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Discussion



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Reply to comments by Y. Zhu: K-feldspar in clinopyroxene from Grt-Cpx silicate rocks of the Kokchetav Massif[☆]

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1. Introduction

During the past decade, the origin of potassium feldspar (Kfs) in ultrahigh-pressure (UHP) rocks has drawn the attention of many workers because Kfs only occurs as blebs and microveins in clinopyroxene (Cpx) and never is associated with other minerals. The Cpx + Kfs paragenesis occurs in eclogitic nodules from kimberlitic pipes (cf. Reid et al., 1976) and in the UHP metamorphic rocks of the Kokchetav Massif, Siberia (e.g., Sobolev and Shatsky, 1990; Perchuk et al., 1995; Zhang et al., 1997). Superficially, the Cpx + Kfs paragenesis appears similar in rocks of different origins and compositions. However, detailed studies show that the composition of Cpx, the shape of the Kfs blebs and their distribution in the Cpx host are different in the rocks of different origin. We demonstrated wide variations of potassium content in Cpx from the specific Fe-rich, diamond-free, coarse-grained garnet (Grt)-Cpx rocks from the

E-mail addresses: llp@geol.msu.ru (L.L. Perchuk), oleg@iem.ac.ru (O.G. Safonov), jmb@na.rau.ac.za (J.M. Barton). Kumdy-Kol Mine in the Kokchetav Complex (Perchuk et al., 1996; 2002; Bindi et al., 2003). The K₂O content in cores and centres of K-*Cpx* inclusions in garnet is nearly constant, but drops dramatically at their rims. We explained this sharp decrease by simultaneous crystallization of *Kfs* with new generation of the *Cpx* (*Cpx*2). The K₂O concentration in *Cpx*2 is similar to that of the low potassium *Cpx*1. Therefore, the *Cpx*2 should contain more *Kfs* blebs. *Kfs* blebs of different shapes, comprising 4–5 vol.%, are observed in the central portions of the *Cpx*2 grains, while *Kfs* blebs never occur in potassiumfree, *Cpx* coronas (*Cpx*3).

The systematic zoning and sequence of crystallization of minerals in the rocks led us to conclude that they originally crystallized from a silicate melt at a depth of about 200 km. Subsequent evolution of these rocks resulted from ascent and cooling (Perchuk et al., 2002). However, in addition to K-*Cpx*, *Grt* also contains small, well-preserved carbonate inclusions; moreover, calcite likewise occurs in the matrix. Based on these observations, we suggested an initial coexistence of separate carbonate and silicate melts but did not comment on the primary nature of these melts (Perchuk et al., 2002).

The crystallization of potassium-bearing clinopyroxene (K-*Cpx*) at the liquidus in diverse silicate and carbonate–silicate systems is supported by the results

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of UHP experiments (Edgar and Vukadinovic, 1993; Mitchell, 1995; Edgar and Mitchell, 1997), including those systems whose compositions are close to those of the Kokchetav rocks (Safonov et al., 2002). The origin of the *Kfs* blebs within *Cpx*2 suggests the reaction:

 $KAlSi_2O_6(in Cpx) + [SiO_2]_{melt} \Rightarrow KAlSi_3O_8$ (1) or

Ca(Fe,Mg)Si₂O₆·*n*KAlSi₂O₆ (in *Cpx*)+[SiO₂]_{melt} ⇒ *n*KAlSi₃O₈ + Ca(Fe,Mg)Si₂O₆ because no eskolaite (*Esk*) component (Ca_{0.5} $\square_{0.5}$ AlSi₂O₆) was observed in numerous *Cpx*2 analyses. It should be mentioned that we thoroughly tested the "*Esk* reaction" (Luth, 1997) in application to the formation of *Cpx*2 + *Kfs* assemblage and concluded that "... *KCpx* (*Cpx*1) from garnet-Cpx rocks of the Kokchetav Complex does not contain the *Esk* end-member" (Perchuk and Yapaskurt, 1998; Perchuk et al., 2002, p. 103). Therefore, the reaction:

$$3 \text{KAISi}_2\text{O}_6 + 2 \text{Ca}_{0.5} \Box_{0.5} \text{AISi}_2\text{O}_6$$

$$= 3KAIS_{13}O_8 + CaAl_2S_1O_6 \tag{2}$$

or K-Jadeite in Cpx (K-Jad)+Ca-Eskola end member (Esk)=K-feldspar (Kfs)+Ca-Tschermakite (Tsch) is not valid for the diamond-free, coarse-grained rocks occurring in the Kumdy-Kol Mine.

