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Oriented kokchetavite compound rods in clinopyroxene of Kokchetav ultrahigh-pressure rocks

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ABSTRACT

Two microdiamond-bearing samples, a dolomite marble and a garnet-clinopyroxene rock, from the Kokchetav ultrahigh-pressure metamorphic terrane were selected in the present study to explore the possible origin of $KAlSi_3O_8$ rod inclusions oriented along the *c*-axis of clinopyroxene host.

The $KAlSi_3O_8$ rod inclusions at clinopyroxene cores, where K_2O content is high in the range of 0.5–1.0 wt.%, are mostly fine-grained with a rod width less than 1 μm. AEM studies showed that the $KAlSi_3O_8$ phase in most rod inclusions is kokchetavite. K-feldspar is present only in a few cases, probably the result of phase transformation/recrystallization from kokchetavite during rock exhumation. Electron diffractions further showed that kokchetavite rods are oriented parallel to clinopyroxene [001] direction and they exhibit the same epitaxial relation with the clinopyroxene host in both samples with the (Al, Si)O_4 tetrahedra chains along the hexagonal *a*-axis of kokchetavite parallel to the single SiO_4 chain along the *c* axis of clinopyroxene; i.e., $[1\bar{2}10]_{Ko}//[001]_{Cpx}$ and $(0001)_{Ko}//(100)_{Cpx}$. It is interesting to note that kokchetavite is always in association with phengite, tremolite, β-cristobalite, Si-rich (Al, K, Ca-bearing) low crystallinity phase, ±Si–Ca (Cl, As) phase, ±calcite, ±apatite, ±lollingite ($FeAs_2$), forming compound rods. Furthermore, all these phases are also present within submicron-scale polyphase inclusion pockets in garnet within garnet-clinopyroxene rock sample. These kokchetavite compound rods are therefore most likely to have resulted from melt/fluid-clinopyroxene interactions leading to epitaxial deposition rather than exsolution *sensu stricto* from the clinopyroxene host. The suggested melt/fluid would have an "external" and/or an "internal" origin related to rock partial melting involving phengite breakdown.

Discrete phlogopite and phengite needle-like inclusions with a needle width less than 1 μm, as well as phlogopite–phengite and kokchetavite-mica intergrowth needles, are also not uncommon in clinopyroxene cores. There are specific crystallographic orientation relationships among phases. These micas might have formed earlier than kokchetavite and have exsolved from clinopyroxene host, although the mass balance issue during exsolution and the temporal relation between phlogopite and phengite needles remain to be settled.

Clinopyroxene rims generally contain mica needles only. Domains near fractures with coarse-grained kokchetavite compound rods or with coarse-grained phlogopite + quartz needles are not uncommon. These clinopyroxene rims/domains are low in K_2O (<0.5 wt.%) and their inclusions are most probably a result of precipitation/recrystallization from late-stage(s) infiltrated fluid-clinopyroxene interactions.

1. Introduction

Despite its large ionic radius, potassium accommodated within clinopyroxene lattice structure in a substantial amount (up to ∼3.6 wt.% K_2O) has been observed in clinopyroxene within kimberlite, in clinopyroxene inclusions in diamonds, and in clinopyroxene within diamondiferous ultrahigh-pressure (UHP) rocks (Bishop et al., 1978; Sobolev and Shatsky, 1990; Harlow and Veblen, 1991; Shatsky et al., 1995; Liou et al., 1998; Katayama et al., 2002; Perchuk et al., 2002; Bindi et al., 2003). Experimental work also confirmed that clinopyroxene can uptake ∼5.6 wt.% K_2O at 7 GPa and 1250 °C (Harlow, 1997; Bindi et al., 2002; Safonov et al., 2003, 2005). On the other hand, recent studies on UHP terranes have repeatedly reported that K-minerals, such as K-feldspar, phengite and phlogopite, occur as oriented needles/lamellae in clinopyroxene. These

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needles/lamellae were inferred to have resulted from decompression exsolution of a K-rich clinopyroxene from great depths during rock exhumation (Zhang et al., 1997; Schmädicke and Müller, 2000; Katayama et al., 2002; Zhu and Ogasawara, 2002; Zhu, 2003; Bozhilov et al., 2009; Dobrzhinetskaya et al., 2009).

In studying polyphase inclusion pockets in clinopyroxene and garnet from a garnet-clinopyroxene rock (KD-1) of the Kokchetav UHP terrane, Hwang et al. (2004) unexpectedly found that one mineral, which has a chemical composition of $KAlSi_3O_8$, is structurally different from any known K-feldspar polymorphs. The lattice structure of the mineral was identified to be a hexagonal system with a = 5.27 Å and c = 7.82 Å. This mineral, as a new K-feldspar polymorph and in association with phengite/β-cristobalite/quartz/glass(±phlogopite/calcite/titanite/zircon) in polyphase inclusions, was therefore named as kokchetavite and was interpreted to be most likely metastable precipitates from a melt phase. One interesting question that follows is whether the commonly quoted oriented "K-feldspar" needles in clinopyroxene of Kokchetav UHP terrane are actually "kokchetavite" needles. Representative samples from the Kokchetav UHP terrane were therefore selected for analytical electron microscopic (AEM) analysis in the present study to delineate this issue. The results of the present study show that the oriented needles are actually composed of kokchetavite, as well as phengite, tremolite, β-cristobalite and Si-rich (Al, K, Ca-bearing) low crystallinity phase, which cast doubts on the exsolution origin for these compound needles.

