

1 **Effect of second Si-O vibrational overtones/combinations on quantifying water in**
2 **silicate and silica minerals using infrared spectroscopy, and an experimental**
3 **method for its removal**

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15

16 **Abstract**

17 Infrared spectroscopy (IR) is the most widely used analytical tool to quantify trace
18 water in silicate and silica minerals. A prerequisite for highly accurate IR measurements
19 of trace water is a good understanding of the effect of the second Si-O vibrational
20 overtones/composition bands (2nd Si-O VOCBs) on the water peaks. Silicate and silica
21 minerals can be divided as isolated (Q⁰), paired (Q¹), ring (Q²), chain (Q¹ or Q²), sheet
22 (Q³) and framework (Q⁴) structures according to the polymerization of their SiO₄
23 tetrahedral units, and the 2nd Si-O VOCBs of these different structural types attain
24 different vibrational features which are expected to affect the water peaks to different
25 extents. Here, we selected olivine (Q⁰) and α -quartz (Q⁴) as two endmember-like
26 structural examples, performed extensive IR measurements on both pristine and heat-
27 treated thin sections prepared for these two minerals, and explored the vibrational
28 features of the 2nd Si-O VOCBs. We have found that the 2nd Si-O VOCBs are well

29 separated from the water peaks in olivine, but severely overlap with the water peaks in
30 α -quartz, confirming the different roles that the 2nd Si-O VOCBs play in quantifying
31 trace water in silicate and silica minerals with different structural polymerizations. To
32 remove the influence of the 2nd Si-O VOCBs (or any other species rather than water),
33 an experimental protocol has been successfully developed, as approved by some
34 fundamental equations and verified by the data of α -quartz in the literature. This
35 development should lead to significant accuracy improvement in quantifying trace
36 amounts of water in Earth and planetary materials.

37

38 **Keywords** α -quartz • infrared spectroscopy • olivine • second Si-O vibrational
39 overtones/composition bands • silicate and silica minerals • water quantification

40

41 **Introduction**

42 Water is a key component of the Earth. On its surface, water dominates nearly all critical
43 processes, geological, meteorological and biological. In its interior, water tremendously
44 influences its melting (Asimow and Langmuir 2003; Liu et al. 2006), deformational
45 (Mackwell and Paterson 1985; Hirth and Kohlstedt 1996), electrical (Yoshino et al.
46 2006; Yang 2012), thermal (Hofmeister 2004) as well as seismic properties (Song et al.
47 2004; Schmandt et al. 2014), controls many important geological processes such as
48 plutonism, volcanism, convection and tectonics, and plays a vital role in the evolution
49 history of the Earth. With the hydrosphere making up only approximately 0.023% of
50 the Earth's mass (Kennish 1989), the majority of the Earth's water is supposed to be
51 stored in the materials of the Earth's interior, especially in those so-called nominally
52 anhydrous minerals (NAMs, i.e., minerals with no hydrogen required in their formulas;
53 Bell and Rossman 1992; Smyth and Jacobsen 2006).

54 Due to its disproportionally large effect, water in the NAMs should be quantified
55 as accurately as possible. Unlike other cations, hydrogens in the NAMs do not occupy
56 conventional crystallographic sites, but bond with oxygens to form hydroxyl groups or
57 water molecules. Infrared spectroscopy (IR) is highly sensitive to water (detection limit
58 < 0.5 wt ppm H_2O ; Peslier et al. 2017), capable to identify different species of water
59 (both H_2O and OH^- ; Aines and Rossman 1984) and determine the crystallographic
60 orientations of the O-H dipoles (Koch-Müller et al. 2001), and has world-wide
61 instrumental accessibility. Consequently, IR is presently the most ideal tool for accurate
62 water-quantification in the NAMs (Yan and Liu 2021).

63 Most NAMs are silicate and silica minerals. The basic structural units of these
64 minerals are SiO_4 tetrahedra. On the basis of polymerization of the SiO_4 tetrahedra
65 (number of bridging oxygen per tetrahedron, denoted as Q^n ; Putnis 1992), the structures
66 of these minerals can be grouped into isolated (Q^0), paired (Q^1), ring (Q^2), chain (Q^1 or
67 Q^2), sheet (Q^3) and framework (Q^4) groups (Fig. 1). It has long been known that as Q^n
68 increases, the mean distance of the Si-O bonds of the SiO_4 tetrahedra is not constant

69 but reduces (Liebau 1985). Consequently, the strength of the Si-O bonds changes, and
70 the Si-O fundamental stretching vibrations occur at different energies, from
71 wavenumbers as low as $\sim 521 \text{ cm}^{-1}$ to wavenumbers as high as $\sim 1316 \text{ cm}^{-1}$ (e.g., Hemley
72 1987; Freeman et al. 2008; Supplementary Table S1). Correspondingly, the first and
73 second Si-O vibrational overtones/combination bands (respectively termed as 1st Si-O
74 VOCBs and 2nd Si-O VOCBs hereafter) should appear in large energy ranges as well,
75 with the former and the latter mostly occurring from ~ 1000 to 2500 cm^{-1} and from
76 ~ 1500 to 3700 cm^{-1} , respectively. The 2nd Si-O VOCBs thus have the potentials to
77 overlap with the water peaks of the NAMs (usually appearing from ~ 3000 to 3750 cm^{-1} ;
78 ¹; Bell and Rossman 1992; Rossman 2006). They should be weak vibrational features,
79 but may strongly influence the water-quantifying process of the IR method.

80 To reveal the potential influences of the 2nd Si-O VOCBs, we have chosen olivine
81 (Ol; Q^0) and α -quartz (α -Qz; Q^4) as two extreme cases to conduct a detailed IR
82 investigation. The SiO_4 tetrahedra are fully isolated in Ol but fully polymerized in α -
83 Qz (Fig. 1). It is thus expected that the Si-O bonds in these two minerals may show the
84 largest difference in their bonding characteristics, leading to the largest difference in
85 the energies of the 2nd Si-O VOCBs. Consequently, the interaction between the 2nd Si-
86 O VOCBs and the O-H stretching modes may vary to its maximum degree, and then
87 can be well exposed. To achieve this goal, we carried out extensive IR analyses on Ol
88 and α -Qz thin sections with large ranges of sample thickness, and conducted a
89 prolonged heat-treating experiment with one α -Qz thin section. Indeed, our
90 experimental observations have demonstrated that as the SiO_4 tetrahedron becomes
91 more polymerized, the impact of the 2nd Si-O VOCBs on the water quantification
92 becomes more significant. In order to get rid of the influence of the 2nd Si-O VOCBs,
93 we have further arrived at some fundamental equations which lead to a new
94 experimental scheme for accurately quantifying water in Earth and planetary materials.
95 Adopting this new method, the accuracy of the IR measurements of trace water can be
96 significantly improved.

97

98

99 **Experimental details**

100

101 Ol and α -Qz specimens and thin section preparation

102 The Ol crystals used in this study were separated from a spinel lherzolite xenolith

103 enclosed in the Cenozoic basalts around the Hannuoba region, North China Craton.

104 According to Yang et al. (2008), they should have an Mg# of ~ 89 , and contain no

105 discernable water. Some optically clear crystals, with neither visible cracks nor

106 mineral/fluid inclusions, were selected for our IR measurements. Two types of thin

107 sections were prepared. On one hand, 12 Ol plates, randomly cut out of some of the

108 clear crystals and with unknown crystallographic orientations, were mounted and then

109 doubly-polished to a roughly similar sample thickness of ~ 2 mm. They were used to

110 examine the influence of different crystallographic orientations on the 2nd Si-O VOCBs.

