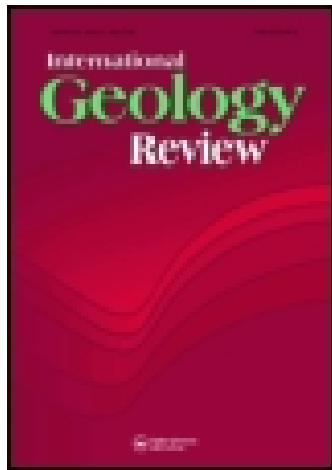


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Yongfeng Zhu ^a & Yoshihide Ogasawara ^b

^a Peking University

^b Waseda University

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Phlogopite and Coesite Exsolution from Super-Silicic Clinopyroxene

YONGFENG ZHU¹

*Institute of Geochemistry, School of Earth and Space Sciences, Peking University, Beijing 100871, China and
Department of Earth Sciences, Waseda University, Tokyo 169-8050, Japan*

AND YOSHIHIDE OGASAWARA

Department of Earth Sciences, Waseda University, Tokyo 169-8050, Japan

Abstract

We document the exsolution of phlogopite and coesite/quartz from pre-existing super-silicic clinopyroxene in dolomite marble from the Kokchetav massif, northern Kazakhstan. The exsolution texture was formed by clinopyroxene decomposition through the reaction $(3\text{enstatite} + 2\text{KAlSi}_2\text{O}_6)_{\text{cpx}} = \text{phlogopite} + 4\text{coesite}$. Phlogopite exsolution must have occurred at pressures less than 8.0 GPa (at 1000°C), where the garnet + super-silicic clinopyroxene + phlogopite assemblage was stable, based on experimentally defined phase relations. Observations described in this report suggest that the precursor clinopyroxene was stable at pressures higher than 8 GPa (>1000°C), implying that the dolomite marble was subducted to mantle depths greater than 240 km. Such profound subduction could be an important mechanism to transport abundant H₂O and potassium into the deep Earth.

Introduction

DEEP SUBDUCTION OF crustal material significantly affects mantle convection and Earth dynamics (e.g., Ernst, 2001). During this process, important amounts of H₂O and potassium may be transported into the deep mantle, which affects its rheology. Exsolution textures, formed during the exhumation of a subducted slab, constitute an indicator of ultra-high pressure (UHP) metamorphism (e.g., Liou et al., 1998). Exsolution lamellae of quartz (e.g., Smith, 1984) and garnet (e.g., Smyth et al., 1989) in clinopyroxenes are well documented for UHP eclogites. A much more complex exsolution texture was identified by Schmadicke and Muller (2000); they described quartz + oligoclase + K-white mica lamellae in omphacite from an Erzgebirge eclogite, and demonstrated that such an exsolution texture was formed at pressure >3 GPa as a result of Ca-Eskola decomposition. Their interpretation is consistent with the mechanism proposed by Katayama et al. (2000) for quartz exsolution from super-silicic clinopyroxene. Here we report an unusual exsolution texture in clinopyroxene from the Kokchetav UHP dolomite marble, propose a mechanism for phlogopite and coesite exsolution (different from the commonly accepted quartz exsolution mechanism), and discuss the implications for deep subduction as well as potassium recycling.

Geologic Background and Sample Descriptions

Rocks from the Kokchetav UHP massif have been extensively studied (e.g., Shatsky et al., 1995; Zhang et al., 1997; Maruyama and Parkinson, 2000; Dobrzhinetskaya et al., 2001) inasmuch as these rocks have been subducted into the mantle from continental crust levels, experienced UHP metamorphism, and then were exhumed to the Earth surface. The Kokchetav UHP massif consists of several metamorphosed lithotectonic units with Precambrian protolith ages, intruded by Ordovician island-arc granites and gabbros, and overlain by Devonian volcanoclastic rocks, Carboniferous–Triassic shallow-water marine and lacustrine deposits (Dobretsov et al., 1995). The Kumdylkol region is situated in the central part of the Kokchetav UHP massif, where pelitic gneiss, eclogite, and various marbles crop out. Diamond-bearing dolomite marble, coexisting with eclogite lenses (Ogasawara et al., 2000), is coarse,

