

Article

In Situ High-Pressure Raman Spectroscopic, Single-Crystal X-ray Diffraction, and FTIR Investigations of Rutile and TiO₂II

Xiaofeng Lu ^{1,2}, Shuchang Gao ^{1,2}, Peiyan Wu ^{1,2}, Ziyu Zhang ¹, Li Zhang ^{1,*}, Xiaoguang Li ³ and Xueqing Qin ⁴¹ School of Earth Sciences and Resources, China University of Geosciences, Beijing 100083, China² Center for High Pressure Science and Technology Advanced Research, Beijing 100193, China³ State Key Laboratory of Lithospheric Evolution, Institute of Geology and Geophysics, Chinese Academy of Sciences, Beijing 100029, China⁴ Institute of Geology, Chinese Academy of Geological Sciences, Beijing 100037, China

* Correspondence: li.z.zhang@cugb.edu.cn

Abstract: In ultrahigh-pressure (UHP) metamorphic rocks, rutile is an important accessory mineral. Its high-pressure polymorph TiO₂II can be a significant indicator of pressure in the diamond stability field. In the present study, in situ high-pressure Raman spectroscopic measurements of natural rutile in UHP eclogite from the main hole of the Chinese Continental Scientific Drilling Project (CCSD) have been conducted up to ~16 GPa. Rutile and recovered TiO₂II have also been analyzed via single-crystal X-ray diffraction and FTIR spectroscopy. The results indicate that (1) the phase transition from rutile to baddeleyite-type TiO₂ terminates at about 16 GPa under compression at ambient temperature; (2) the metastable TiO₂II in the exhumated UHP rocks formed during deep continental subduction can be characterized by a highly distorted octahedral site in the crystal structure. X-ray powder diffraction analyses (with Cu K α radiation) at ambient conditions are sufficient for identifying the lamellae of TiO₂II within natural rutile based on the angles (2 θ) of two strong peaks at 25.5° and 31.5°; (3) rutile and recovered TiO₂II in the continental slabs can contain certain amounts of water during deep subduction and exhumation. The estimated water contents of rutile in the present study range from 1590 to 1780 ppm of H₂O by weight. In the crystal structure of TiO₂II, hydrogen can be incorporated close to the long O–O edges (>2.5143 Å) of the TiO₆ octahedra. Further studies on the pressure–temperature stability of hydroxyls in rutile and TiO₂II may help to understand the transportation and release of water in subducted continental slabs.

Keywords: rutile; TiO₂II; in situ high-pressure Raman spectroscopy; X-ray diffraction; FTIR spectroscopy



Citation: Lu, X.; Gao, S.; Wu, P.; Zhang, Z.; Zhang, L.; Li, X.; Qin, X. In Situ High-Pressure Raman Spectroscopic, Single-Crystal X-ray Diffraction, and FTIR Investigations of Rutile and TiO₂II. *Minerals* **2023**, *13*, 703. <https://doi.org/10.3390/min13050703>

Academic Editor: Daniel Hummer

Received: 6 April 2023

Revised: 14 May 2023

Accepted: 19 May 2023

Published: 21 May 2023



Copyright: © 2023 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<https://creativecommons.org/licenses/by/4.0/>).

1. Introduction

Rutile (ideal formula: TiO₂) is an important accessory mineral in ultrahigh-pressure metamorphic rocks formed during deep continental subduction [1,2]. According to previous investigations of water in nominally anhydrous minerals (NAMs), rutile can hold up to 0.28 wt% of H₂O in the form of structural OH [3,4]. Therefore, it is also expected to be a potential host phase of water in subducting continental slabs.

Rutile has a tetragonal structure with space group of *P*₄₂/*mnm*. It is made up of only one octahedral site that is commonly occupied by Ti⁴⁺ (Figure 1). Previous in situ X-ray diffraction experiments at ambient temperature at a pressure of up to 60 GPa [5,6] showed that rutile begins to transform to its high-pressure polymorph with the monoclinic baddeleyite (ZrO₂) structure (space group *P*₂₁/*c*) at about 12 GPa under compression. Upon the release of pressure, baddeleyite-type TiO₂ converts at 7 GPa into TiO₂II (space group *Pbcn*), which is another high-pressure polymorph of rutile with the orthorhombic α -PbO₂ structure (Figure 1) and is metastable at a normal pressure. The baddeleyite-type TiO₂ is 11.3(9)% denser than rutile and TiO₂II is 2.1(3)% denser than rutile. The

estimated zero-pressure bulk moduli are 230(20), 260(30), and 290(20) for rutile, TiO₂II and baddeleyite-type TiO₂, respectively [6].

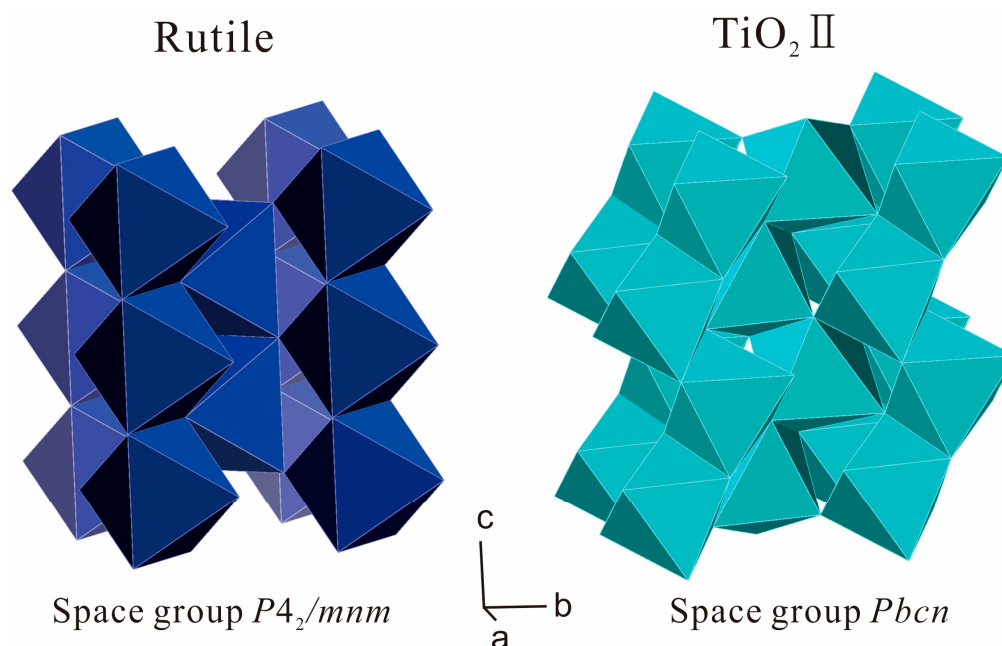


Figure 1. Projection of crystal structures (consisting of TiO₆ octahedra) of rutile and TiO₂II based on the single-crystal X-ray diffraction analyses in this study.