111 On the other hand, one of the 12 Ol plates was randomly selected, and repeatedly

112 mounted, thinned down to certain thickness and analyzed by IR. This practice aimed at

113 the effect of sample thickness on the 2nd Si-O VOCBs.

114 The α -Qz crystal used in this study and that one used in He et al. (2019) to

115 investigate the fundamental IR absorption features belonged to the same crystal cluster

116 collected from Donghai County of Jiangsu Province, China. It was a clear, colorless

117 and euhedral α -Qz prism (~ 60 mm in height and ~ 18 mm in diameter), without any

118 visible fracture or inclusion. Its composition is almost 100% SiO₂ (13 electron

119 microprobe analyses). It contains low levels of Li (54(5) wt ppm), B (0.8(4) wt ppm),

120 Na (19(5) wt ppm), Al (873(81) wt ppm) and Ti (1.4(2) wt ppm), as suggested by eight

121 laser-ablation inductively-coupled-plasma mass-spectrometry analyses (for the

122 technical details, see Yan et al. (2021a)). Its crystallographic orientation was readily

123 ascertained by resorting to its perfect morphology. One crystal plate perpendicular to

124 the optical axis ($\perp[0001]$; Z-cut) was cut out of this crystal, and then repeatedly

125 mounted, thinned down (from ~2991 to 90 μm) and analyzed by IR for 20 times.
126 Previous experimental and theoretical studies (e.g., Kats 1962; Shinoda and Aikawa
127 1993; Stalder and Konzett 2012; Jollands et al. 2020) have suggested that the OH
128 dipoles in α -Qz are oriented almost perpendicular to the optical axis. This crystal plate
129 is thus suitable for our purpose, examining the effect of the 2nd Si-O VOCBs on the
130 water peaks.

131 The technical details in preparing the parallel-sided, stand-alone, doubly-polished
132 thin sections for later heat-treating experiments and IR measurements were generally
133 similar to those reported in Liu et al. (2017) and Yan et al. (2021b). They are thus not
134 repeated here. The accuracy in the thickness measurement of the thin sections was
135 approximately $\pm 2 \mu\text{m}$.

136

137 Heat-treating experiment of α -Qz thin section at 1 atm

138 Another *Z*-cut thin section (~1198- μm -thick) was cut out of the α -Qz crystal, doubly-
139 polished, and then heated at ambient *P* by using a KSL-1100X muffle furnace. To avoid
140 the room-*P* α - β phase transition of Qz (Hu et al. 2011), we chose a heat-treating
141 temperature of 500 °C. The crystal plate was laid on a Pt foil, placed near the hot
142 junction of the controlling K-type thermocouple of the furnace, heated up to 500 °C
143 with a ramp of 5 °C/min, and heated for 1109.5 h (or ~46 d). The accuracy of the
144 temperature measurement in the heat-treating experiment should be better than $\pm 5 \text{ }^\circ\text{C}$
145 (Ma et al. 2021). The heat-treating process was interrupted three times (at accumulated
146 heat-treating times of 164.5, 359.5 and 557.5 h) by removing the crystal plate out of the
147 furnace, cooling it in air, and analyzing it with IR.

148

149 IR measurements

150 Fourier transform infrared spectra (FTIR) were recorded at ambient *P-T* conditions
151 using unpolarized transmitted light with a Nicolet iN10 MX IR Microscope installed at
152 the High-Pressure Laboratory of Peking University (Tang et al. 2014). The IR beam

153 emitted by a high-energy Ever-GloTM infrared source was reflected via a standard KBr
154 beam splitter and focused through sample plate onto a liquid-nitrogen-cooled MCT
155 detector. To avoid surface contamination by room-air humidity, our thin sections were
156 always stored in an oven at 110 °C prior to being analyzed. A clean BaF₂ sample holder
157 was used to facilitate our IR measurements. IR data were acquired in the wavenumber
158 range of 4000–675 cm⁻¹ with a spectral resolution of 4 cm⁻¹. A squared sampling area
159 of 100 × 100 or 150 × 150 μm² was used, and 512 IR scans were accumulated for every
160 individual analysis, both for the background and for the sample (with the background
161 analyzed first).

162 For the IR analyses performed on the heat-treated α -Qz Z-cut thin section, the same
163 part of the crystal plate was probed. This is important. As pointed out by Kats (1962),
164 euhedral α -Qz crystals do not usually show complete compositional homogeneity
165 which may lead to poor internal consistency in the results. Moreover, different parts of
166 a nominally parallel crystal plate may practically attain some small fluctuation in their
167 real thickness (Liu et al. 2020). For the IR analyses performed on the α -Qz crystal plates
168 with different thicknesses, similarly, the analyzed parts were kept as close to the central
169 part as possible.

170 The baselines of the IR spectra were manually corrected, as exemplified in Fig. 2.
171 We conducted a spline-fit correction to all IR spectra collected from the Ol crystal plates
172 by using the Fityk software (Wojdyr 2010), and a linear correction to all IR spectra
173 collected from the α -Qz crystal plates by employing the OMNIC 8.2 software. The IR
174 features of interest, both for Ol and α -Qz, always contain multiple components. The
175 determination of the position and absorbance of these component peaks was
176 accomplished by deconvoluting the baseline-corrected spectra into multiple Gaussian-
177 Lorentzian components with the PeakFit V4.12 software, as shown in Fig. 2.

178 With the Beer-Lambert law, the water content of our α -Qz was estimated using the
179 unpolarized transmission FTIR measurements. Adopting the routine treatment that all
180 peaks in the energy range from 3650 to 3250 cm⁻¹ are related to water (e.g., Müller and

181 Koch-Müller 2009; Thomas et al. 2009; Stalder et al. 2017; Potrafke et al. 2019, 2020),
182 the total absorbance was approximated as $2 \times A_{(\text{unpol}, Z\text{-cut})}$ (Paterson 1982; Pankrath 1991;
183 Stalder and Konzett 2012), with $A_{(\text{unpol}, Z\text{-cut})}$ representing the integral absorbance in the
184 unpolarized IR spectra taken from the Z-cut thin sections. Using the Qz-specific
185 calibration of Thomas et al. (2009; $89000(15000) \text{ L mol}^{-1}_{\text{H}_2\text{O}} \text{ cm}^{-2}$), the initial H₂O
186 content of our α -Qz was estimated as $\sim 23(5)$ wt ppm.

187

188

189 **Experimental results**

190

191 The Ol case: 2nd Si-O VOCBs and their interaction with water peaks

192 As one extreme case, Ol has its SiO₄ tetrahedra non-bonded to each other and sharing
193 no oxygen atoms (Birle et al. 1968; Fig. 1). Its intense fundamental IR- and Raman-
194 active Si-O stretching vibrational modes appear at $\sim 993\text{--}838 \text{ cm}^{-1}$ (Noel et al. 2006;
195 Wang et al. 2015) and at $\sim 966\text{--}828 \text{ cm}^{-1}$ (Servoin and Piriou 1973; Kolesov and Geiger
196 2004), respectively (see Supplementary Table S1). Accordingly, its weak 1st Si-O
197 VOCBs are expected to locate at $\sim 1986\text{--}1656 \text{ cm}^{-1}$, as experimentally confirmed by
198 Jamtveit et al. (2001), Asimow et al. (2006), and Wang et al. (2015). In the case of the
199 2nd Si-O VOCBs, they are anticipated to occur near $\sim 2979\text{--}2484 \text{ cm}^{-1}$, but had not been
200 experimentally demonstrated before this study.

