Precipitates of α-cristobalite and silicate glass in UHP clinopyroxene from a Bohemian Massif eclogite

Tina R. Hill¹, ², Hiromi Konishi¹#, Franklin Hobbs¹, Seungyeol Lee¹, and Huifang Xu¹ *

¹ Department of Geoscience, University of Wisconsin-Madison, Madison, Wisconsin 53706, U.S.A.
² Bruker Nano, Inc., 5465 E. Cheryl Parkway, Madison, WI, 53711

# Present address: Department of Geology, Niigata University, 8050 Ikarashi 2-no-cho, Nishi-ku, 12 Niigata 950-2181, Japan.

* Corresponding author: Prof. Huifang Xu

E-mail: hfxu@geology.wisc.edu
Tel: 608-265-5887
ABSTRACT

Low pressure metastable nano-scale crystals of α-cristobalite have been observed epitaxially-exsolved in cores of UHP clinopyroxene from the Bohemian Massif, Czech Republic. SAED patterns and HRTEM images detail the close structural relationship between host clinopyroxene and α-cristobalite precipitate: \([001]_{\text{Di}} \parallel [010]_\alpha, (010)_{\text{Di}} \sim \parallel (101)_\alpha\). TEM results indicate that α-cristobalite exsolved from host clinopyroxene. Non-crystalline Al-bearing silicate phases, also exsolved from UHP clinopyroxene, possesses Al/Si ratios close to eutectic compositions in the system NaAlSi$_3$O$_8$-SiO$_2$-H$_2$O system. Presence of glass exsolution suggests a high temperature formation environment and presence of water. The α-cristobalite formed in a localized low-pressure, micro-environment formed through exsolution of vacancies and excess silica from the host pyroxene lattice. This micro-environment may be a result of negative density changes due to excess lower density silica exsolving from higher density pyroxene during an exsolution process that involved no localized volume change. Interface-controlled exsolution via lattice matching at the diopside/cristobalite interface, and stability changes and melting point depression due to nano-scale size effects contributed to formation and persistence of this metastable phase. Amphibole in association with α-cristobalite and some non-crystalline silicate phases may be a clue to localized water quantities; silica exsolution with amphibole may have formed below the eutectic temperature and at a later stage than non-crystalline silicate phases without amphibole. Silica rods in Nové Dvory clinopyroxenes were previously thought to be quartz; however, our investigation reveals a variety of low pressure, high temperature, and/or metastable phases greatly affected by the presence of vacancy and OH in clinopyroxenes. The results will help us better understand OH in the UHP pyroxene and even water release in the mantle.
INTRODUCTION

Discoveries of coesite (Smith 1984) and microdiamond in the Kokchetav Massif (Sobolev and Shatsky 1990) have clearly established that rocks of continental origin were subjected to ultrahigh-pressure metamorphism (UHPM), which required their subduction to a depth of not less than 80-120 km (Chopin 1984; Smith 1984; Schreyer et al. 1987; Sobolev and Shatsky 1990; Xu et al. 1992; Coleman and Wang 1995; Dobrzynetskaya et al. 1995; Wain 1997; Ye et al. 2000; Van Roermund et al. 2002; Carswell et al. 2006; Dobrzynetskaya et al. 2006). It is in these deeply-subducted terranes that micro- and nano-scale minerals within stable host minerals such as garnet and pyroxene are often preserved, even though prograde textures and mineral parageneses are typically obliterated during exhumation from great depth. Micro- and nano-scale minerals of these orogenic terranes are of particular interest to investigators because they are windows to the special conditions required to develop UHPM terranes when no other evidence persists, and aids in elucidating the geodynamic processes endured by them.

Crystallographically-oriented silica rods exsolved in clinopyroxene, many coexisting with amphibole, are well-documented from ultrahigh-pressure (UHP) terranes around the world: (Bakun-Czubarow 1992; Bi, et al. 2018; Smith 1984; Gayk et al. 1995; Wain 1997; Katayama et al. 2000; Schmadicke and Muller 2000; Tsai and Liou 2000; Dobrzynetskaya et al. 2002; Zhu and Ogasawara 2002; Klemd 2003; Song et al. 2003; Janak et al. 2004; Sajeev et al. 2010; Dokukina and Konilov 2011; Konilov et al. 2011; Song et al. 2018). Although there is at present evidence of HP (and not UHP) clinopyroxenes possessing these crystallographically-oriented silica precipitates in the Blue Ridge Mountains, USA, the Kontum Massif, central Vietnam, and the Greek Rhodope (Page et al. 2005; Anderson and Moechner 2007; Nakano et al. 2007a; Nakano et al. 2007b; Proyer et al. 2009; Faryad and Fisera 2015; Li et al. 2018), in the dearth of
other UHP evidence the siliceous rods are often used as indicators of rocks experiencing UHP conditions. The breakdown textures of clinopyroxene and its chemical variations may help us to investigate pre- and post-peak rock evolution of the host rock.

Reports of silica exsolution in clinopyroxene have previously been identified by micro- and macroscale techniques as either coesite or quartz (Bakun-Czubarow 1992). For instance, Zhang et al. (2005) demonstrated that silica exsolution took place in the coesite stability field and that the coesite easily transforms to quartz during retrograde metamorphism. More recently, High-resolution transmission electron microscopy (HRTEM) investigation of crystallographically-oriented silica in clinopyroxenes of the Kokchetav Massif discovered anomalous low pressure silica polymorphs (the first confirmed natural occurrence of keatite) in UHP pyroxene (Hill et al. 2013), but no coesite or quartz.

This study characterized crystallographically-oriented silica in clinopyroxenes from an eclogite of well-established UHP origin from the Bohemian Massif to confirm mineral phase identification of silica exsolution and to understand the processes of this occurrence more thoroughly. As in the Hill et al. (2013) study, this HRTEM investigation has found neither of the expected higher density silica polymorphs coesite or quartz. Instead, low-density and low-pressure phases α-cristobalite and Na-Al silicate glass are observed exsolved from UHP diopside. We explore possible mechanisms of formation for the metastable, low P, low T α-cristobalite and Al-bearing silica glass.

The terms exsolution, precipitate, and inclusion are used interchangeably by researchers to describe the phenomenon of crystallographically-oriented silica within pyroxene. We opt for “exsolution” in this manuscript to imply that the siliceous rods are likely formed from breakdown of the clinopyroxenes during exhumation. Further information about this is found in
the Discussion section. We have, at times still used the word precipitate as a descriptor when the use of the term “exsolvent” is somewhat cumbersome.

