OH defects in coesite and stishovite during ultrahigh-pressure metamorphism of continental crust

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Abstract

The high-pressure silica polymorphs coesite and stishovite were synthesized under water-saturated conditions from a natural granitic composition doped with Li and B. Experiments were performed in a Multi-Anvil apparatus between 4 and 9.1 GPa and 900 and 950 °C, based on the conditions of a subducting continental crust as realistic for the ultrahigh-pressure metamorphic units Dora Maira and Kochetav massifs. Run products consisted of coesite/stishovite + kyanite ± phengite ± omphacite, and quench material. The synthesized silica polymorphs were successively analyzed by infrared spectroscopy, electron microprobe, and Secondary-Ion Mass Spectrometry (SIMS). No hydrous defects were observed in coesite synthesized at 4 GPa and 900 °C, whereas coesite grown at higher pressures revealed a triplet of infrared absorptions bands at 3575, 3523, and 3459 cm⁻¹, two minor bands at 3535 and 3502 cm⁻¹, and a small band at 3300 cm⁻¹ that was only visible at 7.7 GPa. The total amount of Al was charge-balanced by H and the other monovalent cations. However, the band triplet could not be associated with AlOH defects, while the band doublet was inferred to BOH defects and the small band probably corresponded to interstitial H. Stishovite displayed one dominant band at 3116 cm⁻¹ with a shoulder at 3170 cm⁻¹, and a minor band at 2665 cm⁻¹, probably all associated with AlOH defects. BOH defects were not observed in stishovite, and LiOH defects were neither observed in coesite nor stishovite, probably because of preferential partition of Li in other phases such as omphacite. The total amount of defect protons increased with pressure and with metal impurity concentrations. The general increase in OH defects in silica polymorphs with increasing pressure (this study) contrasted the negative pressure trend of OH in quartz observed previously from the same starting material, and revealed an incorporation minimum of OH in silica polymorphs around the quartz/coesite phase transition.

Keywords Coesite · Stishovite · OH defects · IR spectroscopy · Phengite

Introduction

Silica (SiO₂) is the most important component in the Earth's crust and silica polymorphs are common mineralogical phases occurring in a wide range of geological environments. Quartz is the second most abundant phase in the Earth's crust (12 modal % according to Ronov and Yaroshevsky 1969) and is an important constituent of many igneous, sedimentary, and metamorphic rocks. During continental collision, small continental fragments of

the continental crust may experience subduction to great depths, leading the transformation of quartz into high-pressure silica polymorphs coesite and stishovite under ultrahigh-pressure (UHP) metamorphic conditions. In nature, this was first discovered inside a quartzite from the Dora Maira massif in the Western Alps, where natural coesite was detected as inclusions in garnet (Chopin 1984). Similar to quartz, coesite and stishovite may incorporate water as hydrous defects, and thus may serve as water carrier to the Earth's mantle. The previous studies based on infrared (IR) spectroscopic investigations on hydrous defects in both synthetic coesite and stishovite suggested that protons can be accommodated as hydrogarnet defects, (4H)_{Si}, AlOH and BOH defects, and interstitial defects. Hydrogarnet defects are inferred from the substitution of one Si⁴⁺ with four H⁺, whereas AlOH and BOH defects derive from the coupled substitutions that involve Si⁴⁺, trivalent cations (Al³⁺ and

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B³⁺), and H⁺. The main hydrous feature observed in IR spectra recorded from coesite, three bands at 3573, 3523–3520, and 3459 cm^{−1} (Mosenfelder 2000; Koch-Müller et al. 2001), were interpreted as (4H)_{Si} defects. Additional hydrous defects in coesite are displayed by two bands at 3535 and 3500 cm^{−1} (Koch-Müller et al. 2003; Deon et al. 2009) that were assigned to BOH defects, and two smaller bands at 3300 and 3210 cm^{−1} (Koch-Müller et al. 2001) that were initially assigned to AlOH defects, although no correlation between the concentrations of Al and H from these bands could be established (Koch-Müller et al. 2003). Stishovite with minor amounts of metal impurities displayed mainly three bands in the IR spectrum at 3311, 3240–3238, and 3111 cm^{−1} (Pawley et al. 1993; Bromiley et al. 2006; Litasov et al. 2007), while only a large broadband at 3111 cm^{−1} with a shoulder at 3160–3180 cm^{−1} was detected in stishovite with high contents of Al (Pawley et al. 1993; Chung and Kagi 2002; Bromiley et al. 2006; Litasov et al. 2007). In both cases, the band at 3111 cm^{−1} with shoulder band at 3160–3180 cm^{−1} was interpreted either as AlOH defects (Pawley et al. 1993; Chung and Kagi 2002) or as interstitial H influenced indirectly by interstitial Al as a result of the next-nearest-neighbour (NNN) effect (Bromiley et al. 2006), whereas the bands at 3311 and 3240–3238 cm^{−1} were assigned to interstitial H that occur only with at very low concentrations of Al (Bromiley et al. 2006). Nevertheless, stishovite tends to incorporate increasing amounts of protons with increasing pressures and temperatures, and proton incorporation in stishovite shows a strong correlation to Al contents (Pawley et al. 1993; Bromiley et al. 2006; Litasov et al. 2007). Beside the wealth of information on OH defects in coesite and stishovite and their IR-absorption band assignment, hitherto only one study used natural material (Chung and Kagi 2002), and no experiments that follow a realistic geotherm of a subducting slab have been performed yet. Therefore, the aim of the present work is to investigate the formation of OH defects in coesite and stishovite from a natural granitic material under experimental conditions that reflect a realistic geotherm of a subducting continental crust fragment. The experimental condition chosen here is based on natural examples such as the Dora Maira (Chopin 2003)

and the Kokchetav (Zhang et al. 1997) massifs. Finally, the results from the present study are compared to the defect inventory of quartz synthesized previously from the same starting material (Frigo et al. 2016), to evaluate the potential of silica polymorphs as carrier for light elements (H, B, and Li) to the Earth's interior.