Presumably, Zhu (2003) did not read our paper (Perchuk et al., 2002) carefully and therefore incorrectly understood our conclusion about the origin of Kfs blebs in the Cpx2. This appears to be the only



Fig. 1. Backscattered images of potassium-bearing *Cpx* included into garnet of the Fe-rich, diamond-free, coarse-grained *Grt-Cpx* rock from the Kumdy-Kol Mine, the Kokchetav Complex. No *Kfs* blebs are present.

reason for their criticism of our idea concerning the role of reaction (1) in the formation of *Kfs* blebs. On the other hand, the comments of Zhu allow us to expand our discussion of this very interesting problem.

2. The rock types discussed

In our papers we outlined the above rock type in which the K-rich Cpx1 at liquidus is changed by the crystallization of the Cpx2 with the Kfs blebs (Perchuk et al., 1996; 2002). These rocks occur as large boudins and lenses in Grt-Bio diamondiferous gneisses. Major rock-forming minerals in these boudins and lenses are Fe–Ca garnet ($X_{Mg}^{Grt} = 0.05 - 0.15$; $X_{Ca}^{Grt} = 0.75 - 0.80$) and Cpx ($X_{Mg}^{Cpx} = 0.4 - 0.6$). Primary garnet contains inclusions of the euhedral K-Cpx (Fig. 1). This K-Cpx shows systematic chemical zoning (Perchuk et al., 2002). Primary K-Cpx never coexists with Kfs. Cpx2 forms large, up to centimeter in size, porphyroblasts (or porphyroclasts?) and rare euhedral fine grains included in Grt containing Kfs blebs (Fig. 2a and b). On one hand, the Kfs inclusions in garnet (Fig. 2a) suggest that the crystallization of garnet continues after the formation of Cpx2, and on the other, Kfs blebs are not the products of the Cpx1 exsolution. The Cpx3 which does not contain Kfs blebs surrounds Cpx2 (Fig. 2b). In some

samples, Cpx2 porphyroblasts contain rare quartz inclusions of 5–10 µm in size, amounting to less than 1 vol.%. Besides the blebs and intergrowths, Kfs occurs as late (Kfs2) microveins crosscutting all generations of Cpx (Perchuk et al., 2002). The Kfs of all generations is pure orthoclase. Outside of the porphyroblasts, Cpx3 forms intergrowths with Kfs(Fig. 2b), resembling eutectic relationships. Titanite and rutile are common primary accessories in the rocks. No epidote, chlorite nor albite occur either in blebs within Cpx2, or in any other primary form.

Thus, the mineral and bulk compositions of the Fe-rich Cpx-Grt silicate rocks discussed in our papers (Perchuk et al., 1996; 2002) strongly differ from those in the Mg-rich *marble* described in Zhu's paper. Although we never mentioned a protholith of the rock, Zhu attributes to us the idea that the formation of the Cpx-Grt bearing silicate rock resulted from "melting of a metamorphic rock." We have to reiterate that the Kumdy-Kol Mine portion of the Kokchetav massif is characterized by different types of magmatic and metamorphic UHP rocks. Therefore, in order to make a decision on the origin of Kfs blebs in silicate rocks, we cannot use compositional and textural characteristics of metamorphic rocks. The comparison of chemistry of Cpx occurring in silicate rocks (our case) and those occurring in carbonate rocks (Zhu's case) has no significance.



Fig. 2. Backscattered images of Cpx2 and Cpx3 in the Fe-rich, diamond-free, coarse-grained Grt-Cpx rock from the Kumdy-Kol Mine, the Kokchetav Complex. (a) Very fine inclusions of Kfs in Cpx2 included in garnet. (b) Mineral zoning around garnet: (1) symplectites of Grt with Kfs2, (2) symplectites of Cpx2 with Kfs2, and (3) the Kfs blebs-free Cpx3 coronas.



Fig. 3. The diagram demonstrating principal difference between compositions of *Cpx* from silicate rock (Perchuk et al., 1996; 2002) and marble (Zhu, 2003) in terms of Ca content in the M2 site. Open circles represent data points of *Cpx* from silicate rock (Perchuk et al., 1996, 2002); closed circles represent data points of *Cpx* from marble (Zhu, 2003).