GEOLOGIC BACKGROUND AND SAMPLE DESCRIPTION

Orogenic peridotite bodies are components of metamorphic terranes in most major mountain systems. Some peridotite lenses contain (or contained) garnet-bearing assemblages, particularly where they occur within eclogite-facies metamorphic crustal rocks that recrystallized at high (HP) or ultrahigh (UHP) pressures. They are rich in petrological, mineralogical and geochemical information about the interaction of the mantle with the crust during mountain building (Brueckner and Medaris 1998, 2000; Rampone and Morten 2001; Scambelluri et al. 2008; Spengler et al. 2009). This study focuses on clinopyroxenes of the Nové Dvory eclogite from the Gföhl nappe (340 Ma (van Breemen et al. 1982)), a nappe within the Bohemian Massif in the Czech Republic. Clinopyroxenes in this eclogite exhibit crystallographically-oriented silica in their cores. It is also within the UHP range. Calculated $P-T$ estimates of the Gföhl nappe mantle garnet peridotite (which hosts the thin layers of the Nové Dvory eclogite) have been calculated at 875–1150°C, 3.3–6 GPa (Medaris et al. 2006). In addition to calculated UHP pressures, microdiamonds have been found as inclusions in garnet, kyanite, and zircon in the Eclogite-Gneiss Unit (Massonne 1998). Coesite has also been found in the Eclogite-Gneiss Unit (Massonne 2001).

The Nové Dvory eclogite is fine- to medium-grained, massive, and generally equigranular. It is composed primarily of Mg-Fe-garnet and Ca-rich clinopyroxene (between omphacite and diopside) (Table 1). A transmitted light micrograph of the rock (eclogite) (Fig. 1a) demonstrates the predominance of garnet and pyroxene. Thin rims of Na-rich clinopyroxene
are observed in electron backscatter images surrounding pyroxenes (arrows, Fig. 1a). Observed accessory minerals are rutile,apatite, zircon, iron sulfides, and iron oxides (possible retrograde phases ilmenite and Mg-bearing ilmenite). Some later-stage retrograde reactions (pyroxene-plagioclase symplectites and amphiboles) are observed at grain boundaries (Fig. 1a), otherwise, the rock is relatively fresh displaying only minor fracturing and alteration.

A plane polarized light image with a clinopyroxene grain oriented at some angle to the $c$-axis (Fig. 1b) displays siliceous phases concentrated in the core. In this orientation silica appears as elongated dark euhedral lines. In contrast, when clinopyroxenes are oriented with the $c$-axis parallel to the viewing direction, they appear as dark euhedral dots. This shape change with differing orientations of pyroxene demonstrates that the precipitates are crystallographically-oriented within the pyroxene lattice. A pyroxene grain boundary at the upper left in Fig. 1b (black circle) demonstrates that silica rods are few near grain boundaries.

**EXPERIMENTAL METHODS**

High-resolution TEM (HRTEM) images and selected-area electron diffraction patterns (SAED) were obtained utilizing an FEI Titan aberration-corrected S/TEM at the University of Wisconsin-Madison at 200 kV accelerating voltage. In addition to clinopyroxene (CPX) chemical compositions from the electron microprobe, compositions of silica precipitates were also analyzed by means of X-ray energy-dispersive spectroscopy (EDS) with small spot sizes in HRTEM mode using an EDAX EDS system on the FEI Titan S/TEM. Major element compositions of bulk CPX crystals were determined via wavelength dispersive spectrometry performed with the five spectrometer Cameca SX51 electron microprobe at the University of Wisconsin-Madison. Analytical operating conditions were 15 kV.
accelerating voltage, Faraday cup current of 20 nA, and 20 s counting times per element. Beam
spot size was 1 μm. Samples and standards were coated with ~20 nm carbon. Microprobe
analytical standards were: hematite for Fe, augite for Ca, olivine for Mg, rutile for Ti, chromite
for Cr, Mn-olivine for Mn, and hornblende for Si, Na, Al, and K.

Clinopyroxene lattice parameters were refined from X-ray diffraction (XRD) patterns by
means of least squares analysis using MDI, Inc. Jade 9.0 software. XRD patterns were collected
with a Rigaku Rapid II X-ray diffraction system with a 2-D image plate (Mo Kα radiation), with
an accelerating voltage of 50kV, a current of 50 mA, and a 0.1mm diameter collimator.
Diffraction data were collected on an image-plate detector. Two-dimensional images were then
integrated to produce conventional 2-theta -intensity patterns using Rigaku’s 2DP software.

Polished petrographic thin sections (30 μm thick) of the previously described CPX grains
were examined to find pyroxenes oriented parallel to the c-axis. Clinopyroxene grains were cut
out and thinned to ~20 μm by hand with silicon carbide grinding disks. Grains were then
mounted on molybdenum TEM grids. These foils were thinned to electron transparency via Ar⁺
ion milling in a Fischione 1010 ion mill.

RESULTS

Transmission electron microscope results

A bright-field (BF) TEM image details a nano-crystal of α-cristobalite (Fig. 2).

Dominant pyroxene crystallographic planes observed in the [001]Di orientation are labeled {010}
and {110}. These planes govern α-cristobalite crystal morphology, which appears in almost all
cases as a euhedral ‘negative’ pyroxene shape. The SAED pattern (Fig. 2b) was calibrated with
clinopyroxene lattice parameters calculated from collected X-ray diffraction data from a single
crystal of clinopyroxene, then refined via least squares method. Those parameters are: $a = 9.630$
Å, \( b = 8.818 \, \text{Å}, \ c = 5.244 \, \text{Å}, \ \alpha = \gamma = 90^\circ, \ \beta = 106.2^\circ \). The SAED pattern confirms host diopside, [001], is epitaxially-oriented with \( \alpha \)-cristobalite, [010]. Cristobalite \( hkl \)'s are denoted with white numbers and white arrows; diopside is labeled with black numbers and arrows in a white rectangle. Simulated diffraction patterns (DP) with indexing of both phases observed in the collected SAED pattern. Only \( \alpha \)-cristobalite and diopside are shown for clarification in Fig. 2d, e, and f, respectively. Spots which appear in the \( \alpha \)-cristobalite SAED pattern (001, 002, 003) are labeled as X’s in the simulated DP (Fig. 2e, f). These are typically at extinction due to screw axis (4\( _1 \)) but appear due to multiple diffraction effects.