In situ high-pressure spectroscopic studies [7–9] indicated that the phase transition from rutile to baddeleyite-type TiO₂ begins at 13 GPa and terminates at 21 to 23 GPa at room temperature. Upon decompression, the baddeleyite-type TiO₂ to TiO₂II transition occurs around 7 GPa and terminates at about 5 GPa. In addition, previous investigations of high-pressure and high-temperature phase equilibria of TiO₂ showed that the phase boundary between rutile and TiO₂II changes from having a negative slope to having a positive slope with increasing temperature at about 6 GPa and 850 °C [10]. Therefore, in natural ultrahigh-pressure (UHP) metamorphic rocks, widely observed nano-crystal lamellae of TiO₂II within (or coexisting with) rutile can be a significant indicator of pressure in the diamond stability field [11–13].

To better understand the high-pressure behavior and crystal structure of rutile and its high-pressure polymorphs in continental slabs during ultra-deep subduction and exhumation, in situ high-pressure Raman spectroscopic measurements of rutile in UHP eclogite collected from continental subduction environment have been conducted up to ~16 GPa in the present work. Natural rutile and recovered TiO₂II have also been analyzed via single-crystal X-ray diffraction and FTIR spectroscopy.

2. Sample Description and Experimental Methods

Natural rutile (Ti_{0.988}Fe_{0.011}O₂) was collected from an UHP eclogite (no. B132R114P1a) in the main hole of the Chinese Continental Scientific Drilling Project (CCSD) in a supracrustal rock slab, which was subducted to a depth of over 100 km and then exhumed to the surface during continental collisional orogeny [14,15]. The eclogite is composed of fresh medium-grained garnet, omphacite, phengite, and minor rutile (Figure 2) and has experienced peak metamorphic *P-T* conditions greater than 3 GPa and 700 °C [15].

In situ high-pressure Raman spectroscopic measurements were conducted using a symmetric-type diamond anvil cell (DAC) with a pair of type IIa diamond anvils (culet of ~0.3 mm in diameter). A rhenium gasket was pre-indented to have a thickness of ~60 µm, and a hole of a diameter of ~0.15 mm was drilled as the sample chamber. A rutile sample with the size of 40 × 40 × 30 µm was selected and loaded into the sample chamber together

with two ruby spheres. Argon (Ar) was loaded as a pressure-transmitting medium. The potential pressure gradients are estimated to be lower than 0.2 GPa at pressures up to 20 GPa [16]. Raman spectra were collected with a HORIBA LabRAM HR Evolution laser Raman spectrometer at Institute of Geology, Chinese Academy of Geological Sciences, in the wavenumber range of 100 to 1200 cm^{-1} (spectral resolution of 1 cm^{-1}), using 10 accumulations and a 5 s exposure time with a 20 $\times$ microscope objective. All spectra were excited by a 532 nm solid-state laser at a power of 100 mW. Pressure was calculated from the shift of the ruby R1 luminescent line [17]. The frequencies (cm^{-1}) of the bands in the spectra from in situ high-pressure Raman spectroscopic measurements are listed in Table 1.

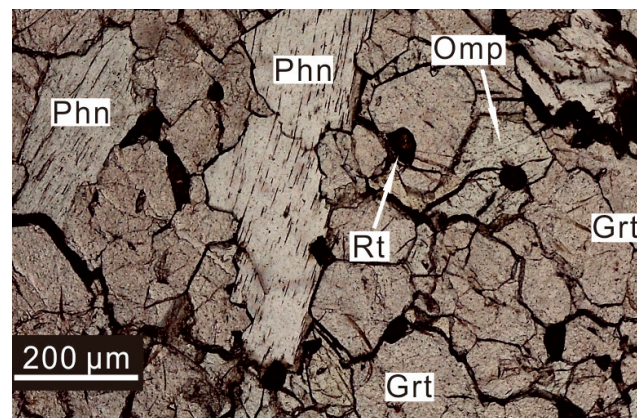


Figure 2. Micro-photographs of eclogite (no. B132R114P1a) from the main hole of the Chinese Continental Scientific Drilling Project. Abbreviations: Rt = rutile, Phn = Phengite, Grt = Garnet, Omp = Omphacite.

Table 1. Frequencies (cm^{-1}) of the bands in the spectra from in situ high-pressure Raman spectroscopic measurements.

Pressure (GPa)	Phase 1 (Rutile)											
2.2	232.80	452.85	614.03	-	-	-	-	-	-	-	-	-
4.1	239.46	459.78	620.86	-	-	-	-	-	-	-	-	-
7.5	248.66	469.17	633.03	-	-	-	-	-	-	-	-	-
8.2	251.21	473.11	638.38	-	-	-	-	-	-	-	-	-
9.7	253.77	477.56	644.70	-	-	-	-	-	-	-	-	-
10.8	-	481.55	648.59	-	-	-	-	-	-	-	-	-
Phase 2												
12.4	-	-	-	449.38	485.44	598.69	654.41	-	-	-	-	-
13.2	-	-	-	453.34	487.90	599.17	657.32	-	-	-	-	-
13.8	179.33	320.30	382.16	457.30	489.38	603.04	658.92	-	-	-	-	-
14.1	182.43	321.81	381.16	460.76	490.36	604.49	660.23	-	-	-	-	-
14.6	181.91	322.32	381.16	464.72	489.87	603.62	659.26	-	-	-	-	-
Phase 3 (baddeleyite-type TiO_2)												
16.0	159.17	221.01	264.99	323.33	351.05	408.63	439.47	492.33	634.01	660.71	702.25	833.26
15.2	159.69	221.53	267.02	325.86	351.55	407.64	438.97	492.33	630.60	658.77	698.88	833.26
14.7	159.17	220.50	263.46	324.85	349.54	406.14	437.98	491.84	630.11	659.74	697.43	830.90
14.0	154.51	218.96	262.95	324.34	349.04	402.65	436.94	490.86	628.17	658.29	696.47	830.43
13.6	152.44	217.43	261.42	324.34	347.03	402.15	436.00	490.86	627.19	657.80	697.43	830.90
13.0	151.92	217.94	262.95	329.89	347.03	399.66	435.00	489.87	626.22	654.90	695.51	828.54
10.5	142.58	209.72	258.87	320.80	346.02	390.17	430.53	486.92	602.37	650.53	690.20	822.88
Phase 4												
8.2	142.58	180.88	252.23	289.40	315.75	378.15	449.38	478.54	573.97	614.03	640.33	-
7.1	128.56	183.46	253.25	289.91	314.74	374.15	439.96	471.14	569.11	605.46	623.06	-
Phase 5 (TiO_2 II)												
5.0	178.82	288.89	318.28	374.65	439.47	555.97	592.40	624.76	-	-	-	-
0.0	174.17	287.37	315.75	365.12	431.03	538.90	575.91	612.22	-	-	-	-

