\text{K}(\text{Al},\text{Cr})\text{Si}_2\text{O}_6\text{-Cpx}_{\text{ss}}$	5 to 15 GPa, 1000-1500 °C Kcpx1 to Kcpx20	Harlow (1997), Wang & Takahashi (1999)
Si-wadeite (or K-wadeite)	$\text{K}_2\text{Si}_4\text{O}_9$	from 6 GPa @ 1000 °C to ~12 GPa @ 1500 °C	Yagi et al. (1994), Harlow (1997)
K-cymrite (or sanidine hydrate)	$\text{KAlSi}_3\text{O}_8 \cdot n\text{H}_2\text{O}$ ( $n \leq 1$ )	from 2.5 GPa @ 400 °C  to 8 GPa @ 1200 °C	Fasshauer et al. (1997), Thompson et al. (1998) This work
KMgF <sub>3</sub> -perovskite	$\text{KMgF}_3$	to ≥8 GPa @ 1400 °C	Harlow (2002)
Al-rich phase	$[\text{K},\text{Na}]_{0.9}[\text{Mg},\text{Fe}]_2[\text{Mg},\text{Fe},\text{Al},\text{Si}]_6\text{O}_{12}$	≥ 24 GPa @ 1700-1800 °C	Gasparik & Litvin (2002)
K-phase 1	$(\text{K},\text{Na})_2\text{Mg}_4\text{Si}_4\text{O}_{13}$	16? GPa @ 1600 °C? to 20 GPa @ <1900 °C	Wang & Takahashi (2000), Gasparik & Litvin (2002)
K-hollandite	$\text{KAlSi}_3\text{O}_8$	from ~9 GPa @ >1000 °C to >25 GPa @ >1600 °C	Yagi et al. (1994), Urakawa et al. (1994), Wang & Takahashi (1999)
K-Ti silicates	$\text{K}_4\text{Ti}_2\text{Si}_7\text{O}_{20}$ to  $\text{K}_4\text{TiSi}_8\text{O}_{20}$	from 6 GPa @ 1100-1400 °C	Mitchell (1995)

**AMPHIBOLE – <sup>M4</sup>K-SUBSTITUTED POTASSIC RICHTERITE**

This amphibole, sometimes called K-richterite or KK-richterite (ideally  $\text{K}[\text{KCa}]\text{Mg}_5\text{Si}_8\text{O}_{22}[\text{OH},\text{F}]_2$ ), has been produced from Di + Phl and K-rich peridotitic compositions at  $P > 7$  to 15 GPa (see Table 1), above

which it breaks down to phase X 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  $\text{KMgF}_3$  (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, 2002). Amphibole is a major potential

reservoir in the upper mantle at depths exceeding ~ 200 km.

### **PHASE X**

Phase X, a potassium di-magnesium acid disilicate ( $[\text{K}_{1-x-n}]_2[\text{Mg}_{1-n}\text{M}^{3+}_n]_2\text{Si}_2\text{O}_7\text{H}_{2x}$ ), was discovered in synthesis products in various studies at  $T=1150-1400^\circ\text{C}$  and  $P = 9-17\text{ GPa}$  (e.g., Luth, 1997; Harlow, 1997; Konzett and Ulmer, 1999). 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  $\text{H}_2\text{O}$  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  $\square_2\text{Mg}_2\text{Si}_2\text{O}_7-(\text{K}\square)\text{Mg}_2\text{Si}_2\text{O}_7\text{H}-\text{K}_2\text{Mg}_2\text{Si}_2\text{O}_7\text{H}_2$ , where the center part of the solid solution series appears to be the most stable portion at the conditions examined so far.

### **K-HOLLANDITE**

$\text{KAlSi}_3\text{O}_8$ , in which Al and Si are both 6-coordinated, is stable from ~ 9 GPa through condition of the lower mantle and appears to be the main K-rich solid-phase reservoir for potassium through the transition zone to the lower mantle. One inclusion in diamond (Kankan, Guinea) has been reported where K-hollandite might have been the precursor (Stachel et al., 2000).

### **KMGF<sub>3</sub> PEROVSKITE**

$\text{KMgF}_3$  (and F-bearing clinohumite and chondrodite) is stable up to at least 10 GPa and 1400 °C as subsolidus breakdown products of phlogopite upon increasing  $P$  (Harlow, 2002), thus some phlogopite (or melts) may be a reaction product of these phases upon uplift.