Composition is straightforward. The silica precipitate EDS spectrum displays only silicon and oxygen peaks (Fig. 2c). Both the TEM images and the SAED pattern reveal homogeneous pyroxene structure with \( C2/c \) symmetry. Ordered omphacite lamellae (\( P2/n \ symmetry) known to occur in clinopyroxene structures were not observed. In addition, nano-scale amphibole occurs at the \( \alpha \)-cristobalite interface; the crystals display excellent pyroxene/amphibole lattice matching (Fig. 2g). In this HRTEM lattice image of all three phases, the cristobalite can be seen in the midst of transforming to an amorphous phase as a result of damage from the electron beam. This happened more quickly at the amphibole/pyroxene interfaces, where no cristobalite lattice can be observed. In Fig. 2a, a planar boundary marked (101)\( \alpha \) is observed in the cristobalite and explained in Fig. 3, where black arrows denote the location of the boundary in (a-c). Boxes denote areas of Fast Fourier Transform (FFT) patterns (Fig. 3c) on either side of the boundary in the HRTEM lattice image (Fig. 3a) and demonstrate that the planar boundary is the cristobalite twin plane (101). The amphibole and host diopside are labeled in (a) for reference. A schematic representation of the \( \alpha \)-cristobalite lattice with twinned unit cells outlined in black (b) shows the near-perfect lattice fit on either side of the composition plane.
A second category of siliceous precipitates are non-crystalline Al-bearing silicate phases enclosed by the euhedral negative pyroxene shape. They are quite common; a select four are shown in Fig. 4. Dominant euhedral CPX planes are sharp and clear; however, SAED patterns from precipitates (e.g., Fig. 4b) generally show diffuse rings indicative of amorphous phases. A ring with weak intensity and some possible diffraction spots are attributed to crystallites of an unidentified mineral that was quickly destroyed by the electron beam. There is no other evidence of this mineral. The only chemical constituents observed via EDS (Fig. 4c) are Si, O, and Al. Al/Si ratios in the exsolved silica in Fig. 4 (as shown by EDS) range from 0.1 to 0.2. Preferential loss of alkali elements and low-atomic-number elements, such as Na and K, and during analytical electron microscopy gives rise to characteristically low count rates for those elements. In addition, with a focused probe for X-ray analyses such as used in this investigation, the damage rate to the sample is exacerbated by a high current density and results in the loss of these elements during X-ray collection (Ma et al. 1998). No amphiboles (or other H₂O-rich phases) are observed in the non-crystalline silica in Fig. 4, unlike the cristobalite or the third category of siliceous precipitates, which is non-crystalline, but also possesses amphibole (Fig. 5).

This group of siliceous phases (Fig. 5(a)) possess very similar features to the non-crystalline siliceous phases in Fig. 4, with one main difference: the presence of amphibole at the pyroxene/silica interface. Fig. 5 shows one of the siliceous, Al-bearing glass phases with amphibole. The EDS spectrum (c) displays an Al peak as in the non-crystalline phase in Fig. 4. Euhedral negative pyroxene morphology of the silica is still observed here, and, although the SAED pattern (Fig. 5d) shows this image is oriented at [T01]₄₋, at an angle to CPX c-axis, the interface between diopside and the amphibole precipitate can still be seen to be coherent. Broad diffuse rings are observed in the silica SAED pattern (Fig. 5b), establishing that the silicate is
amorphous. White arrows in this SAED pattern point to a distinct faint ring representative of multiple small crystals. The extremely weak diffraction ring likely stems from the minerals indicated by black arrows in the white precipitate center (Fig. 5a). Identity of these minerals is unknown as they quickly disappeared under the energy of the electron beam. Inspection of the CPX/amphibole interface (Fig. 5e) illustrates the excellent lattice matching between the single and double chain silicates, and FFT patterns of both minerals further detail their crystallographic relationship: \([T01]_{\text{Di}} \parallel [100]_{\text{Amp}}\). A chemical formula calculated from the EDS spectrum using Cliff-Lorimer-based \(k\)-factors (Fig. 5f). This formula confirms a sodic-calcic amphibole (OH is assumed, not measured by EDS):

\[
\text{Na}_{0.64}(\text{Na}_{0.26}\text{Ca}_{1.64}\text{Fe}_{0.10})(\text{Mg}_{3.06}\text{Fe}_{0.99}\text{Al}_{0.95})(\text{Si}_{6.68}\text{Al}_{1.32})\text{O}_{22}(\text{OH})_2.
\]

It is also of note that multiple crystals of phyllosilicates were observed in close proximity to some siliceous precipitates (Fig. 6a, b) in this investigation. In these precipitates, the shape of the non-pyroxene crystals is modified from the typical euhedral ‘negative’ pyroxene shape, with the sheet silicates fully covering the siliceous phase (Fig. 6a), but not the pyroxene. Dominant pyroxene planes, specifically \{010\} and \{110\} are highly degraded and the familiar euhedral negative pyroxene shape is unrecognizable. The composition (EDS spectrum taken from the area in (b)) is that of a talc-like phyllosilicate with ~9 Å (001) lattice fringes (Fig. 6c), and the SAED pattern (e) confirms pyroxene plus diffraction rings from multiple talc-like crystals.

**Electron microprobe results**

Table 1 presents recalculated electron microprobe (EMPA) data from a representative clinopyroxene grain in the Bohemian Massif eclogite. All clinopyroxenes analyzed via EMPA exhibit silica precipitates in their cores. Standard deviation and standard error of these data are
reported (SDEV= Standard deviation, SERR=Standard error, and n=17). Oxygen was
calculated, not measured, and all calculations are normalized to six O atoms.

Almost all CPX analysis locations show sufficient Al to fill $^{IV}\text{Al}$, the rest fills $^{VI}\text{Al}$. The
clinopyroxene is highly calcic (~Di$_{68}$, between diopside and omphacite), with very little to no K.
UHP (non-stoichiometric) clinopyroxenes are characterized by significant cation deficiencies,
with cations equaling <4 total cations/6 oxygen; this has been well-established in the literature
(Smyth 1980; McCormick 1986; Proyer et al. 2004; Day and Mulcahy 2007; Konzett et al.
2008b; Zhao et al. 2011). Here, we broadly constrain possible vacancy content in clinopyroxene
grains by assuming cation deficiencies exist in the structure as vacancies (cations + vacancies =
four). Iron was measured via EMPA, and structural formula calculations involving only Fe$^{2+}$
resulted in cations sum to ~ 4 or even slightly larger than 4, permitting no possible calculation of
potential vacancy content. natural UHP clinopyroxenes, it is highly unlikely that all iron is Fe$^{2+}$,
and some usefulness is found in estimating some amount of Fe$^{3+}$ (Deer et al 1966) to calculate
formulae. In general, Fe$^{3+}$ is not measured, it is estimated by charge balance; in fact, these
authors found no instances of measured Fe$^{3+}$ data for the Nové Dvory eclogitic clinopyroxenes.
A comparable UHP clinopyroxene bulk composition was found in another UHP regime—the
Norwegian UHP clinopyroxenes of the Hareitland eclogite possess extremely similar bulk
clinopyroxene compositions. Calculated Fe$^{3+}$ data from Mysen (1972) show 1.1-1.7 wt. % Fe$^{3+}$
in the Hareitland eclogitic clinopyroxenes. Utilizing this as a proxy and making the assumption
that 2% of the total iron was Fe$^{3+}$ in the UHP Nové Dvory clinopyroxenes, we tabulate both
measured Fe$^{2+}$ and assumed 2% Fe$^{3+}$ amounts in Table 1. The host pyroxene is close to
stoichiometric.
The occurrence of α-cristobalite and Na-Al-bearing silicate glass in UHP pyroxene raises several questions. First, did the cristobalite form as β-cristobalite (as commonly happens) and transform to α-cristobalite? Secondly, did the cristobalite form within its own range of metastability (~200-275 °C (Hatch and Ghose 1991)) or at UHP pyroxene stability? Thirdly, we interpret both the silica glass and α-cristobalite, which exhibit similar morphology, as primary exsolution phases—what mechanism may have formed these low-density phases, and is the same mechanism responsible for both?