¹Corresponding author; email: yzhu@geoms.geo.pku.edu.cn

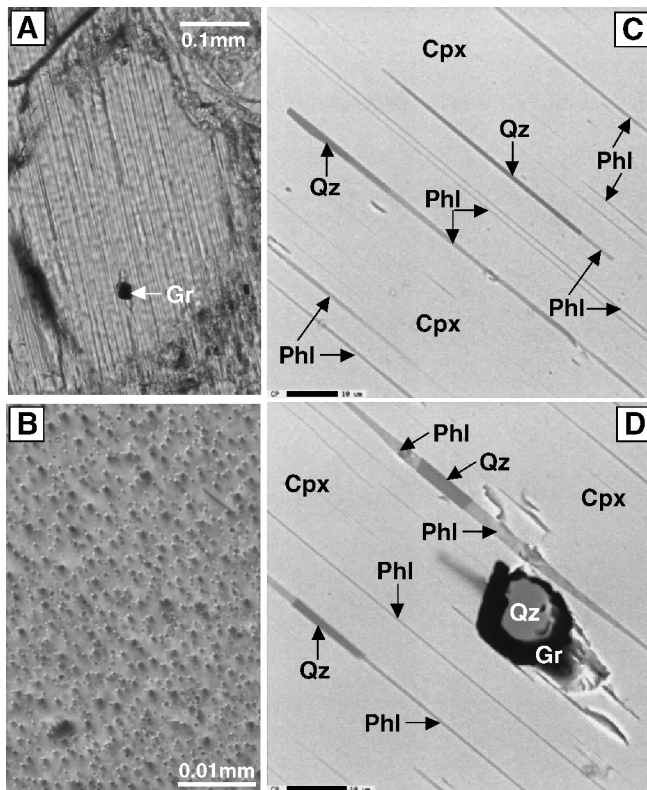


FIG. 1. A. Microphotograph showing a clinopyroxene containing abundant lamellae, and a single graphite inclusion, plane-polarized light. B. Cross-section of the lamellae in clinopyroxene, plane-polarized light. C and D. Back-scattered electron (BSE) images showing lamellae composed of phlogopite and quartz in clinopyroxene. The phlogopite and quartz coexist even in a single lamella. A rare graphite + quartz inclusion occurs in clinopyroxene (D). The scale bars in C and D represent 10 μm . Abbreviations: Cpx = clinopyroxene; Phl = phlogopite; Qz = quartz/coesite; Gr = graphite.

equigranular, and heterogeneous in terms of dolomite and silicate mineral contents. Silicates constitute up to 50 vol % of the bulk rocks. Besides dolomite, garnet + clinopyroxene assemblages are most abundant, and account for more than 40 vol% of the bulk rocks. Most garnet and clinopyroxene grains contain microdiamond inclusions. Clinopyroxene (15–30 vol%, 0.2–2.0 mm in size) occurs as a major silicate mineral in the Kokchetav diamond-bearing dolomite marble. The assemblage of clinopyroxene + garnet together with diamond inclusions was thought to represent the peak metamorphic phases (Zhang et al., 1997; Ogasawara et al., 2000).

Clinopyroxene contains abundant lamellae, which are very thin and rigorously parallel to each other with regard to orientation and homogeneity

(Fig. 1A). In some cases, the cross-sections of lamellae were investigated (Fig. 1B). By combining the images of lamellae and their cross-sections, we can demonstrate that the exsolved lamellae are needle-like rods. The lamellae typically have widths less than 1 μm ; such tiny lamellae consist of phlogopite only. However, some lamellae are thicker than 1 μm , and these consist of phlogopite and quartz/coesite (Figs. 1C–D). The coexistence of phlogopite and coesite even in a single lamella strongly suggests that phlogopite and coesite exsolved simultaneously from the precursor clinopyroxene. In rare cases, inclusions consisting of quartz and graphite occur in clinopyroxene (Fig. 1D). The petrological significance of these inclusions is still unclear, but the quartz in such inclusions is different from the quartz/coesite lamellae coexisting with phlogopite.