### **K-CYMRITE**

K-cymrite (or hydrous hexsanidine- $\text{KAlSi}_3\text{O}_8 \cdot n\text{H}_2\text{O}$ ,  $n \leq 1$ ) is stable from 2.5 GPa at 400 °C to 1000 °C and ~6 GPa, depending upon water content, where it reacts to Si-wadeite ( $\text{K}_2\text{Si}_4\text{O}_9$ ) + kyanite + silica +  $\text{H}_2\text{O}$  or melt; the reaction boundary has positive slope of ~2.5 MPa/°C and is similarly placed to the anhydrous reaction sanidine  $\rightleftharpoons$  K-wadeite + kyanite + silica. In experiments with a mixture of Di + sanidine + Phl, K-cymrite was found at 6-8 GPa and 1200 °C coexisting with Cpx + Phl  $\pm$  kyanite  $\pm$  enstatite. K-cymrite formation appears to be highly dependent upon  $\text{H}_2\text{O}$  content (activity) of the system; experiments indicate it is not stable at supersolidus conditions. Considering the strong effect  $\text{H}_2\text{O}$  has on lowering melting temperatures, K-cymrite may be restricted to relatively high  $P/T$  conditions and may react

to sanidine upon equilibration or uplift. Study on K-cymrite continues.

### **K-Ti-SILICATE**

Perhaps related to  $\text{BaTi}_9\text{O}_{20}$  (hollandite-like structure), a phase with apparent formula  $\text{K}[\text{Si,Ti}]_9\text{O}_{20}$  was produced from sanidine-phlogopite lamproite in experiments at  $>4.5\text{ GPa}$  and  $<1400-1500^\circ\text{C}$  (Mitchell, 1995). These K-Ti silicates bear a passing resemblance to members of the crichtonite group, particularly mathiasite,  $[\text{K,Ca,Sr}][\text{Ti,Cr,Fe,Mg}]_{21}\text{O}_{38}$ , which are formed by kimberlite-related (?) metasomatism in the upper mantle (Haggerty et al., 1983).

### **SI-WADEITE**

Si-wadeite (or K-wadeite –  $\text{K}_2\text{Si}_4\text{O}_9$ ) is a common product in K-rich experiments with stability from 6 to  $>12\text{ GPa}$ , typically limited by reactions forming sanidine, K-cymrite, or K-hollandite. There are no citations of K-wadeite in natural samples, although the mineral wadeite,  $\text{K}_2\text{ZrSi}_3\text{O}_9$ , found in alkaline rocks and carbonatites, may be stable at high pressure.

### **(21)-MHP**

The mixed-chain (21)-hydrous clinopyribole, nominally  $\text{KNa}_2\text{Ca}_2\text{Mg}_6\text{AlSi}_{12}\text{O}_{34}(\text{OH})_2$  – a combination of K-richterite plus 2 omphacite formulae, was found in experiments on a KNCMASH bulk composition by Konzett and Fei (2000). Recent work with compositions approximating its own composition, (21)-MHP is stable from 5-18 GPa and 1100-1600 °C (Konzett and Japel, in press); moreover, potassium has been shown to be necessary to produce this clinopyribole.

### **K-PHASE-1**

$(\text{K,Na})_2\text{Mg}_4\text{Si}_4\text{O}_{13}$  and related K-rich phases have been reported at high  $P$  in experiments (see Table 1) but the low-melting temperature (sub-geotherm) make them unlikely candidates as a sink or sampleable phase in the mantle.

### **AL-RICH PHASE**

A phase with a composition like  $[\text{K,Na}]_{0.9}[\text{Mg,Fe}]_2[\text{Mg,Fe,Al,Si}]_6\text{O}_{12}$  with up to ~7 wt%  $\text{K}_2\text{O}$  has been reported in experiments (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 (Hutchinson, 1997).

## ACKNOWLEDGEMENTS:

The authors apologize to researchers who have not been directly cited in this manuscript, but concerns for length led to this decision. In the final version we will address the missing citations. We gratefully acknowledge the National Science Foundation (EAR-9314819 & EAR-9903203) for support of this research.

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