The potential use of OH-defects in enstatite as geobarometer

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Abstract

In this study single crystals of pure enstatite ($\text{Mg}_2\text{Si}_2\text{O}_6$) were synthesized under water-saturated conditions at 4 and 8 GPa and 1150 °C with variable silica activity, leading to phase assemblages enstatite + forsterite, enstatite, or enstatite + coesite. Run products were investigated using an FTIR-spectrometer equipped with a focal plane array detector enabling IR-imaging with a lateral pixel resolution of 2.7 μm . IR spectra within the OH-absorption region show two different groups of absorption bands: group 1 (wavenumbers at 3592 cm^{-1} and 3687 cm^{-1}) show strongest absorptions for $E||n_r$, whereas group 2 (wavenumbers at 3067 cm^{-1} and 3362 cm^{-1}) show strongest absorptions for $E||n_r$. The groups are related to different defect types, group 1 to tetrahedral defects (T-site vacancies) and group 2 to octahedral defects (M-site vacancies). The intensity ratio of the bands within one group (i.e. A_{3067}/A_{3362} and A_{3592}/A_{3687}) and the intensity ratio of $E||n_r$ and $E||n_a$ in group 2 bands remains constant within error. In contrast the intensity ratio of group 2 to group 1 absorption bands (e.g., $(A_{3362})/(A_{3687})$) is sensitive to the SiO_2 -activity and pressure. On the basis of the results of this and previous studies, a barometer for pure orthoenstatite coexisting with forsterite can be formulated:

$$P[\text{GPa}] = 1.056 + \sqrt{\frac{1.025 - A_{(3362)} / [A_{(3362)} + A_{(3687)}]}{0.009}},$$

where $A_{(3362)}$ and $A_{(3687)}$ is the integral absorbance of the component $E||n_i$ of the absorption bands at 3362 cm^{-1} and the component $E||n_p$ of the absorption band at 3687 cm^{-1} , respectively.

Keywords: enstatite, hydrogen, IR imaging, high pressure, geobarometer

Introduction

Significant amounts of water are stored in the Earth's upper mantle by incorporation in nominally anhydrous minerals (NAMs), such as olivine and pyroxene. According to many studies in the previous decades water is dissolved as hydrogen point defects. The concentration can be determined and the defect type can be discriminated by infrared spectroscopy (e.g., Wilkins and Sabine 1973, Bell and Rossman 1992). The mechanism of incorporation is crucial to understand the physical properties of the Earth's mantle (Hirth and Kohlstedt 1996). Absorption bands at high wavenumbers have previously been assigned to Si-vacancies (V_{Si}) charge balanced by protons, and absorption bands at low wavenumbers can be assigned to Mg-vacancies (V_{Mg}) charge balanced by protons, as suggested for olivine (Matveev et al., 2001, Lemaire et al. 2004, Kovács et al. 2010), orthoenstatite (Prechtel and Stalder 2010), clinoenstatite (Withers and Hirschmann 2007) and diopside (Stalder and Ludwig 2007).

This study is focussed on the effect of pressure (P) and silica activity (a_{SiO_2}) on the defect chemistry of pure, synthetic enstatite. Syntheses of enstatite ($Mg_2Si_2O_6$) single crystals were performed within the MgO - SiO_2 - H_2O system under water saturated conditions at different pressure and variable a_{SiO_2} with the aim to assess the potential of OH-defects in enstatite as a geobarometer.

In order to get additional information on the nature of the observed OH-defects, dehydration experiments were performed by repeated heating of one single crystal at 800°C .

Experimental and analytical procedure

Starting compositions

Five different starting mixtures with different Mg/Si-ratios (Table 1) were prepared from $\text{Mg}(\text{OH})_2$ (AlfaAesar) and SiO_2 (AlfaAesar, 99.995%). Approximately 20 mg of the starting material was welded in a platinum capsule with an outer (inner) diameter of 3.0 (2.6) mm and a length of 4.5 mm. All capsules were weighed, pierced, dried, and weighed again after the experiment in order to check for any loss of fluid. All successful runs produced enstatite crystals up to $1100 \times 800 \times 500 \mu\text{m}$ in size, together with water and amorphous quench material. In most runs either forsterite or coesite occurred as additional phase. In some runs no additional crystalline phase could be detected (Table 1).

