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Mg and Fe distribution between ternary solid solutions of clinopyroxenes and bioite

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To construct the mineral thermometer using CPx-Bi association the data of magnesium and iron distribution between these minerals are necessary. This equilibrium for binary clinopyroxenes of diopside-hedenbergite range has been experimentally studied [*Kovalsky et al*, 2008, 2009]. The purpose of our work was to study the dependence of aegirine minal entrance on the properties of clinopyroxene solid solution and magnesium and iron distribution in *Bi–CPx* pair.

Cation exchange experiments were carried out at 750°C and 1.5 kbar in hydrothermal conditions. For activation of equilibrium achievement the solution of intense mineralizing agent – potassium fluoride (KF concentration was ~10 wt %) has been used. The oxygen potential corresponded to the iron–wustite equilibrium or equilibrium of graphite with water fluid [*Gramenitsky et al,* 2000]. Experiments duration was 45 days. As initial materials the synthetic solid solutions of ternary clinopyroxenes (*CPx*-3) and synthesized at 650°C and 1.5 kbar phlogopite and annite have been used. The approach to the equilibrium was carried out from two sides. The initial minerals compositions and results of cation exchange experiments are presented in table 1.

Based on the cation exchange experiments the isotherm of Mg and Fe distribution between *CPx*-3 and Bi has been obtained (fig. 1). Mg distribution coefficient between clinopyroxene and biotite (K_D) is described by equation of third order: $\ln(K_D) = 0.65 + 3.30*x - 5.763*x^2 - 1.0911*x^3$ (±0.40), where x is magnesium mole fraction in clinopyroxene ($x=Mg/(Mg+Fe^{2+})$). Used this equation the energy parameters of nonsymmetrical Margules model for description of excess energy of mixing of clinopyroxene solid solutions (*Aeg–D–Hed* system, aegirine mole fraction is 0.2±0.04) have been calculated: W1 = -48.5 (16.2) and W2 = 24.1 (2.5) kJ/mole. Earlier the equilibrium *CPx–Bi* for binary clinopyroxene solid solutions was studied [*Kovalsky et al*, 2008, 2009] and practically ideal miscibility in diopside-hedenbergite range was shown. So, we can conclude that nonideality of diopside–hedenbergite solid solution increases with entrance of aegirine minal. Based on the Perchuk`s data [*Perchuk,* 1970] of natural clinopyroxene and biotite paragenesis the excess energies of mixing of clinopyroxenes have been calculated for 750°C isotherm (fig. 2). Based on our experimental data, calculations using Perchuk`s [*Perchuk,* 1970] and Kovalsky`s [*Kovalsky et al*, 2008, 2009] works we estimated the integral excess energies of mixing (tabl. 2).

Table 1. The experimental results of Mg and Fe exchange between clinopyroxene (*CPx*-3) and biotite (*Ann–Phl* range) at 750°C and 1.5 kbar. $K_D=[X_{Mg}^{CPx3}*(1-X_{Mg}^{Bi})]/[(1-X_{Mg}^{CPx3})* X_{Mg}^{Bi}]$

№	X_{mg}^{CPx3} until/exp	X_{mg}^{Bi} until/exp	X_{mg}^{CPx3} after/exp	Variation	X_{mg}^{Bi} after/exp	Variation	K_D	$\ln(K_D)$
6424	0.50	1.0	0.73	0.70÷0.75	0.91	0.90÷0.93	0.267	-1.319
6431	0.83	0.0	0.65	0.62÷0.66	0.42	0.40÷0.43	2.565	0.942
6433	0.80	0.0	0.43	-	0.22	0.20÷0.23	2.675	0.984
6489	0.83	0.5	0.66	0.63÷0.77	0.63	0.59÷0.67	1.140	0.131
6490	0.05	1.0	0.68	0.64÷0.72	0.63	0.62÷0.63	1.248	0.221
6491	0.05	0.5	0.55	0.47÷0.55	0.42	0.42÷0.45	1.689	0.523
6492	0.60	1.0	0.68	0.65÷0.69	0.82	0.81÷0.83	0.466	-0.762
6499	0.50	0.00	0.43	0.41÷0.45	0.22	0.21÷0.23	2.675	0.984
6501	0.83	0.00	0.45	0.38÷0.46	0.29	024÷0.30	2.003	0.695
6505	0.5	1.0	0.74	0.60÷0.74	0.80	0.80÷0.82	0.711	-0.340