Experimental and analytical methods

Starting material

Coesite and stishovite were synthesized in a chemical system that consisted of natural granite (68.90 wt% SiO₂, 14.87 wt% Al₂O₃, 6.35 wt% K₂O, 3.05 wt% Na₂O, 2.51 wt% Fe₂O₃, 1.56 wt% CaO, 0.50 MgO, 0.27 wt% TiO₂, 0.08 wt% MnO, and 0.04 wt% P₂O₅), synthetic quartz (Alfa Aesar 99.995%), and natural schorl tourmaline. All the components were separately crushed into powder and mixed in two steps: first, by preparing a mixture of natural granite and synthetic quartz in the proportion of 1:1, and second, by adding 5 wt% of powdered schorl tourmaline to the mixture. 7–20 mg of starting material was then loaded together with 0.3–1.2 mg water into a platinum capsule (Table 1), yielding water content of 1.5–6.0 wt% in the starting mixture. The capsule was then welded shut and weighted before and after being placed in the oven for observing a possible water loss.

High-pressure experiments

Experiments were performed at 900–1100 °C and 4 to 9.1 GPa in a 1000-ton Walker-type Multi-Anvil (MA) press at the Institute of Mineralogy and Petrography of Innsbruck. Two MA assemblages have been used to cover the whole-pressure range, both of which consisted of a MgO + 5% Cr₂O₃ octahedron combined with a graphite furnace and eight tungsten carbide cubes with truncated edges. Experiments at lower pressures were performed with a 25/15 (octahedron edge length/truncation edge length) assembly, whereas an 18/11 assembly was employed for experiments at higher pressures. Natural and sintered gaskets

Table 1 Experimental conditions and starting material

Run #	OEL/TEL	Capsule (mm)	P (GPa)	final <i>T</i> (°C)	<i>t</i> (h)	Run products
E47	25/15	Pt 3.0	4	900	24	coe + ph + omp + ky + quench
E48	25/15	Pt 3.0	5	900	64	coe + ph + omp + ky + quench
E51	25/15	Pt 3.0	6	950	36	coe + ph + omp + ky + quench
E52	25/15	Pt 3.0	7	950	36	coe + ph + omp + ky + quench
E65	18/11	Pt 2.0	7.7	950	70	coe + omp + ky + quench
E63	18/11	Pt 2.0	8.4	950	72	coe + st + omp + ky + quench
E62	18/11	Pt 2.0	9.1	950	64	st + ky + quench

coe coesite, *st* stishovite, *ph* phengite, *omp* omphacite, *ky* kyanite

were employed to support the 25/15 and 18/11 assemblies, respectively. Both assemblies were pressure calibrated at high temperatures by reproducing the quartz–coesite (Bose and Ganguly 1995), the CaGeO_3 garnet–perovskite structure (Ono et al. 2011), and the coesite–stishovite (Akaogi et al. 1995)-phase transitions. Temperatures were controlled using Pt_{100} – $\text{Pt}_{90}\text{Rh}_{10}$ thermocouples for the 25/15 assembly, and W_{97}Re_3 – $\text{W}_{75}\text{Re}_{25}$ thermocouples were used for the 18/11 assemblies. The junction of the thermocouples was placed 1 mm below the center of the assembly and was separated by a MgO disk from the platinum capsule. Pressures and temperatures were monitored electronically over the whole duration of the experimental runs. All successful runs were pressurized and heated simultaneously to the highest PT conditions, since the initial runs suffered from leaking capsules whenever the temperature was not raised before the final pressure was reached. Moreover, some experiments (E63, E62, and E65) were pressurized and heated in two steps, to grow coesite from quartz first, and second to transform coesite into stishovite. Temperature was raised up to 1100 °C, maintained for 5 h, and then decreased to 900 or 950 °C with rate of 4 °C/hour, aiming to improve the growth of the silica polymorph phases. The final temperature was hold for 24–72 h and then quenched by shutting off the power supply. Finally, each experiment was decompressed overnight. Detailed information of the experimental conditions is reported in Table 1.

After each experiment, the capsule was recovered from the high-pressure assembly, weighed, pierced, dried, and weighed again to check for fluid loss. Run products were finally extracted from the capsule and then examined under a petrographic microscope.

Run products

High-pressure silica polymorphs usually formed euhedral crystals. Coesite always consisted of pseudo-hexagonal crystals (Fig. 1a), exhibiting either lath or tabular shapes. Furthermore, coesite crystals showed a very low interference color under orthoscopic illumination and a biaxial nature under conoscopic illumination. In contrast, stishovite

Fig. 1 Pseudo-hexagonal coesite synthesized at 4 GPa (**a**) and elongated stishovite synthesized at 9.1 GPa (**b**)

displayed elongated needles (Fig. 1b) with comparably high interference colors and uniaxial nature, characteristic to tetragonal crystals. In the run at 8.4 GPa, both coesite and stishovite were detected (Fig. 2), meaning that the experiment was performed close to the phase transitions of coesite to stishovite. The existence of coesite and stishovite was furthermore checked and confirmed by Raman spectroscopy.