201 Fig. 3 shows the unpolarized IR spectra ($\sim 2800\text{--}2400 \text{ cm}^{-1}$) taken from those Ol
202 crystal plates (~ 2 mm thick) randomly cut out of our Ol crystals. In general, there are
203 five IR peaks constantly observed at $\sim 2748, 2661, 2615, 2505$ and 2491 cm^{-1} , and one
204 additional peak occasionally found at $\sim 2568 \text{ cm}^{-1}$. Presumably due to the variation of
205 the crystallographic orientation of the Ol crystal plates, the intensities of these IR peaks
206 attain some variations, but their positions are generally fixed. Since the water peaks of
207 Ol usually appear in a very different energy range, i.e., $\sim 3630\text{--}3160 \text{ cm}^{-1}$ (e.g., Lemaire

208 et al. 2004; Wang et al. 2020; Supplementary Table S1), these 2nd Si-O VOCBs should
209 have no effect on quantifying water.

210 Additionally, the third Si-O vibrational overtones/combination bands (3rd Si-O
211 VOCBs hereafter) should have no effect on quantifying the water content of Ol, as
212 [experimentally demonstrated by Mosenfelder et al. \(2011\)](#). They should appear at
213 higher wavenumbers than those shown in Fig. 3, possibly overlap with the water peaks,
214 but must be too weak to affect the water peaks in any ways. The evolution of the 1st and
215 2nd Si-O VOCBs with sample thickness is shown in Fig. 4. The dependence of the
216 integral absorbance area of the 2nd Si-O VOCBs on the plate thickness is demonstrated
217 in Fig. 5. The thickness of the Ol crystal plates usually employed in water-quantifying
218 IR measurements is commonly less than 200 μm (e.g., Jamtveit et al. 2001; Kovács et
219 al. 2010), so that the integral absorbance area of the 2nd Si-O VOCBs should be less
220 than 0.5 cm^{-1} (Fig. 5). Furthermore, the 1st Si-O VOCBs are commonly ~ 100 times
221 weaker than the fundamentals (Bowey and Hofmeister 2005), the 2nd Si-O VOCBs are
222 also ~ 100 times weaker than the 1st Si-O VOCBs (Fig. 4; the ratio of the integral
223 absorbance areas is ~ 0.0060 for the spectrum collected with the 452- μm -thick sample,
224 and ~ 0.0036 for the spectrum collected with the 200- μm -thick sample), and the 3rd Si-
225 O VOCBs are expected to be ~ 100 times weaker than the 2nd Si-O VOCBs. It follows
226 that for a ~ 200 - μm -thick Ol sample, the integral absorbance area of the 3rd Si-O VOCBs
227 should largely be less than 0.005 cm^{-1} , i.e., completely negligible in the water
228 quantification.

229

230 The α -Qz case: 2nd Si-O VOCBs and their interaction with water peaks

231 As the other extreme case, α -Qz has its all SiO_4 tetrahedra linked together, via oxygen-
232 sharing, to form a three-dimensional framework (Fron del 1962; Fig. 1). Its Si-O bonds
233 are thus stronger than those in Ol, resulting in relatively higher energies for the normal
234 Si-O stretching vibrational modes. Indeed, these fundamental IR-active and Raman-
235 active Si-O stretching vibrational modes occur at ~ 1249 – 697 cm^{-1} and ~ 1231 – 695 cm^{-1}

236 ¹, respectively (e.g., Ocaña et al. 1987; He et al. 2019; Supplementary Table S1), much
237 higher than those in Ol. Consequently, the 1st Si-O VOGBs of α -Qz locate at higher
238 energies, i.e., $\sim 2470\text{--}1390\text{ cm}^{-1}$, as observed by Kats (1962) and Shinoda and Aikawa
239 (1994). Similarly, the 2nd Si-O VOGBs should appear at higher energies, probably in
240 the energy range of $\sim 3747\text{--}2085\text{ cm}^{-1}$. They may hence overlap with the water peaks
241 from ~ 3650 to 3250 cm^{-1} (Aines and Rossman 1984; Kronenberg 1994; Table 1 and
242 Supplementary Table S1).

243 Figure 6a displays the general IR features of α -Qz in the energy range of
244 $3800\text{--}3000\text{ cm}^{-1}$, as collected from our Z-cut thin sections (thickness varying from ~ 90
245 to $2991\text{ }\mu\text{m}$). Eight IR peaks at ~ 3530 , 3511 , 3482 , 3437 , 3403 , 3378 , 3312 and 3199
246 cm^{-1} constantly show up, but two peaks at ~ 3400 and $\sim 3585\text{ cm}^{-1}$ never appear. A broad
247 peak at $\sim 3400\text{ cm}^{-1}$ was occasionally observed and attributed to trace water molecules
248 in α -Qz (Aines and Rossman 1984; Rovetta et al. 1986). A sharp peak at $\sim 3585\text{ cm}^{-1}$
249 was more frequently observed and assigned to hydrogarnet defects (4H^+ replacing Si^{4+} ,
250 or $(4\text{H})_{\text{Si}}$ defects) in α -Qz (e.g., Chakraborty and Lehmann 1976; Paterson 1986;
251 Rovetta 1989; Stalder and Konzett 2012).

252 The eight IR peaks have different spectroscopic characteristics (Fig. 2b and Table
253 1), and different origins. There are severe interactions between the IR peaks of different
254 origins, which may affect the water-quantifying process with the IR method.

255 The IR peak at $\sim 3199\text{ cm}^{-1}$ is relatively weak and diffusive (full-width at half
256 maximum-height, or FWHM, being $\sim 49\text{ cm}^{-1}$), and can be confidently assigned as a 2nd
257 Si-O VOGB, following Kats (1962), Dodd and Fraser (1965), Kronenberg et al. (1986),
258 Bachheimer (1998), Müller and Koch-Müller (2009), Jollands et al. (2020), etc. Biró et
259 al. (2016) had another interpretation, and attributed this peak to tetrahedrally-
260 coordinated surface-absorbed water molecules. Nevertheless, this peak does not
261 represent any hydrogen defects in α -Qz, and should be excluded in water-quantifying
262 (Müller and Koch-Müller 2009; Stalder 2021). Further, the Qz-specific IR calibration
263 of Thomas et al. (2009) has been established on this basis.

264 The IR peak at $\sim 3312 \text{ cm}^{-1}$ is even more diffusive than that at $\sim 3199 \text{ cm}^{-1}$ (Fig. 2b
265 and Table 1; FWHM = $\sim 73 \text{ cm}^{-1}$), a phenomenon previously observed by Müller and
266 Koch-Müller (2009; FWHM = $66(17) \text{ cm}^{-1}$). It implies at least two components for this
267 peak. Indeed, it has long been recognized that one 2nd Si-O V_{OCB} and one water peak
268 related to Al in α -Qz ($\text{H}^+ + \text{Al}^{3+}$ replacing Si^{4+} , or $(\text{H} + \text{Al})_{\text{Si}}$ defects) occur around this
269 energy (Kats 1962; Bachheimer 1998; Jollands et al. 2020). What remains uncertain is
270 the relative contributions of these two components, resulting in two different treatments
271 of the peak at $\sim 3312 \text{ cm}^{-1}$, i.e., one-component peak (water peak only; e.g., Thomas et
272 al. 2009; Stalder et al. 2017) or two-component peak (Jollands et al. 2020; Fig. 6a).
273 Existing heat-treating experiments (e.g., Kats 1962; Bachheimer 1998) could have
274 provided some constraints on this issue if the experimental details such as sample
275 thickness, heat-treating temperature and heat-treating time had been reported: without
276 these details, the residual water contents in the heat-treated samples could not be
277 critically assessed.