Single crystals of natural rutile (about $60 \times 40 \times 30 \mu\text{m}$ in size) and recovered TiO_2II (about $40 \times 40 \times 30 \mu\text{m}$ in size) (Figure 3) were mounted on glass fibers for single-crystal X-ray diffraction measurements, respectively. Intensity data were collected with a Bruker D8 Venture diffractometer at Center for High Pressure Science and Technology Advanced Research, Beijing, using APEX4 software. An X-ray ($\lambda = 0.71073 \text{ \AA}$) was conducted with a I μ S 3.0 generator using a rotating Mo anode. Crystal structures were refined from the intensity data via SHELXL-2018 [18] in the package WINGX [19]. The refinements were based on the scattering factors and absorption coefficients for Ti^{4+} and O^{2-} from the International Tables for Crystallography, Volume C [20]. The refined unit cell parameters and atom positions of rutile and TiO_2II are given in Table S1. We calculated X-ray powder diffraction patterns for the Cu K α radiation ($\lambda = 1.5405 \text{ \AA}$) of rutile and TiO_2II from the crystal structure data collected via single-crystal X-ray diffraction, using the program CrystalDiffract. These are compared in Figure 4.

Unpolarized infrared spectra of three natural rutile samples and recovered TiO_2II were collected at ambient conditions in the wavenumber range of 3000 to 3800 cm^{-1} , using a Bruker INVENIO-R FTIR spectrometer with a $15\times$ objective on the HYPERION 1000 microscope at Institute of Geology and Geophysics, Chinese Academy of Sciences. Each spectrum was accumulated over 128 scans with a 2 cm^{-1} resolution. The calculation of the water contents referred to [21], using Lambert–Beer’s Law in the form $c = a/\varepsilon$, wherein the absorption coefficient $a = A/t$, and where c is the water concentration ($\text{mol}\cdot\text{L}^{-1}$), ε is the integrated molar absorption coefficient ($\text{L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$), A is the measured absorbance, and t is the thickness (cm) of the measured crystal plate. The unpolarized absorbance of randomly oriented grains in this study is estimated to be one-third of the sum of the three principal absorbances [22].

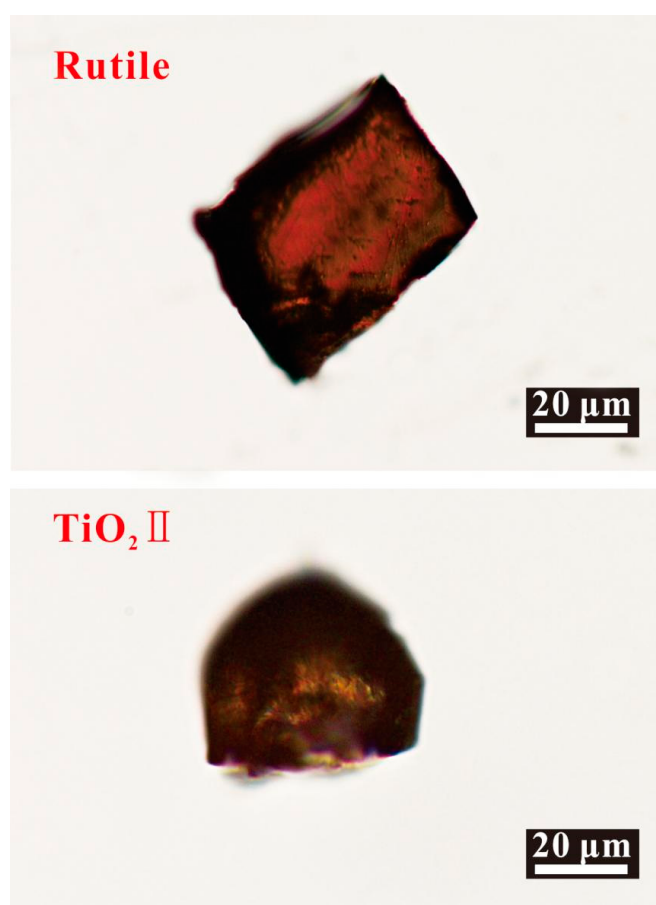


Figure 3. Photomicrographs of natural rutile and recovered TiO_2II in this study.