After the characterization of the run products, several samples were selected and prepared for the following purposes: (1) characterization and quantification of the OH defects via IR spectroscopy, (2) analysis of major trace elements by electron microprobe, and (3) analysis of light elements such as Li and B by Laser Ablation—Inductively Coupled Plasma—Mass Spectrometry (LA–ICP–MS). LA–ICP–MS analyses were performed at the Institute of Mineralogy, University of Münster, using a 193 nm excimer laser (Analyte G2, Photon Machines) connected to a ThermoFisher Element 2 single collector mass spectrometer. However, because of the high purity of the silica polymorphs and their transparency, the energy of the laser beam was not transmitted to the sample samples and ablation was not successful. Therefore, concentrations of Li and B were further detected by Secondary-Ion Mass Spectrometry (SIMS) at the Institute of Earth Sciences, University of Heidelberg.

To perform polarized IR measurements, the largest synthesized crystals of both coesite and stishovite were hand-picked, embedded in a thermoplastic resin, and aligned parallel to their main refractive indices using a petrographic microscope with conoscopic illumination. The oriented crystal wafers were then manually polished on both sides and the resin was removed by dissolution in acetone. Thicknesses of the prepared wafers were measured with a mechanical

Fig. 2 BSE image of the run products from the experiment E63, consisting of euhedral stishovite, coesite, omphacite, and quenched material (porous-dendritic material around the crystals)

Mitutoyo micrometer with an accuracy of $\pm 2 \mu\text{m}$. The identification of the refractive indices n_α , n_β , and n_γ in coesite was accomplished in two steps: (1) by conoscopic illumination to verify that a symmetric section through the indicatrix was prepared, and (2) in orthoscopic illumination using a compensator (550 nm) to identify the relative value of both refractive indices. Therefore, three sections were inspected (Table 2): the section perpendicular to the acute bisectrix (which is very close to the (001) plane and exhibits the refractive indices n_α – n_β), the section perpendicular to the obtuse bisectrix (which is identical to the (010) plane and exhibits the refractive indices n_β – n_γ), and the section parallel to the optical axes plane (which is in the [h0l] zone and exhibits the refractive indices n_α – n_γ). In all cases, conoscopic illumination shows a centered image through the indicatrix, where two isogyres meet (and divide) in the center of the view field. In the section perpendicular to the acute bisectrix, the angular range of isogyre appearance was

much larger than in the other two sections. However, due to the small birefringence and the small size of the crystals, the quality of the conoscopic figures was not clear enough to distinguish between the two last mentioned sections. Nonetheless, it was possible to recognize whether one of the bisectrices was centered in the view field of the conoscopic image. The small birefringence ($\Delta_{\text{max}} = 0.005$) gave mostly rise to interference grey colours, and never exceeded red I. Based on the observation on the crystal section perpendicular to the acute bisectrix (which could unequivocally be defined and where n_α and n_β are exhibited), spectra parallel to these direction were recorded and used as reference for further measurements. Finally, lattice overtones of all IR spectra (Fig. 3) were related to their respective direction and cross-checked for all samples (for lattice overtones, see next section).

In case of stishovite grown at 9.1 GPa, small elongated crystals were individually selected, placed parallel to their

Table 2 Polarized IR measurements of coesite, stishovite, and omphacite

Sample #	P (GPa)	Thickness (μm)			A_i (mm^{-1})	H ₂ O (wt ppm)
Coesite		$\parallel$ (h0l)	$\parallel$ (010)	$\parallel$ (001)		T et al. (09)
E47coe1	4	–	57	–	–	< 10
E47coe2	4	–	55	–	–	< 10
E48coe3	5	96	56	–	72	21
E52coe1	7	119	48	–	119	34
E52coe2	7	78	65	–	115	33
E65coe1	7.7	110	99	–	223	64
E65coe2	7.7	–	68	78	201	58
Sample #	P (GPa)	Thickness (μm)			A_i (mm^{-1})	H ₂ O (wt ppm)
Stishovite		(hki0)				T et al. (09)
E63st2	8.4	160			3489	298
E63st3	8.4	140			4350	371
E63st4	8.4	155			5986	511
E63st5	8.4	158			4593	392
E63st6	8.4	68			3515	300
E62st2	9.1	45			4712	402
E62st3	9.1	35			2861	244
E62st8	9.1	40			3306	282
E62st9	9.1	49			1280	109
E62st10	9.1	43			3386	289
E62st13	9.1	49			2521	215
E62st17	9.1	46			2791	238
Sample #	P (GPa)	Thickness (μm)			A_i (mm^{-1})	H ₂ O (wt ppm)
Omphacite		$\parallel$ (010)	$\parallel$ (100)			L&R (97)
E63omp1	8.4	125	96		230	149

A_i integral total absorbance

T et al. (09) calibration from Thomas et al. (2009)

L&R (97) calibration from Libowitzky and Rossman (1997)

Fig. 3 Polarized IR spectra of the lattice overtones of coesite (coe) and stishovite (st). Overtones of quartz (qz) are shown for comparison (Stalder et al. 2017)

c-axis, and analyzed parallel to their main refractive indices without further preparation, since their thickness was too small for any kind of preparation. In this case, their thickness was calculated from the interference colors.

Additional phases such as phengite, omphacite, kyanite, and skeletal quench material were also observed in the run products. Except for one crystal of omphacite from the experimental run E63, these phases were too small to get properly prepared for polarized IR spectroscopy as individual and oriented crystal sections.