High pressure experiments

Synthesis of orthoenstatite ($\text{Mg}_2\text{Si}_2\text{O}_6$) single crystals were performed at 4 and 8 GPa in a 1000 t press equipped with a Walker-type multi anvil module using 25/15 assemblies made of $\text{MgO} + 5\% \text{Cr}_2\text{O}_3$ with a graphite-furnace. The temperature was measured with a Pt_{100} - $\text{Pt}_{90}\text{Rh}_{10}$ thermocouple, and both pressure and temperature were computer-controlled during the entire duration of the runs. The temperature was raised to 1300°C and held for 3 h followed by a decrease to 1150°C at a rate of 10°C/h . Synthesis runs were terminated by shutting off the heating power, yielding a quench rate more than 200°C/s , followed by a pressure-release over night. In order to estimate the thermal gradient an additional run in the system diopside-enstatite at the same conditions was carried out. The thermal gradient over the length of the capsule was monitored using the Ca-in-Opx-geothermometer (Brey and Köhler 1990). In this way, the temperature gradient is estimated to be below 50°C over the length of the capsule. Experimental and calibration conditions of pressure and temperature are similar to those described by Rubie et al. (1993) and Keppler and Frost (2005) and are estimated to be accurate within $\pm 5\%$.

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79 Phase identification

80 Run products were inspected under an optical microscope and analysed by micro-Raman
81 spectroscopy to verify the orthorhombic structure of the enstatite (Ulmer and Stalder 2001)
82 and to identify additional crystalline phases (i.e. forsterite or coesite). Raman spectra were
83 obtained with a Horiba Jobin Yvon LabRam-HR 800 confocal Raman spectrometer using the
84 514.5 nm emission line of a 30 mW Ar⁺- laser and an Olympus 100x objective. Furthermore,
85 the entire charge was analysed (without further preparation or grinding) by X-ray diffraction
86 using a Bruker-AXS D8 powder diffractometer equipped with an energy dispersive SOL-X
87 detector in parallel beam optics mode, or a Siemens D5000 powder diffractometer with a
88 scintillation counter in Bragg-Brentano geometry in the 2 θ range between 2° and 60° (Cu-K α
89 radiation, generator settings: 40kV/40mA, step size: 0.02° 2 θ , counting time per step: 3s). For
90 phase identification the PDF-4 database was used. In any individual run one or two of the
91 following crystalline phases were identified (Table 1): enstatite (En) (card nr. 00-019-768),
92 coesite (Coe) (00-014-0654) and forsterite (Fo) (04-007-7321).

93

94 Preparation

95 Single crystals of enstatite were handpicked, embedded in a thermoplastic resin and aligned
96 parallel (010) (i.e. a section perpendicular to the obtuse bisectrix) using a polarization
97 microscope with conoscopic illumination. All crystals were polished double-sided to a
98 thickness of 85 to 320 μ m. After preparation, the thermoplastic resin was removed by rinsing
99 in acetone. The thickness of each crystal was measured with a mechanical micrometer with an
100 accuracy of $\pm$ 2 μ m. Details concerning crystal sizes and orientations are given in Table 1.