TABLE 1. Representative Compositions of Host Clinopyroxene (cpx) and Phlogopite Lamellae (phl)

Oxides, wt%	cpx	cpx	cpx	cpx	cpx	cpx	cpx	cpx	cpx ¹	phl	phl	phl	phl	phl	phl
SiO ₂	54.86	55.41	54.71	55.49	55.54	53.94	54.54	54.42	39.44	39.07	39.61	40.18	38.65	39.66	39.66
TiO ₂	0	0	0	0	0	0	0.01	0.02	1.40	1.35	1.09	1.14	1.34	1.58	1.58
Al ₂ O ₃	1.05	0.92	0.93	1.49	1.20	1.71	1.43	1.49	14.55	14.95	14.41	14.16	17.71	17.70	17.70
MgO	16.81	16.71	17.63	16.51	16.90	16.79	16.83	16.68	23.64	23.26	21.54	21.43	20.69	20.69	20.69
MnO	0.08	0.22	0	0.11	0.07	0.04	0.04	0.07	0	0.14	0.11	0	0.02	0	0
FeO	1.13	0.80	1.12	1.32	1.27	2.76	1.95	2.10	4.32	4.36	5.04	4.41	3.82	3.85	3.85
Cr ₂ O ₃	0.07	0	0.06	0	0	0.03	0	0.02	0.02	0	0	0.09	0.03	0	0
CaO	24.72	24.71	24.29	24.27	24.84	23.74	24.11	24.09	0.13	0.22	1.58	2.15	0.33	0.17	0.17
Na ₂ O	0.23	0.24	0.31	0.28	0.23	0.32	0.26	0.29	0.22	0.20	0.13	0.14	0.03	0.02	0.02
K ₂ O	0.41	0.26	0.34	0.49	0.29	0.29	0.54	0.33	9.51	9.88	9.56	9.46	10.18	9.81	9.81
Total	99.36	99.27	99.39	99.96	100.34	99.62	99.71	99.51	93.23	93.43	93.07	93.16	92.80	93.48	93.48
Cations															
O	6	6	6	6	6	6	6	6	6	22	22	22	22	22	22
Si	1.999	2.014	1.991	2.006	2.001	1.971	1.986	1.985	5.708	5.663	5.784	5.842	5.609	5.684	5.684
Ti	0	0	0	0	0	0	0	0.001	0.152	0.147	0.120	0.125	0.146	0.170	0.170
Al ^{IV}	0	0	0.009	0	0	0.029	0.014	0.015	0.292	0.337	0.216	0.158	0.391	0.316	0.316
Al ^{VI}	0.045	0.053	0.031	0.063	0.051	0.044	0.047	0.049	2.190	2.217	2.263	2.268	2.638	2.673	2.673
Mg	0.913	0.905	0.956	0.890	0.908	0.914	0.913	0.907	5.101	5.027	4.689	4.645	4.476	4.421	4.421
Mn	0.002	0.007	0	0.003	0.002	0.001	0.001	0.002	0	0.017	0.014	0	0.002	0	0
Fe	0.034	0.024	0.034	0.040	0.038	0.084	0.059	0.064	0.523	0.528	0.615	0.536	0.464	0.461	0.461
Cr	0.002	0	0.002	0	0	0.001	0	0	0.002	0	0	0.010	0.003	0	0
Ca	0.965	0.962	0.947	0.940	0.959	0.929	0.940	0.941	0.020	0.034	0.247	0.335	0.051	0.026	0.026
Na	0.016	0.017	0.022	0.020	0.016	0.023	0.018	0.021	0.062	0.056	0.037	0.039	0.008	0.006	0.006
K	0.019	0.012	0.016	0.023	0.013	0.014	0.025	0.015	1.756	1.827	1.781	1.754	1.885	1.793	1.793
Total	3.996	3.981	4.007	3.984	3.988	4.010	4.005	4.000	15.806	15.854	15.765	15.712	15.675	15.551	15.551
Mg/(Mg+Fe)	0.961	0.967	0.966	0.954	0.957	0.914	0.938	0.932	0.907	0.902	0.882	0.897	0.906	0.905	0.905

¹Average composition of host clinopyroxene analyses (n = 49).