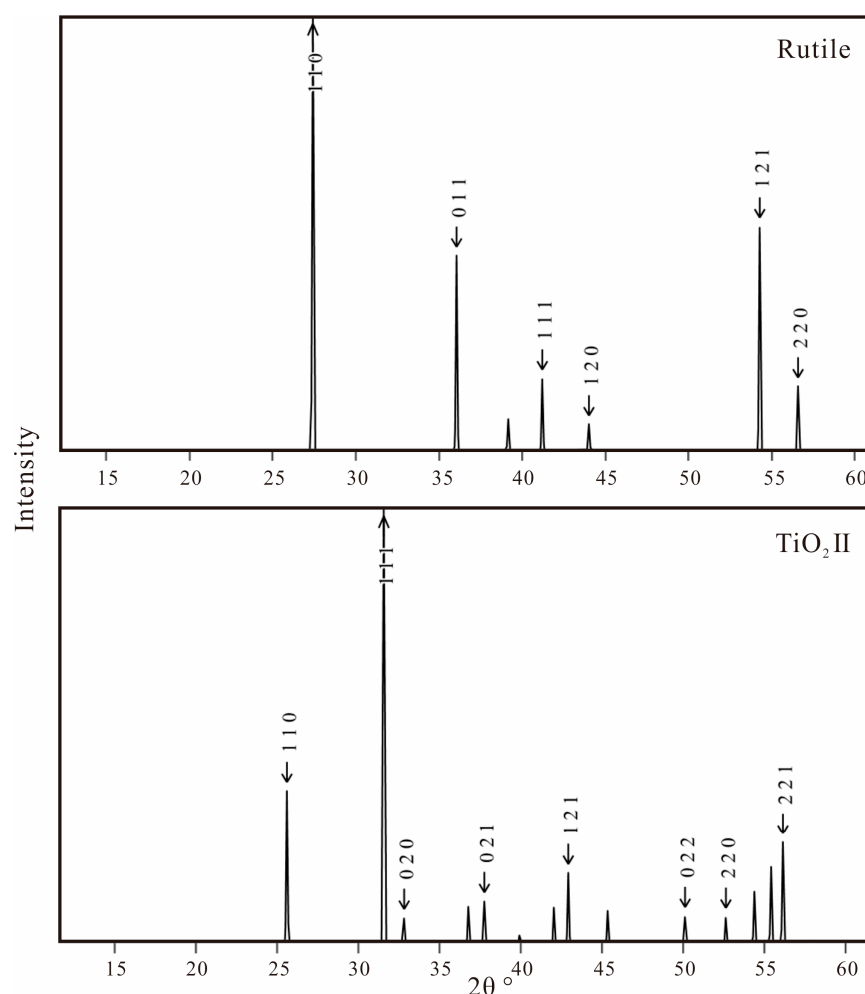


Figure 4. The calculated X-ray powder diffraction patterns for Cu K α radiation ($\lambda = 1.5405 \text{ \AA}$) of rutile and TiO₂ II.

3. Result and Discussion

3.1. In Situ High-Pressure Raman Spectroscopy

Under ambient condition, as shown in Figure 5, the Raman spectrum of rutile in this study exhibits seven bands at 135, 235, 325, 360, 445, 610 and 830 cm^{-1} . The broad band at 235 cm^{-1} is ascribed to multi-phonon scattering, which indicates the disordered crystal structure of rutile at 1 atm [1,8,23]. The two strong bands at 445 and 610 cm^{-1} are attributed to the O-Ti-O bending vibration and asymmetric Ti-O stretching vibration, respectively. The two weak bands at 135 and 830 cm^{-1} are due to the rotation of the TiO₆ octahedra and symmetric Ti-O stretching vibration, respectively [1,7,9,24].

In the Raman spectra collected in the in situ high-pressure experiment (Figure 6 and Table 1), three strong bands at 235, 445, and 610 cm^{-1} can be observed, while the bands initially located at 135, 325, 360, and 830 cm^{-1} can hardly be detected due to their relatively low intensity. At elevated pressures up to 10.8 GPa, the bands at 445 and 610 cm^{-1} linearly shift to higher frequencies without discontinuity (Figure 7a), indicating the continuous and steady compression of the TiO₆ octahedra. In accordance with previous observations [7,8], the intensity of the 235 cm^{-1} band decreases with increasing pressure (Figure 6a). This decrease can be explained by the increased ordering of the crystal structure under compression [8]. At pressures above 13.2 GPa, a number of new, sharp bands instantaneously appear in the spectrum (Figure 6a), implying the beginning of the rutile-to-baddeleyite-type TiO₂ transition. At about 16 GPa, the Raman spectrum displays 12 bands at 159, 221, 264, 323, 350, 408, 440, 492, 634, 660, 702, and 833 cm^{-1} (Figure 6a and Table 1).

These bands are consistent with the previously reported vibrational modes of baddeleyite-type TiO_2 [7,9,25], indicating the termination of the transition.

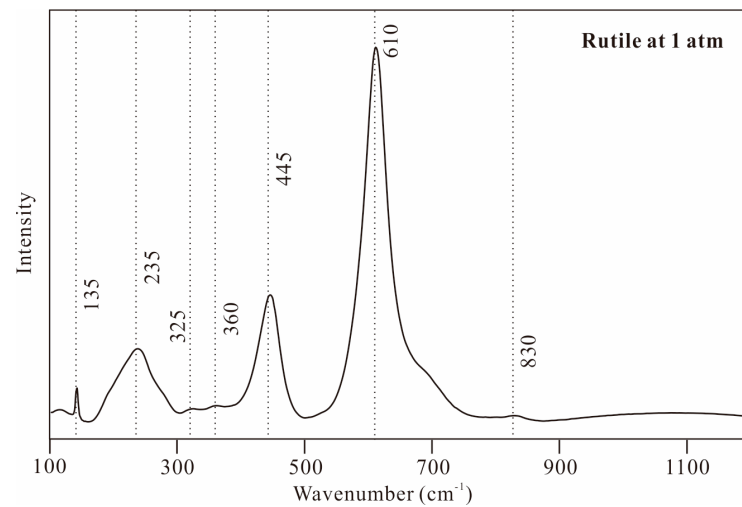


Figure 5. The Raman spectrum of rutile in the wavenumber range of 100 to 1200 cm^{-1} under ambient conditions.

