Interpretation of Kcpx and CaEs in Clinopyroxene from Diamond Inclusions and Mantle Samples

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Clinopyroxene (Cpx) has many potential components that make it a monitor of aspects of the growth environment: chemistry, coexisting phases, and conditions. This is particularly important in the upper mantle where high-variance phases like amphibole, mica, and melt or fluid are either rarely or not preserved in samples that reach Earth's surface as xenocrysts, grains in xenoliths, or inclusions in diamonds. Recent multianvil experiments provide some new constraints and insights into environments of clinopyroxenes, particularly with respect to potassium clinopyroxene (KAlSi₂O₆ or KCrSi₂O₆ –Kcpx), calcium-Eskola (Ca_{0.5}AlSi₂O₆–CaEs), and calcium-Tschermaks (CaAlAlSiO₆ – CaTs) components.

Kcpx: Reports of Kcpx component in clinopyroxenes from the mantle, abundantly reported in the kimberlite/xenolith/diamond literature, have proven (finally) to be real and the result of high pressure (Harlow and Veblen, 1991; Edgar and Vukadinovic, 1995; Harlow, 1997, Luth, 1997), although there is some uncertainty about the extent of solid solution (SS) and partitioning between Cpx and other phases. Synthetic Kcpx content can reach ~20 mol% (4.2 to 4.7 wt% K2O) in both DiKoKcpx and DiJdKcpx intermediate (Diso-Di40) SSs at 1400-1500 °C and 10-11 GPa coexisting with a K-rich carbonate or glass or KAlSi₃O₈ (Harlow, 1997, and new data). Pressure has a much more important effect than temperature except when Cpx coexists with Opx which leads to increased En content of Cpx at higher T and reduced Kcpx solubility. Larger unit cell volumes and mixing disorder appear to facilitate Kcpx solutions at the same conditions; thus, partitioning can be effected by the Cpx composition, particularly for En-rich or Jd-rich compositions (see Harlow, 1997). Partitioning of K between Cpx and K-carbonate, $^{Cpx/carb}D_{K}$, or silicate melt, $^{Cpx/melt}D_{K}$, generally ranges from .03 to .07 for P from 5 to 11 GPa and T from 1400 to 1500 °C for Di-Jd-K-carbonate or Di-Ko-K-carbonate (Harlow, 1997), which can be compared to $C_{px/melt}D_K$, values up to 0.19 (Edgar and Vukadinovic, 1995) for lamproite magma at 1200 °C and 5 GPa decreasing ten-fold upon increasing T, and from 0.022 at 1400 °C @ 5 GPa to 0.11 at 1600 °C @ 11 GPa for Di-Phl melting (Luth, 1997). Experiments have yielded Cpx with Kcpx contents far above values reported in natural crystals, so we can infer that these natural samples have not experienced the same combination of high pressure and coexisting high K activity. Moreover, the Kcpx contents can be used to examine the pressure estimates, suggest coexisting K-rich phases during growth, and judge the experiments.

Vacancies in Cpx—CaEs: Smyth and co-workers have shown the importance of cation vacancies in Cpx, largely attributable to CaEs content, an indicator of high pressure for a Cpx + silica or anorthite (An) + silica assemblage (Smyth, 1980; McCormick, 1986; Smyth et al. 1991). Gasparik (1986) has measured Di-CaTs-CaEs ternary solutions for starting assemblages of anorthite + Cpx and anorthite + quartz + Cpx in the range 1.5 to 3.2 GPa and 1200 to 1450 °C, finding a roughly linear increase CaEs and CaTs contents (~3 to 1 : CaTs to CaEs) with pressure for the univariant reaction Di+An=garnet (Gar) + kyanite (Ky). Natural examples with such ratios except at near-zero values of CaEs, however, are rare. In experiments reported here, substantial CaEs component in Cpx has been produced in the ternary Di-Jd-Or (actually $Or_{97}Ab_3$) which is conspicuously sensitive to the breakdown of KAlSi₃O₈ feldspar (Or) to KSi-wadeite (K₂Si₄O₉) + Ky + coesite with increasing

pressure (~ 6 GPa @ 1000 °C) which then converts to a single hollandite-structure phase (~ 9 GPa @ 1000 °C; Yagi et al., 1994). A sampling of results follows:

Exper.	Contents	P (GPa)	T (°C)	Phases + Cpx	Di	Jd	Ксрх	CaTs	CaEs	En
GG566	Di+Or	6	1400	Glass	76	10	1	5	0	7
GG566	Di+Or	6	1400	Glass	69	18	1	5	0	7
GG535	Di+Or	8.5	1500	Ky, Glass	28	37	5	8	14	7
GG535	Di+Or	8.5	1500	Ky, Glass	49	24	7	5	8	6
GG606	Di+Or	9	1500	Gar, Ky, Glass	42	23	5	8	16	7
GG606	Di+Or	9	1500	Gar, Ky, Glass	50	16	3	10	12	9
BB367	Di+Or	9.5	1500	Ky, K-Wad, Sil	39	25	19	4	10	3
BB367	Di+Or	9.5	1500	Ky, K-Wad, Sil	37	25	11	4	14	5
BB367	Di+Or	9.5	1500	Ky, K-Wad, Sil	25	39	18	4	10	4
GG544	Di50Jd50+Or	10	1500	Ky, K-Wad?, Sil	21	52	8	1	13	5
GG544	Di50Jd50+Or	10	1500	Ky, K-Wad?, Sil	57	30	7	0	4	2
GG544	Di ₅₀ Jd ₅₀ +Or	10	1500	Ky, K-Wad?, Sil	73	15	10	1	0	1
TT155	Di+Or	11	1400	K-Hollandite	73	10	15	0	2	0
TT155	Di+Or	11	1400	K-Hollandite	56	25	17	0	1	0

Pressure favors both CaEs and Kcpx content in the assemblages, but the presence of <u>both</u> an aluminous phase and silica, rather than just bulk composition, is very important to CaEs enrichment and perhaps somewhat to CaTs content. CaTs, a high-T component, drops upon rising P. These data do not clearly show partitioning w.r.t. K (28 wt% K_2O in K-Wad and 16 wt% in Or).

Cpx in diamonds: A characteristic typical of some Cpx inclusions in diamonds is their measurable K content, as well as for Cpx in Group I and diamondiferous eclogites (McCandless and Gurney, 1989). A cursory examination shows that omphacite inclusions from Sloan, Monastery, Orapa, Argyle, and Copetown have a high-end range of 0.6 to 0.9 wt% K₂O with \leq CaEs₂, suggesting coexistence with a melt/fluid of 1.2 to 30 wt% K₂O without coexisting Ky (or corundum?); this author would lean toward more K-rich melt/fluids. Some omphacite inclusions from Arkangelsk (Sobolev et al., 1997) contain both significant CaEs component, up to 9%, and Kcpx, to 8%, suggesting both a K-rich fluid/solid phase and something like Ky coexisted. Few ultramafic Cr-diopsides are K-rich, and the richest are from the Koffiefontein pipe (Rickard et al., 1989) with 0.6 and 1.6 wt% K₂O suggesting perhaps both high pressure, > 5 GPa, and K-rich coexisting phase, > 25 wt% K₂O, both unusual.

Cpx coexisting with phlogopite: Data from Luth (1997) yield a $^{Cpx/Phl}D_K$ of 0.013 to 0.08 from 1250 to 1400 °C and 3 to 8 GPa increasing upon P and perhaps decreasing upon T in Cpx Di₋₉₀En₋₇ - CaTs₁₋₄Kcpx₁₋₄ CaEs₀. That is comparable to this author's experiments with natural phases that yield Cpx of Di₈₃₋₇₅Jd₅₋₁₀En₋₇CaTs₁₋₂Kcpx₁₋₃CaEs₀, however, addition of K-bicarbonate maintains Phl to 1500 °C and 10 GPa with apparent $^{Cpx/Phl}D_K$ of 0.07 to 0.09 and Cpx Di₇₇₋₇₀En₂₃₋₂₆Jd₁CaTs₁ - Kcpx₃₋₄CaEs₀. Data from the literature on xenoliths with 0.01 to 0.07 wt% K₂O in diopsidic Cpx coexisting with Phl (e.g., Carswell, 1989) are not consistent with coexistence at mantle conditions, whereas the inclusions of Phl and Cpx (0.48 wt% K₂O) in the F70 diamond from the Finsch pipe of Gurney et al. (1979) are consistent with an equilibrium pair at about 1200 °C and 5 GPa.

Cpx in kyanite eclogite: Many of the Cpx analyses with cation deficiencies are from Ky or corundum eclogites or grospydites (e.g., Smyth, 1980; Smyth et al., 1991) and many have 0.05 to 0.2 wt% K_2O (e.g., $Di_{36}Jd_{45}CaEs_{10}CaTs_5En_3Kcpx_1$). Using the range of partition coefficients above, K-content in Cpx would suggest, a coexisting phase with up to 10 wt% K_2O ; CaEs/CaTs above unity suggests

other than anorthite breakdown as the control. From the experimental results above, a phase more like K-feldspar, perhaps phengite or Phl (~10 wt.% K_2O), could be the missing phase (fictive or real) to yield K-rich Cpx in these rocks.

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