In order to test the models in terms of reaction (2), we must compare the predominant substitution mechanisms in K-*Cpx* (*Cpx*1) and *Cpx*2. *Cpx*1 and the *Cpx*2 from marbles "…are characterized by higher content of Ca" (Dobretsov et al., 1971, p. 176) that completely occupies the M2 site. Fig. 3 illustrates this pattern, while the *Cpx* from *Grt-Cpx* bearing silicate rock show a lack of Ca with respect to K, Na, Fe and Mg, suggesting saturation of the M2 site by K and Na instead of Ca with the charge compensation by Al and Fe³⁺ in the M1 site. The excess Ca in the M2 site of *Cpx*1 from marble (Fig. 3) suggests that the *Esk* component is not characteristic of the primary *Cpx* in the rock.

Any model addressing the formation of K-*Cpx* must demonstrate clear evidence for (Fe, Mg)Si₂O₆–KAlSi₂O₆ solid solution in *Cpx*1. Furthermore, in order to use reaction (2), the Ca_{0.5} $\Box_{0.5}$ AlSi₂O₆ component in the primary *Cpx*1 must occur, while *Cpx*2, the product of reaction (2), (i) must be *Tsch*-rich and (ii) must contain *Kfs* blebs.

3. Cpx from the silicate rock

From our observations, *Cpx* crystallized in three generations. The first one, K-*Cpx* (Perchuk et al., 1995; 1996), occurs as inclusions in garnet, and never

contains *Kfs* blebs. *Cpx2* contains little or no potassium (Perchuk et al., 2002) but contains up to 4-5 vol.% *Kfs* blebs. *Cpx3* surrounds *Cpx2*, and contains neither K₂O nor *Kfs* blebs. However, it forms symplectites with orthoclase (Fig. 2). Thus, all three generations of *Cpx* differ in morphology, and presumably, in chemical composition. Apart from a brief discussion by Perchuk et al. (1995), a significant number of chemical analyses of all three generations of *Cpx* have not been published. We take this opportunity to do so.

Most of the Cpx compositions were determined using a CamScan electron microscope fitted with a well-standardized EDS Link AN10/85S (Department of Petrology, Moscow State University). Additional analyses were made using a wave-length Camebax SX50 instrument at the Institute of Experimental Mineralogy and a JEOL JXA 8600 instrument at the Dipartimento di Scienze della Terra, Università di Firenze. More than 130 and 110 probe analyses were produced for Cpx1 and Cpx2, respectively, as well as a few dozen analyses of Cpx3. Representative analyses of all three generations of Cpx from coarse grained Grt-Cpx silicate rocks from the Kumby-Kol Mine are shown in the Table 1.

The following scheme was applied to recalculate the *Cpx* formula (per 6 oxygen atoms) for site occupancy: $A1^{T}=2$ -Si, $A1^{M1}=A1-A1^{T}$, $Fe^{3+}=Na-(A1-2)$. A1^T-K)-2·Ti, $(Mg+Fe)^{M1}=1-(A1^{M1}+Cr+Ti+Fe^{3+})$, Mg^{M1}= X_{Mg}^{Cpx} ·(Mg+Fe)^{M1}, Fe^{M1}= $(1-X_{Mg}^{Cpx})$ ·(Mg+ Fe)^{M1} (tentatively assuming uniform distribution of Mg and Fe between M1 and M2), Mg^{M2}=Mg-Mg^{M1}, Fe^{M2}=Fe-Fe^{M1}, $\Box^{M2}=1-(Ca+Na+K+Mn+Mg^{M2}+Fe^{M2})$. Admitting that \Box^{M2} can be compen-

sated via the introduction of other cations in M1 (i.e., Cr, Fe³⁺) in addition to Al^{M1} to form *Esk*-like components (Ca_{0.5} $\Box_{0.5}$ AlSi₂O₆, Ca_{0.5} $\Box_{0.5}$ FeSi₂O₆, Ca_{0.5} $\Box_{0.5}$ CrSi₂O₆), we have calculated an excess cations in M1 over KAlSi₂O₆, NaAlSi₂O₆, CaAl₂SiO₆, NaFeSi₂O₆, etc.: (Al^{M1}+Cr+Ti+Fe³⁺)-K-Na-

Table 1

The chemical compositions clinopyroxenes from garnet-pyroxene silicate rocks of the Kumdy-Kol Mine, Kokchetav massif

