

Evidence of the Existence of High-Alumina Clinopyroxene (Tschermakite) in Garnet Pyroxenites from the Kokchetav Massif, Kazakhstan

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The unique manifestation of high- and ultrahigh-pressure collisional metamorphism, the Kokchetav Massif in northern Kazakhstan, represents a fragment of Proterozoic crust in the Central Asian foldbelt [1, 2]. The subsidence of the western part of the massif during the Middle Cambrian subduction to a depth no less than 140 km, where the pressure >40 kbar and the temperature was >900°C, resulted in the formation of diamond in metasedimentary rocks [3]. The eastern part of the massif sank to shallower depths. This can be judged from the absence of diamond. However, the discovery of coesite-bearing schists suggests subsidence to depths no less than 80 km [4]. During Upper Cambrian exhumation, the subducted crust was deformed, imbricated into tectonic slices shifted with respect to each other, and affected by retrograde metamorphism [2, 3]. The newly formed melange represents a rock assemblage metamorphosed under ultrahigh to low pressures [1, 2].

Garnet pyroxenites associated with harzburgites, eclogites, and amphibolites were found among the schists and quartzites of the Zerenda Group, in the eastern part of the Kokchetav Massif, 3–5 km west of the Settlement of Enbek-Berlik. Their chemical and mineral compositions and geological structure are described in [5–8]. The pyroxenites experienced retrograde metamorphism. They represent coronites with numerous anorthite–zoisite–spinel–magnetite–corundum pseudomorphs after an unknown mineral. Macroscopically, pseudomorphs have dark gray or black color, sharp boundaries, and irregular, ovoid, or rhomboid shape. Their size varies from fractions to 5–7 mm in size. They consist of ultrafine-grained mineral aggregate with grain size varying from 1 to 20 μm . They are commonly separated from the heteroblastic groundmass of orthopyroxene by anorthite/zoisite and cordierite rims (Fig. 1). Occasionally, these rims are absent. Garnet porphyroblasts are partially or completely replaced by anorthite–orthopyroxene–cordierite–spinel/magnetite symplectite. The Al/Si ratio is 0.65–

0.66 in garnet and 0.69 ± 0.02 in symplectite, indicating the inert behavior of Al and Si during replacement [8]. Ashworth *et al.* [8] assumed that, like in symplectites, Al and Si were nearly immobile during pseudomorph formation. Since the Al/Si ratio measured over the area is between 1.61 and 1.93, the formation of pseudomorphs was attributed to replacement of kyanite porphyroblasts. However, this assumption cannot explain the presence of Ca and significant amounts of anorthite and zoisite. Based on the invariability of the Al/Si ratio, we believe that anorthite–zoisite–spinel/magnetite–corundum pseudomorphs developed after clinopyroxene with a very high Al content. The approximate chemical composition of the clinopyroxene is suggested by results of the analysis of three pseudomorphs in 16 randomly selected points ($\sim 0.1 \text{ mm}^2$ in area) on a Camebax scanning microprobe. Data presented in the table show that the Al/Si ratio in pseudomorphs is within 1.50–1.83. They also demonstrate a strong negative correlation in Al–Si and Ca–Mg pairs. Sum totals in the table are less than 100% due to the incomplete error correction during measurement of heterogeneous crystalline structure (microdispersion aggregate of several

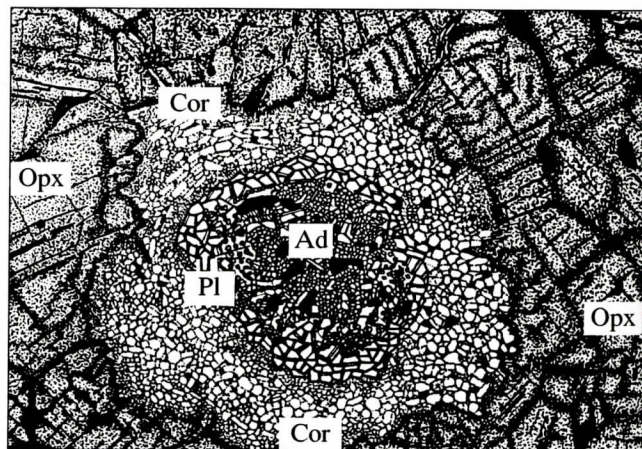


Fig. 1. Cross section of anorthite–zoisite–spinel/magnetite–corundum pseudomorphs (Ad) rimmed by anorthite (Pl) and cordierite (Cor) in the orthopyroxene groundmass of coronite. Sketch of thin section. Horizontal size is 2.9 mm.

