



Experimental evidence of bulk chemistry constraint on SiO₂ solubility in clinopyroxene at high-pressure conditions



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ARTICLE INFO

Article history:

Received 7 May 2014

Accepted 23 January 2015

Available online 17 February 2015

Keywords:

Ultrahigh-pressure metamorphism

Supersilicic clinopyroxene

Eskola component

Octahedral silicon

M2 vacancy

ABSTRACT

We have experimentally confirmed that the solubility of SiO₂ in clinopyroxene at ultrahigh-pressure metamorphic conditions is buffered by coesite and kyanite. The present findings were derived from high-pressure experiments on metapelite glass, powdered andesite and eclogite glass under anhydrous conditions. The metapelite glass and powdered andesite were recrystallised in boron nitride capsules at 8 GPa and 1100–1500 °C. The eclogite glass was heated in an AuPd capsule, both ends of which were welded, at 3 GPa and 1000 °C.

Clinopyroxene nucleated from metapelite glass, the bulk composition of which is saturated in both SiO₂ and Al₂SiO₅ components plotting within the *Jd* (Na,K)(Al,Cr)(Si,Ti)₂O₆–*Qtz* (Si,Ti)O₂–*Grt* M₃(Al,Cr)₂(Si,Ti)₃O₁₂–*Als* (Al,Cr)₂(Si,Ti)O₅ tetrahedron (M = Fe, Mn, Mg, Ni, Zn, Ca), coexists with garnet, coesite and kyanite. The average excess silica content of the clinopyroxene ranges from 23.4 to 35.4 mol%. In contrast, an andesite experiment saturated in SiO₂ but undersaturated in Al₂SiO₅ within the *Jd*–*Qtz*–*Aug* M(Si,Ti)O₃–*Grt* tetrahedron produced clinopyroxene, garnet and coesite but no kyanite. The average excess silica in the clinopyroxene was 9.7–15.5 mol%, which is comparable to previous experimental data. Experiment on the eclogite glass with similar composition to andesite yielded clinopyroxene, garnet and coesite. An average excess silica content in clinopyroxene counts 6.4 mol%, which is much lower than that obtained from the andesite.

The SiO₂ content of clinopyroxene coexisting with garnet, coesite and kyanite is much higher than that of clinopyroxene coexisting with garnet and coesite without kyanite. Although the temperature dependence is unclear, the SiO₂ solubility increases with pressure and Fe/(Fe+Mg). Clinopyroxene forms the solid solution series *Jd*–*Es* □_{0.5}M_{0.5}Al(Si,Ti)₂O₆ and *Aug*–*Es*, rather than *Jd*–*Ts* MAl₂(Si,Ti)O₆ and *Es*–*Ts* joins. Our experimental data suggest the probable existence of octahedral Si which may accompany the M2 vacancies in clinopyroxene.

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1. Introduction

A non-stoichiometric supersilicic clinopyroxene is characterised by silicon accounting for more than two per formula unit normalised to six oxygen atoms (e.g., Smith and Cheeney, 1980). Such non-stoichiometry is attributed to the partial substitution with Ca–Eskola hypothetical end-member resulting from M2 vacancies and incorporation of the excess SiO₂. The supersilicic clinopyroxene is stabilised at pressures higher than 3 GPa but is unstable at lower pressures (e.g., Smyth, 1980).

Despite a large amount of experimental data (Gasparik, 1986; Konzett et al., 2008; Okamoto and Maruyama, 2004; Ono and Yasuda, 1996; Wood and Henderson, 1978), the thermodynamic properties of supersilicic clinopyroxene remain ambiguous, and the SiO₂ solubility in clinopyroxene has yet to be exactly formulated as a function of intensive variables such as pressure, temperature and composition.

Therefore, it is of urgent need to perform a series of experiments under ultrahigh-pressure metamorphic conditions in order to reveal the thermodynamic behaviours, especially the solid solution relation of supersilicic clinopyroxene. In this study we examined SiO₂ solubility in clinopyroxene in terms of the chemical trend among components of supersilicic clinopyroxene and its dependence on pressure and bulk chemistry, using three bulk compositions: granulite-facies metapelite, high-magnesian andesite and kyanite-bearing quartz eclogite.