Generation	K-Cpx1									
Sample Spot	Kum-39 L_A3	Kum-40 L_A1	Kum-40 L_A2	Kum-40 40-8-1	Kum-40 40-8-2	Kum-02 3058	Kum-02 3057	Kum-02 2179		
									SiO ₂	51.39
TiO ₂	0.06	0.15	0.16	0.13	0.11	0.03	0.01	0.03		
Al ₂ O ₃	0.65	1.42	1.48	2.12	0.74	1.16	1.24	1.13		
FeO	17.91	17.21	17.31	16.90	16.65	14.10	14.11	14.45		
MnO	0.38	0.48	0.51	0.33	0.53	0.35	0.14	0.32		
MgO	6.92	6.91	6.85	6.87	7.46	9.15	8.91	9.04		
CaO	21.94	22.65	22.92	21.40	22.07	22.55	22.56	22.70		
Na ₂ O	0.16	0.12	0.10	0.35	0.24	0.15	0.32	0.19		
K ₂ O	0.57	0.50	0.45	1.09	0.72	1.11	1.10	1.10		
Total	99.98	99.87	100.32	99.93	99.45	100.00	100.00	100.00		
Cations ratios (per 6 ox	vgens)									
Si	2.007	1.973	1.969	1.977	1.996	1.982	1.988	1.974		
Ti	0.002	0.004	0.005	0.004	0.003	0.001	0.000	0.001		
Al	0.030	0.065	0.068	0.097	0.034	0.053	0.056	0.052		
Fe	0.585	0.563	0.564	0.550	0.545	0.454	0.454	0.467		
Mn	0.013	0.016	0.017	0.011	0.017	0.011	0.005	0.010		
Mg	0.403	0.403	0.398	0.399	0.435	0.526	0.511	0.521		
Ca	0.918	0.949	0.957	0.893	0.926	0.931	0.930	0.940		
Na	0.012	0.009	0.008	0.026	0.018	0.011	0.024	0.014		
K	0.028	0.025	0.022	0.054	0.036	0.055	0.054	0.054		
Results of calculation										
$X_{M\alpha} = Mg/(Mg + Fe)$	0.411	0.423	0.420	0.430	0.454	0.564	0.556	0.566		
Fe ³⁺	0.007	0.014	0.014	0.022	0.022	0.048	0.046	0.067		
Al ^T	0.000	0.027	0.031	0.023	0.004	0.018	0.012	0.026		
Al ^{M1}	0.030	0.038	0.037	0.074	0.030	0.034	0.044	0.026		
K+Na	0.040	0.034	0.030	0.081	0.054	0.066	0.078	0.068		
$Al^{M1} + Cr + Ti + Fe^{3+}$	0.039	0.057	0.056	0.100	0.055	0.083	0.090	0.093		
$[K + Na + Ca + Mn]^{M2}$	0.971	0.999	1.003	0.984	0.998	1.009	1.013	1.019		
$[Mg + Fe]^{M1}$	0.961	0.943	0.944	0.900	0.945	0.917	0.910	0.907		
Mg ^{M1}	0.395	0.399	0.396	0.387	0.429	0.517	0.506	0.513		
Fe ^{M1}	0.566	0.544	0.548	0.513	0.516	0.400	0.404	0.394		
Mg ^{M2}	0.008	0.003	0.001	0.012	0.006	0.009	0.005	0.008		
Fe ^{M2}	0.011	0.005	0.002	0.015	0.007	0.007	0.004	0.006		
Total cations	3.997	4.007	4.007	4.011	4.011	4.024	4.023	4.033		
[T]	2.007	2.000	2.000	2.000	2.000	2.000	2.000	2.000		
[M1]	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000		
[M2]	0.990	1.007	1.007	1.011	1.011	1.024	1.023	1.033		
Vacancies in [M2]	0.010	0.000	0.000	0.000	0.000	0.000	0.000	0.000		

(continued on next page)

Table 1 (continued)