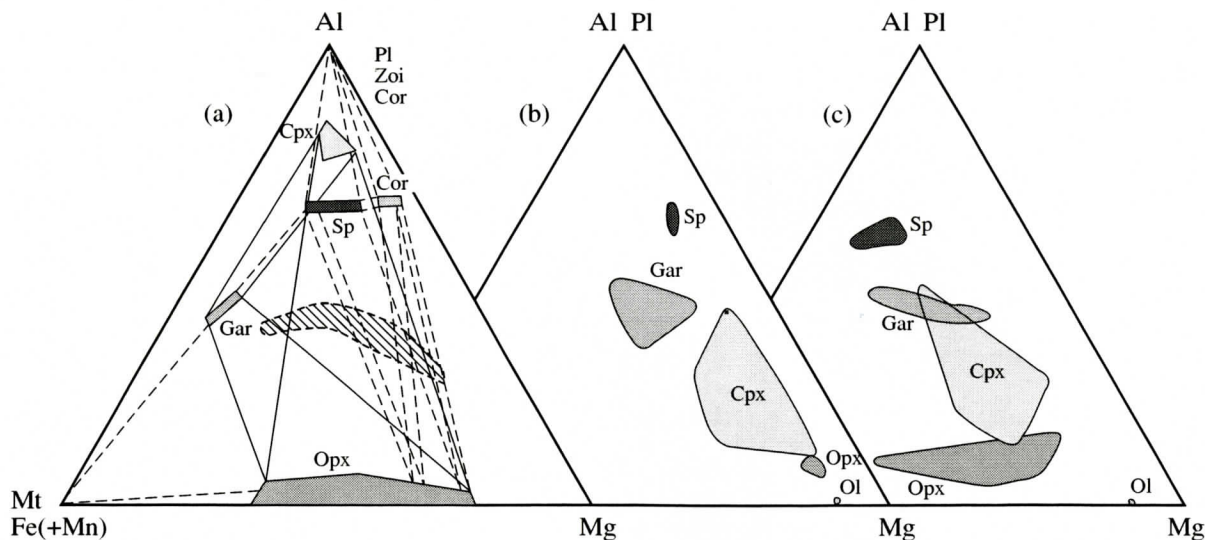


Fig. 2. (a) Mg–Al–Fe(+Mn) phase diagram for garnet pyroxenites from the Kokchetav Massif. Solid lines connect the coexisting primary minerals represented by garnet (Gar), orthopyroxene, and inferred clinopyroxene (Cpx), while dashed lines connect the younger minerals: plagioclase, zoisite (Zoi), spinel (Sp), magnetite (Mt), corundum (Cor), and cordierite (Cor). Clinopyroxene compositions are taken from microprobe determinations in the table. Compositions of other minerals are taken from [5, 8]. Shaded field shows chemical compositions of garnet pyroxenites and coronites after [5]. (b, c) Mg–Al–Fe(+Mn) phase diagrams, showing compositions of coexisting minerals in garnet pyroxenites from Beni Bousera Pluton, Morocco [10], and from lower crustal xenoliths in the Hungarian volcanic rocks [11]; (Ol) olivine.

phases) [9] and presence of OH-bearing mineral (zoisite).

Pseudomorphs presumably resulted from simple breakdown of peraluminous clinopyroxene. For example, the breakdown reaction in the Si–Al–Ca–Fe system for Sample 35-6 (table) and other minerals taken from [8] can be written according to the phase rule as follows: 0.85 clinopyroxene = 0.44 plagioclase (91% anorthite) + 0.01 zoisite + 0.30 spinel (54% hercynite) + 0.01 magnetite. In the Si–Al–Mg–Fe system, clinopyroxene is also generally broken down into plagioclase and spinel, occasionally with corundum and/or magnetite. Compositional variations of clinopyroxene provoke changes of reaction coefficients and products. The variations of component contents are mainly related to the primary compositional heterogeneity of clinopyroxene porphyroblasts with some contribution of Mg, Fe, and Al redistribution during formation of cordierite rims. This is distinctly expressed in the pseudomorph boundaries. One can see that spinel is liberated from anorthite and zoisite, while cordierite rims grow during interaction of spinel with orthopyroxene groundmass (Fig. 1).

The proportions of Fe and Al mole fractions in apoxyroxenite coronite are shown in the Al–Fe–Mg diagram (Fig. 2a). It also demonstrates the composition of clinopyroxene in equilibrium with garnet and orthopyroxene. We suppose that the clinopyroxene was a precursor of anorthite–zoisite–spinel/magnetite–corundum pseudomorphs. Clinopyroxenes from high-pressure garnet pyroxenites [10, 11] contain significantly less Al (Figs. 2b, 2c). However, in specific high-Al and

low-Na rocks, high pressure and temperature promote the formation of clinopyroxene phase, in which Al significantly dominates over Si in the form of tschermakite molecule $(Ca,Mg,Fe)Al_2SiO_6$. Experimental data indicate that such a peraluminous clinopyroxene can originate at a pressure of 10–15 kbar and temperature of 1000–1100°C or somewhat lower [12, 13].

We determined the formation temperature for harzburgites located near coronites described above. The orthopyroxene–olivine–spinel geothermometer [14] yielded 840 and 780°C, respectively, for samples R-118-A-98oe and R-118-98 analyzed in [5]. Based on these temperatures, we can determine the formation pressure for garnet orthopyroxenite, which is also located near the coronites. The pressure estimated from the Harley orthopyroxene–garnet geobarometer [15] for Sample R-118-Be-98e is 14–15 kbar. Hence, the maximum *PT* conditions for pyroxenites later transformed into coronites are estimated at ~800°C and 14–15 kbar. They are close to those determined experimentally for the Ca–Mg–clinopyroxene tschermakite [12, 13]. The presence of Fe in this system presumably widens its stability field. These data support the assumption that anorthite–zoisite–spinel/magnetite–corundum pseudomorphs formed after clinopyroxene.