Crystallographically-oriented silica in clinopyroxene from high- and ultrahigh-pressure pyroxenes, such as that investigated here, is widely interpreted to be the result of a complex combination of rock bulk composition, $P$, and $T$ with a generally-accepted exsolution mechanism of excess silica from host clinopyroxene during decompression via the reaction:

$$2\text{Ca}_0.5\square_0.5\text{AlSi}_2\text{O}_6 = \text{CaAl}_2\text{SiO}_6 + 3\text{SiO}_2 + \square$$

($\text{Ca}_0.5\square_0.5\text{AlSi}_2\text{O}_6 = \text{CaEskola (CaEs) vacancy solid solution in pyroxene, and } \square = \text{vacancy}$)

(Smyth 1980; Liou et al. 1998; Katayama et al. 2000; Dobrzhinetskaya et al. 2002; Klemd 2003; Zhang et al. 2005; Konzett et al. 2008a; Zhao et al. 2011). Substitution of CaEs component into pyroxenes results in non-stoichiometry, and pyroxene may then dissolve excess silica charge balanced by vacancies in M sites (Wood and Henderson 1978). Day and Mulcahy (2007) document clear evidence that vacancy consumption in non-stoichiometric clinopyroxene can release free silica. Vacancies are not the only way to result in pure silica from pyroxenes. Smith (2006) demonstrates that it is also theoretically possible to exsolve pure SiO$_2$ from non-stoichiometric pyroxene other than by the CaEs formula mechanism and leave behind
stoichiometric compositions. However, the non-stoichiometric character of HP/UHP clinopyroxene is well-established (Smyth 1980; McCormick 1986; Proyer et al. 2004; Day and Mulcahy 2007; Konzett et al. 2008b; Zhao et al. 2011), and we can conclude with some confidence that vacancies were most likely present in the UHP pyroxenes of the Bohemian Massif eclogite prior to decompression. These mechanisms produce silica irrespective of silica polymorph, and exsolution may not produce and maintain α-cristobalite and Na-Al-silicate glass phases to the exclusion of other silica polymorphs. Exsolution of excess silica from non-stoichiometric pyroxenes is merely the beginning of the answer, and formation of these unusual phases is likely an intricate combination of many processes.

In addition to excess silica, evidence of hydroxyl (water) observed in this investigation may play a part in the vacancy content and the particular polymorph exsolved in the CPX structure. Experimental studies have documented the incorporation of varying amounts of hydroxyl in synthetic clinopyroxene (Skogby and Rossman 1989; Skogby 1994), as well as natural clinopyroxenes (Skogby et al. 1990; Smyth et al. 1991; Bell et al. 1995; Koch-Muller et al. 2004; Katayama et al. 2006). It is reasonable to assume that OH was present in Nové Dvory clinopyroxenes. Observed micro- and nano-scale amphiboles are evidence of at least a sufficient amount of OH to transform clinopyroxene to amphibole, and to produce a siliceous melt during expulsion of excess silica and OH. Smyth et al. (1991) found a positive correlation between hydroxyl content and cation vacancy concentration in pyroxene from mantle-derived eclogite in the Roberts Victor kimberlite pipes. Katayama and Nakashima (2003) reported water contents as high as 3000 ppm in omphacite within a diamond-grade eclogite from the Kokchetav massif, Kazakhstan, although they assert this could be overestimated as much as 30%. Much lower OH
quantities are also known—31-60 ppm in diamond-bearing eclogite xenoliths of the Mir
kimberlite pipe (Koch-Müller et al. 2004).

Cristobalite and silicate glass

High- (or β-) cristobalite is the stable low pressure polymorph of SiO$_2$ between 1470°C and its anhydrous melting point at ~1828°C, but exists in a metastable form down to ~275°C. There, it undergoes a rapid and reversible displacive transition to the metastable phase α- (low-) cristobalite (Hatch and Ghose 1991). Beta-cristobalite is cubic (denoted below as subscript ‘c’) (Fd$\bar{3}$m); α-cristobalite is tetragonal (P4$_1$2$_1$2$_1$).

Metastable silica phases are not uncommon in nature, and cristobalite can be found in a variety of volcanic and metamorphic environments. Low- (or, α-) cristobalite is often found in volcanic ejecta, lunar rocks and meteorites due to quenching (Christie et al. 1971), and metastable cristobalite can also crystallize authigenically within sedimentary deposits as opal-CT (Jones and Segnit 1971). Planar boundaries and microstructures within cristobalite are physical evidence of the β→α transition. Microstructures in α-cristobalite following the β→α transition are well documented by Hatch and Ghose (1991), and via electron microscopy (Lally et al. 1978). None of these β→α transformation microstructures described above are observed in Fig. 2, indicating that this silica polymorph may have formed as α-cristobalite, not the expected higher density polymorphs coesite or quartz previous researchers have reported in UHP clinopyroxenes. Although none of the above transformation microstructures were observed in the Nové Dvory clinopyroxene, a single planar boundary along (101) in the α-cristobalite crystal is observed in Fig. 2. Planar boundaries along (10$l$)$_1$ have been observed in previous studies (Withers et al. 1989), but the exact nature of these boundaries and their relationship with β-
cristobalite is still unclear. Diopside surfaces likely served as sites for heterogeneous nucleation and epitaxial growth of cristobalite. Although there is evidence for the (101) boundary to be interpreted as a growth twin, it is possible this may be an inherited twin (not a transformation twin) from the β-phase (Lemmens et al. 2000). Thus, we cannot rule out the possibility that the cristobalite transformed from the high temperature β- to α- cristobalite. It may be that the crystal is simply too small to display all of the transformation microstructures typical of this transformation.