Generation	Cpx2 (with	Kfs inclusion)		Cpx3			
Sample	Kum-02	Kum-39	Kum-39	Kum-39	Kum-2	Kum-39	
Spot	2141	2221	2213	436	421	429	
SiO ₂	51.87	50.06	50.08	50.18	52.56	51.17	
TiO ₂	0.05	0.00	0.01	0.00	0.00	0.00	
Al ₂ O ₃	0.68	0.37	0.35	0.48	0.38	0.22	
FeO	13.51	19.36	18.91	21.15	13.44	18.27	
MnO	0.38	0.27	0.51	0.74	0.28	0.40	
MgO	9.74	6.64	6.54	4.88	10.26	6.92	
CaO	23.24	22.96	23.32	22.47	22.90	22.95	
Na ₂ O	0.28	0.30	0.27	0.00	0.00	0.00	
K ₂ O	0.24	0.05	0.02	0.10	0.18	0.00	
Total	99.99	100.01	100.01	100.00	100.00	99.93	
Cations ratios (per 6 oxy	vgens)						
Si	1.989	1.976	1.977	1.995	2.006	2.003	
Ti	0.001	0.000	0.000	0.000	0.000	0.000	
Al	0.031	0.017	0.016	0.022	0.017	0.010	
Fe	0.433	0.639	0.624	0.703	0.429	0.598	
Mn	0.012	0.009	0.017	0.025	0.009	0.013	
Mg	0.556	0.391	0.385	0.289	0.583	0.404	
Ca	0.954	0.971	0.986	0.957	0.936	0.962	
Na	0.021	0.023	0.020	0.000	0.000	0.000	
K	0.012	0.002	0.001	0.005	0.009	0.000	
Results of calculation							
$X_{Mg} = Mg/(Mg + Fe)$	0.574	0.396	0.396	0.291	0.576	0.403	
Fe ³⁺	0.021	0.042	0.037	0.000	0.000	0.000	
Al ^T	0.011	0.017	0.016	0.005	0.000	0.000	
Al ^{M1}	0.020	0.000	0.000	0.018	0.017	0.010	
K+Na	0.033	0.025	0.021	0.005	0.009	0.000	
$Al^{M1} + Cr + Ti + Fe^{3+}$	0.042	0.042	0.037	0.018	0.017	0.012	
$[K+Na+Ca+Mn]^{M2}$	1.000	1.005	1.024	0.987	0.954	0.976	
$[Mg+Fe]^{M1}$	0.958	0.958	0.963	0.982	0.983	0.988	
Mg ^{M1}	0.550	0.379	0.381	0.286	0.566	0.398	
Fe ^{M1}	0.408	0.579	0.582	0.696	0.416	0.590	
Mg ^{M2}	0.006	0.012	0.004	0.003	0.017	0.006	
Fe ^{M2}	0.005	0.018	0.005	0.007	0.012	0.008	
Total cations	4.010	4.028	4.026	3.996	3.989	3.993	
[T]	2.000	1.993	1.993	2.000	2.006	2.003	
[M1]	1.000	1.000	1.000	1.000	1.000	1.000	
[M2]	1.010	1.035	1.033	0.996	0.983	0.990	
Vacancies in [M2]	0.000	0.000	0.000	0.004	0.017	0.010	

Al^{IV}. If the *Esk* component is indeed present, the excess cations in M1 should be in positive correlation with vacancies \Box^{M2} in the proportion 2:1.

Using this scheme, all analyses were recalculated to the end-member compositions to check the concentration of Esk in both Cpx1 and Cpx2. If Cpx1 is a potential source of silica for producing the Kfs

blebs + Cpx2, both the *Esk* and K-*Jad* components occur in Cpx1. In other words, excess cations in the M1 site must correlate with vacancies in the M2 site in proportion 2:1. As mentioned above, some potassium in Cpx1 is compensated in the M1 site by other Fe³⁺, Cr, and Ti, while the rest is KAlSi₂O₆ end-member. By attributing all other cations as possible end-mem-

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Fig. 4. Correlation between K and $AI^{VI} = AI^{M1} - AI^{T} - (Na + Fe^{3+} + 2Ti + Cr)$ in K-*Cpx* and suggesting predominantly isomorphic substitution in the solid solution (Fe,Mg)Si₂O₆-KAlSi₂O₆. Open circles represent data points of *Cpx* from Fe-rich, diamond-free, coarse-grained *Grt-Cpx* rocks from the Kumdy-Kol Mine, the Kokchetav Complex; the closed circles reflect analyses from marble collected from the same Mine (see Table 1 in Zhu's paper). It is clearly seen that all closed circles differ significantly from the (Fe,Mg)Si₂O₆-KAlSi₂O₆ solid solution, as well as from other data points (open circles). *Cpx*1: inclusions of euhedral *Cpx*1 in garnet; *Cpx*2: matrix clinopyroxene containing *Kfs* blebs. Open circles represent data points of *Cpx* from silicate rock (Perchuk et al., 1996, 2002), closed circles represent data points of *Cpx* from marble (Zhu, 2003); asterisks reflect rims of the *Cpx*2 grains from the *Grt-Cpx* rocks (see Fig. 6, *Cpx*3). Methods of calculation are discussed in the text.