101

102 FTIR spectroscopy

Mid infrared absorption spectra were recorded at room temperature in transmission mode using a Bruker Vertex 70 FTIR spectrometer, which was continuously flushed with dried air to minimise water-vapour background, coupled to a Hyperion 3000 microscope equipped with (1) a usual nitrogen-cooled MCT-D316-025 (mercury cadmium telluride) detector – in the following called single element detector – and (2) a nitrogen-cooled focal plane array (FPA) detector consisting of 64 x 64 MCT-D364 detectors. A silicon carbide (SiC) globar was used in combination with a KBr beam splitter and a ZnSe wire grid polarizer. For measurements with the single element detector each spectrum was acquired by 64 scans in the 550 - 8000 cm^{-1} range with a spectral resolution of 2 cm^{-1} . The FPA detector enables FTIR imaging of an area measuring 170 x 170 μm with a lateral pixel resolution of 2.7 μm . Using a FPA-detector, the locus of the measured point is determined by the position of the detector itself and no optical aperture is necessary. Thus the spatial resolution of the MIR-signal is only limited by the wavelength of the IR-radiation (i.e., 3.3 μm at 3000 cm^{-1}). For each spectrum 64 scans in the 850 - 3950 cm^{-1} range were acquired with a spectral resolution of 4 cm^{-1} . Data reduction was performed using OPUS 6.5 software (Bruker) by defining the left and right margin of an absorption band, i.e. 3010-3160 cm^{-1} , 3310-3410 cm^{-1} , 3575-3630 cm^{-1} , and 3665-3710 cm^{-1} , respectively. Between these two points a linear baseline was subtracted, and the area of the absorption band was calculated using the integration tool of the OPUS software. In addition to the analysis of the OH-bands, the overtones of the lattice vibrations between 1250 cm^{-1} and 2350 cm^{-1} (Jamtveit et al. 2001) were recorded in order to confirm the alignment of the sample. For FPA analyses the values were colour-coded and graphically displayed as a map. Areas on the crystal, which are penetrated by cracks or inclusions could be easily detected, and avoided as regions for measurements with the IR single element detector.

Dehydration experiments

In order to check, whether the different observed OH-defects exhibit differences in their thermal stability and dehydration behaviour, crystal EN020c1 was placed in a gold crucible and annealed at 800 °C in air in several steps. After each thermal treatment single element IR-measurements were performed on the crystal to monitor the proceeding dehydration. In addition IR-images were recorded for visualisation of the degassing process.

In pure enstatite hydrogen incorporation is accomplished by two different point defects. One point defect is associated with the octahedral M-site vacancy (V_M), charge balanced by two interstitial protons H_i :

the other point defect can be assigned to the tetrahedral T-site vacancy (V_T) and can be described as:

where the notation of Kröger and Vink (1956) is applied. ^X indicates that the associated point defect is charge balanced, whereas $\cdot$ and $\prime$ indicates positive and negative charges, respectively.

Results

Two groups of absorption bands were observed. Bands of group 1 (at 3592 cm⁻¹ and 3687 cm⁻¹) show strongest absorptions for E||n_r, whereas bands of group 2 (at 3067 cm⁻¹ and 3362 cm⁻¹) show strongest absorptions for E||n_r (Fig. 1). The shape of the spectra with the polarization direction E||n_r was always similar to E||n_r, but the absorbance was constantly lower by approximately a factor of two (Prechtel and Stalder 2010).

For constant starting compositions the intensity ratio of group 2 and group 1 absorption bands changes systematically with increasing pressure (Fig. 1), and the resulting phase assemblages shift to more silica rich crystalline phases, in the sequence En + Fo → En → En + Coe (Fig.

2). Furthermore, at constant pressure a correlation between the intensity ratio of group 2 to group 1 bands and the silica content is observed (Fig. 2).

In this study our principal interest is the ratio of absorption bands $[A_{(3362)}/(A_{(3362)}+A_{(3687)})]$ and therefore detailed calculations for water contents were not performed systematically. Example calculations for crystal En037c1 yielded values around 450 ppm using the method of Libowitzky and Rossmann (1997).

Dehydration

Time-dependent thermal treatment at 800 °C led to a significant reduction of integral absorbances (Table 2 and Fig. 3 + 4). The diffusivity was calculated using the solution of Fick's second law for one-dimensional diffusion in a solid medium with a homogeneous initial concentration bounded by two parallel planes (Carslaw and Jaeger 1959, Ingrin et al. 1995):

$$\frac{c_{av}}{c_0} = \frac{8}{\pi^2} \cdot \sum_{n=0}^{\infty} \frac{1}{(2n+1)^2} \cdot e^{\left(\frac{-Dt(2n+1)^2 \pi^2}{4L^2}\right)} \quad (3),$$

where c_{av} is the average concentration across the whole thickness of the crystal plate, c_0 the initial concentration of the diffusing species, D the diffusion coefficient, t the time and $2L$ the thickness of the sample. Results are shown as solid lines in Fig. 3.