278 There are two more IR peaks related to the $(\text{H} + \text{Al})_{\text{Si}}$ defects in α -Qz, at ~ 3378
279 and $\sim 3437 \text{ cm}^{-1}$ (Kats 1962; Pankrath 1991; Stalder 2021). Although good agreement
280 on their origins has been reached and consistent treatment in water-quantifying has been
281 applied, there is potential uncertainty about the peak at $\sim 3437 \text{ cm}^{-1}$: it is a rather
282 diffusive peak (Fig. 2b). Its FWHM, observed as $\sim 46 \text{ cm}^{-1}$ by Müller and Koch-Müller
283 (2009) and by this study (Table 1), is much larger than that of the water peak at ~ 3378
284 cm^{-1} (less than $\sim 30 \text{ cm}^{-1}$). Taking into account the Al and Li abundances in our sample
285 (873(81) versus 54(5) wt ppm), it may hence contain two components, with the major
286 one related to the $(\text{H} + \text{Al})_{\text{Si}}$ defects and the minor one related to some Li-specific
287 hydrogen defects (Kats 1962). The Al and Li abundances in the samples investigated
288 by Müller and Koch-Müller (2009) ranged up to ~ 100 and 12 wt ppm, respectively.

289 The peaks at ~ 3403 , ~ 3482 and $\sim 3511 \text{ cm}^{-1}$ shown in Fig. 2b and Fig. 6a are also
290 likely related to the Li-specific hydrogen defects in α -Qz (Kats 1962; Baron et al. 2015;

291 Frigo et al. 2016; Stalder 2021). As previously observed, the peak at $\sim 3482\text{ cm}^{-1}$ is the
292 most obvious one.

293 The IR peak at $\sim 3530\text{ cm}^{-1}$ is weak and diffusive, and thus subjected to large
294 uncertainty (Fig. 2b and Table 1). According to Kats (1962), it can be assigned to some
295 Na-specific hydrogen defects in α -Qz (19(5) wt ppm Na in our sample).

296 Briefly, the IR peak at $\sim 3199\text{ cm}^{-1}$ is a 2nd Si-O VOCB, the six IR peaks at 3378,
297 3403, 3437, 3482, 3511 and 3530 cm^{-1} are related to various hydrogen defects, and the
298 IR peak at $\sim 3312\text{ cm}^{-1}$ may be caused both by the Si-O vibrations and by the O-H
299 vibrations in α -Qz.

300 The relationship between the absorbance of these IR peaks and the sample
301 thickness may shed light on the relative contributions to the formation of the IR peak
302 at $\sim 3312\text{ cm}^{-1}$ made by the Si-O vibrations and by the O-H vibrations (Fig. 6b). It is
303 well known that a negative correlation between the molar absorption coefficients and
304 wavenumbers exists for the water peaks (e.g., Paterson 1982; Skogby and Rossman
305 1991; Libowitzky and Rossman 1997; Yan and Liu 2021). This implies that the
306 dependences of the water peaks at lower energies on sample thickness (e.g., the slope
307 of the broken line for the 3378 cm^{-1} peak in Fig. 6b) should be larger than those of the
308 water peaks at higher energies (e.g., the slope of the broken line for the 3511 cm^{-1} peak
309 in Fig. 6b). Clearly, the slope of the IR band at $\sim 3312\text{ cm}^{-1}$ for our α -Qz is much
310 comparable to that of the water peak at 3378 cm^{-1} and remarkably different to that of
311 the 2nd Si-O VOCB at $\sim 3199\text{ cm}^{-1}$ (Fig. 6b), suggesting that our IR band at $\sim 3312\text{ cm}^{-1}$
312 is largely a water peak. In contrast, its counterpart in some of the IR spectra reported
313 for Qz by Jollands et al. (2020; e.g., those two shown in Fig. 6a), appearing at a much
314 lower energy of $\sim 3293\text{ cm}^{-1}$, is mostly a 2nd Si-O VOCB.

315 Additionally, the 2nd Si-O VOCBs of α -Qz are likely intense enough to affect the
316 water peaks. As demonstrated by Wang et al. (2015) and He et al. (2019), the Si-O
317 fundamentals of α -Qz are much stronger than those of Ol, which can be readily
318 explained by a higher density of the SiO_4 polyhedron in the former than in the latter.

319 Naturally, much stronger 1st Si-O VOCBs and 2nd Si-O VOCBs are expected for α -Qz.
320 More importantly, the 1st Si-O VOCBs of α -Qz are unusually strong (Fig. 7): as
321 obtained from the IR spectrum of the 7- μ m-thick thin section, the ratio of the integral
322 absorbance areas of the 1st Si-O VOCBs (2100–1400 cm⁻¹) and the fundamentals
323 (1400–675 cm⁻¹) is \sim 0.116, which is about ten times larger than the commonly
324 anticipated value \sim 0.01 (Bowey and Hofmeister 2005); the integral absorbance areas
325 are respectively \sim 34.578 and \sim 298.893 cm⁻¹. Due to the positive correlation between
326 the 1st Si-O VOCBs and the 2nd Si-O VOCBs, the 2nd Si-O VOCBs of α -Qz are expected
327 to be unusually intense, and potentially influence the water peaks.

328

329 The α -Qz case: further evidence from heat-treating experiment

330 In principle, the roles that a 2nd Si-O VOCB and an O-H stretching vibration play in the
331 formation of an IR feature can be discriminated by performing heat-treating experiment
332 (see Supplementary Fig. S1). If the heat-treating duration is long enough, water will be
333 fully driven out, so that an IR peak fully aroused by the O-H vibration will progressively
334 reduce its intensity and eventually reach zero absorbance (Supplementary Fig. S1a),
335 that fully caused by the Si-O vibration will retain its intensity (Supplementary Fig. S1b),
336 and that with a mixed origin will slowly decrease its intensity but never reach zero
337 absorbance (Supplementary Fig. S1c).

338 Figure 8a shows the IR spectra (from \sim 3650 to 3000 cm⁻¹) collected from the thin
339 section heat-treated at 500 °C. Figs. 8b–8i show the trends between the peak heights
340 and the accumulated heat-treating durations for the eight IR peaks at \sim 3199, 3312, 3378,
341 3403, 3437, 3482, 3511 and 3530 cm⁻¹. Clearly none of the IR peaks reached zero
342 absorbance.

343 To aid the interpretation of the results, water diffusion curves have been calculated
344 by adopting a one-dimension diffusion model. This is justified simply because the
345 thickness of the sample is much smaller than its width. As our heat-treating experiment
346 progressed, the crystal plate slowly dehydrated, and the averaged water concentration

347 (c_{av}) across the crystal plate as a function of heating time could be expressed as follows
348 (Carslaw and Jaeger 1959; Ingrin et al. 1995):

349
$$c_{av} = \frac{8c_0}{\pi^2} \sum_{n=0}^{\infty} \frac{1}{(2n+1)^2} \exp\left(-\frac{Dt(2n+1)^2\pi^2}{(2L)^2}\right) \quad (1),$$

350 where c_0 is the initial concentration of water, D is the diffusion coefficient at 500 °C, t
351 is the heating time and $2L$ is the thickness of the crystal plate. The diffusion coefficient
352 at 500 °C obtained for the Z -axis direction of α -Qz by Kats (1962; $2.4 \times 10^{-14} \text{ m}^2 \text{ s}^{-1}$) is
353 used in our calculation. The results are shown as solid curves in Figs. 8b–8i. To account
354 for the fact that different hydrogen species in α -Qz may behave differently (Kats 1962;
355 Kronenberg and Kirby 1987), additional calculations have been executed with 10 times
356 larger and 10 times smaller diffusion coefficients.