bers (hedenbergite, diopside, jadeite, aegerine and negligible amount of *Tsch*) in *Cpx*1 at $Si + Al^{IV} = 2$, an excellent positive correlation of potassium with Al^{VI} in M1 in the *Cpx*1 was found (Fig. 4). Fig. 4a illustrates that, apart from potassium jadeite, KAl- Si_2O_6 , is the only end-member that contains Al in the M1 site of Cpx1, an indication that no Eskcomponent is present in Cpx1. Therefore, the Kfs blebs cannot be formed by reaction (2) in the silicate rocks because of absence of the Esk component in Cpx1. Because the maximal content of potassium in Cpx2 is similar to minimal content in Cpx1 (Perchuk et al., 2002), a K-Al diagram for Cpx2 (Fig. 4b) demonstrates perfect correlation of K with Al for centers and cores, while compositions of rims are characterized by deviation from the K = AI line. This deviation suggests the presence of the Esk end-member in Cpx2. Both Cpx1 (inclusions in Grt) and Cpx2 (Cpx with blebs) from marble, used by Zhu (2003), are plotted in Fig. 4 for comparison. The comments on Fig. 4a are extra, while diagram b in this figure needs the special discussion that will be done in a corresponding section of this paper. This relationship suggests the presence of some amount of the *Esk* component but no vacancies in the M2 site. However, the average number of cations in this site is about of 1.01, with an average occupation of the M2 site of about of 0.99. The T position of *Cpx*2 from silicate rock is almost totally occupied by Si (average value from 107 analyses is about 1.99). This suggests presence of negligible amount of the *Tsch* in the *Cpx*2. This is further evidence for the displacement of reaction (2) to the left side for *Cpx*2 from silicate rocks. All these chemical evidence are supported by the presence of the *Kfs* blebs in garnet (Fig. 2a), which cannot be the products of the *Cpx*1 exsolution.

No potassium is present in Cpx3. This is practically pure salite that crystallized simultaneously with garnet of a composition different from Grt1 by containing a more andradite end-member, suggesting that final crystallization of the rock took place close to the Earth's surface.

4. Cpx from marble

Figs. 3 and 4 clearly illustrate that the Cpx from marble are compositionally different from those of the Grt-Cpx silicate rocks. In addition to the higher Ca (Fig. 3), all Cpx from marbles show higher Mg number $(X_{Mg}^{Cpx} = 0.86 - 0.94)$ at very low potassium (Fig. 4). As mentioned above, in order to produce the Kfs blebs by reaction (2), primary K-Cpx must contain (1) distinct amount of potassium and (2) corresponding concentration of the Esk molecule, while Cpx2 containing the Kfs blebs must be potassium-free and Tsch-rich. However, both the Cpx1 (inclusions) and Cpx2 (matrix with blebs) described by Zhu are similar in compositions (Fig. 3 in their paper). In addition, there is no correlation between K and Al either in Cpx1 or Cpx2. Fig. 4 clearly demonstrates that Kfs blebs cannot be produced from the potassium-free Cpx1 in marble. But perhaps Cpx1 in marble contains Esk component, allowing the production of Kfs blebs by intracrystalline reaction (2). The M2 site of Cpx1from marble is almost totally occupied by Ca, Na, K, and Mn (in Cpx1 this total reaches 1.004). Zhu and Ogasawara do not state how the Esk content was calculated. Nevertheless, if this end-member occurred in Cpx1 before exsolution, Cpx2 as a product of reaction (2), must be undersaturated in Si, because of the Tsch content. However, an average crystallochemical formula of Cpx2 in Table 1 of Zhu's paper shows Si = 2.001. It may be that single compositions of Cpx^2 form a trend after reaction (2), suggesting an increase of the Tsch component at the expense of the Esk component? In this case, a negative correlation between Si and the Esk component Al^{M1} should be observed in Cpx2 from marble. However, such a correlation is not a characteristic of this Cpx (Fig. 5). Moreover, Fig. 5 shows a weak positive correlation between these compositions of all Cpx, in which Al^{M1} >Na+K. This suggests an increase of the *Esk* component in Cpx2 and Cpx3, contradicting the shift of reaction (2) to the right. Thus, Cpx2 from marble shows a standard content of Si and no negative correlation between Si and Al^{M1}, while Cpx1 has no vacancies in M2, i.e. no Esk component in the solid solution.