During dehydration an additional absorption band emerged at 3573 cm⁻¹. The absorbance of this band remained always below 1 % of the total absorbance of the spectrum, and therefore was not further considered.

Discussion

Band assignment

Group 1 and group 2 absorption bands can be assigned to different types of OH-defects. Since the intensity of group 1 bands increase with decreasing silica in the system, the most plausible explanation for their occurrence are protons in an environment favoured by low silica activity, i.e., associated with Si-vacancies. The dominance of group 1 OH-absorption bands has previously been observed in clinoenstatite at high pressure (Bolfan-Casanova et al. 2000) and at low silica activity (Withers and Hirschmann 2007). In orthoenstatite these bands – though not dominant – have been reported at low silica activity (Rauch and Keppler 2002). In contrast, group 2 bands are suggested to reflect M-site vacancies, because they are dominant at high silica activity (i.e. low MgO-activity). Additional group 2 bands to those observed in this study have been reported in pure orthoenstatite at temperatures between 700 and 1000 °C (Mierdel and Keppler 2004). It has been suggested that these bands represent a local modification of the pyroxene structure, possibly as lamellae of a monoclinic pyroxene. However, these additional group 2 bands have neither been observed at 1100 °C in Mierdel and Keppler 2004 nor in this study, and therefore are not further considered.

Pressure dependence

The difference between IR spectra of enstatite crystals synthesized at 4 GPa compared to the ones synthesized at 8 GPa (Fig. 1) may be applicable as geobarometer. In the following the ratio of the integral intensity of group 2 absorption bands and the integral intensity of group 1 absorption bands are regarded. Since the intensity ratio within each group is constant within error, only the strongest bands of each group (i.e. 3362 cm⁻¹ and 3687 cm⁻¹) were taken into account and plotted against the starting composition (Fig. 2). Specifically, in our calculations only the component $E||n_p$ for the group 1 band and $E||n$ for the group 2 band was considered. At a given starting composition the ratio of absorbances decreases with increasing pressure, and at constant pressure the ratio increases with increasing silica content in the starting material. Furthermore, it is observed that at a given starting composition, the crystalline phase

assemblage is shifted from En + Fo to En or from En to En + Coe (Fig. 2). This implies that the MgO/SiO₂ ratio in the hydrous melt or aqueous fluid increases with increasing pressure, in accord with Takahashi (1986) and Stalder et al. (2001). The results of this study furthermore reveal that also the enstatite crystals have a higher Mg/Si (i.e., a lower fraction of Mg-vacancies relative to Si-vacancies) with increasing pressure. This change in composition, however, is only revealed in the IR-spectra where the vacant M- and T-sites are recorded, and not with electron microprobe, where the total amount of Si and Mg is measured.

Both phenomena, the chemistry of the fluid and the defect structure of the pyroxene, can be explained by the same reason: the activity of silica compared to MgO changes with pressure, and in order to attain an equilibrium with a certain silica content in the melt or fluid (or Si-vacancy to Mg-vacancy ratio in enstatite) the assemblage has to be buffered by solid phases with higher silica content with increasing pressure.

In order to explain the slopes exhibited in Fig. 2 we suggest the following theoretical approach: In the two component system MgO-SiO₂ it would be expected that the silica activity is either buffered by the assemblage En + Fo or by En + Coe (Fig. 5 upper left), and the phase field for unbuffered En is restricted to an infinitesimally small composition range. With respect to the OH-defects in enstatite, in a system containing only traces of water (a “dry” system) we would expect an abrupt change (Fig. 5 upper left) rather than a continuous change of defect ratio as observed in Fig. 2. However, in the three component system MgO-SiO₂-H₂O the field enstatite + melt is divariant (Fig. 5 right) and a continuous change of octahedral defects (Mg-vacancies) to tetrahedral defects (Si-vacancies) is expected (Fig. 5 lower left), as observed in Fig. 2. Nevertheless, in the buffered part of the three component system (En + Fo + L or En + Coe + L) constant values of defect ratios are expected at constant pressure and temperature. Taking this into account it can be assumed, that the positive trend observed in Fig. 2 through the field of unbuffered enstatite is correct, while in the buffered environments a constant value is expected. De facto our data in the buffered