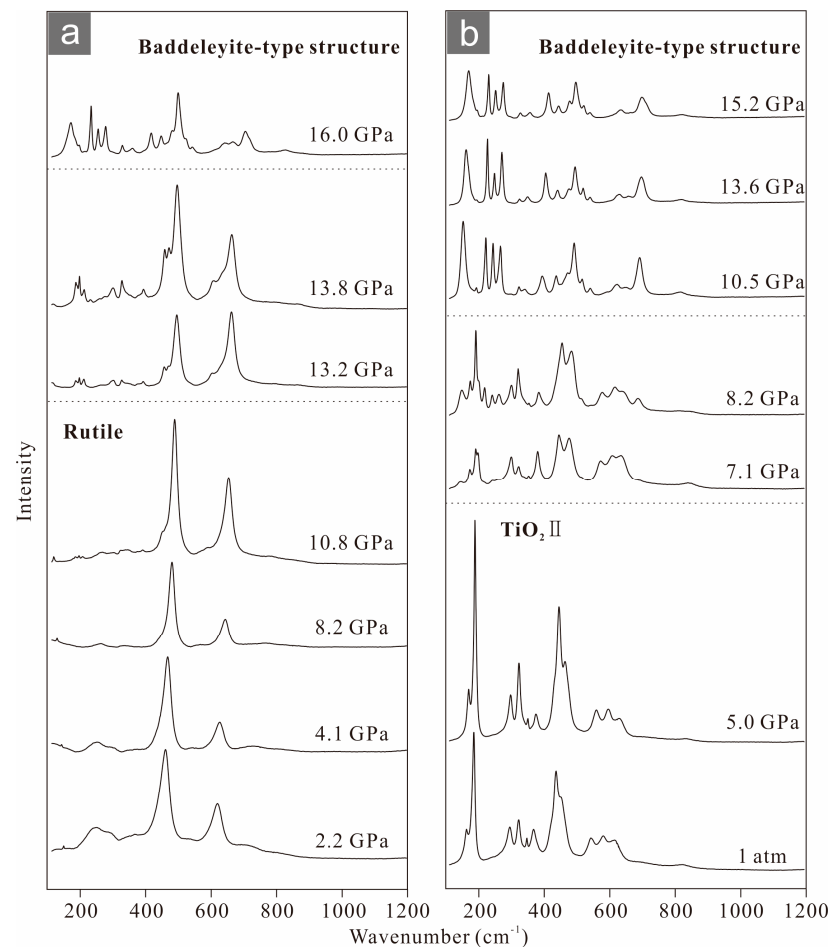


Figure 6. Representative Raman spectra of rutile with varying pressure under (a) compression and (b) decompression.

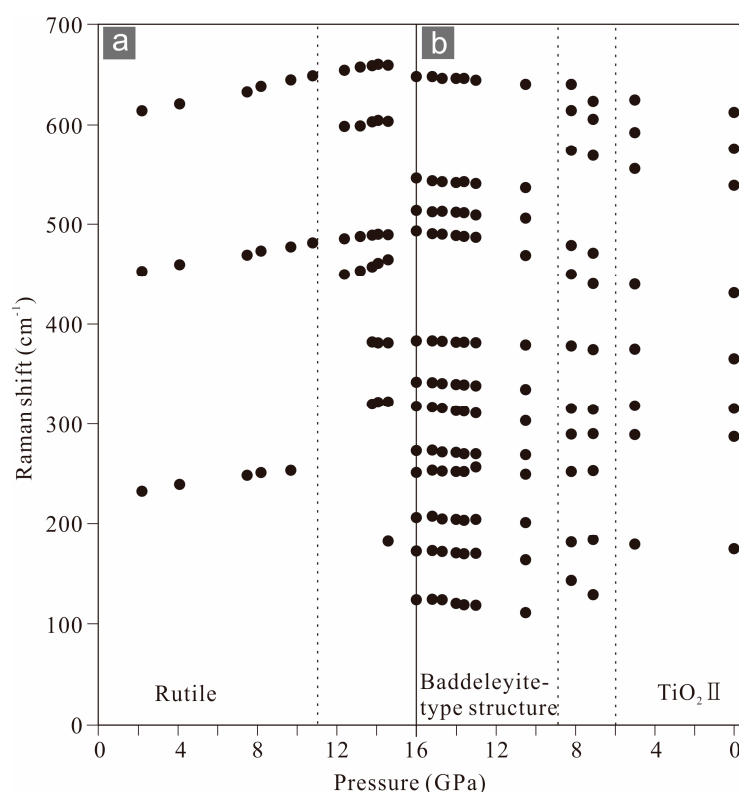


Figure 7. Variations in band frequencies in the Raman spectra with varying pressure under (a) compression and (b) decompression.

As shown in Figures 6b and 7b, Raman bands of baddeleyite-type TiO_2 linearly shift to lower frequencies with decreasing pressure down to 10 GPa without notable discontinuity and band broadening, revealing that the crystal structure of baddeleyite-type TiO_2 is still stable during decompression. In addition, there is no observable increase or decrease in the intensities of the bands upon the release of pressure. In the pressure range of about 9 to 6 GPa, the bands exhibit a highly non-linear shift with an abrupt change in frequency due to the phase transition from baddeleyite-type TiO_2 to TiO_2II . The intensities of the bands change anomalously with the appearance of a number of new bands (Figures 6 and 7). In accordance with the reported vibrational modes of TiO_2II [7–9], the Raman spectrum shows eight bands at 178, 288, 318, 374, 440, 555, 592, and 624 cm^{-1} at about 5 GPa (Figure 6b and Table 1), demonstrating the termination of the phase transformation. All these bands are still visible in the Raman spectrum of the recovered TiO_2II at 1 atm. However, the two strong bands at about 178 and 440 cm^{-1} decrease in intensity after the pressure is released, implying that their intensities can be pressure-dependent (Figure 6b).

The present work shows that the pressure interval (13 to 16 GPa) of the rutile to baddeleyite-type TiO_2 transition at ambient temperature is significantly narrower than that (12 to 21 GPa) reported in previous studies [7,9]. In addition, a transition in rutile can also be observed to begin at about 7 GPa [8], implying a wider pressure interval. Therefore, more work is needed to determine the potential influence of kinetic factors (such as minor impurities, grain size, pressure medium and length of time under pressure) on this phase transition. In addition, at room temperature, the transformation may reflect a slow rate of abrupt transition [8]. Further high-pressure and high-temperature experiments are expected to reveal the equilibrium phase boundary among these rutile polymorphs.

3.2. Single-Crystal X-ray Diffraction Analyses

According to single-crystal X-ray diffraction measurements in this study (Table 2), the average Ti–O distance of the octahedral site (1.9574 Å) in recovered TiO_2II is similar

to that in rutile (1.9599 Å), whereas TiO₂II has smaller TiO₆ octahedra, compared to rutile (Figure 8). As shown in Figure 8 and Table 2, the central Ti⁴⁺ in the octahedral site in rutile is bonded to four oxygens at an identical distance (1.9467 Å), which is slightly shorter than the lengths of other two Ti-O bonds (1.9863 Å). However, in the crystal structure of TiO₂II, two Ti-O bonds (2.0368 Å) are much longer than the other two (1.8874 Å) in a plane. As a result, the estimated mean octahedral quadratic elongation [26] and octahedral angle variance of the octahedral site in TiO₂II are significantly larger than those in rutile (Figure 8 and Table 2), indicating that the recovered TiO₂II has more distorted TiO₆ octahedra than rutile does under ambient conditions [27]. As shown in Figure 4, X-ray powder diffraction analyses (with Cu K α radiation) are expected to identify the lamellae of TiO₂II within natural rutile under ambient conditions based on the angles (2 θ) of two strong peaks at 25.5° and 31.5°.

Table 2. Site geometry and occupancy parameters for rutile and TiO₂II.