Silicate glass can be found in many environments. Nanometer-size P/K-rich silica glass inclusions are found in microdiamond from gneisses of the Kokchetav and Erzgebirge massifs (Hwang et al. 2006). These are interpreted as former melt inclusions that reflect the chemical character of their host rocks and may have been generated through partial melting of gneissic rocks and/or dehydration/decarbonation processes in marble (Hwang et al. 2006). Pertinent to this investigation, highly silicic glass inclusions are found commonly present in Mg-rich minerals (olivine and pyroxene) of xenolithic terrestrial upper mantle rocks and have many similarities with glass inclusions from mafic minerals of achondritic meteorites (Varela et al. 1998).

Mechanisms of formation—silicate glass

As shown above, the non-stoichiometric character of UHP clinopyroxene has been well-established. If exsolution of excess silica is intimately linked to the non-stoichiometry of UHP clinopyroxene, it is possible that both non-crystalline Al-bearing silicate phases and α-cristobalite nucleated and exsolved from Ca-Es-bearing clinopyroxene. Simultaneous expulsion of OH held within the clinopyroxene structure at high temperatures most likely caused the partial
melting of silica that created Na-Al-silicate glass phases, and growth of amphiboles associated
with α-cristobalite. It is at this point in the story that formation mechanisms of α-cristobalite and
silica glass diverge slightly.

We propose that the glass precipitates in this study (Figs. 4, 5) are likely formed through
partial melting of the silica and albite components, as silica, a jadeite component, and OH are
expelled from the pyroxene lattice. Although silica-rich, aluminous alkali-rich glasses have been
found in Mg-rich minerals of both terrestrial upper mantle rocks and achondrites, mechanisms of
formation in the two cases are different. Varela et al. (1997) observed that although many
processes were likely to have contributed to their formation—low-degree partial melting,
precipitation from silicate-loaded fluids, fractional crystallization and liquid immiscibility, or
residual glass from a parent magma—glass inclusions in olivine and pyroxene of upper mantle
peridotites were more likely related to a very low degree of partial melting. Precipitation from
silicate-loaded fluids can be ruled out in the formation of glass in the Nové Dvory eclogite and
garnet pyroxenite, as it is more often associated with fractures and cross-cutting grain boundaries
that suggest migration of fluids through the grain, not isolated precipitation in cores of grains.
And, as can be seen in Fig. 1, the cores of clinopyroxenes in the rock are quite fresh, without
obvious subsequent alteration. Fractional crystallization and liquid immiscibility may be ruled
out on the basis that this phenomenon is typically extremely FeO-rich and, with these
compositions, is generally found in lunar environments. Table 1 compositions show these
pyroxenes possess some FeO, but may not be enriched enough for that. Residual glass from a
parent magma can also be ruled out. Varela et al. (1997) state that silica-rich glass inclusions in
upper mantle xenoliths are incompatible with this genesis, as residual melts that form glass likely
represent independent components trapped during crystallization of primary magma components.
Although Na is not observed now as it disappears quickly under the electron beam and can be difficult to capture, the potential presence of Na allows for us to consider the Al-bearing glass as a mixture of albite and silica components in a silica-albite eutectic system. The calculated range of Al/Si ratios (0.1-0.2) from the glasses is close to the eutectic composition in the NaAlSi$_2$O$_8$-SiO$_2$-H$_2$O (Ab + Qz + H$_2$O) system—at 0.1 GPa and 800 °C (Wen and Nekvasil 1994). The eutectic temperature at low pressures is similar for hydrous versus anhydrous conditions—at 1 bar, the temperatures of the eutectics are shown to be 1007 °C and 1009 °C, respectively. In a H$_2$O-saturated system, which is not the case here, an increase in pressure causes the temperature of the eutectic to drop—at 7 kbar, the eutectic is 682 °C. In an anhydrous system, a pressure increase to 7 kbar causes the eutectic temperature to increase dramatically to 1132 °C, and at 15 kbar (1.5 GPa), the eutectic moves to 1228 °C. Calculated $P$-$T$ estimates of the UHP mantle garnet peridotite which hosts the thin layers of the Nové Dvory eclogite are 875–1150 °C, 33–60 kbar (Medaris et al. 2006). At our calculated Al/Si ratio range of 0.1-0.2, the temperature of the eutectic in an anhydrous system which is similar to a hydrous system, as mentioned above, (at 5 kbar) is ~1100°C, as shown by Wen and Nekvasil (1994). This temperature is possible for glass formation. Figure 8 is a diagram illustrating the pressure difference between the precipitates (curve c) and the host minerals (curve b). Melt inclusions will be over-pressured (curve a) with respect the host mineral and precipitates will be under-pressured with respect to the host mineral.

It is unlikely that the glass-forming components (jadeite component, silica, vacancy, and OH) were expelled from the clinopyroxene lattice at peak metamorphic $P$-$T$. Rather, they may have been expelled at varying high temperatures post-metamorphic peak during decompression, when these elements formed a melt at the eutectic. In fact, modeling of thermal boundary conditions of exhumation rates in UHP rocks has shown that in the absence of lateral heating,
rocks exhuming from great depth always cool or decompress isothermally, and the main cooling period at shallower crustal levels follows the main period of exhumation (Grasemann et al. 1998). We may use the modeling results of Grasemann et al (1998) to propose that a glass formed at the eutectic in the Ab + Qz + (low) H₂O system with an Al/Si ratio of 0.1-0.2 may have formed at many different depths along the exhumation pathway. To narrow the temperature range in which the glass formed, we must also consider contributing factors that likely lowered the temperature at which the melt can form. See the section entitled “Contributing factors that aid in α-cristobalite and silica glass formation” for a discussion of these factors.