5. Discussion and conclusions

Compositional differences preclude the direct comparison of rocks and minerals described by us with those described by Zhu (2003). Most Cpx inclusions in garnets from the Grt-Cpx rocks are potassium-rich, while those from marble are potassium-free. No *Esk* component is found to pose as a possible donor of silica in Cpx1 of the silicate rocks (Table 1). If a rock does not



Fig. 5. Diagrams showing no negative correlation between content of Si and the rest of AI^{M1} presumably bounded in *Tsch* component as a product of reaction (2). Open circles represent data points of *Cpx* from silicate rock (Perchuk et al., 1996; 2002); Closed circles represent data points of *Cpx* from marble (Zhu, 2003).



Fig. 6. Backscattered images of Kfs blebs showing no systematic shapes or compositional distributions in Cpx2 and they do not occur along Cpx2 cleavage. Diamond-free coarse-grained Grt-Cpx rock from the Kumdy-Kol Mine, the Kokchetav Complex.

Kok-700

contain primary potassium- and *Esk*-bearing *Cpx* (*Cpx*1), there is no chance for it to contain *Kfs* blebs as an exsolution product. No *Tsch* component is present in *Cpx*2 from the silicate rock (Table 1). Since *Cpx*2, as a possible exsolution product of reaction (2) does not contain *Tsch*, therefore the reaction (2) cannot reflect a mechanism of the formation of *Kfs* blebs in *Cpx*2.

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Fig. 4b demonstrates small (0.005) but systematic deviation of 19 of 107 Cpx2 data points from the K = AI line for the Ca(Fe, Mg)Si₂O₆-KAlSi₂O₆ solid solution. All these data relate to rims of the Cpx2 grains from Grt-Cpx rocks (Cpx3). This deviation suggests extra Al is bonded neither with K, nor with some other components from the M1 and M2 sites. The only explanation can be that we have to assume the existence of "clinocorundum" Al2Al2O6 in M2 of Cpx2 from the silicate rock. However, this component cannot be a characteristic of the Cpx2 solid solution from marble because both M1 and M2 are oversaturated by cations. For example, the total of Ca + Na + Kin the M2 site in average Cpx^2 from marble equals 1.004. Even if we assume that the extra Al represents the Esk end-member in Cpx2, it indicates the displacement of reaction (2) to the left, i.e. consumption of the Kfs blebs rather than their formation.

Thus, the data presented above demonstrate the error produced by comparison of the *Kfs* blebs in the rocks of different origin. The saying goes: "How misleading appearances are sometimes," sighed a little hedgehog getting off the shoe brush. Our model of the

crystallization of Kfs blebs in the Cpx2 from a silicate liquid is the only alternative unless the Kfs blebs (see Fig. 6) form after the reaction, involving a fluid:

$$Ca(Fe, Mg)Si O_6 \cdot nKAlSi_2O_6(in Cpx) + [SiO_2]_{fluid}$$

$$\Rightarrow nKAlSi_3O_8 + Ca(Fe, Mg)Si_2O_6$$
(3)

In addition to alkalis, such a mantle-derived fluid is rich in silica (Navon et al., 1988; Schrauder and Navon, 1994; Israeli et al., 1998). Because sanidine is not stable at a pressure above 60 kbar (e.g., Urakawa et al., 1994), we suggested that reaction (1) takes place at relatively low pressures (Perchuk et al., 2002), outside of field stability of the K-*Cpx*. At present, however, no experimental data exist for (1), (2) and (3). Hopefully, these data will appear in the near future.

References

- Bindi, L., Safonov, O.G., Yapaskurt, V.O., Perchuk, L.L., Menchetti, S., 2003. Ultrapotassic Cpx from the Kumdy-Kol microdiamond mine, Kokchetav Complex, Kazakhstan: occurrence, composition and crystal-chemical characterization. Am. Mineral. 88, 464–468.
- Dobretsov, N.L., Kochkin, Yu.N., Krivenko, A.P., Kutolin, V.A., 1971. Rock-Forming Pyroxenes Nauka Press, Moscow. 452 pp.
- Edgar, A.D., Mitchell, R.H., 1997. Ultra high pressure-temperature melting experiments on an SiO₂-rich lamproite from Smoky Butte, Montana: derivation of siliceous lamproite magmas from enriched sources deep in the continental mantle. J. Petrol. 38, 457–477.