FTIR spectroscopy

Polarized spectra were collected at room temperature in transmission mode using a Bruker Vertex 70 FTIR spectrometer coupled to a Hyperion 3000 microscope, a nitrogen-cooled MCTD316-025 (mercury cadmium telluride) detector, a global light source, a KBr beamsplitter, and a wire grid polarizer. Analysis spots were chosen taking care to avoid cracks, mineral, melt, or fluid inclusions in the selected crystals. For these purposes, measurements were performed on areas that varied from $30\text{ }\mu\text{m} \times 30\text{--}80\text{ }\mu\text{m} \times 80\text{ }\mu\text{m}$. Depending on the analyzed area, 32 scans were collected for background and sample measurements of large areas, and 300–1000 for small areas.

Polarized measurements were performed parallel to the main refractive indices of each sample on the same spot by rotating the polarizer by 90° . Practically, for coesite, measurements for $n\alpha$ and $n\gamma$ were performed on the (h0l) plane, measurements for $n\beta$ and $n\gamma$ on the (010) plane, and one exceptional measurement was performed parallel to $n\alpha$ and $n\beta$ on the (001) plane (Table 2, sample E65coe2). Measurements for $n\omega$ and $n\epsilon$ of stishovite were performed on a plane from the zone (hki0). In this publication are also reported for the first time the overtones of the lattice vibrations of oriented coesite and stishovite crystals (Fig. 3). These features can be also used in the future for verifying the correct orientation of the samples. To characterize the pleochroism of the OH defects in coesite, additional polarized measurements were executed on a coesite synthesized at 7 GPa by turning the polarizer in 22.5° steps.

Electron microprobe

Textures from run products were inspected under a JEOL JXA-8100 electron microprobe (Fig. 2), and major and minor element chemistry of coesite, stishovite, and coexisting phases were determined using 15 kV acceleration voltage. Concerning the beam current, different analytical conditions were used depending on the measured material: (1) 50 nA beam current on coesite and stishovite for a better counting statistics of the Al-K α line, and (2) 5 nA beam current on phengite and omphacite. A defocused beam of $10\text{ }\mu\text{m}$ diameter was used in both types of analyses. As standards, the following minerals were used: Si: quartz, Al: corundum, K: orthoclase, Na: jadeite, P: apatite, Fe: almandine, Mg: periclase, Ca: diopside, Ti: rutile, and Mn: rhodonite.

Secondary-ion mass spectrometry

Li, B, and Al concentrations of coesite, stishovite, and omphacite were measured using CAMECA ims3f ion microprobe at the Institute of Earth Sciences, University of Heidelberg. O^- primary ions with a net energy of 14.5 keV and a beam current of $\sim 10\text{ nA}$ were focused to a spot diameter of $\sim 15\text{ }\mu\text{m}$ on the sample. Positive secondary ions were accelerated to 4.5 keV and the energy acceptance of the double-focussing mass spectrometer was set to $75 \pm 20\text{ eV}$ (energy filtering). The mass resolving power M/DM was ~ 1000 (10%) and the secondary ions were detected by an electron multiplier in counting mode. Because of the small sample sizes and to reduce the influence of B surface contamination (Marschall and Ludwig 2004), the area analyzed was limited to a diameter of $\sim 6\text{ }\mu\text{m}$ using a $400\text{ }\mu\text{m}$ field aperture and a nominal imaged field of $25\text{ }\mu\text{m}$. Li, B, and Al concentrations in the unknown samples were calculated using the ion yield relative to Si (RIY) which was determined using

Fig. 4 Polarized IR spectra of coesite parallel to the main refractive indices α , β , and γ

the NIST SRM610 glass (concentrations were taken from Pearce et al. 1997). The energy filtering method was used to reduce the matrix effect (Ottolini et al. 1993).

IR lattice vibration overtones

The lattice vibration overtones of oriented quartz, coesite, and stishovite are shown in Fig. 3. Lattice vibration overtones of oriented coesite are very similar along the three main refractive indices. However, similar to quartz (Stalder et al. 2017), there are subtle, but significant, differences in the absorption band around 1948 cm^{-1} and in the region $1600\text{--}1800\text{ cm}^{-1}$. Lattice vibration bands of stishovite are observed towards lower wavenumbers than quartz and coesite. Perpendicular to the c-axis (parallel to ω), lattice overtones are dominated by one absorption band at 1346 cm^{-1} , while parallel to the c-axis (parallel to ϵ), a doublet at 1346 and 1389 cm^{-1} is revealed.

IR band assignment and determination of water content as OH defects

Coesite No absorption bands are observed in coesite synthesized at 4 GPa, whereas faint bands are observed at 5 GPa and more intense bands are observed in coesite grown from 5 to 7.7 GPa (Fig. 4a–c), confirming the trend of former studies (Mosenfelder 2000; Koch-Müller et al. 2001). Conversely, the polarized spectra of this study exhibit different anisotropies than observed by Koch-Müller et al. (2001). Three specific absorption features are revealed: (1) one triplet at 3575 , 3523 and 3459 cm^{-1} , (2) a doublet at 3535 (visible only parallel to α) and 3502 cm^{-1} , and (3) one band at 3300 cm^{-1} that was visible only along β (Fig. 4-b). The IR spectra from the run samples E48, E52, and E65 were successively deconvoluted using the software PeakFit, to separate the triplet band (3575 , 3523 , and 3459 cm^{-1}) from the two minor bands 3535 and 3502 cm^{-1} . Polar diagrams of OH-absorption bands of coesite synthesized at 7 GPa parallel to (h0l) and (010) reveal a strong pleochroism (Fig. 5a, b). In section $\parallel(h0l)$, maximum and minimum absorbances are parallel to the main refractive indices α and γ , in accord to the prerequisite that, in a monoclinic crystal, one refractive index—in this case α —is strictly coupled to the crystallographic b-axis. In section $\parallel(010)$, the band at 3535 cm^{-1} is almost parallel to γ , whereas the bands at 3459 and 3523 cm^{-1} exhibit maximum absorptions between β and γ . In contrast to Koch-Müller et al. (2001), the band at 3575 cm^{-1} (not shown in Fig. 5) exhibited no clear maximum and minimum absorptions. All absorption

bands gradually tend to get stronger with pressures, except the band at 3502 cm^{-1} that shows its maximum absorbance at 7 GPa.