Mechanisms of formation—α-cristobalite

The key to α-cristobalite formation may the stability of the CPX lattice during subduction and exhumation. Metastable cristobalite has previously been found in high pressure garnet granulite from Gore Mountain, New York. This cristobalite within garnet likely originated as small trapped samples of hydrous Na-Al-siliceous melt where diffusive loss of water from the inclusions under isothermal, constant volume conditions may have resulted in a large enough internal pressure decrease to promote the metastable crystallization of cristobalite (Darling et al. 1997). In the Nové Dvory eclogite as in the Gore Mountain garnet, a crystal may form under constant volume conditions due to the high tensile strength and low thermal expansivity/compressibility of diopside compared with α-cristobalite (Berman 1988). No evidence of volume change is observed in the Nové Dvory clinopyroxenes in optical (Fig. 1) or HRTEM (Fig. 2) micrographs as a result of silica polymorphic transformations or changes in density from host clinopyroxene (~3.3 g/cm³) to cristobalite (2.32 g/cm³). Darling et al. (1997)
attribute formation of low pressure cristobalite to an open system in which mass is removed from
the system, causing lowered pressure. We hypothesize a locally-closed system at the point of
silica exsolution in the case of the α-cristobalite crystal in Fig. 2. Exsolution of vacancies
(assumed density of ~0.0 g/cm\(^3\)) that coalesce may cause a void and aid in this localized density
decrease. The density of the surrounding pyroxene (~3.3 g/cm\(^3\)) minus precipitated α-cristobalite
(2.32 g/cm\(^3\)) plus a potential coalesced vacancy void (0.0 g/cm\(^3\)) is a negative change of ~ 1
g/cm\(^3\). An arrow in Fig. 2 points to a potential void at the interface of silica and pyroxene. We
interpret this as an area of expelled, coalesced vacancies. If we interpret Fig. 2 in such a way as
to assume overall volume is preserved in clinopyroxene during silica exsolution, and assume
simultaneous vacancy expulsion and coalescence, a low pressure micro- or nano-environment
may be generated at any depth in response to density changes, perhaps via a reaction similar to
this:

\[
2\text{Mg}_{1.5} \square_{0.5} \text{Si}_2\text{O}_6\text{H} \rightarrow 1.5\text{Mg}_2\text{Si}_2\text{O}_6 + \square + \text{SiO}_2 + \text{H}_2\text{O}
\]

Vacancies are point defects in the crystal structure that create non-stoichiometry and are
also notoriously difficult to image with the TEM. We can assume the unstable vacancies have
been expelled from the destabilized pyroxene lattice and cannot be imaged in situ. Fortunately,
cases exist in which point defects form clusters and have been imaged readily with TEM
methods (Veblen and Cowley 1994). We believe this may be the mechanism which aids in
forming a low pressure micro-environment. As in the case of the Gore Mountain garnet, this
interpretation requires that the host mineral (clinopyroxene) maintain a pressure differential
between the small inclusions and the outside of the clinopyroxene. This pressure differential, in
addition to the high tensile strength and low thermal expansivity/compressibility of the
clinopyroxene (Berman 1988) likely serves to preserve micro- and nano-scale stable and
metastable minerals within the clinopyroxene during exhumation. Results of recent synthetic
fluid inclusion studies on quartz demonstrate that high pressure differences can be maintained
over small distances at high temperatures in cases where the internal inclusion pressure is lower
than external confining pressure (Sterner and Bodnar 1989; Vityk et al. 1995). In this way,
metastable phases such as α-cristobalite and the siliceous non-crystalline phases may persevere
to the surface from any depth.

This mechanism has been used by these authors (Hill et al, 2013) to explain another
instance of silica exsolution from UHP diopside in the Kokchetav Massif. In this diopside, low-
pressure keatite with accompanying amphibole was identified, also with no evidence of volume
change within the clinopyroxene crystal. Formation of α-cristobalite is favored over keatite in
the Nové Dvory eclogite as a result of higher temperatures than Kokchetav Massif garnet
pyroxenite.

Contributing factors that aid in α-cristobalite and silicate glass formation

Although it appears likely that both α-cristobalite and silica glass initiated formation in a
similar manner, the crystalline nature of α-cristobalite requires a different formation environment
than glass. Already discussed is the low-pressure micro-environment that may have been
produced by vacancy expulsion/coalescence and subsequent density decrease under constant
volume conditions, thus creating a suitable $P$ and $T$ for α-cristobalite. A number of other factors
may have contributed to the formation of metastable α-cristobalite.

Favorable interface energy due to excellent lattice matching and nano-scale size effects
may have played integral parts in lowering the nucleation and crystallization energy.

Generation/exsolution of metastable phases takes place when the kinetically-preferred path
differs from the preferred thermodynamic path (Baricco et al. 2004). In this way, exsolution of a
metastable phase may be preferred over a more stable phase. Mineral nano-particles commonly
behave differently as a function of their size within the nano-scale range. Mineral nano-particles
also behave differently than larger micro- and macroscopic crystals of the same structure and
composition. At the nano-scale, three factors compete to stabilize a given polymorph: enthalpy
of polymorphic transition, surface enthalpy, and enthalpy of hydration (Barnard and Xu 2008;
Hochella et al. 2008). Navrotsky et al. (2004) reported that competition between surface
enthalpy and the energetics of phase transformation leads to the general conclusion that
polymorphs that are metastable as micron-sized or larger crystals can often be
thermodynamically stabilized at the nano-scale. Nanocrystals of protoennetstite within plagioclase
are quenchable and stable at low-temperature (Xu et al. 2017a). This phenomenon has been
observed in TiO$_2$ polymorphs, aluminum and iron oxides, and oxyhydroxides (Navrotsky 2003;
Navrotsky et al. 2004; Chen and Fu 2006; Barnard and Xu 2008; Navrotsky et al. 2009; Lee and
Xu 2016; Lee et al. 2016). Thus, we infer metastable nano-scale α-cristobalite may be stabilized
in part due to its small size.

Additionally, the size at which a nano-scale mineral forms/melts is temperature
dependent. Extensive research has shown that decreasing particle size also decreases the
temperature at which the particle forms (Barnard and Xu 2008; Barnard et al. 2009). This
melting/crystallization point depression occurs for nearly all free nanoparticles, e.g. Au, TiO$_2$, Pt
(Barnard et al. 2009; Barnard et al. 2011), and for some nano-particles embedded in a matrix.
Melting point depression is also observed as a function of dimension (Zhang et al. 2000).