fields deviate slightly from this theoretical consideration. The most probable explanation is the occurrence of chemical gradients within the capsule and a zonation of the enstatite crystals itself (in terms of defect chemistry) generated during the growth. Such a zonation of the crystal itself has recently been documented with IR imaging (Prechtel and Stalder 2010). The ratios of absorbances can also be displayed as contours in a plot of pressure against SiO₂-content of the starting material (Fig. 6). To be consistent with the approach describe above (Fig. 5) two corrections within this plot have to be performed. Firstly, the values in the fields with enstatite and a coexisting phase (En + Fo or En + Coe) have to be constant. Secondly, the ratio of absorbances approaches a value of 1 when coesite is the coexisting phase. The modified diagram with smoothed values for the ratio of absorbances within the field of En + Fo is shown in Fig. 7. From the contour lines derived from Fig. 7 for the assemblage En + Fo a barometer can be established (Fig. 8):

$$P[GPa] = 1.056 + \sqrt{\frac{1.025 - A_{(3362)}/[(3362)+(3687)]}{0.009}} \quad (4).$$

This barometer so far is only applicable for pure orthoenstatite coexisting with forsterite and only up to 8 GPa, because of the transition to clinoenstatite at higher pressures (Ulmer and Stalder 2001). It has to be noted that data for 2.5, 4 and 8 GPa were derived from samples quenched from 1150 °C and the data at 6 GPa was derived from samples quenched from 1250 °C (Prechtel and Stalder 2010). Even if it has been suggested that the total solubility of OH in enstatite increases with temperature (Mierdel and Keppler 2004, Grant et al. 2007), it has to be mentioned that the defect ratio and not the total solubility of OH is considered here. Apparently the 6 GPa data point fits well into the proposed equation, and therefore the temperature difference of 100 °C seems not to play an important role, for the ratio of group 1 to group 2 bands.

Although the barometer presented here is not yet applicable to nature, it is a basis for studying more complex systems containing trivalent cations such as Fe³⁺, Al³⁺ and Cr³⁺. Trivalent

cations are crucial for the incorporation of OH in orthopyroxene natural systems, and for the formulation of an applicable geobarometer their systematic changes of group 1 and group 2 OH-absorption bands with pressure have to be investigated. Enstatite doped with different trivalent cations synthesised at 2.5 GPa have already been reported (Stalder et al. 2005), and defect interactions dependent on silica activity (and therefore also on pressure) have been proposed. In a more broad sense, the pressure dependence of defect ratios can probably also be applied to other nominally anhydrous minerals relevant to the Earth's mantle. For example, in synthetic forsterite, group 2 bands fade out with increasing pressure, while group 1 bands show a continuous increase (Bali et al. 2008).

With the approach presented in this study, the pressure and therefore the depth of origin can be estimated based on the analysis of one single crystal. A possible application is in the field of diamond prospecting, where a study of the OH in olivine as indicator for high pressure was performed recently (Matveev and Stachel 2009). It is important to remember another finding of this study: the absorbance ratio of group 1 and group 2 bands stays more or less constant during dehydration. This means that crystals partially dehydrated during ascent will furnish the same results as the unmodified crystals when the barometer established above is applied.

Thermal stability of the OH-defects

Using the equations from Carslaw and Jaeger (1959) and Ingrin et al. (1995) the diffusion coefficient at 800 °C and 1 atmosphere can be determined as $-\log D = 14.4 \pm 0.2$ (Fig. 3), which is in good agreement with diffusion law determined by Stalder and Skogby (2003). The most plausible interpretation for the synchronous decrease of group 1 and group 2 bands is a similar diffusivity of V_{Mg} and V_{Si} .