$$\ln(K_D) = 0.65 + 3.30*x - 5.763*x^2 - 1.0911*x^3 \ (\pm 0.40) \qquad (1)$$

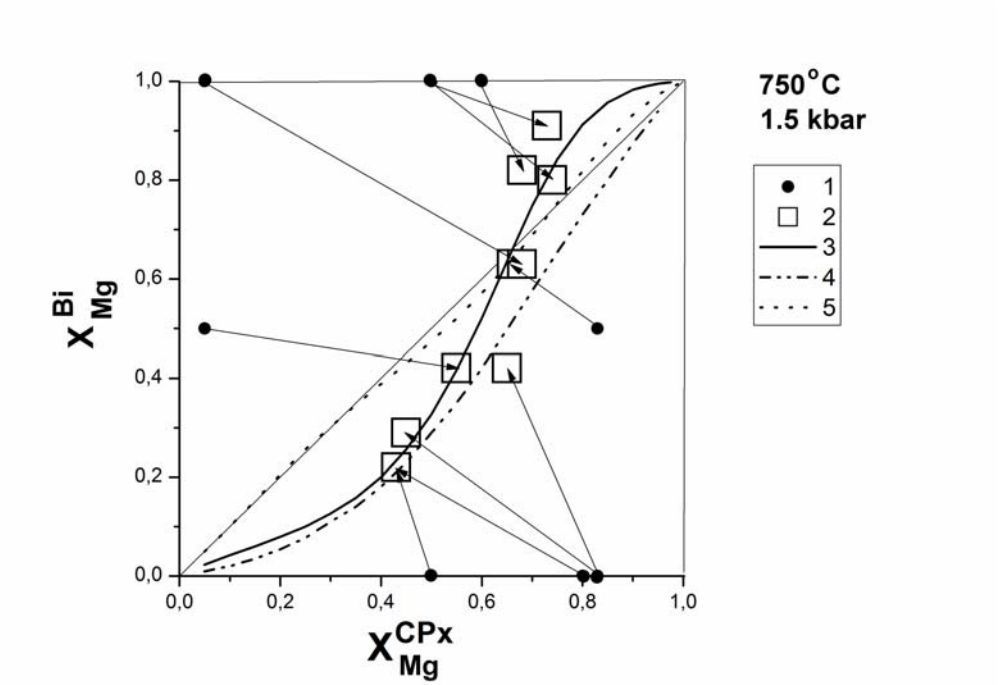

Fig. 1. Mg, Fe distribution between ternary solid solution of CPx (*Aeg–-Di–Hed*, X_{Aeg}=0.2) and biotite. 1– initial compositions of *CPx* and *Bi*; 2 – equilibrium compositions of *CPx* and *Bi* after experiments; 3 – isotherm of Mg, Fe distribution between *CPx* and *Bi* (our data); 4 – isotherm of Mg, Fe distribution between *CPx* and *Bi* (natural paragenesis [*Perchuk,* 1970]); 5 – isotherm of Mg, Fe distribution between binary *CPx* and *Bi* [*Kovalsky et al*, 2008]