The melting point depression can be dramatic. As the particle shrinks to the nanoscale,
the interfacial energy ($\gamma$) penalty becomes significant when compared to total bulk energy ($\Delta H$).
This, in turn, destabilizes the particle with respect to the melt (DeHoff 2006). Assuming an \( l \times l \) x \( 3l \) rectangle particle shape as observed in TEM (Fig. 4), this destabilizing effect for a pure silica glass results in nearly a 300˚C melting temperature depression for an \( l = 50 \) nm particle as the melting temperature drops from 1723˚C to 1430˚C. The same calculations for \( l = 100 \) and 200 nm yield a 140˚C and 70˚C depression, respectively:

\[
\lambda_m = \frac{3\gamma M}{\rho_s \Delta H}
\]

\[
T_m(l) = T_m(\infty) \left[ 1 - \lambda_m \frac{l}{\ell} \right]
\]

where, \( l \) (length), \( \gamma \) (interfacial energy) = 4.4 J/m\(^2\), \( M \) (molar mass) = 60.08 g/mol, \( \rho_s \) (density) = 2.203E6 g/m\(^3\), \( T_m(\infty) = 1996 \) K (1723˚C), \( \Delta H \) (bulk enthalpy of fusion) = 50.55 kJ/mol

In combination with nano-scale size effects, mechanisms of exsolution are closely related to the types of interfaces that develop between two phases. The geometry of the substrate in epitaxial mineral growth is known to cause growth of phases not stable at existing \( P-T-X \) conditions. The morphology of silica glass and \( \alpha \)-cristobalite is certainly dominated by the clinopyroxene lattice (Figs. 2, 4, 5), and a high degree of lattice match between the two likely serves to stabilize the nano-scale \( \alpha \)-cristobalite crystal. The structural relationship of \( \alpha \)-cristobalite with diopside derived from the SAED pattern (Fig. 2a) is schematically-represented in Fig. 7. In all models \([001]_{\text{CPX}} \parallel [010]_{\alpha \text{-cristobalite}} \). Here we show \((010)_{\text{CPX}} \sim \parallel (-101)\alpha \) (Fig. 7a) and \((TT0)_{\text{CPX}} \sim \parallel (100)\alpha \) (Fig. 7b). These models illustrate that diopside and silica lattices join with little to no bending of the silica tetrahedra. Diopside \((010)\) is parallel to \( \alpha \)-cristobalite \((\bar{1}01)\), and Fig. 7d illustrates the close lattice match with unit cell dimensions: \( d_{100} \) of diopside is 9.3 Å, while \( \alpha \)-cristobalite \( d_{101} \) 4.04 Å. This is a mere 5% difference over just two unit cells of diopside.
and three unit cells of α-cristobalite, where 5d_{101α} (5 x 4.04 Å) is approximately equal to 2d_{100CPX} (2 x 9.3 Å). In addition, very minor mismatch between α-cristobalite and diopside likely minimizes the nucleation energy which aids a favorable configuration of silica tetrahedra.

The presence of amphibole in association with α-cristobalite and some glass precipitates may be a clue to localized water quantities. Silica glass exsolution with amphibole may have formed below the eutectic temperature and at a later stage than glass precipitates without amphibole. Nano-crystals of α-cristobalite plus amphibole likely possessed less localized water than the glass precipitates and may have formed after glass precipitates with and without amphibole. The amphibole in Fig. 3 appears to have been encompassed by the exsolving silica rather than transforming from pyroxene along the edge. A possible explanation is that the diopside expelled only a small amount of water at this locality and only a nano-scale portion of the pyroxene rehydrated to amphibole.

In this paper, we propose that the unique properties of HP/UHP pyroxenes discussed above (excess silica balanced by structural vacancies, OH held within the lattice and expelled during precipitate formation) drive exsolution from the clinopyroxene structure and form silicate minerals and melts. In addition, we interpret the silicate glass Al/Si ratios of 0.1-0.2 to correlate well with Al-bearing silicate glasses forming from a siliceous melt at high temperature on the eutectic in the Ab-Qz-H₂O system. A slightly later stage and lower temperature, the metastable low density silica polymorph α-cristobalite nucleated on diopside planes that served as sites for solid state heterogeneous nucleation and epitaxial growth. Assuming that the pyroxene (a stable crystal) has not experienced volume change at the point of low density silica exsolution, a metastable phase may form and persist within the host due to an internal pressure decrease.
Thus, a low pressure micro-environment may be created at the point of low density cristobalite formation.

Later stage alteration of silica precipitates

Some silica precipitates in this investigation are observed to have altered to talc-like phyllosilicates (Fig. 6). This appears similar to exsolved silica altered to high-silica sheet silicates from UHP clinopyroxene of the Kokchetav Massif (Hill et al. 2013). Here, as in the Kokchetav Massif, the dominant planes of the euhedral clinopyroxene have degraded and are nearly unrecognizable (Fig. 6a). Multiple crystals of sheet silicates in random orientation show a composition that is unexplainably high in silica (Fig. 6c), where no silica precipitate is observed. Due to the similarities of the two cases, we continue to interpret the sheet silicates as a later stage alteration of silica by replacement reaction due to fluid migration, similar to the results of Dobrzhinetskaya et al. (2009), localized on silica during rock retrogression. Refer to Hill et al. (2013) for a more detailed explanation.

IMPLICATIONS

Nano-scale investigation of formation processes of precipitates of silicate glass and cristobalite/amphibole intergrowths in UHP pyroxene may be important to help us better understand OH (or water) in eclogitic host pyroxene during subduction, and its ultimate release in the mantle. As geologists have little access to minerals from UHP terranes to study, the findings here have great significance for investigation of rocks that weren’t commonly believed to exist a mere 20-30 years ago. This study revealed vacancies and OH in high-pressure pyroxene that formed during subduction. When the host rock is exhumed, the incorporated OH
migrates out from the UHP pyroxene structure together with vacancies and excess silica in multiple forms of glass and cristobalite / amphibole precipitates. If the pyroxene-bearing slab subducts further into the mantle, the pyroxene may release the incorporated OH into mantle during its phase transformation to garnet and/or perovskite structures. The subsequent effects on mantle rocks are worthy of investigation.

Characterization of nano-scale phases inside UHP rocks is also significant for understanding the larger scale geodynamics of collisional terranes, particularly when unexpected (metastable) phases make an appearance. Geologic processes occurring deep in the Earth and under UHP conditions are difficult to recognize due to subsequent retrogressive reactions and fluid and deformation events experienced by rocks during exhumation. Only by identifying minerals and their mechanisms of exsolution at the nano-scale to track the path of these rocks can we understand in detail the processes operating deep in the Earth. Silica precipitates in Nové Dvory clinopyroxenes were previously thought to be quartz; however, our investigation reveals a variety of low pressure, high temperature, and/or metastable phases greatly affected by the presence of water in clinopyroxenes. The high tensile strength and low thermal expansivity / compressibility of diopside serves to preserve phases typically unlikely to make it to the surface without recrystallizing. When compared to observed silica phases, this may mean that the exsolved phases have little to no effect on the rheology of the exhuming rock but could affect the interpretation of the $P$-$T$ path. Some low-density precipitates containing Na and K may be formed through similar precipitation processes, instead of melt inclusions. $P$-$T$ evolution for the precipitates and inclusions are very different. The precipitates are under-pressured with respect to the host mineral. However, the melt inclusions are over-pressured.
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FIGURE CAPTIONS

Figure 1. Plane polarized light photomicrograph of Bohemian Massif eclogite (a) and clinopyroxene (b). The rock (a) is dominated by garnets (black) and clinopyroxenes (most other grains in the image). Arrows point to decompression garnet/CPX and CPX/CPX symplectites; the symplectites are generally thin and the CPX grains are quite fresh, with little alteration. The lack of alteration can be seen in the cores of the clinopyroxenes (b), which are filled with siliceous precipitates. In this orientation viewed at an angle to the c-axis, the precipitates appear primarily as rods and some dots (likely rods on end). Precipitates are concentrated in the grain core, with few precipitates in the rims near grain boundaries. A black circle denotes one of the CPX grain boundaries at the top left of (b), where there is a much lower concentration of precipitates. Note that no optical evidence of volume change (i.e., cracking due to less dense phase transformation) surrounds the precipitates.