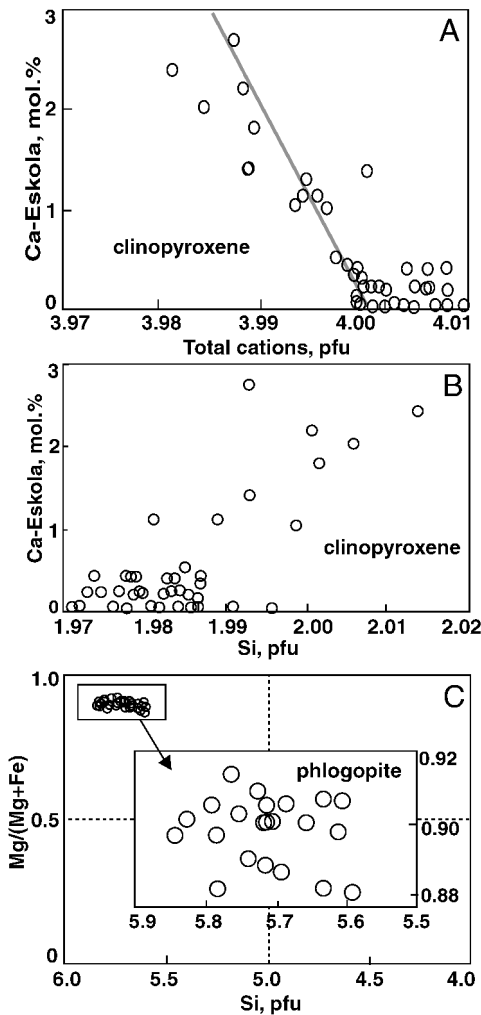


FIG. 2. Compositional variations of host clinopyroxene (A, B) and exsolved phlogopite lamellae (C). The reference line in A represents the ideal relation between Ca-Eskola component and cation vacancies (from Smyth, 1980).

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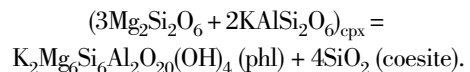
All textural relationships described here were investigated employing a JEOL Superprobe 8900 using the backscattered-electron (BSE) image mode, combined with wavelength-dispersive X-ray spectroscopy (WDS). The analyses conditions were 15 kV, 1nA, with probe diameter of 1 μm and a counting time of 40s for every element. Representative compositions of host clinopyroxene and phlogopite lamellae are listed in Table 1. Eight pyroxene

end-members (Ca-Eskola, Ca-Tschermak, jadeite, acmite, augite-diopside + hedenbergite, orthopyroxene = enstatite + ferrosilite, $\text{Na}(\text{Mg}, \text{Fe})_{0.5}\text{Ti}_{0.5}\text{Si}_2\text{O}_6$, and KAlSi_2O_6) were assumed, and calculated based on the method of Smyth (1980), assuming $\text{Fe}^{3+} = \text{Na} (\text{Al} - 2 \text{IVAl} - \text{K})$. The calculated KAlSi_2O_6 components vary from 0.7 to 3.3 mol%, with an average of 1.5% (49 analyses). Ca-Eskola components in clinopyroxene vary between 0 and 2.7 mol%, with an average of 0.5%, and negatively correlate with total cations (Fig. 2A, Table 1). Similar to super-silicic clinopyroxene in the Kokchetav eclogites and pelitic gneisses (Katayama et al., 2000), the amount of Ca-Eskola components in the studied dolomite marble increases roughly with the number of cation vacancies. This therefore suggests that Ca-Eskola components can account for the clinopyroxene composition. The Si contents in clinopyroxene are close to 2.0, with an average of 1.985 pfu (Table 1). Some analyses have Si contents higher than 2.0 pfu (Fig. 2B). Although no correlation exists between Ca-Eskola components and Si contents, the analyses with higher Si contents generally contain relatively higher Ca-Eskola components (Fig. 2B). This observation indicates that high-Si clinopyroxene contains relatively large numbers of vacancies.

Phlogopite lamellae are close to the phlogopite end-member composition. Mg/(Mg+Fe) ratios higher than 0.88 and Si values higher than 5.50 pfu are observed (Fig. 2C).

Discussion

Quartz exsolution from the precursor clinopyroxene is explained by decomposition of the Ca-Eskola component as the reaction of $2\text{Ca-Eskola} = \text{CaSi}_2\text{O}_6 + 3\text{quartz}$ (Katayama et al., 2000). This mechanism obviously cannot explain the observed phlogopite-coesite exsolution texture in clinopyroxene. We propose that phlogopite lamellae coexisting with coesite are the decomposition products of combined enstatite and KAlSi_2O_6 components in super-silicic clinopyroxene, based on the following mass-balanced reaction:



This reaction explains the coexistence of phlogopite and coesite lamellae observed in the studied clinopyroxene (Fig. 1). Although the formation of phlogopite and coesite lamellae consumed enstatite