Stishovite All polarized IR spectra display one dominant and asymmetrical absorption band at 3116 cm^{-1} , one band at 3170 cm^{-1} that emerged as a shoulder on the strongest absorption peak, and a less intense band at 2665 cm^{-1} (Fig. 6). These absorption bands are strongly polarized parallel to the $n\omega$ refractive index (perpendicular to the c axis). Two additional smaller bands at 3529 and 3595 cm^{-1} are observed at 9.1 GPa. However, since these bands were observed only in few crystals, whose spectra exhibited broad isotropic bands from fluid inclusions, they were probably caused by inclusions and, therefore, not further considered.

Water contents were calculated using the Lambert–Beer equation in combination with the integrated extinction coefficients of coesite and stishovite from mineral-specific calibration of Thomas et al. (2009). Results deviate from values which would be obtained if other calibrations (Patterson 1982; Pawley et al. 1993; Libowitzky and Rossman 1997) would be used (Fig. 7). For determining the water concentration in omphacite, the calibration of Libowitzky and Rossman (1997) was used.

Concentrations of $<10\text{ wt ppm H}_2\text{O}$ are estimated for coesite synthesized at 4 GPa, while 21–58 wt ppm H_2O are determined from 5 to 7.7 GPa. Water concentrations in

Fig. 6 Polarized IR spectra of stishovite parallel to the main refractive indices $n\omega$ and $n\epsilon$

stishovite are higher at 8.4 GPa (376 wt ppm H_2O) than at 9.1 GPa (246 wt ppm H_2O , Table 2).

Polarized IR spectra on one crystal of omphacite synthesized at 8.4 GPa revealed 149 wt ppm water. Therefore, at 8.4 GPa, water tends to partition preferentially into stishovite ($D_{\text{H}}^{\text{st/omp}} \sim 2.5$).

Electron microprobe and SIMS results

Chemical compositions of major and trace elements coesite, stishovite, omphacite, and phengite are reported in Table 3.

Aluminum is the most abundant trace element in both high-pressure silica polymorphs and concentrations tend to rise with pressure. At conditions where both high-pressure silica polymorphs are in equilibrium (i.e. at 8.4 GPa), aluminum is preferentially incorporated in stishovite, which also comprises the highest Al concentration in this study (1.15 wt% Al_2O_3). The maximum concentration of Al in coesite is of 0.22 wt% Al_2O_3 (corresponding to 1165 wt ppm Al or 2601 Al/10⁶Si), which is more than one order of magnitude higher than reported in some previous studies (Mosenfelder 2000; Koch-Müller et al. 2001, 2003). Al in stishovite is slightly lower than observed in the previous studies (1.64 wt% Al_2O_3 in Pawley et al. 1993, and 1.32 wt% Al_2O_3 in; Chung and Kagi 2002), but much lower than in stishovite synthesized at higher pressure and temperature conditions (7.62 wt% Al_2O_3 at 20–25 GPa and 1200–1400 °C in Litasov et al. 2007). In addition to aluminum, coesite also accommodates trace amounts of Na and

Fig. 5 Pleochroism of OH-absorption bands of coesite plotted as polar graphs $||(\text{h}0\text{l})$ (a) and $||(\text{010})$ (b). Bands at 3459, 3523, and 3502 cm^{-1} are represented by circles, diamonds, and triangles, respectively

Fig. 7 Comparison of water concentrations calculated from different calibrations for **a** coesite and **b** stishovite. Calibrations from Koch-Müller et al. (2001) are shown as white triangles, KM(01), Paterson (1982) as grey triangles, P(82), Libowitzky and Rossman (1997) as black triangles, L&R(97), and Pawley et al. (1993) as white diamonds, P(93). Dashed lines represent the water ratios between the selected calibrations and the calibration of Thomas et al. (2009)

K, reaching concentrations of 0.13 wt% K_2O and 0.04 wt% Na_2O . Conversely, the incorporation of Li is rather limited in coesite and stishovite, attaining a maximum of 19.8 ppb Li in coesite (Table 3). Lithium is preferentially incorporated in other phases such as omphacite, which comprised up to 207 wt ppm Li at 8.4 GPa. Boron, sufficiently incorporated

in coesite to be observed as BOH defects (Koch-Müller et al. 2003; Deon et al. 2009), reaches concentrations up to 17 wt ppm in coesite, while concentrations in stishovite are below 1 wt ppm B.