357 As expected, the results of our heat-treating experiments have put further
358 constraints on the origins of those IR peaks in the energy range of 3800 to 3000 cm^{-1} .
359 On one hand, Fig. 8a does not show any significant change in the overall pattern of the
360 IR spectra as the heat-treating process advances. On the other hand, Figs. 8b–8i clearly
361 demonstrate rather different behaviors for the individual IR peaks. Due to the fast
362 transport rate of Li in α -Qz (Kronenberg and Kirby 1987), the IR peaks at ~ 3403 , 3482
363 and 3511 cm^{-1} caused by the Li-specific hydrogen defects steadily decrease their
364 intensity, and the experimentally observed trends generally match the curves calculated
365 by the one-dimension diffusion model (Figs. 8e, 8g, 8h). The mobile Na-specific
366 hydrogen defects in α -Qz behave similarly (Fig. 8i). On the contrary, the IR peak at
367 $\sim 3199 \text{ cm}^{-1}$ assigned as a 2nd Si-O VOGB does not show much intensity reduction, and
368 the experimentally observed trend significantly deviates from the calculated curve (Fig.
369 8b). It is well known that the Al-specific hydrogen defects in α -Qz are extremely stable
370 at temperatures like 500 °C (Kats 1962), so that their IR peaks may behave much similar
371 to the 2nd Si-O VOGB rather than typical water peak. Indeed, the IR peaks at ~ 3312 ,
372 3378 and 3437 cm^{-1} show little intensity decrease, and their trends significantly deviate
373 from the calculated curves (Figs. 8c, 8d, 8f). Nevertheless, all these three IR peaks
374 simultaneously decrease their intensities at the initial stage of the heat treatment and

375 show no much change at later stages, implying that they have similar origins. It is
376 interesting to see that the IR peak at $\sim 3312\text{ cm}^{-1}$, which contains a minor component
377 aroused by the Si-O vibration, shows a slightly weaker intensity reduction, as compared
378 to the two peaks at 3378 and 3437 cm^{-1} .

379 Summarily, the observations made with the heat-treating experiment support our
380 previous assignments of the IR peaks in the energy range of $3800\text{--}3000\text{ cm}^{-1}$. The
381 coexistence in similar energy ranges of the 2nd Si-O VOCBs and the water peaks in α -
382 Qz inevitably leads to strong interaction which can affect the water-quantifying process
383 of IR.

384

385 **Discussions**

386 Effect of overlapping IR features on quantifying water and an experimental method for
387 its removal

388 Quantifying water with the IR method employs the Beer-Lambert law. According to
389 this law, the integral absorption area (A_i) of a species in a material (i) is related to the
390 concentration of this species (c_i) and the thickness of the sample (d), as following:

$$391 \quad A_i = c_i \times d \times \varepsilon_i \quad (2),$$

392 where ε_i is the integrated molar absorption coefficient. To make Eq. (2) useful to water
393 quantification, much work has been devoted to establishing material-specific IR
394 calibrations, i.e., determining $\varepsilon_{\text{H}_2\text{O}}$ values for different materials (e.g., Bell et al. 1995,
395 2003; Johnson and Rossman 2003; Thomas et al. 2009; Koch-Müller and Rhede 2010).
396 Determining $\varepsilon_{\text{H}_2\text{O}}$ can be straightforward, provided that the water content of some
397 standards of the material in interest is accurately quantified by some independent
398 method, the sample thickness is precisely measured, and the water peaks do not overlap
399 with any other IR peaks of a different origin. On the other hand, it can be complicated
400 when the water peaks intensely overlap with the IR signals of another species, e.g., the
401 2nd Si-O VOCBs of α -Qz (Fig. 6a). These extra IR signals are usually hard to remove
402 so that frequently they have to be treated as water signals. The thus-calibrated material-

403 specific $\varepsilon_{\text{H}_2\text{O}}$ is hence somewhat impaired and may lead to large uncertainty when
404 used to quantify trace water.

405 With the case of α -Qz as an example, we demonstrate below that the effect of the
406 extra overlapping IR signals aroused by another species i rather than water can be
407 successfully removed, real mineral-specific $\varepsilon_{\text{H}_2\text{O}}$ and ε_i can be obtained, and highly
408 accurate measurements with IR for trace water can be feasible.

409 Three α -Qz standards with different water contents ($c_{\text{H}_2\text{O}-1}$, $c_{\text{H}_2\text{O}-2}$ and $c_{\text{H}_2\text{O}-3}$)
410 are shown in Fig. 9. At any specific sample thickness, the as-measured integral
411 absorbance (A_{total}) contains two components, one for the O-H vibrations ($A_{\text{H}_2\text{O}}$) and
412 the other for the 2nd Si-O VOCBs ($A_{\text{Si-O}}$), so that $A_{\text{total}-1} = A_{\text{Si-O}} + A_{\text{H}_2\text{O}-1}$,
413 $A_{\text{total}-2} = A_{\text{Si-O}} + A_{\text{H}_2\text{O}-2}$ and $A_{\text{total}-3} = A_{\text{Si-O}} + A_{\text{H}_2\text{O}-3}$. As the ratio of $A_{\text{H}_2\text{O}}$ to
414 A_{total} is obviously not constant, the calibration should lead to different $\varepsilon_{\text{H}_2\text{O}}$ values.
415 In other words, $\varepsilon_{\text{H}_2\text{O}}$ should be dependent on $c_{\text{H}_2\text{O}}$.

416 To further explore this dependence, we rewrite Eq. (2) into

$$417 \quad \varepsilon_i = A_i / (c_i \times d) \quad (3),$$

418 and then have

$$419 \quad \varepsilon_{\text{total}} = (A_{\text{H}_2\text{O}} + A_{\text{Si-O}}) / (c_{\text{H}_2\text{O}} \times d) \quad (4)$$

420 for the water-in-Qz IR calibration process. Expanding Eq. (4) yields the following
421 equation,

$$422 \quad \varepsilon_{\text{total}} = \varepsilon_{\text{H}_2\text{O}} + (A_{\text{Si-O}}/d) / c_{\text{H}_2\text{O}} \quad (5),$$

423 with $\varepsilon_{\text{total}}$ being a nominal value which is usually obtained from the IR calibration
424 experiments, and $\varepsilon_{\text{H}_2\text{O}}$ being a true value which is commonly undetermined though.

425 Clearly, $A_{\text{Si-O}}/d$ in Eq. (5) is the integrated molar absorption coefficient for the 2nd Si-O
426 VOCBs in α -Qz (i.e., $\varepsilon_{\text{Si-O}}$), and must be constant. Eq. (5) thus resembles the function

$$427 \quad y = a + b/x \quad (6),$$

428 with y representing $\varepsilon_{\text{total}}$ from the IR calibration experiment, x standing for $c_{\text{H}_2\text{O}}$ of the
429 standards, and a and b being two constants. It follows that the true value of $\varepsilon_{\text{H}_2\text{O}}$ may
430 be approximately obtained by calibration experiments performed on some water-rich

431 standards. As to the $\varepsilon_{\text{Si-O}}$, it should be better constrained with experiments performed
432 on standards with zero water.