2. Previous studies

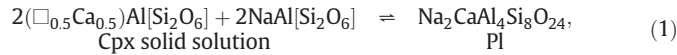
Franchi (1902) described clinopyroxene + plagioclase symplectites in eclogite of the Alps and observed the reaction jadeite + quartz → albite (Godard, 2001) and interpreted the replacement of omphacite by symplectites in eclogite as resulting from jadeite exsolution. Eskola (1921) further developed this interpretation. He described myrmekite-like intergrowths of clinopyroxene and plagioclase in Norwegian eclogites and proposed that a former jadeite-bearing clinopyroxene was replaced by diopside and plagioclase. He also introduced the term “pseudojadeite” for the molecule (Ca,Mg)(Al,

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$\text{Fe}_2\text{Si}_4\text{O}_{12}$, which is equivalent to the present-day “Ca-Eskola” hypothetical end-member (Khanukhova et al., 1976), pointing out the existence of clinopyroxene within the jadeite–acmite–diopside–“pseudojadeite”–silica system. Vogel (1966) hypothesised that symplectitic intergrowths of clinopyroxene and plagioclase result from isochemical breakdown of supersilicic clinopyroxene as follows:



where \square is a vacancy and $(\square_{0.5}\text{Ca}_{0.5}\text{Al}[\text{Si}_2\text{O}_6])$ is the Ca-Eskola end-member (CaEs).

Omphacite containing oriented needles or rods of quartz has been found in eclogite xenoliths from kimberlite pipes (e.g., Smyth, 1980) and from many eclogites in continent–continent collisional metamorphic belts, including the Norwegian Caledonides (Smith, 1984), the Bohemian Massif (Bakun–Czubarow, 1992; Schmädicke and Müller, 2000), the Alpe Arami, Switzerland (Dobrzhinetskaya et al., 2002; Green et al., 2000), the Kokchetav Massif, Kazakhstan (Katayama et al., 2000; Shatsky et al., 1985; Zhu and Ogasawara, 2002) and the Sulu region, China (Tsai and Liou, 2000; Zhang et al., 2005). In these collisional metamorphic belts, coesite, diamond, or coesite + diamond provides direct evidence of ultrahigh-pressure metamorphism. Quartz needles in clinopyroxene have been interpreted as the exsolution from supersilicic clinopyroxene indicating ultrahigh-pressure conditions, if the host rock contains other ultrahigh-pressure phases such as coesite, microdiamond, talc, K-rich clinopyroxene and/or Na-rich garnet (Klemd, 2003; Page et al., 2005).

The quartz needles would exsolve from CaEs-bearing supersilicic clinopyroxene during exhumation following this reaction (Katayama et al., 2000; Smyth, 1980; Zhang et al., 2005):



Katayama et al. (2000) provided the first evidence for significant amounts of Ca-Eskola dissolved in clinopyroxene under ultrahigh-pressure metamorphic conditions. They reported that clinopyroxene inclusions in zircons from eclogites and biotite gneisses of the Kokchetav Massif contained up to 10 and 18 mol% $(\square_{0.5}\text{Ca}_{0.5}\text{Al}[\text{Si}_2\text{O}_6])$, respectively. Chopin (1984) described the partial breakdown of jadeitic pyroxene associated with coesite-bearing pyrope in ultrahigh-pressure rocks from the Dora-Maira Massif; this jadeitic pyroxene contains a slight excess of Al relative to Na, and shows a sum of cations of 3.981, lacking 0.019 cations from pyroxene stoichiometry based on a 6-oxygen structural formula. The deficiency in the sum of cations indicates the excess silica in the clinopyroxene. Similarly, Bruno et al. (2002) have found jadeitic clinopyroxene with an average content of 13 mol% $(\square_{0.5}\text{Ca}_{0.5}\text{Al}[\text{Si}_2\text{O}_6])$ in a metagranite from the Dora-Maira Massif. Proyer et al. (2004) identified clinopyroxene with a low Ca-Eskola component (2–5 mol%) from the kyanite–talc–coesite eclogites of the Dabie Shan ultrahigh-pressure orogen. These clinopyroxenes are characterised by significant cation deficiencies, with values as low as 3.91 cations per formula unit normalised to six oxygen atoms.

Kushiro (1969) first synthesised clinopyroxene with excess SiO_2 . He obtained a single clinopyroxene phase for an initial composition of up to 50 wt% anorthite in the diopside–anorthite system at 2.7 GPa and 1350 °C. Mao (1971) showed that $\text{NaAlSi}_2\text{O}_6$ – $\text{CaAl}_2\text{SiO}_6$ clinopyroxene can contain as much as 7.5 wt% excess SiO_2 at 4.0 GPa and 1100–1700 °C, and that the solubility of SiO_2 in clinopyroxene is highly sensitive to pressure. This suggests that the excess SiO_2 content in clinopyroxene is a potential geobarometer. Mori and Green (1976) reported that diopside shows minor solid solution towards either SiO_2 or Mg_2SiO_4 at 3.0 GPa, depending on the bulk composition in the CaO – MgO – SiO_2 system. Wood and Henderson (1978) identified substantial M1 vacancies in aluminous clinopyroxene as a form of $\text{Ca}(\square_{0.33}\text{Al}_{0.66})[\text{Si}_2\text{O}_6]$ in the