Discussion

Mechanism of trace elements incorporation

Compared to former studies, the present work reports the highest concentrations of trace elements in coesite, probably due to the employment of natural granitic powder as starting material. Similarly to quartz, trace elements may be incorporated by coupled substitutions of Si^{4+} by one trivalent (M^{3+}) and one monovalent (M^+) cation (Müller and Koch-Müller 2009; Frigo et al. 2016). In fact, concentrations of M^{3+} (i.e. Al and B) in coesite display a linear correlation with M^+ (H, Na, and K) in the ratio of 1:1 (Fig. 8a) and thus suggest that, in coesite synthesized in this study, both types of cations are charge-balanced and that the coupled substitution $Si^{4+} = M^{3+} + M^+$ is fulfilled. By contrast, concentrations of M^{3+} and M^+ of stishovite plot on the right side of the 1:1 slope, suggesting that Al^{3+} is partly charge-balanced by H^+ , and partly charge-balanced by other mechanisms, such as the formation of oxygen vacancies (Hirose et al. 2005; Bromiley et al. 2006), e.g.

where V_O represents an oxygen vacancy, Al'_{Si} an Al^{3+} on the tetrahedral site, and Si_{Si}^x (and O_O^x) Si^{4+} (and O^{2-}) in the undisturbed stishovite lattice (according to the Kröger–Vink notation, Kröger and Vink 1956). The 1:1 correlation between the cations M^{3+} and M^+ in coesite synthesized in this study (Fig. 8a) may suggest that the dominant hydrous feature in coesite (i.e., the triplet at 3575, 3523, and 3459 cm^{-1}) is related to the Al contents. The correlation Al/H_{triplet} in coesite is not obvious (Fig. 8b). However, all the averages of the single data point are plotted below the 1:1 slope, which not excludes the hypothesis that Al and H bond together to form AlOH defects in coesite. Al concentrations in coesite and stishovite are in all cases about two orders of magnitude higher than H concentrations (Fig. 9), as already observed for quartz synthesized from the same starting material (Frigo et al. 2016).

Correlation between Al- and OH-absorption bands of coesite

Based on the results of the present study, the dominant hydrous feature in coesite is the triplet at 3575, 3523, and 3459 cm^{-1} . The band assignment of this absorption feature was interpreted as hydrogarnet defects (Mosenfelder 2000;

Table 3 Trace element concentrations in coesite, stishovite, phengite, and omphacite from EPMA and SIMS analyses

No.	<i>n</i>	EPMA	<i>n</i>											SIMS	
			Coesite											Coesite	
		Na ₂ O (wt%)	MgO (wt%)	Al ₂ O ₃ (wt%)	SiO ₂ (wt%)	P ₂ O ₅ (wt%)	K ₂ O (wt%)	CaO (wt%)	TiO ₂ (wt%)	MnO (wt%)	FeO (wt%)	tot (wt%)	Al ₂ O ₃ (wt%)	Li (ppb)	B (ppm)
E47	18	0.03±0.02	b.d.l.	0.03±0.02	100.0±0.3	b.d.l.	0.02±0.01	b.d.l.	b.d.l.	b.d.l.	b.d.l.	100.1±0.3	n.a.	n.a.	n.a.
E48	12	b.d.l.	b.d.l.	0.02±0.01	100.2±0.3	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	100.3±0.3	n.a.	n.a.	n.a.
E51	10	0.04±0.02	b.d.l.	0.13±0.09	99.6±0.5	b.d.l.	0.13±0.04	b.d.l.	b.d.l.	b.d.l.	b.d.l.	99.9±0.4	n.a.	n.a.	n.a.
E52	14	b.d.l.	b.d.l.	0.22±0.15	99.4±0.5	b.d.l.	0.04±0.03	b.d.l.	b.d.l.	b.d.l.	b.d.l.	99.7±0.5	n.a.	n.a.	n.a.
E65	55	b.d.l.	b.d.l.	0.03±0.02	99.0±0.4	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	99.1±0.4	9	0.04±0.04	19.8±6.3
E63	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	2	0.07±0.08	6.8±0.1
															10.9±0.0
No.	<i>n</i>	Stishovite	<i>n</i>											Stishovite	
		Na ₂ O (wt%)	MgO (wt%)	Al ₂ O ₃ (wt%)	SiO ₂ (wt%)	P ₂ O ₅ (wt%)	K ₂ O (wt%)	CaO (wt%)	TiO ₂ (wt%)	MnO (wt%)	FeO (wt%)	tot (wt%)	Al ₂ O ₃ (wt%)	Li (ppb)	B (ppm)
E63	96	b.d.l.	b.d.l.	1.15±0.31	99.6±0.5	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	100.8±0.4	13	0.87±0.22	4.4±1.3
E62	10	b.d.l.	b.d.l.	0.80±0.09	99.8±0.2	b.d.l.	0.03±0.01	b.d.l.	b.d.l.	b.d.l.	b.d.l.	100.7±0.2	2	0.79±0.08	2.8±0.6
No.	<i>n</i>	Phengite	<i>n</i>											Phengite	
		Na ₂ O (wt%)	MgO (wt%)	Al ₂ O ₃ (wt%)	SiO ₂ (wt%)	P ₂ O ₅ (wt%)	K ₂ O (wt%)	CaO (wt%)	TiO ₂ (wt%)	MnO (wt%)	FeO (wt%)	tot (wt%)	Al ₂ O ₃ (wt%)	Li (ppb)	B (ppm)
E47	1	0.3	3.7	26.5	50.3	b.d.l.	11.2	b.d.l.	0.5	b.d.l.	0.20	92.8	n.a.	n.a.	n.a.
E48	30	b.d.l.	3.1±0.4	27.0±0.8	50.8±1.3	b.d.l.	11.3±0.2	b.d.l.	0.48±0.07	b.d.l.	b.d.l.	92.9±0.9	n.a.	n.a.	n.a.
E51	14	0.11±0.06	2.2±0.3	26.7±0.9	49.7±1.0	b.d.l.	11.7±0.2	b.d.l.	0.45±0.06	b.d.l.	0.28±0.06	91.3±0.9	n.a.	n.a.	n.a.
E52	11	b.d.l.	3.2±0.2	24.1±0.4	50.9±0.9	b.d.l.	11.5±0.4	b.d.l.	0.42±0.03	b.d.l.	0.18±0.03	90.6±0.9	n.a.	n.a.	n.a.
No.	<i>n</i>	Omphacite	<i>n</i>											Omphacite	
		Na ₂ O (wt%)	MgO (wt%)	Al ₂ O ₃ (wt%)	SiO ₂ (wt%)	P ₂ O ₅ (wt%)	K ₂ O (wt%)	CaO (wt%)	TiO ₂ (wt%)	MnO (wt%)	FeO (wt%)	tot (wt%)	Al ₂ O ₃ (wt%)	Li (ppb)	B (ppm)
E65	16	12.5±0.4	1.8±0.4	22.4±0.7	58.5±0.4	b.d.l.	b.d.l.	2.8±0.4	b.d.l.	b.d.l.	b.d.l.	98.4±0.5	n.a.	n.a.	n.a.
E63	27	12.7±0.2	1.7±0.2	22.7±0.6	58.1±0.8	b.d.l.	b.d.l.	2.6±0.3	b.d.l.	0.15±0.03	b.d.l.	98.0±1.1	2	n.a.	n.a.