433 The water-in-Qz IR calibration by Thomas et al. (2009) did generate highly
434 variable $\varepsilon_{\text{total}}$, from which an averaged value of $89000(15000) \text{ L mol}_{\text{H}_2\text{O}}^{-1} \text{ cm}^{-2}$ was
435 obtained. Their data, as plotted in Fig. 10, clearly show a correlation between $\varepsilon_{\text{total}}$ and
436 $c_{\text{H}_2\text{O}}$. Fitting these data to Eq. (5), we obtain $\varepsilon_{\text{H}_2\text{O}} = 78899(10661) \text{ L mol}_{\text{H}_2\text{O}}^{-1} \text{ cm}^{-2}$
437 and $\varepsilon_{\text{Si-O}} = 786940(759295) \text{ l mol}_{\text{SiO}_2}^{-1} \text{ cm}^{-2}$. Obviously $\varepsilon_{\text{Si-O}}$ is poorly constrained.

438 Alternatively, $\varepsilon_{\text{Si-O}}$ can be much better determined by using the IR analyses on two
439 nearly dry Qz crystals from Jollands et al. (2020; Q6L5 and Q6L7). These IR analyses,
440 shown as curves in the bottom of Fig. 6a, display two peaks (~ 3378 and 3293 cm^{-1}) at
441 wavenumbers between 3650 and 3250 cm^{-1} . Assumed as water peaks, they would have
442 altogether indicated $\sim 3(1)$ wt ppm water. Yet, a quick comparison of these two peaks to
443 the water peaks of our much water-rich α -Qz samples (with $\sim 23(5)$ wt ppm H_2O)
444 reveals that the major peak at $\sim 3293 \text{ cm}^{-1}$ is largely caused by the Si-O vibrations rather
445 than by water (Fig. 6a). Nevertheless, the minor peak at $\sim 3378 \text{ cm}^{-1}$ implies some water
446 in their Qz, likely close to zero though. Ignoring this trace water, we obtain $\varepsilon_{\text{Si-O}} =$
447 $592.0(696) \text{ L mol}_{\text{SiO}_2}^{-1} \text{ cm}^{-2}$ (Fig. 11).

448 With $\varepsilon_{\text{Si-O}} = 592.0(696) \text{ L mol}_{\text{SiO}_2}^{-1} \text{ cm}^{-2}$, we can use Eq. (5) to make corrections
449 to the data from Thomas et al. (2009). Removing its dependence on the water content,
450 $\varepsilon_{\text{total}}$ becomes equal to $\varepsilon_{\text{H}_2\text{O}}$, attaining $88279(5669) \text{ L mol}_{\text{SiO}_2}^{-1} \text{ cm}^{-2}$ (Fig. 10). This
451 value is in remarkable agreement with that from Thomas et al. (2009;
452 $89000(15000) \text{ L mol}_{\text{H}_2\text{O}}^{-1} \text{ cm}^{-2}$). This agreement, however, is likely a coincidence:
453 without those data obtained from the water-rich standards (i.e., less affected by the 2nd
454 Si-O VOCBs), their calibration would have resulted in a much larger averaged value.
455 Nevertheless, the water-in-Qz IR calibration by Thomas et al. (2009) can be directly

456 applied to α -Qz with water contents covered by their IR calibration experiments (Fig.
457 10; $c_{\text{H}_2\text{O}} > \sim 38$ wt ppm).

458 No doubt that compared to the value of $\varepsilon_{\text{H}_2\text{O}}$ ($78899(10661) \text{ L mol}_{\text{H}_2\text{O}}^{-1} \text{ cm}^{-2}$),
459 the value of $\varepsilon_{\text{Si-O}}$ ($592.0(696) \text{ L mol}_{\text{SiO}_2}^{-1} \text{ cm}^{-2}$) is very small. Since the H_2O content in
460 common silicate and silica minerals are usually a few to a few tens of wt ppm whereas
461 the SiO_2 contents are usually a few tens of wt%, however, the effect of the 2nd Si-O
462 VOCBs on quantifying water can be enormous, especially for the materials with trace
463 amounts of water.

464 With $\varepsilon_{\text{H}_2\text{O}} = 78899(10661) \text{ L mol}_{\text{H}_2\text{O}}^{-1} \text{ cm}^{-2}$ and $\varepsilon_{\text{Si-O}} =$
465 $592.0(696) \text{ L mol}_{\text{SiO}_2}^{-1} \text{ cm}^{-2}$, trace water in α -Qz can now be accurately quantified. For
466 α -Qz with 15, 10 and 5 wt ppm water measured by applying the water-in-Qz IR
467 calibration of Thomas et al. (2009), our new approach indicates ~ 14 , 8 and 2 wt ppm
468 water, respectively (Fig. 11). Ignoring the effect of the 2nd Si-O VOCBs, trace water in
469 α -Qz can be substantially overestimated indeed (e.g., by $\sim 150\%$ for the α -Qz
470 containing 2 wt ppm H_2O). For an accurate IR measurement on water-poor α -Qz, we
471 thus suggest a simultaneous application of $\varepsilon_{\text{H}_2\text{O}}$ and $\varepsilon_{\text{Si-O}}$. The water-in-Qz IR
472 calibration by Thomas et al. (2009) can also be applied, provided that those extra IR
473 peaks aroused by another species rather than water can be carefully identified and their
474 absorptions can be reasonably well removed.

475

476 Potential applications of the new approach

477 For the water-quantification technique of IR, the principles and the example given
478 above demonstrate that even with the water peaks severely overlapped by other IR
479 signals of a different species, it is still feasible to make highly accurate IR
480 measurements on water-poor samples. A jointed application of the absorption
481 coefficients for both water and the additional species is the key. It is believed that our
482 new approach should have wide applications.

483 Our new approach can be applied to the silicate and silica minerals with interacting
484 water peaks and 2nd Si-O VOCBs. The length of the Si-O bonds in silicate and silica
485 minerals ranges from $\sim 1.60 \text{ \AA}$ to $\sim 1.64 \text{ \AA}$ (Putnis 1992). As the SiO₄ tetrahedra become
486 more polymerized, it generally decreases, e.g., from $\sim 1.634(20) \text{ \AA}$ in O1 (Q⁰; Birle et
487 al. 1968) to $\sim 1.6092(7) \text{ \AA}$ in α -Qz (Q⁴; Levien et al. 1980). Accordingly, the Si-O bonds
488 strengthen, and the fundamental Si-O vibration modes attain higher energies. Indeed,
489 this is usually the case (Fig. 1 and Supplementary Table S1), with the maximum
490 frequency of the fundamental Si-O vibration modes being $< \sim 1000 \text{ cm}^{-1}$ for the isolated
491 structures (Q⁰), $< \sim 1100 \text{ cm}^{-1}$ for the chain structures (Q¹ or Q²), $< \sim 1150 \text{ cm}^{-1}$ for the
492 sheet structures (Q³) and $< \sim 1250 \text{ cm}^{-1}$ for the framework structures (Q⁴). The only
493 possible exception is the ring silicates (Q²; Fig. 1 and Supplementary Table S1), which,
494 rather unfortunately, show very high frequency for their fundamental Si-O vibration
495 modes (up to $\sim 1200 \text{ cm}^{-1}$). Clearly, interaction between the 2nd Si-O VOCBs and water
496 peaks of the silicate and silica minerals is a very common phenomenon.