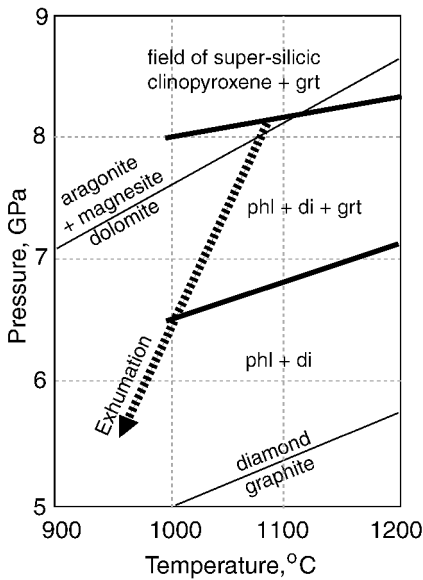


FIG. 3. Pressure-temperature diagram for phlogopite-clinopyroxene-garnet assemblages from the Kokchetav diamond-bearing dolomite marble. The diamond-graphite boundary is from Kennedy and Kennedy (1976); the dolomite decomposition boundary is based on Sato and Katsura (2001). Other phase boundaries are from Sudo and Tatsumi (1990) and Luth (1997). Phlogopite exsolution occurred during exhumation from pressures >8 GPa (see text for details).

and KAlSi_2O_6 components in precursor clinopyroxene, the studied clinopyroxene with exsolution textures still contains up to 3.3 mol% KAlSi_2O_6 components. This indicates that the precursor clinopyroxene must have been even more K-rich. The analyzed K_2O contents in clinopyroxene vary between 0.16 and 0.72 wt% (with an average of 0.33 wt%, Table 1). High-K clinopyroxene is stable at high pressure based on experimental studies (e.g., Harlow, 1997; Luth, 1997). Clinopyroxene with $\text{K}_2\text{O} > 0.5$ wt% in the diopside-phlogopite system is stable at pressures >7.5 GPa (Luth, 1997).

Early experiments suggested that stoichiometric phlogopite cannot survive at pressure higher than 7 GPa ($\sim 1000^\circ\text{C}$) based on experimental studies (Tronnes, 1990; Luth et al., 1993). At high temperatures ($>1200^\circ\text{C}$), both pure phlogopite and the phlogopite + enstatite assemblage undergo partial melting at 5 GPa (Sato et al., 1997), and phlogopite + clinopyroxene will partially melt at higher temperatures ($>1350^\circ\text{C}$) at the same pressure conditions (Luth, 1997). The assemblage phlogopite + diopside

transforms to the phlogopite + diopside + garnet assemblage at pressures of >6.5 – 7.4 GPa (at >1000 – 1300°C), and the latter is stable up to 8.0 – 8.5 GPa at the same temperature ranges (Sudo and Tatsumi, 1990; Luth, 1997). Thus either phlogopite in the diopside + garnet assemblage must be “off composition” and stabilized at pressures greater than that for pure phlogopite, or some of the phase equilibrium results must be in error. Here we accept the latest results by Luth (1997).

The observed phlogopite + clinopyroxene assemblage coexists with garnet in the studied dolomite marble. The phlogopite + clinopyroxene + garnet assemblage can survive in a wide pressure range from 6.5 to 8.0 GPa (at 1000°C , Fig. 3). Phlogopite and coesite exsolution from the pre-existing super-silicic clinopyroxene should take place at pressures less than 8 GPa (1000°C) based on the phase diagram shown in Figure 3. The precursor clinopyroxene must have formed in a higher-pressure environment (>8.0 GPa, $>1000^\circ\text{C}$), because exsolution textures formed during pressure decrease. This is consistent with the observations made by Zhu and Ogasawara (2002), demonstrating that dolomite decomposition to magnesite + aragonite occurred in the Kokchetav dolomite marble.

Conclusions

Phlogopite and coesite lamellae in super-silicic clinopyroxene formed as the decomposition products of enstatite + KAlSi_2O_6 components in clinopyroxene at pressures lower than about 8.0 GPa (at 1000°C). The pre-exsolution super-silicic clinopyroxene must have been stable at pressures of >8 GPa. This suggests that the studied dolomite marble reached depths >240 km in the mantle, and brought H_2O and potassium into the deep Earth. This process may effect the rheology of the mantle, and probably is an important factor triggering the generation of potassic magmas. The “lamproite” cropping out in the Kokchetav UHP massif (Zhu et al., 2002) probably is related to such potassium recycling.

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