systems $\text{CaAl}_2\text{SiO}_6$ – SiO_2 and $\text{CaAl}_2\text{SiO}_6$ – $\text{CaMgSi}_2\text{O}_6$ at 2.5–3.2 GPa and 1400–1500 °C. The experimental results obtained from the $\text{CaMgSi}_2\text{O}_6$ – $\text{CaAl}_2\text{SiO}_6$ – $\text{Ca}_{0.5}\text{AlSi}_2\text{O}_6$ clinopyroxene coexisting with anorthite and quartz at 1.4–3.04 GPa and 1200–1400 °C (Gasparik, 1984a,b, 1986), and at 3.5–7.0 GPa and 1200 °C (Zharikov et al., 1984) suggest that the degree of non-stoichiometry in pyroxene is highly pressure-sensitive and that non-stoichiometric pyroxene should be a stable component of natural clinopyroxene, particularly in the presence of excess SiO_2 . Zhao et al. (2011) obtained similar results from high-pressure experiments on Ca-Eskola solubility in clinopyroxene in the Na_2O – CaO – MgO – Al_2O_3 – SiO_2 system. In the Zhao et al. (2011) experiments, the amount of SiO_2 in clinopyroxene coexisting with garnet, kyanite and coesite increases with pressure up to about 6 GPa, slightly decreases as pyroxene progressively dissolves to garnet at 8 GPa, and decreases sharply in the stability field of stishovite at 10–12 GPa.

3. Experimental procedures

3.1. Starting materials

3.1.1. Bulk chemistry

Despite the field evidence that ultrahigh-pressure metamorphic rocks are mainly composed of quartzofeldspathic and pelitic gneisses, marbles, and quartzites, together with minor mafic eclogites and garnet peridotites (Liou et al., 1998), most of the experimental studies carried out to clarify the phase relations among ultrahigh-pressure minerals have been performed on the composition of mid-oceanic ridge basalts (MORB) at pressures above 5 GPa (e.g., Konzett et al., 2008; Okamoto and Maruyama, 1998, 2004; Ono and Yasuda, 1996).

In order to examine the effects of pressure and bulk chemistry on the SiO_2 solubility in clinopyroxene and to get information on the mineral texture observed in the run products derived from different types of precursors, the following samples are used as starting materials: (1) vitrified granulite-facies metapelite from the Tertiary Hidaka metamorphic belt in Hokkaido, Japan (Osanai et al., 1992); (2) pulverised high-magnesian augite–bronzite–olivine andesite from Ibuki-jima Island, Miocene Setouchi volcanic belt in northeastern Shikoku, Japan (Osafune, 1990; Sato, 1981); (3) vitrified kyanite-bearing quartz eclogite, deriving from basic volcanoclastic rocks of the Higashi-Akaishi mass of the Sanbagawa belt, central Shikoku, Japan (Enami, 2000; Miyamoto et al., 2007; Takasu, 1989; Wallis et al., 2000).

The chemical compositions of the starting materials, given in Table 1, show a variable X_{Mg} of 0.423 (metapelite), 0.702 (andesite) and 0.564 (eclogite). As is shown in Fig. 1, the bulk chemistry can be expressed in the system $\text{Qtz}(\text{Si,Ti})\text{O}_2$ – $\text{MO}(\text{Fe,Mn,Mg,Ni,Zn,Ca})\text{O}$ – $\text{Crn}(\text{Al,Cr})_2\text{O}_3$ – $\text{Jd}(\text{Na,K})(\text{Al,Cr})(\text{Si,Ti})_2\text{O}_6$. The metapelite plots within the Jd – Qtz – Grt $\text{M}_3(\text{Al,Cr})_2(\text{Si,Ti})_3\text{O}_{12}$ – $\text{Als}(\text{Al,Cr})_2(\text{Si,Ti})\text{O}_5$ tetrahedron, whereas the andesite and the eclogite plot within the Jd – Qtz – Aug $\text{M}(\text{Si,Ti})\text{O}_3$ tetrahedron. These three rocks also plot within the Jd – Qtz – Aug – Es $\square_{0.5}\text{M}_{0.5}(\text{Al,Cr})(\text{Si,Ti})_2\text{O}_6$ tetrahedron. Here, Ti, Cr and K are added to Si, Al and Na, respectively (see also Section 4.2). As is discussed in Sections 4.1 and 5.1, the differences in the bulk chemistry of the starting materials reflect the differences in the assemblage of the run products and those in the chemical composition of clinopyroxene: clinopyroxene coexisting with the garnet–coesite–kyanite assemblage from the metapelite glass shows higher excess silica content than that with garnet and coesite but no kyanite from the powdered andesite and eclogite glass.

3.1.2. Preparation of starting materials

First, the rock samples were ground to 60-mesh powder (about 0.4 mm in size). This coarse powder was ground in an agate mortar in ethyl alcohol for 1 h. Finally, the rock sample was pulverised to a size of about 10–50 μm , so that about 50% of the particles were less than 30 μm in size. The finely powdered metapelite was fused in a graphite capsule at 1.0 GPa and 1400 °C for 4 min using a piston–cylinder

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