Figure 2. (a) Bright-field TEM image of α-cristobalite nano-crystal. Dominant euhedral diopside planes and α-cristobalite (101)α twin plane are labeled; nano-scale amphibole at cristobalite/diopside interface indicated with white arrow at top left of precipitate. White arrow at bottom of image highlights an area of great strain contrast, and may be a void. (b) SAED pattern details epitaxial orientation of diopside (black arrows/numbers on white box) with α-cristobalite (white arrows/numbers). (c) EDS spectrum from just the α-cristobalite nano-crystal. Simulated diffraction patterns (DP) with indexing of (d) both phases observed in the SAED pattern, only α–cristobalite (e), and only diopside (f). Diffraction spots from α-cristobalite spots which appear in the SAED (001, 002, 003), labeled as X’s in the simulated diffraction pattern, are typically at extinction but appear due to multiple diffraction. (g) HRTEM image of nano-scale amphibole at interface of diopside and α-cristobalite.

Figure 3. (a) HRTEM image showing cristobalite domains in a twin relationship. Twin plane (101) corresponds to (111) in β-cristobalite. White squares are locations of Fast Fourier Transform (FFT) patterns in (c), which detail the crystallography on either side of the (101) twin plane. (b) Schematic representation of the α-cristobalite lattice with twinned unit cells in black; black arrows in (a, b, c) denote the location of the twin plane.
Figure 4. (a) Bright field TEM image of non-crystalline siliceous precipitate exhibiting “negative” pyroxene morphology. Dominant pyroxene planes evident in crystalline silica precipitates are also evident here. (b) Diffraction pattern is from the glass precipitate in (a). Ring with weak intensity, and possible diffraction spots are attributed to crystallites of an unidentified mineral that was quickly destroyed by the electron beam; (c) EDS spectrum from precipitate in (a). All non-crystalline precipitates possess Al in addition to Si, just as in this spectrum. (d-f) More examples of Al-bearing non-crystalline silica precipitates with negative pyroxene morphology.

Figure 5. (a) Non-crystalline siliceous precipitate in negative pyroxene shape surrounded by diopside (dark area). (b) SAED pattern shows evidence of a faint ring (white arrows point to the ring) likely contributed by the small crystals indicated by black arrows in the non-crystalline precipitate. (c) EDS spectrum shows there is some Al in the precipitate. (d) Diopside SAED pattern. (e) HRTEM image and (g, h) FFT patterns of diopside and Na-Ca-amphibole across the interface, respectively, detailing crystallographic orientation and excellent lattice fit of the single/double chains. (f) EDS spectrum from amphibole exhibits Na and Al.

Figure 6. (a) Low magnification TEM image and (b) HRTEM image of multiple sheet silicate crystals in diopside. Note euhedral [001] pyroxene shape of former silica precipitate is degraded, with few recognizable pyroxene planes evident. (c) EDS spectrum taken from the area in (b) showing Mg, Fe, and Al peaks, in addition to a large silica peak. Carbon peak is from carbon coating on sample. (d) SAED pattern from diopside. (e) SAED pattern from diopside and multiple mica crystals (f) SAED pattern from talc-like nano-crystals showing (001) reflections.

Figure 7. (a-d) Schematic representation of the structural relationship between diopside and α-cristobalite based upon SAED pattern. (a-c) are same orientation. (a, b) illustrate that diopside and cristobalite lattices join at the interface with little to no bending or rotation of silica tetrahedra. (a) (010)\textsubscript{Di} \parallel (-101)\textsubscript{α}. (b) (-1-10)\textsubscript{Di} \parallel (100)\textsubscript{α} (c-d) close lattice fit at the interface in (a, b) is shown utilizing unit cells of both crystals, where (100)\textsubscript{Di} is approximately \parallel (101)\textsubscript{α}. (c) 5d\textsubscript{101a} = 20.2 Å \sim \parallel 2(a \cdot \sinβ) d\textsubscript{100CPX} = 18.6 Å. (d) this diagram is the orientation in (c) rotated 90 degrees to look at CPX [010], and illustrates the structural match between 5d\textsubscript{101a} = 20.2 Å ~
The slight mismatch may cause the observed strain at the interface between diopside and cristobalite (Fig. 2a).

Figure 8: A diagram illustrating the pressure difference between the precipitates (curve c) and the host minerals (curve b). Melt inclusions will be over-pressured (curve a) with respect the host mineral. Modified from Burnham and Davis (1974).

**TABLE CAPTION**

Table 1. Recalculated EMPA clinopyroxene analyses from Bohemian Massif CPX grain, calculated with an assumed (not measured) Fe content of 2 wt. % $\text{Fe}_2\text{O}_3$, $\text{FeO} = \text{Fe} - 2 \text{ wt }\%$ $\text{Fe}_2\text{O}_3$. Measurements made with 1μm beam. Oxygen calculated, all calculations based on 6 O. Potential calculated vacancy component $= ([])$.  

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Fig. 2
Fig. 3
Fig. 4
Fig. 5
Fig. 8
### Table 1. Recalculated EMPA clinopyroxene analyses from Bohemian Massif CPX grain, calculated with an assumed (not measured) Fe content of 2 wt. % Fe$_2$O$_3$; FeO = Fe – 2 wt % Fe$_2$O$_3$. Measurements made with 1μm beam. Oxygen calculated, all calculations based on 6 O.

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Notes for Table 1:
- bd = below detection
- $\square$ = vacancy component
- * 2 wt. % Fe$_2$O$_3$ chosen for calculations, not measured
- Oxygen calculated

Statistics:
- AVG= average
- STDV= standard deviation
- SERR= standard error
- Cations per 6 O

Potential calculated vacancy component = (1).