Rutile		TiO ₂ II	
Average bond length	1.9599	Average bond length	1.9574
Octahedral volume	9.9127	Octahedral volume	9.7171
Octahedral angle variance	29.4997	Octahedral angle variance	66.5861
Mean octahedral quadratic elongation	1.0085	Mean octahedral quadratic elongation	1.0203
<Ti-O> (2)	1.9863	<Ti-O> (2)	1.8874
<Ti-O> (4)	1.9467	<Ti-O> (2)	1.9481
<O-O> edge	2.7812	<Ti-O> (2)	2.0368
<O-O> edge (shared edge)	2.5284	<O-O> edge	2.8360
<O-O> edge	2.9607	<O-O> edge	2.8873
<O-O> distance	3.8934	<O-O> edge	2.9488
<O-O> distance	3.9726	<O-O> edge	2.7310
Occupancy	1	<O-O> edge (shared edge)	2.5143
		<O-O> edge	2.7168
		<O-O> edge	2.6509
		<O-O> distance	3.8317
		Occupancy	1

Note: the bond length and atom distance are measured in Å.

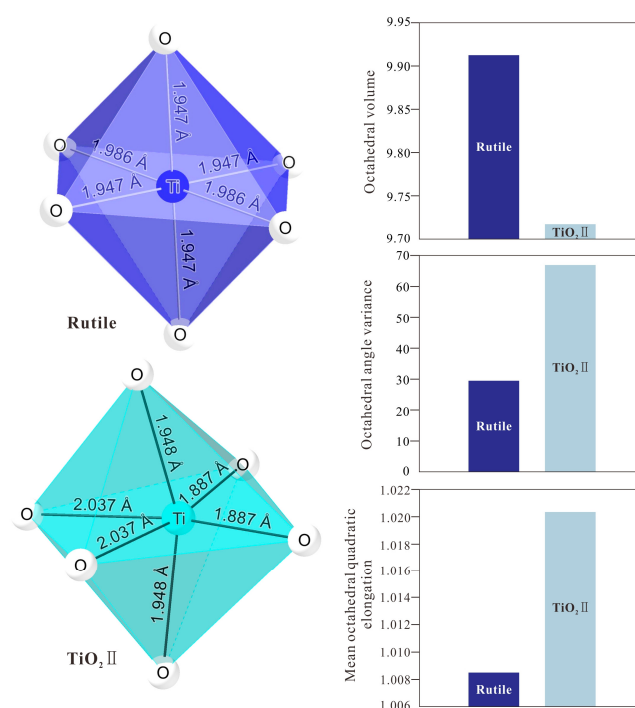


Figure 8. Structural representations and geometry parameters of octahedral sites in rutile and TiO₂II.

3.3. FTIR Spectroscopy

The representative mid-infrared spectrum of natural rutile in this study displays three absorption bands at 3280, 3295, and 3320 cm^{-1} in the wavenumber range of 3000 to 3800 cm^{-1} (Figure 9a). All these bands are ascribed to the O-H stretching vibration [2–4]. The main O-H band at 3280 cm^{-1} can be observed in the infrared spectra of both natural and synthetic rutile [1,2,4,28]. This band is attributed to H incorporated close to the shared O-O edge (the shortest edge of the TiO_6 octahedron) and is not associated with any substitutional defects in the crystal structure [29,30]. However, the two weak O-H bands at 3320 and 3295 cm^{-1} are, respectively, related to Ti^{3+} and Fe^{3+} impurities at the octahedral site [2,29,31]. The water contents of three rutile samples are estimated to be 1590, 1620, and 1780 ppm of H_2O by weight, respectively. The maximum water content of rutile generally increases with increasing inferred temperature and pressure [3]. Therefore, rutile from the UHP eclogite in this study has a relatively high water solubility compared to that of other crustal rocks. For instance, the maximum reported water concentration of rutile in pegmatite is only 820 ppm of H_2O by weight [3,21].

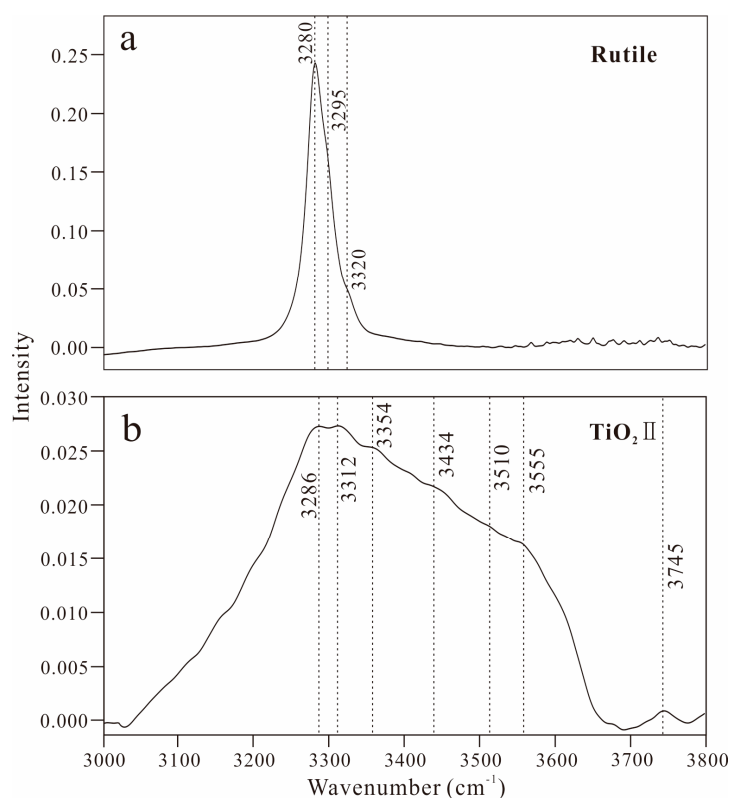


Figure 9. Representative mid-infrared absorption spectra of (a) natural rutile and (b) recovered TiO_2II under ambient conditions. The spectrum of rutile was normalized to 30 μm thickness but was vertically offset.