Planar defects

An alternative explanation for the group 1 band at 3687 cm^{-1} would be the existence of planar defects. Several features would strengthen such an interpretation: (1) the most suitable orientation of phases with sheet-structure in pyroxenes is parallel to the crystallographic b-axis (Koch-Müller et al. 2004), (2) the OH-dipole vector in such lamellae would be oriented parallel to the crystallographic a-axis (i.e., parallel to n_x) of the pyroxene, (3) the wavenumber of the observed OH absorption band in enstatite is close to the OH absorption band of brucite (3690 cm^{-1}), (4) the thermal stability of brucite increases with increasing pressure and reaches 1150 °C at 8 GPa (Johnson and Walker 1993). Even if brucite is not stable under most of the synthesis conditions chosen in this study, it may be possible that single domains survive (or are incorporated) at higher temperatures, similar to humite-lamellae in olivine (Hermann et al. 2007). However, several points argue against an interpretation involving brucite-type planar defects: (1) the results of the 6 GPa samples derived at higher temperatures should strongly deviate from the trend shown in Fig. 8, (2) the thermal stability of the defects causing the group 1 bands should show a different behaviour to the group 2 bands (which is not the case), and (3) group 1 has two bands showing a constant intensity ratio over all specimens investigated here and brucite lamellae cannot explain the occurrence of the other group 1 band at 3592 cm^{-1} .

Planar defects could be identified by transmission electron microscopy (TEM), but for samples with OH-contents as reported here, less than one elementary cell of brucite out of 1000 elementary cells of enstatite would be expected. If there were lamellae their distribution must be homogenous on the scale of a few μm , since otherwise they would have been revealed by IR-imaging.

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418 Figure captions

419 **Fig. 1** IR spectra of OH-bands of two enstatite crystals synthesized from the same starting
 420 composition ($\text{Bc}_{55}\text{Qz}_{45}$) at different pressure (4 GPa: En027c1, 8 GPa: En037c1). The
 421 polarisation direction is indicated at the respective spectrum. The absorbance is normalised to
 422 1 mm thickness

423

424 **Fig. 2** Ratio of the integral absorbance $A_{3362}/(A_{3362}+A_{3687})$ plotted against the SiO_2 content in
 425 the starting composition. For the band at 3362 cm^{-1} only $\text{E}||\text{n}_i$ was taken into account and for
 426 the band at 3687 cm^{-1} only $\text{E}||\text{n}_p$. The approximate stability fields of En + Fo, En, and En +
 427 Coe are separated by dotted curves. Each pressure shows its own trend (4 GPa: diamonds, 6
 428 GPa: circles, 8 GPa: squares). Data at 6 GPa are from Prechtel and Stalder (2010)

429

430 **Fig. 3** Development of integral absorbances (A) of two OH-bands normalised to the initial
 431 integral absorbance (A_0) during thermal treatment at 800 °C of crystal En020c1. The

absorption band around 3687 cm^{-1} is representative for group (1), while the absorbance band around 3362 cm^{-1} is representative for group (2). Calculated curves for different diffusivities D (displayed as $-\log D$) are shown as solid lines. Data points are listed in Table 2

Fig. 4 IR images of crystal En020c1 before thermal treatment at $800\text{ }^{\circ}\text{C}$, and after 3h, 12h, 30h, 46h, and 70h. Total absorbances in the wavenumber range $3310\text{ cm}^{-1} - 3410\text{ cm}^{-1}$ are colour-coded according to the scale bar to the right (not normalised to thickness). Note the emerging and propagating crack in the upper right acting as a sink for OH during thermal treatment. Each pixel ($2.7\text{ }\mu\text{m} \times 2.7\text{ }\mu\text{m}$) contains the full information of an IR spectrum and can be extracted separately. Each figure consists of 16 (4×4) sequentially recorded IR images, covering a surface of $680\text{ }\mu\text{m} \times 680\text{ }\mu\text{m}$