2. Geological background and sampling

The Kokchetav Massif is a large (300 × 150 km), fault-bounded metamorphic complex of Proterozoic protolith age in northern Kazakhstan. In the central part of this massif, seven tectonic melange units, resulting from collision between the Siberian platform and the Vendian-Ordovician island arc, have been collectively named as the Zerenda Series (Shatsky et al., 1995). The diamondiferous UHP rocks occur in unit I of the Zerenda Series, which consists of a variety of crystalline schist, gneiss, eclogite, amphibolite, garnet–pyroxene rock, quartzite, marble and rare garnet peridotite. Abundant in situ microdiamonds have been found as inclusions in garnet, zircon, and clinopyroxene in biotite gneiss, garnet–pyroxene rock and dolomite marble. Most of the protoliths of diamondiferous rocks were of supracrustal origin with a 2.2–2.3 Ga Sm–Nd model age (Shatsky et al., 1999). The peak metamorphic P–T conditions have been estimated at around 5.8–6.5 GPa and 900–1100 °C. The age of the peak metamorphism has been determined to be around 530–540 Ma (Hermann et al., 2001; Katayama et al., 2001). The suggested P–T path of these Kokchetav UHP rocks is shown in Fig. 1.

Two samples were selected in the present study. One is a dolomite marble (KD-82) and the other is a garnet–clinopyroxene rock (KDD-26). Oriented "$KAlSi_3O_8$" needles/rods are commonly present within clinopyroxene of these two samples. Microdiamond inclusions and polyphase mineral inclusions were also observed within garnet. Both samples were collected from an underground mining gallery at Kumdy-Kol, Kokchetav. The gallery had been constructed for microdiamond mining in 1981–1986 and was refurbished in 2002. The lithologic characteristics of this mining gallery were well documented by previous investigators (Parkinson et al., 2002; Shatsky et al., 1995; Sobolev et al., 2003). Detailed geological map and section of Kumdy-Kol deposit including underground gallery were given by Sobolev et al. (2003). Briefly speaking, granitic gneiss, biotite gneiss and dolomite marble are the major rock types. Garnet–clinopyroxene rock occurs as layers up to 10 m thick within granitic and biotite gneisses (Shatsky et al., 1995). On the basis of geochemical characteristics, Shatsky et al. (1999) concluded that most Kokchetav UHP rocks might have been subjected to complicated partial melting processes yet to be studied.

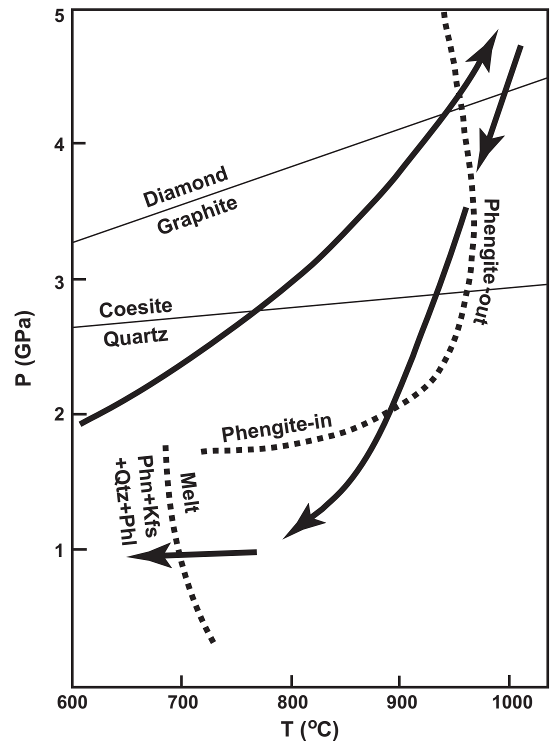

Fig. 1. The suggested P–T path of the Kokchetav UHP rocks (after Hermann et al., 2001). Also shown are reaction Coesite = Quartz after Hemingway et al. (1998); reaction Diamond = Graphite after Kennedy and Kennedy (1976), Phengite-in/out curve after Auzanneau et al. (2006); and melting curve in the KMASH system: Phengite + K-feldspar + Quartz + Phlogopite = Melt, after Massonne and Schreyer (1987).

3. Analytical methods

Petrographic thin-sections were prepared from both samples for optical polarized microscopic and scanning electron microscopic (SEM, JEOL JSM-7000F at 15 kV) observations. Twenty-six thin foils for analytical electron microscopic (AEM) studies were prepared from petrographic thin sections. Clinopyroxene or garnet grains with needles and inclusion pockets under optical microscope were first clamped between two copper rings to ensure sample integrity, followed by argon-ion-beam milling (Gatan, PIS) to perforation (operation condition: 4.0 kV, 9° incident angle). Additional 30 AEM samples with the thickness of 100 nm were further prepared by applying the focused ion beam technique (FIB, SMI-3050) for AEM–EDX analyses of semi-quantitative chemical compositions of minerals. Crystal structures/orientations and microstructures were obtained using a transmission electron microscope (TEM) (JEOL JEM-3010) operated at 300 kV. The selective area electron diffraction (SAED) patterns were taken along various zone axes to determine the crystal system. The transmission electron microscope was equipped with an energy dispersive X-ray (EDX) spectrometer (Oxford EDS-6636) with an ultrathin window and a Si(Li) detector, capable of detection of elements from boron to uranium.

4. Results

4.1. OM and SEM observation

Sample KD-82 is a medium- to coarse-grained dolomite marble with an equigranular granoblastic texture. It contains 60–65%