In the IR spectrum of recovered TiO_2II under ambient conditions, seven bands at 3286, 3312, 3354, 3434, 3510, 3555, and 3745 cm^{-1} can be observed (Figure 9b). All these bands are consistent with the reported bands of TiO_2II in the range of 3000 to 3800 cm^{-1} [7], implying that TiO_2II in the continental slabs can also contain certain amounts of water. The bands at 3354, 3434, 3510, 3555, and 3745 cm^{-1} are probably associated with longer O-O edges or O-O distances (>2.5143 Å) (Table 2), indicating the relatively weak effects of hydrogen bonding ($\text{O-H}\cdots\text{O}$) on O-H stretching [32–34]. Since the broad bands around 3400 to 3450 cm^{-1} can also be due to liquid water (or sub-microscopic fluid inclusions) in NAMs [3], the possibility that water molecules are taken up by TiO_2II after a phase transition occurs cannot be excluded. Since several hundred parts per million of water

in NAMs can trigger original partial melting of HP and UHP rocks [35], further studies on the pressure–temperature stability of hydroxyls in rutile and TiO₂II may also help to understand the transportation and release of water in continental slabs during deep subduction and exhumation.

4. Conclusions

(1) In situ high-pressure Raman spectroscopic measurements of natural rutile in an UHP eclogite indicate that the phase transition from rutile to baddeleyite-type TiO₂ terminates at about 16 GPa under compression at ambient temperature. The estimated pressure interval (13 to 16 GPa) of the transition is significantly narrower than that (12 to 21 GPa) reported in previous studies. Kinetic factors are expected to have influences on this transition at room temperature.

(2) According to single-crystal X-ray diffraction analyses, in the exhumated UHP rocks formed during deep continental subduction, the metastable TiO₂II can be characterized by highly distorted octahedra in the crystal structure. Under ambient conditions, X-ray powder diffraction analyses (with Cu K α radiation) are sufficient to identify the lamellae of TiO₂II within natural rutile based on the angles (2 θ) of two strong peaks at 25.5° and 31.5°

(3) Infrared spectroscopic investigations demonstrate that rutile and recovered TiO₂II in the continental slabs can contain certain amounts of water during deep subduction and exhumation. The estimated water contents of rutile in this study range from 1590–1780 ppm H₂O by weight. The bands with high frequencies (>3350 cm^{−1}) in the IR spectrum of recovered TiO₂II are probably attributed to H incorporated close to the long O–O edges (>2.5143 Å) of the TiO₆ octahedra.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/min13050703/s1>. Table S1: Unit-cell and atom position parameters for rutile and TiO₂II.

Author Contributions: L.Z. suggested the basis of the paper; X.L. (Xiaofeng Lu) and L.Z. wrote the paper; X.L. (Xiaofeng Lu) and S.G. performed in situ high-pressure Raman spectroscopic measurements. L.Z. and P.W. performed single-crystal X-ray diffraction analysis; X.L. (Xiaoguang Li) and Z.Z. performed infrared spectroscopic investigations; X.L. (Xiaofeng Lu) discussed the methods and results; X.Q. performed Raman spectroscopic measurements under ambient conditions. All authors have read and agreed to the published version of the manuscript.

Funding: This study was supported by the National Natural Science Foundation of China (nos. 42172044 and 41802035).

Data Availability Statement: The unit-cell and atom position parameters for rutile and TiO₂II have been added in the supplementary material file.

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Wang, S.; Zhang, J.H.; Smyth, J.R.; Zhang, J.F.; Liu, D.; Zhu, X.; Wang, X.; Ye, Y. Crystal Structure, Thermal Expansivity and High-Temperature Vibrational Spectra on Natural Hydrous Rutile. *J. Earth Sci.* **2020**, *31*, 1190–1199. [\[CrossRef\]](#)
2. Yang, Y.; Xia, Q.K.; Feng, M.; Gu, X.Y. In situ FTIR investigations at varying temperatures on hydrous components in rutile. *Am. Miner.* **2011**, *96*, 1851–1855. [\[CrossRef\]](#)
3. Johnson, E.A. Water in Nominally Anhydrous Crustal Minerals: Speciation, Concentration, and Geologic Significance. *Rev. Mineral. Geochem.* **2006**, *62*, 117–154. [\[CrossRef\]](#)
4. Vlassopoulos, D.; Rossman, G.R.; Haggerty, S.E. Coupled substitution of H and minor elements in rutile and implications of high OH contents in Nb- and Cr-rich rutile from the upper mantle. *Am. Miner.* **1993**, *78*, 1181–1191.
5. Endo, S.; Sato, H.; Tang, J.; Nakamoto, Y.; Kikegawa, T.; Shimomura, O.; Kusaba, K. Baddeleyite-type high-pressure phase of TiO₂ and its stable P–T region. *High-Press. Res. Appl. Earth Planet. Sci.* **1992**, *67*, 457–461.
6. Gerward, L.; Olsen, J.S. Post-rutile high-pressure phases in TiO₂. *J. Appl. Cryst.* **1997**, *30*, 259–264. [\[CrossRef\]](#)
7. Chen, F.; Su, W.; Li, X.G.; Hu, X.M.; Gao, J. In situ high temperature and high-pressure investigation of crystal structure and OH of rutile in jadeite quartzite from the Dabie Mountains, China. *Acta Petrol. Sin.* **2021**, *37*, 3893–3902.
8. Mammone, J.F.; Sharma, S.K.; Nicol, M. Raman study of rutile (TiO₂) at high pressure. *Solid State Commun.* **1980**, *34*, 799–802. [\[CrossRef\]](#)