Fig. 5 Schematic drawing of the $\text{MgO-SiO}_2\text{-H}_2\text{O}$ -system at high pressure and temperature (right panel). When only traces of water are present (“dry system”), the silica activity changes abruptly around the stoichiometric composition of enstatite, and an abrupt change in the ratio of band 2 to band 1 OH-absorbances is expected (upper left panel). In contrast, in the nominally wet system a divariant field enstatite + melt (grey area) exists, and the silica activity may be unbuffered. Consequently, the silica activity and the ratio of band 2 to band 1 OH-absorbances increases continuously (lower left panel). Bc = brucite, Fo = forsterite, En = enstatite, Coe = coesite, L = melt

Fig. 6 Contours of the ratio of octahedral to tetrahedral defects (as $A_{(3362)}/(A_{(3362)} + A_{(3687)})$) as a function of pressure and silica content in the starting material. Data points are labelled with the observed absorbance ratio. Phase assemblages are shown with different symbols, i.e., En + Fo (triangles), En (diamonds), and En + Coe (squares). Data at 6 GPa are from Prechtel and Stalder (2010)

458

459 **Fig. 7** Contours of the ratio of octahedral to tetrahedral defects (as $A_{(3362)}/(A_{(3362)} + A_{(3687)})$) as
460 a function of pressure and silica content in the starting material. The graph is based on Fig. 6
461 and modified according to theoretical considerations (see text). Phase assemblages are shown
462 with different symbols, i.e., En + Fo (triangles), En (diamonds), and En + Coe (squares). Only
463 the buffered field (En coexisting with Fo) is applicable for barometric considerations. Data at
464 6 GPa are from Prechtel and Stalder (2010)

465

466 **Fig. 8** Defect ratio of group 2 to group 1 OH-absorbance bands in orthoenstatite as a function
467 of pressure. The data point at 2.5 GPa (ratio of absorbances = 1) is derived from Stalder and
468 Skogby (2002) and the data point at 6 GPa is from Prechtel and Stalder (2010)

untreated

$t = 3h$

$t = 12h$

$t = 30h$

$t = 46h$

$t = 70h$

Table 1 Details concerning the investigated enstatite single crystals.

run	P [GPa]	wt% H ₂ O	Bc:Qz (mole)	phase assemblage ^{a)}	crystal	size [μm]	thickness [μm]	A ₍₃₀₆₇₎ ^{b)}	A ₍₃₃₆₂₎ ^{c)}	A ₍₃₅₉₂₎ ^{d)}	A ₍₃₆₈₇₎ ^{e)}
FP012 ^{f)}	6	15	50:50	En, (Fo)	En012c1	660x390	200	11.8	19.4	2.6	4.3
FP012 ^{f)}	6	15	50:50	En, (Fo)	En012c4	450x320	220	10.7	17.2	2.4	3.9
FP013 ^{f)}	6	21 ^{g)}	50:50	En, Fo	En013c1	580x420	160	9.2	15.4	1.5	2.6
FP015 ^{f)}	6	12	40:60	Coe, En	*)	< 50x50	< 50	(1.5)	(2.0)	0.0	0.0
FP017 ^{f)}	6	17	55:45	Fo, En	En017c1	280x460	135	6.1	9.5	2.3	4.0
FP017 ^{f)}	6	17	55:45	Fo, En	En017c2	170x195	125	5.7	8.9	1.3	2.3
FP017 ^{f)}	6	17	55:45	Fo, En	En017c3	150x150	100	5.6	8.7	1.2	2.1
FP017 ^{f)}	6	17	55:45	Fo, En	En017c4	200x120	110	3.9	5.9	1.1	1.9
FP020 ^{f)}	6	14	47:53	En	En020c1	600x520	210	17.7	29.5	2.3	3.9
FP020 ^{f)}	6	14	47:53	En	En020c2	350x150	110	10.6	17.7	1.4	2.3
FP027	4	17	55:45	Fo, En	En027c1	80x345	85	5.4	9.1	0.4	0.7
FP027	4	17	55:45	Fo, En	En027c2	110x245	125	3.7	6.3	0.4	0.8
FP028	4	15	50:50	Fo, En	En028c1	585x210	200	11.1	18.7	2.6	1.4
FP029	4	14	47:53	En, (Fo)	En029c1	270x135	100	3.5	6.3	0.2	0.3
FP029	4	14	47:53	En, (Fo)	En029c2	315x170	100	5.7	9.4	0.4	0.6
FP030	4	12	40:60	Coe, En	*)	< 30x30	< 30	(1.5)	(1.9)	0.0	0.0
FP034	8	15	50:50	En, Fo	En034c1	760x370	275	13.1	18.8	3.8	7.4
FP034	8	15	50:50	En, Fo	En034c2	1410x790	350	17.6	24.7	5.6	11.0
FP035	8	14	47:53	En	En035c1	1100x450	320	22.8	34.6	5.3	11.6
FP035	8	14	47:53	En	En035c2	580x180	200	12.0	23.6	2.9	6.2
FP036	8	12	40:60	Coe, En	*)	< 30x30	< 30	(1.5)	(2)	0.0	0.0
FP037	8	17	55:45	En, Fo	En037c1	300x65	120	4.3	6.2	2.5	0.5
FP037	8	17	55:45	En, Fo	En037c2	280x135	120	4.5	6.5	2.6	0.5
FP038	8	13	43:57	Coe, En	En038c1	365x190	220	h)	h)	h)	h)