- Edgar, A.D., Vukadinovic, D., 1993. Potassium-rich Cpx in the mantle: an experimental investigation of K-rich lamproite up to 60 kbar. Geochim. Cosmochim. Acta 57, 5063–5072.
- Israeli, E., Schrauder, M., Navon, O., 1998. On the connection between fluids and mineral inclusions in diamonds. Extended Abstracts, 7th International Kimberlite Conference, Cape Town, pp. 352–354.
- Luth, R.W., 1997. Experimental study of the system phlogopitediopside from 3.5 to 17 GPa. Am. Mineral. 82, 1198–1209.
- Mitchell, R.H., 1995. Melting experiments on a sanidine-phlogopite lamproite at 4-7 GPa and their bearing on the source of lamproitic magmas. J. Petrol. 36, 1455–1474.
- Navon, O., Hitcheon, I.D., Rossman, G.R., Wasserburg, G.J., 1988. Mantle-derived fluids in diamond microinclusions. Nature 325, 784–789.
- Perchuk, L.L., Yapaskurt, V.O., 1998. Mantle-derived ultrapotassic liquids. Russian Geology and Geophysics 39, 1746–1755.
- Perchuk, L.L., Yapaskurt, V.O., Okay, A., 1995. Comparative petrology of diamond-bearing metamorphic complexes. Petrology 3, 238–276.
- Perchuk, L.L., Sobolev, N.V., Yapaskurt, V.O., Shatsky, V.S., 1996. Relics of potassium-bearing pyroxenes from diamond-free pyroxene-garnet rocks of the Kokchetav massif, northern Kasakhstan. Dokl. Ross. Akad. Nauk, Earth Sci. 348, 790–795.
- Perchuk, L.L., Safonov, O.G., Yapaskurt, V.O., Barton, J.M., 2002. Crystal-melt equilibria involving potassium-bearing Cpx as indicator of mantle-derived ultrahigh-potassic melts: an analytical review. Lithos 60, 89–112.
- Reid, A.M., Brown, R.W., Dawson, J.B., Whitfield, G.G., Siebert,

J.C., 1976. Garnet and pyroxene compositions in some diamondiferous eclogites. Contrib. Mineral. Petrol. 58, 203-220.

- Safonov, O.G., Matveev, Yu.A., Litvin, Yu.A., Perchuk, L.L., 2002. Experimental study of some joints in the system CaMgSi₂O₆– (Ca,Mg)₃Al₂Si₃O₁₂–KAlSi₂O₆–K₂(Ca,Mg)(CO₃)₂ at 5–7 GPa in relation to the Genesis of *Grt-Cpx*–carbonate rocks of the Kokchetav Complex, Northern Kazakhstan. Petrology 10 (6), 519–539.
- Schrauder, M., Navon, O., 1994. Hydrous and carbonatitic mantle fluids in fibrous diamonds from Jwaneng, Botswana. Geochim. Cosmochim. Acta 58, 761–771.
- Sobolev, N.V., Shatsky, V.S., 1990. Diamond inclusions in garnets from metamorphic rocks: a new environment for diamond formation. Nature 343, 742–746.
- Urakawa, S., Kondo, T., Igawa, N., Shimomura, O., Ohno, H., 1994. Synchrotron radiation study on the high-pressure and high-temperature phase relations of KAlSi₃O₈. Phys. Chem. Miner. 21, 387–391.
- Zhang, R.Y., Liou, J.G., Ernst, W.G., Coleman, R.G., Sobolev, N.V., Shatsky, V.S., 1997. Metamorphic evolution of diamond-bearing and associated rocks from the Kokchetav Massif, northern Kazakhstan. J. Metamorph. Geol. 13, 479–496.
- Zhu, Y., 2003. Comments on: "Crystal-melt equilibria involving potassium-bearing clinopyroxene as indicator of mantle-derived ultrahigh-potassic liquids: an analytical review" by Perchuk, L.L., Safonov, O.G., Yapaskurt, V.O., Barton Jr., J.M. [Lithos 60 (2002) 89–111]: K-feldspar in metamorphic clinopyroxene, from exsolution to potassium replacement. Lithos. this issue.