9. Xiao, W.S.; Zhang, H.; Tan, D.Y.; Weng, K.N.; Li, Y.C.; Luo, C.J.; Liu, J.; Xie, H.S. Raman characterization of rutile phase transitions under high-pressure and high-temperature. *Spectrosc. Spect. Anal.* **2007**, *27*, 1340–1343.
10. Olsen, J.S.; Gerward, L.; Jiang, J.Z. On the rutile/ α -PbO₂-type phase boundary of TiO₂. *J. Phys. Chem. Solids* **1999**, *60*, 229–233. [\[CrossRef\]](#)
11. Goresy, A.E.; Ming, C.; Gillet, P.; Dubrovinsky, L.; Ahuja, R. A natural shock-induced dense polymorph of rutile with alpha-PbO₂ structure in the suevite from the Ries crater in Germany. *Earth Planet. Sc. Lett.* **2001**, *192*, 485–495. [\[CrossRef\]](#)
12. Meng, D.W.; Wu, X.L.; Fan, X.Y.; Zhang, Z.J.; Chen, H.; Meng, X.; Zheng, J.P. High pressure response of rutile polymorphs and its significance for indicating the subduction depth of continental crust. *Acta Geol. Sin.* **2008**, *82*, 371–376.
13. Wu, X.L.; Meng, D.W.; Han, Y.J. α -PbO₂-type nanophase of TiO₂ from coesite-bearing eclogite in the Dabie Mountains, China. *Am. Miner.* **2005**, *90*, 1458–1461. [\[CrossRef\]](#)
14. Liu, F.L.; Xu, Z.Q.; Xue, H.M.; Meng, F.C. Ultrahigh-pressure mineral inclusions preserved in zircons separated from eclogite and its country-rocks in the main drill hole of Chinese Continental Scientific Drilling Project (0–4500 m). *Acta Petrol. Sin.* **2005**, *21*, 277–292.
15. Zhang, Z.M.; Xiao, Y.L.; Hoefs, J.; Liou, J.G.; Simon, K. Ultrahigh pressure metamorphic rocks from the Chinese Continental Scientific Drilling Project: I. Petrology and geochemistry of the main hole (0–2,050 m). *Contrib. Mineral. Petr.* **2006**, *152*, 421–441. [\[CrossRef\]](#)
16. Klotz, S.; Chervin, J.C.; Munsch, P.; Le Marchand, G. Hydrostatic limits of 11 pressure transmitting media. *J. Phys. D Appl. Phys.* **2009**, *42*, 075413. [\[CrossRef\]](#)
17. Mao, H.K.; Xu, J.; Bell, P.M. Calibration of the ruby pressure gauge to 800-kbar under quasi-hydrostatic conditions. *J. Geophys. Res.* **1986**, *91*, 4673–4676. [\[CrossRef\]](#)
18. Sheldrick, G.M. *SHELXL: Programs for Crystal Structure Analysis*; University of Göttingen: Göttingen, Germany, 2018.
19. Farrugia, L.J. WinGX suite for small-molecule single-crystal crystallography. *J. Appl. Crystallogr.* **1999**, *32*, 837–838. [\[CrossRef\]](#)
20. Prince, E. *International Tables for Crystallography, Volume C: Mathematical Physical and Chemical Tables*, 3rd ed.; Reidel: Dordrecht, The Netherlands, 2004.
21. Maldener, J.; Rauch, F.; Gavranic, M.; Beran, A. OH absorption coefficients of rutile and cassiterite deduced from nuclear reaction analysis and FTIR spectroscopy. *Miner. Petrol.* **2001**, *71*, 21–29. [\[CrossRef\]](#)
22. Kovács, I.; Hermann, J.; O'Neill, H.; Gerald, J.F.; Sambridge, M.; Horváth, G. Quantitative absorbance spectroscopy with unpolarized light: Part II. Experimental evaluation and development of a protocol for quantitative analysis of mineral IR spectra. *Am. Miner.* **2008**, *93*, 765–778. [\[CrossRef\]](#)
23. Lan, T.; Tang, X.L.; Fultz, B. Phonon Anharmonicity of Rutile TiO₂ Studied by Raman Spectrometry and Molecular Dynamics Simulations. *Phys. Rev. B* **2012**, *85*, 094305. [\[CrossRef\]](#)
24. Porto, S.; Fleury, P.A.; Damen, T.C. Raman spectra of TiO₂, MgF₂, ZnF₂, FeF₂, and MnF₂. *Phys. Rev.* **1967**, *154*, 522. [\[CrossRef\]](#)
25. Lagarec, K.; Desgreniers, S. Raman study of single crystal Anatase TiO₂ up to 70 GPa. *Solid State Commun.* **1995**, *94*, 519–524. [\[CrossRef\]](#)
26. Robinson, K.; Gibbs, G.V.; Ribbe, P.H. Quadratic elongation: A quantitative measure of distortion in coordination polyhedra. *Science* **1971**, *172*, 567–570. [\[CrossRef\]](#)
27. Zhang, L.; Smyth, J.R. Crystal chemistry of metal element substitution in olivine and its high-pressure polymorphs: Implications for the upper-mantle and the mantle transition zone. *Earth-Sci. Rev.* **2022**, *232*, 104127. [\[CrossRef\]](#)
28. Johnson, O.; Ohlsen, W.; Kingsbury, P.J. Defects in rutile. III. Optical and electrical properties of impurities and charge carriers. *Phys. Rev.* **1968**, *175*, 1102–1108. [\[CrossRef\]](#)
29. Bromiley, G.D.; Hilairet, N. Hydrogen and minor element incorporation in synthetic rutile. *Mineral. Mag.* **2005**, *69*, 345–358. [\[CrossRef\]](#)
30. Bromiley, G.D.; Shiryayev, A.A. Neutron irradiation and post-irradiation annealing of rutile (TiO_{2-x}): Effect on hydrogen incorporation and optical absorption. *Phys. Chem. Miner.* **2006**, *33*, 426–434. [\[CrossRef\]](#)
31. Khomenko, V.; Langer, K.; Rager, H.; Fett, A. Electronic absorption by Ti³⁺ ions and electronic delocalization in synthetic blue rutile. *Phys. Chem. Miner.* **1998**, *25*, 338–346. [\[CrossRef\]](#)
32. Libowitzky, E. Correlation of O-H stretching frequencies and O-H...O hydrogen bond lengths in minerals. *Monatsh. Chem.* **1999**, *130*, 1047–1059. [\[CrossRef\]](#)
33. Nisr, C.; Leinenweber, K.; Prakapenka, V.; Prescher, C.; Tkachev, S.; Shim, S.-H. Phase transition and equation of state of dense hydrous silica up to 63 GPa. *J. Geophys. Res.-Sol. Earth* **2017**, *122*, 6972–6983. [\[CrossRef\]](#)
34. Xue, X.Y.; Kanzaki, M.; Fukui, H.; Ito, E.; Hashimoto, T. Cation order and hydrogen bonding of high-pressure phases in the Al₂O₃-SiO₂-H₂O system: An NMR and Raman study. *Am. Miner.* **2006**, *91*, 850–861. [\[CrossRef\]](#)
35. Seaman, S.J.; Williams, M.L.; Jercinovic, M.J.; Koteas, G.C.; Brown, L.B. Water in nominally anhydrous minerals: Implications for partial melting and strain localization in the lower crust. *Geology* **2013**, *41*, 1051–1054. [\[CrossRef\]](#)

Disclaimer/Publisher's Note: The statements, opinions and data contained in all publications are solely those of the individual author(s) and contributor(s) and not of MDPI and/or the editor(s). MDPI and/or the editor(s) disclaim responsibility for any injury to people or property resulting from any ideas, methods, instructions or products referred to in the content.