^{a)} En = Enstatite; Fo = Forsterite; Coe = Coesite, order represents abundance. Very minor abundance is displayed in parentheses.

^{b)} Integral absorbance between 3010 and 3160 cm⁻¹ with E||γ. Not normalized to thickness of the wafer.

^{c)} Integral absorbance between 3310 and 3410 cm⁻¹ with E||γ. Not normalized to thickness of the wafer.

^{d)} Integral absorbance between 3575 and 3630 cm⁻¹ with E||β. Not normalized to thickness of the wafer.

^{e)} Integral absorbance between 3665 and 3710 cm⁻¹ with E||β. Not normalized to thickness of the wafer.

^{f)} Data from Prechtel and Stalder (2010)

^{g)} Doped with 13 μg of water in addition to the water from Mg(OH)₂

^{h)} Experiment served to check phase assemblage only

^{*)} No single crystal could be prepared due to the small grain sizes. Therefore a grain mount was prepared, within over more than 40 measurements no evidence of the absorption band at 3687 cm⁻¹ could be detected.

Table 2 Development of the integral absorbances of the OH-bands of crystal En020c1 after each dehydration step.

t [h]	$A_{(3067)}$	A/A_0	$A_{(3362)}$	A/A_0	$A_{(3592)}$	A/A_0	$A_{(3687)}$	A/A_0	$A_{(3573)}$	A/A_0
0	12.76	1.00	21.57	1.00	2.07	1.00	3.88	1.00	0.00	0.00
3	12.77	1.00	21.08	0.98	2.02	0.98	3.29	0.85	0.03	0.18
7	12.32	0.96	20.45	0.95	1.98	0.95	3.27	0.84	0.06	0.30
12	11.88	0.93	19.55	0.91	1.89	0.91	3.17	0.82	0.10	0.53
30	9.93	0.78	16.07	0.74	1.76	0.85	2.88	0.74	0.17	0.93
46	9.01	0.70	14.50	0.67	1.66	0.80	2.75	0.71	0.17	0.90
70	8.51	0.67	13.82	0.64	1.56	0.75	2.56	0.66	0.19	1.00
190	5.93	0.46	9.53	0.44	1.25	0.60	1.97	0.51	0.14	0.74
358	3.77	0.30	6.19	0.29	1.02	0.49	1.62	0.42	0.09	0.46

Times (t) are total dehydration times after the respective dehydration step. For each absorption band two values are indicated, the integral absorbance A (left) and the relative value compared to the initial value A/A_0 (right). For the group 1 bands only the component $E_{||n_\beta}$ and for the group 2 bands only the component $E_{||n_\gamma}$, respectively was considered.