497 In the literature, there have been many specific cases in which whether some
498 enigmatic IR peaks belong to water or to the Si-O vibrations are unclear. The followings
499 are just a few examples. The first case comes with zircon. The infrared peaks at ~ 3200 ,
500 3180 and 3100 cm^{-1} have been assigned as three-photon combination modes
501 (comparable to the 2nd Si-O VOCBs) by Woodhead et al. (1991; stepwise heating
502 experiments), but as water peaks related to either some trivalent cations at the Zr site
503 (M³⁺ + H⁺ replacing Zr⁴⁺) or the hydrogarnet substitution (4H⁺ replacing Si⁴⁺) by
504 Nasdala et al. (2001), Trail et al. (2011), Botis et al. (2013) and De Hoog et al. (2014).
505 The second case comes with ringwoodite, the most abundant mineral in the lower part
506 of the mantle transition zone (Frost 2008; Liu et al. 2016). Much knowledge has been
507 obtained on the IR features of water in ringwoodite (Koch-Müller and Rhede 2010;
508 Bolfan-Casanova et al. 2018; Liu et al. 2020; Liu 2020), but potential influence of its
509 Si-O vibrations has not been adequately well understood. As a matter of fact, the molar
510 absorption coefficient of water in ringwoodite was calibrated for the IR signals in very

511 different wavenumber ranges, being $\sim 4000\text{--}2500\text{ cm}^{-1}$ in Koch-Müller and Rhede
512 (2010), $\sim 3900\text{--}2000\text{ cm}^{-1}$ in Thomas et al. (2015) and $\sim 3730\text{--}2000\text{ cm}^{-1}$ in Bolfan-
513 Casanova et al. (2018). Nevertheless, the large wavenumber spread of the water peaks
514 of ringwoodite warrants severe interaction between the 2nd Si-O VOCBs and the water
515 peaks (Supplementary Table S1). The third case comes with sillimanite. The IR peak at
516 $\sim 3205\text{ cm}^{-1}$, which constitutes $\sim 14(6)\%$ of the total integral absorbance for water
517 (Wilkins and Sabine 1973; Beran et al. 1989), was not observed to reduce its intensity
518 upon heating (Beran et al. 1989). Considering that the frequencies of the fundamental
519 Si-O vibrational modes in sillimanite are as high as $\sim 1195\text{ cm}^{-1}$, this band might be a
520 2nd Si-O VOCB. Furthermore, those broad IR peaks at $\sim 3119, 3176, 3284, 3371, 3484,$
521 3567 cm^{-1} observed on a $\sim 6\text{-mm-thick}$ feldspar sample by Mosenfelder et al. (2015;
522 GRR2651 with $\sim 1.4(3)$ wt ppm H₂O only, as determined by secondary ion mass
523 spectrometry), and that broad IR band near $\sim 3250\text{ cm}^{-1}$ obtained for nepheline by Beran
524 and Rossman (1989; its intensity not affected by annealing, as shown by their Fig. 1)
525 are all likely candidates of the 2nd Si-O VOCBs.

526 Our new approach can also be applied to hydrous silicate and silica melts. The
527 wavenumbers for the fundamental O-H stretching vibrations in these melts can be as
528 low as $\sim 2500\text{ cm}^{-1}$ (Stolper 1982; Liu et al. 2006), and those for the fundamental Si-O
529 stretching vibrations can be as high as $\sim 1200\text{ cm}^{-1}$ (Dalby and King 2006), so that severe
530 interaction between the water peak and the 2nd Si-O VOCBs is expected. Detailed
531 investigation will reveal the effect of the 2nd Si-O VOCBs.

532 IR is the most commonly-used technique to quantify small amounts of water in
533 Earth and planetary materials. However, its application once relied on a precise
534 recognition of the water peaks and a successful removal of the effect of interfering IR
535 features (e.g., the 2nd Si-O VOCBs) of any other species. Even possible sometimes,
536 these operations are highly time-consuming and inconvenient. This study shows that
537 with careful calibration experiments to constrain the absorption coefficients both for

538 water and for additional species, highly accurate IR measurements on trace water can
539 be readily obtained.

540

541

542 **Conclusions**

543 The following conclusions may be drawn from this study:

544 1. The 2nd Si-O VOCBs in Ol locate at wavenumbers lower than $\sim 3000\text{ cm}^{-1}$. They are
545 well separated from the water peaks appearing at wavenumbers higher than ~ 3000
546 cm^{-1} , and should have no effect on quantifying water.

547 2. The 2nd Si-O VOCBs in α -Qz severely overlap with the water peaks in the
548 wavenumber range of 3650 to 3250 cm^{-1} . The IR peak at $\sim 3199\text{ cm}^{-1}$ is a 2nd Si-O
549 VOCB, the six IR peaks at 3378 , 3403 , 3437 , 3482 , 3511 and 3530 cm^{-1} are
550 attributed to various hydrogen defects, and the IR peak at $\sim 3312\text{ cm}^{-1}$ may be
551 aroused both by the Si-O vibrations and by the O-H vibrations. The 2nd Si-O VOCBs
552 in α -Qz should have some effect on quantifying water with IR, and need careful
553 handling.

554 3. With various degrees of polymerization in the structures of the silicate and silica
555 minerals, the overlapping between the 2nd Si-O VOCBs and the water peaks varies,
556 and the effect of the 2nd Si-O VOCBs on the water-quantifying process with IR
557 varies. This also applies to the cases of silicate and silica melts.

558 4. The effect of the 2nd Si-O VOCBs (or some other interfering IR peaks caused by
559 another species) on quantifying water in the silicate and silica minerals (and melts)
560 with IR can be successfully removed, and accuracy in the water quantification can
561 be significantly improved, as theoretically justified by some fundamental equations
562 and experimentally verified by the data of α -Qz in the literature. This new
563 experimental approach should have wide applications.

564

565

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572

573

574 **Supplementary Information**

575 This article contains one supplementary figure (Fig. S1) and [four](#) supplementary tables
576 ([Tables S1, S2, S3 and S4](#)).

577

578

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826

827 **Figure Captions**

828 **Fig. 1** Basic structural units in common silicate minerals, and general wavenumber
829 ranges of their fundamental IR- and Raman-active Si-O stretching vibration modes
830 (averaged from the data in the supplementary Table S1). Note that with increasing
831 polymerization, the number of bridging oxygen per silicate tetrahedron (termed as Q^n)
832 increases whereas the number of non-bridging oxygen (*NBO*) per silicate tetrahedron
833 (termed as *NBO/T*) decreases, accompanied by an overall increase of the frequencies of
834 the fundamental IR- or Raman-active Si-O stretching vibration modes

835

836 **Fig. 2** Examples of baseline correction and Gaussian-Lorentzian deconvolution of the
837 IR absorption spectra collected on crystal plates of (a) Ol (unknown orientation; 2159
838 μm thick) and (b) α -Qz (Z-cut; 2797 μm thick). The baseline of the IR spectra collected