Conclusions. Our study showed that anorthite–zoisite–spinel/magnetite–corundum pseudomorphs in coronites of the Kokchetav Massif developed after high-alumina clinopyroxene (tschermakite) $(Ca,Fe,Mg)Al_2SiO_6$. This phase is stable only at high *PT* parameters. Therefore, it can be replaced by aggregate of later minerals during retrograde metamorphism.

Table 1

Component	Contents, wt %															
	35-A-1	35-A-2	35-A-3	35-A-4	K-1A	K-1B	K-1C	35-1	35-2	35-3	35-4	35-5	35-6	35-7	35-8	35-9
SiO ₂	29.87	30.61	28.66	31.06	29.36	29.59	29.29	31.36	30.59	28.77	30.13	30.94	32.12	29.53	30.68	29.74
Al ₂ O ₃	42.29	39.31	42.83	42.22	45.51	45.22	45.29	42.11	41.55	44.42	43.28	41.07	40.95	41.21	42.01	41.29
TiO ₂	0.03	0.02	0.03	0.03	0.02	0.02	0.02	0.02	0.03	0.04	0.04	0.02	0.02	0.02	0.03	0.02
Cr ₂ O ₃	0.10	0.06	0.09	0.08	0.42	0.38	0.52	0.12	0.10	0.14	0.09	0.09	0.08	0.05	0.14	0.10
FeO	7.90	8.55	8.46	7.26	5.82	5.46	5.29	7.57	8.50	8.53	7.80	8.97	7.21	9.31	7.77	8.05
MgO	4.62	4.32	4.55	3.82	7.52	7.57	7.02	3.80	3.63	5.24	4.19	4.22	3.19	4.11	3.99	4.05
MnO	0.02	0.03	0.02	0.00	0.01	0.00	0.00	0.02	0.02	0.02	0.03	0.03	0.04	0.04	0.01	0.02
CaO	11.97	13.90	12.11	12.73	8.41	8.26	8.68	11.46	12.37	10.01	11.31	12.10	13.62	12.68	12.30	12.75
Na ₂ O	0.20	0.14	0.15	0.19	0.21	0.21	0.27	0.29	0.17	0.17	0.18	0.24	0.20	0.12	0.17	0.13
K ₂ O	0.02	0.02	0.01	0.01	0.01	0.01	0.00	0.19	0.13	0.01	0.02	0.01	0.01	0.01	0.01	0.01
Total	97.02	96.96	96.91	97.40	97.29	96.72	96.38	96.94	97.09	97.35	97.07	97.69	97.44	97.08	97.11	96.16

Calculation on the basis of six oxygen atom																
Si	1.112	1.151	1.073	1.147	1.068	1.079	1.073	1.161	1.141	1.064	1.116	1.148	1.187	1.110	1.139	1.121
Al	1.855	1.743	1.891	1.838	1.950	1.944	1.956	1.837	1.827	1.937	1.889	1.797	1.784	1.825	1.838	1.834
Ti	0.001	0.001	0.001	0.001	0.001	0.001	0.000	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001
Cr	0.003	0.002	0.003	0.002	0.012	0.011	0.015	0.004	0.003	0.004	0.003	0.003	0.002	0.001	0.004	0.003
Fe	0.246	0.269	0.265	0.224	0.177	0.167	0.162	0.235	0.265	0.264	0.241	0.279	0.223	0.293	0.241	0.254
Mg	0.256	0.243	0.254	0.210	0.408	0.412	0.383	0.210	0.202	0.289	0.232	0.234	0.176	0.230	0.221	0.228
Mn	0.001	0.001	0.001	0.000	0.000	0.000	0.000	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.000	0.001
Ca	0.477	0.560	0.486	0.504	0.328	0.323	0.341	0.455	0.494	0.397	0.449	0.481	0.539	0.510	0.489	0.515
Na	0.014	0.010	0.011	0.013	0.015	0.015	0.019	0.021	0.012	0.012	0.013	0.017	0.014	0.009	0.012	0.010
K	0.001	0.001	0.001	0.001	0.000	0.000	0.000	0.009	0.006	0.000	0.001	0.000	0.000	0.001	0.000	0.000
Total	3.966	3.981	3.986	3.940	3.959	3.952	3.949	3.934	3.952	3.969	3.946	3.961	3.927	3.981	3.945	3.967

Notes: Analyses were performed at an accelerating voltage of 25 kV with beam size up to 100 μ m. Standard deviation for impulses recorded from randomly selected points was no more than 8 rel %. The analytical data were processed using the PAP correction program [9]. The total correction of first approximations of intensity ratios of sample and standards was less than 10%, which provided the correction for matrix effects.

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