Errors correspond to the standard deviation
b.d.l. below the detection limit, *n.a.* not analyzed

Fig. 8 **a** Coupled substitutions of H^+ , Na^+ , K^+ , Al^{3+} , and B^{3+} in coesite and stishovite. Small symbols represent single data points, while average data points at each pressure are represented by large symbols. H^+ contents are calculated from IR analyses, B^{3+} from SIMS analyses, and the remaining elements from electron microprobe analyses. Error bars on large elements correspond to the standard deviation of the data points. **b** Correlation between $\text{Al}/\text{H}_{\text{triplet}}$ (triangles) in coesite and $\text{Al}/\text{H}_{\text{total}}$ (circles) in stishovite. Error bars correspond to the standard deviation of the data points

Koch-Müller et al. 2001). Indeed, in Koch-Müller et al. (2001), both Al and H concentrations were simultaneously determined by SIMS and a correlation was not observed, e.g., one coesite crystal was poor in Al (23.9 Al/ 10^6Si) and rich in H (254 H/ 10^6Si). As there was no correlation between Al and H and there was no other charge balancing cation, the triplet band was assigned as hydrogarnet substitution. Based on our results, at the first sight, the band triplet mentioned

Fig. 9 H contents (open circles) and Al contents (black circles) in α - and β -quartz (results from Frigo et al. 2016), in coesite and stishovite at different pressures are shown in log units. Note that hydrogen contents were calculated by dividing the water concentrations by 9. Dashed lines are linear regressions for Al and H. Error bars correspond to the standard deviation. Because of the small standard deviation of H, error bars are within the size of the symbol

above looks similar to the AlOH triplet in quartz (3431, 3379, and 3313 cm^{-1}) shifted by 144 cm^{-1} to higher wave-numbers. However, such linear shift towards higher wave-numbers is not explainable. First, quartz and coesite have totally different structures, and thus, a linear band shift is not expected. Second, in a more dense structure, we would expect shorter O...O distances and thus a shift towards lower vibrational frequencies. Indeed, according to the correlation between O–H frequencies and the bond length $d(\text{O}\cdots\text{O})$ in hydrous minerals, the higher the O–H frequencies, the higher the bond lengths (Libowitzky 1999). Nonetheless, the concentrations of H and the other monovalent cations appear to be essential to charge balance the equivalent amount of Al in coesite (Fig. 7a).

The band at 3300 cm^{-1} was first reported from Mosenfelder (2000), and appears only at pressures above 7 GPa, in good agreement with the present study. This band, which appears at lower frequencies with respect to the other bands, may correspond to the vibration of an interstitial hydrogen defect, since the vibrational frequencies within sites with a greater number of coordination tend to be shifted to lower values. This band probably corresponds in good approximation to the frequencies of the interstitial hydrogen observed in stishovite at 3336 cm^{-1} (Bolfan-Casanova et al. 2000; Bromiley et al. 2006).

Phengite as geobarometer and host of light elements in the mantle

In this work, it was observed that phengite enriched in Si at higher pressures (Table 3). Phengite is a mineral of the solid solution series muscovite(ms)-celadonite(cel), $\text{KAl}_2(\text{AlSi}_3\text{O}_{10})(\text{OH})_2 - \text{K}(\text{Mg}, \text{Fe}^{2+})(\text{Fe}^{3+}, \text{Al})\text{Si}_4\text{O}_{10}(\text{OH})_2$. Phengite tends to get richer in the celadonite end-member (i.e., richer in Si) at higher pressures (Velde 1965), and the correlation between the Si concentrations in phengite depending on pressure and temperature conditions has been widely used as a geobarometer (Massonne and Schreyer 1987). Unfortunately, this specific geobarometer has only been calibrated to pressures ≤ 3 GPa, and thus could not been used for the results of the present work. Though, Si concentrations in phengite from the present study correspond within error to the data set of Domanik and Holloway (1996), who synthesized phengite at similar PT conditions (Fig. 10). Temperature also affects the incorporation of Si, leading to smaller Si content for higher temperatures. The good approximation between the results of this study and Domanik and Holloway (1996) (Fig. 10) suggests that equilibrium took place in our experiments. In nature, phengite is a common and abundant mineral phase in the UHP rocks that is stable within a wide pressure range. Given a suitable composition of the protolith and realistic geothermal conditions, phengite can be stable between 3 and 12 GPa (Schmidt et al. 2004), corresponding to depths of 100 to 350 km. Phengite is, therefore, a very important carrier for light elements such as H, Na, and K from the Earth's crust to the Upper Mantle.