839 from our Ol may be strongly affected by the electronic transition band of Fe^{2+} in the
840 octahedral site (at $\sim 2350 \text{ cm}^{-1}$; Goldman and Rossman 1976; Mosenfelder and Rossman
841 2013). It was corrected by performing a manual spline fit. In contrast, the baseline of
842 the IR spectra acquired from our α -Qz attained a gentle slope, which was readily
843 corrected by a simple linear fit procedure. The IR peak component-deconvolution
844 process was accomplished by using the Peakfit V4.12 software (SPSS Inc.). For a
845 clearer demonstration, the intensity data of the baseline-corrected Ol IR spectra has
846 been multiplied by a factor of 2. Uncorrected raw spectroscopic data: solid black curve;
847 baseline: broken blue curve; corrected raw spectroscopic data: solid blue curve;
848 component peak: broken black curve; sum of component peaks: solid red curve
849

850 **Fig. 3** Unpolarized IR absorption spectra ($\sim 2800\text{--}2400 \text{ cm}^{-1}$) of 12 randomly-cut Ol
851 crystal plates (thickness ranging from 1723 to 2159 μm) with unknown crystallographic
852 orientations. All spectra have been normalized to a sample thickness of 1 cm and
853 vertically offset for the purpose of illustration. In general, six broad peaks can be
854 observed

855

856 **Fig. 4** Unpolarized infrared absorption spectra collected from the Ol thickness-
857 reduction experiments: (a) the 2nd Si-O VOCBs; (b) the 1st Si-O VOCBs. Numbers next
858 to each IR spectrum are the thickness of the crystal plate (in μm) whereas those in the
859 parentheses is the minimum percentage of the transmitted light for the shown energy
860 range. The IR spectra (without baseline correction) have been vertically offset for the
861 purpose of illustration

862

863 **Fig. 5** Dependence on the Ol plate thickness of the integral absorbance of the 2nd Si-O
864 VOCBs. Filled squares stand for the data from the thickness-reduction experiments in
865 which the crystallographic orientations of the Ol plates were the same (unknown though;
866 Fig. 4). Empty circles represent the data from the experiments with randomly-oriented

867 Ol plates (Fig. 3). The broken line, represented by the equation, is drawn through the
868 filled squares only. [See Supplementary Table S2 for the plotted data](#)

869

870 **Fig. 6** Evolution of IR features of α -Qz crystal plate (Z-cut) in response to variation of
871 sample thickness: (a) Unpolarized IR spectra (from 3800 to 3000 cm^{-1}); (b) integral
872 absorbance. Both the 2nd Si-O VOCBs and the O-H stretching vibrations likely occur
873 in the energy range from 3800 to 3000 cm^{-1} . The numbers in blue denote the IR peaks
874 for the hydrogen defects whereas those in red denote those two major 2nd Si-O VOCBs
875 in α -Qz (Kats, 1962; Table 1). For comparison, the IR data for two dry α -Qz crystals
876 from Jollands et al. (2020) are shown as well, with the intensity of their IR signals
877 multiplied by a factor of 5. For each dry α -Qz (top one: crystal Q6L5, 373- μm -thick;
878 bottom one: crystal Q6L7, 388- μm -thick), two polarized spectra (Red: light polarized
879 along the Z-axis; Blue: light polarized along the X-axis) collected from the spot right
880 near the edge of the crystal are plotted (Jollands et al. 2020). All O-H dipoles in α -Qz
881 lie almost normal to the Z-axis, so that the IR spectrum in blue well captures the water
882 signals and the IR spectrum in red well holds the Si-O vibration signals. Numbers next
883 to the spectra represent the plate thickness (in μm). The IR spectra have been vertically
884 offset for the purpose of illustration

885

886 **Fig. 7** Unpolarized infrared absorption spectra collected from α -Qz crystal plate (Z-cut)
887 showing the 1st Si-O VOCBs and fundamental Si-O vibrational bands (down to 675 cm^{-1}).
888 Numbers next to the IR spectra are the thickness of the crystal plates (in μm). Those
889 in the following parentheses, as separated by the semicolons, are the minimum
890 percentages of the transmitted light for the 1st Si-O VOCBs and fundamental Si-O
891 vibrational bands, respectively. The IR data for the samples with thickness ranging from
892 505 to 90 μm are from this study, and the rest are from He et al. (2019). Note that the
893 1st Si-O VOCBs well show up for the samples with thickness less than $\sim 90 \mu\text{m}$ whereas
894 the fundamentals fully emerge for the 7- μm -thick sample plate only (He et al. 2019).

895 The 1st Si-O VOCBs, observed at ~1998, 1966, 1938, 1888, 1866, 1795, 1727, 1680,
896 1607, 1531, 1518 and 1491 cm⁻¹, are in good agreement with Kats (1962). The
897 fundamentals in the shown spectral range were observed at ~1249, 1163, 1067, 801,
898 787 and 705 cm⁻¹ by He et al. (2019). The IR spectra (without baseline correction) have
899 been vertically offset for the purpose of illustration

900

901 **Fig. 8** Evolution with accumulated heat-treating time at 500 °C of IR spectrum (a), and
902 intensity of IR peak at 3199 cm⁻¹ (b), IR peak at 3312 cm⁻¹ (c), IR peak at 3378 cm⁻¹
903 (d), IR peak at 3403 cm⁻¹ (e), IR peak at 3437 cm⁻¹ (f), IR peak at 3482 cm⁻¹ (g), IR
904 peak at 3511 cm⁻¹ (h), and IR peak at 3530 cm⁻¹ (i). Unpolarized IR spectra were
905 collected on the α -Qz Z-cut plate (1198- μ m-thick) heated with different accumulated
906 heat-treating times. Multiple IR peaks severely overlap with each other in this energy
907 range, and thus usually bear relatively large uncertainties in their peak intensities. Also
908 shown are the results predicted by the one-dimension diffusion model for the diffusion
909 process of water in α -Qz at 500 °C, with $D_H = 2.4 \times 10^{-14} \text{ m}^2 \text{ s}^{-1}$ from Kats (1962; the
910 solid curves), with 10 times larger D_H (i.e., $2.4 \times 10^{-13} \text{ m}^2 \text{ s}^{-1}$; the dotted curves) and
911 with 10 times smaller D_H (i.e., $2.4 \times 10^{-15} \text{ m}^2 \text{ s}^{-1}$; the broken curves). See Supplementary
912 Table S3 for the plotted data

913

914 **Fig. 9** Schematic illustration of two components, one for the O-H vibrations (A_{H_2O}) and
915 the other for the 2nd Si-O VOCBs (A_{Si-O}) in three α -Qz with different water contents
916 (c_{H_2O}), in the integral absorbance for the peak-overlapping wavenumber ranges

917

918 **Fig. 10** Correlation between nominal integrated molar absorption coefficient (ϵ_{total}) for
919 water and water content in α -Qz. Filled symbols stand for the data directly from
920 Thomas et al. (2009) whereas empty symbols represent the data after correcting their
921 dependence on water. Red curve, as described by the equation, is drawn through the
922 filled symbols only. Note that the empty symbols nicely fall on the blue horizontal line

923 (denoted as T. S., this study), implying a successful removal of the dependence on water
924 content. The dotted black line is the averaged $\epsilon_{\text{H}_2\text{O}}$ from Thomas et al. (2009; T2009).

925 [See Supplementary Table S4 for the plotted data](#)

926

927 **Fig. 11** Difference in water contents of α -Qz, as obtained by conventional approach
928 (numbers in black) and our new approach (numbers in blue). The squared symbols are
929 the integral absorbances ($3650\text{--}3250\text{ cm}^{-1}$) caused by the 2nd Si-O VOCBs in dry α -Qz
930 (zero water), as obtained from the IR spectra at the bottom of Fig. 6a. The blue lines
931 are obtained by subtracting the red line from the black lines