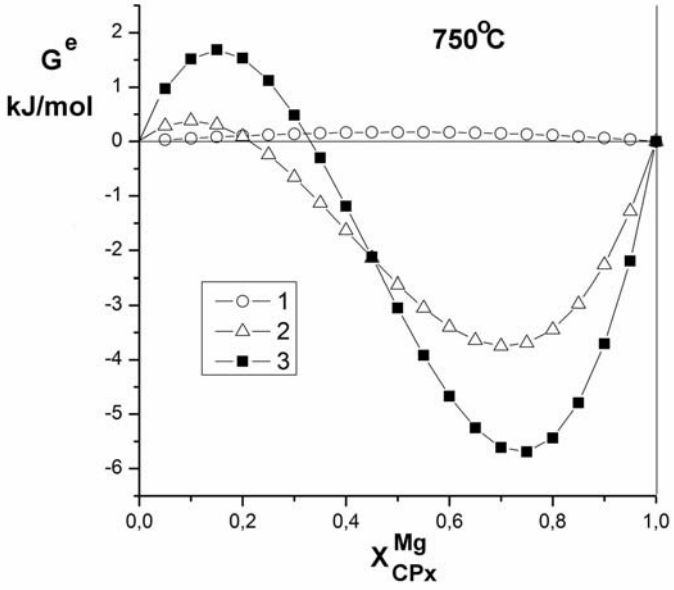

Fig. 2. Concentration dependences of excess mixing energies of clinopyroxenes solid solutions. 1 – binary *CPx* (*Di–Hed* range); 2 – natural *CPx* [*Perchuk,* 1970]; 3 – ternary solid solutions of *CPx* (*Aeg–Di–Hed*, X_{Aeg}=0.2)

It has been shown that values G^e_{int} of diopside-hedenbergite solid solutions depend on entrance of third minal (jadeite or aegirine) linearly (fig. 3.).

Table 2. Dependence of values of integral excess energies of mixing G^e_{int} (kJ/mol) (750°C) of diopside-hedenbergite clinopyroxenes on the content of third minal (jadeite or aegirine)

№	Average composition of *CPx*	(*Aeg*+*Jd*), mol %	G^e_{int} (kJ/mol) (750°C)	Note
1	$(Aeg+Jd)_{0.2}(Di+Hed)_{99.8}$	0.2	0.11	[*Kovalsky, et al.,* 2008, 2009]
2	$Aeg_{5.6}Jd_{8.4}(Di+Hed)_{86}$	14	1.85	[*Perchuk*, 1970]
3	$Aeg_{17.4}Jd_{1.1}(Di+Hed)_{81.5}$	18.5	2.76	This work

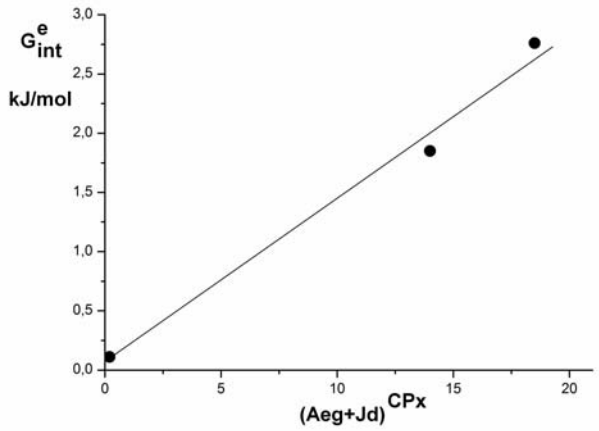

Fig. 3. Dependence of *CPx* integral excess energies of mixing on the jadeite and aegirine minals content

Conclusions

1. The Mg and Fe distribution between clinopyroxene (ternary solid solution of *Di–Hed–Aeg* system; X_{Aeg}^{CPx}=0.2) and biotite (binary solid solution of *Phl–Ann)* has been studied at 750°C and 1.5 kbar in hydrothermal conditions.

2. It has been shown that Mg, Fe^{2+} distribution between clinopyroxene and biotite is unideal; when there is low X_{Mg}^{CPx} , Fe^{2+} enriches biotite, when $X_{Mg}^{CPx} > 0.7$, the inversion takes place and Fe^{2+} redistributes to the *CPx*.

3. Based on the data of Mg, Fe^{2+} distribution between clinopyroxene and biotite the Margules parameters of clinopyroxene mixing model have been calculated; it has been shown that value of integral excess energies of mixing directly correlate with mole fraction of third clinopyroxene minal (aegirine and jadeite).

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