Water partitioning

As discussed above, the water content in all silica polymorphs (from quartz to stishovite) parallels the trend of Al incorporation (Fig. 9), resulting in a minimum of water around the quartz/coesite transition, while both coesite and stishovite exhibit increasing water concentrations with higher pressures. H incorporation, therefore, is mostly controlled by the Al incorporation in the crystalline silica polymorphs. In contrast, granitic melts tend to incorporate higher water concentrations at higher pressures (Johannes and Holtz 1996), until a singular point (the so called second critical endpoint) is reached, where the chemistry of aqueous fluids and hydrous melts converge. This point is located at $\sim 3\text{--}3.5$ GPa and ~ 750 °C for some realistic granitic and metapelitic bulk compositions (Hermann et al. 2006), so runs in the coesite and stishovite field probably all were conducted at supercritical pressure. At (and above) the critical pressure, increasing temperatures will enhance the silicate/water ratios in the supercritical fluid, until a silicate/water ratio close to that of hydrous melts is reached. Given the relative high

Fig. 10 Concentrations of Si as atoms per formula unit (a.p.f.u.) in phengite at different pressures. Open diamonds are data points from this study at 900 °C, open square are data points from this study at 950 °C, and black triangles and black circles, D&H(96), are data points from Domanik and Holloway (1996) at 900 and 1000 °C for comparison

temperatures, the water/silicate ratios in supercritical fluids of the runs reported here were rather constant (within a factor of less than 2) between 4 and 9 GPa. Therefore, water partitioning ($D_{\text{water}}^{\text{crystal/melt}}$) between the quartz and hydrous melt (or supercritical fluid) decreases from 10^{-3} at 0.5 GPa to less than 10^{-4} at 3 GPa, where it reaches its minimum, and increases with increasing pressure to 10^{-3} in the stishovite stability field. Therefore, silica polymorphs alone cannot serve as water carrier to great depths, because they loose all water at the quartz/coesite transition. Nevertheless, during progressive downward migration of a subducting slab, when phengite (the major solid water carrier in this study) decomposes, coesite and stishovite develop to major water carrier in the solid portion of the slab.

Petrological and geodynamical applications

To summarize, the results of the present study depict some aspects of the evolution of a continental crust during subduction at “hot” conditions (i.e., at $T = 900\text{--}1000$ °C). There are several mineralogical phases that contribute to the water transport to great depth, namely the hydrous phase phengite and the nominally anhydrous minerals (NAMs) coesite/stishovite, omphacite, and kyanite (the latter one which in this study was not large enough to be analyzed by FTIR spectroscopy). Phengite is the primary water carrier to mantle depths amongst all occurring mineral phases in the present study. Here, it is stable up to 7.7 GPa, but is known to

be stable up to 11–12 GPa in cold slabs if the temperature does not exceed 650 °C (Schmidt et al. 2004). As phengite decomposes, water is released and may liberate sufficient amounts of water to produce fluids that migrate to shallower and (in case of the reversed isotherms in subduction regimes) hotter regions. The addition of a free aqueous fluid at hot temperatures may, in turn, trigger partial melting (or in case of supercritical behaviour: enhanced dissolution) of the subducting rocks. Contemporaneously, water may partly be incorporated as hydrous defects in NAMs. At 4 GPa and 900 °C, coesite incorporate extremely low amounts of hydrogen, since water is preferentially partitioned into the hydrous melt. Higher pressures promote the incorporation of hydrous features in coesite either via coupled substitution $\text{Si}^{4+} = \text{M}^{3+} (\text{Al}^{3+} \text{ and } \text{B}^{3+}) + \text{H}^+$ or other mechanisms as discussed above. Finally, around 8 GPa, coesite transforms to stishovite, which also incorporates water through the coupled substitution, but in higher concentrations than coesite and omphacite ($D_{\text{H}}^{\text{st/omp}} \sim 2.5$). In contrast, coesite and stishovite are poor in light elements such as Li, which seems to be preferentially partitioned in other mineral phases such as omphacite.

The eclogitization and possible partial melting of the slab lead to the densification (Austrheim 1994; Massonne et al. 2007) and change in rheology (Hermann et al. 2013) of the subducting rock, which are both crucial features for the fate of the subducting rock. Slabs denser than the surrounding mantle are destined to sink to greater depths, while ductile rocks might be preferentially exhumed (Hermann et al. 2013), where inclusions of coesite into stiff minerals (e.g., garnet) are preserved from the back reaction to quartz (Gillet et al. 1984). Indeed, during the past decades, natural coesite was repeatedly found in continental orogens (Chopin 1984; Liou et al. 2004), however, mostly depleted in water (Rossman and Smyth 1990; Mosenfelder 2000; Mosenfelder et al. 2005), probably because OH-rich crystals transform much faster back to quartz (Lathe et al. 2005). By now, natural hydrous coesite have been found only as mineral inclusions in diamonds from Venezuela (Koch-Müller et al. 2003).

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