Title: Concentration of hydroxyl defects in quartz from various rhyolitic ignimbrite horizons: results from unpolarized micro-FTIR analyses on unoriented phenocryst fragments

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Concentration of hydroxyl defects in quartz from various rhyolitic ignimbrite horizons: results from unpolarized micro-FTIR analyses on unoriented phenocryst fragments

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Abstract: Hydroxyl defect concentrations of quartz phenocryst fragments from various rhyolitic pyroclastic density current deposits from the Bükk Foreland Volcanic Area, Hungary, were determined by using micro-FTIR spectrometry. In addition trace-element analysis and SEM cathodoluminescence imaging were performed on the same crystals. Hydroxyl defect-content (expressed in water equivalent) of volcanic quartz ranges from 0.9 ± 0.1 to 2.8 ± 0.4 wt. ppm, which is lower than those in quartz of plutonic (granitic), metamorphic and hydrothermal origin. The incorporation of hydroxyl defect is mainly due to H⁺⁺⁺Al⁺⁺ substitution into Si-tetrahedral vacancies of quartz. Furthermore, the presence of molecular water probably in (nano-)inclusions was proven. The post-eruptive diffusive loss of hydroxyl defects during cooling seems to be the main factor causing the very low concentration of hydroxyl defects. This may be also manifested in the almost homogeneous distribution of hydroxyl defects regardless of the considerable zonation in Al-content, although complete diffusive loss of hydroxyl defects was possibly hindered by the cooling effect of phreatomagmatism (interaction of excess water with magma during eruption) and deposition in a shallow submarine environment.

Moreover, a reasonable linear correlation is observed between the integrated area of Si–O bands (between 2110 and 1440 cm⁻¹) and sample thickness up to ∼300 µm by studying unoriented quartz phenocryst fragments. This may enable the quantitative analysis of hydroxyl defects in separated quartz crystals without the need for preparing oriented thin sections.

Key-words: quartz; micro-FTIR spectrometry; hydroxyl defect; water content; ignimbrite; Bükk Foreland Volcanic Area.

1 Introduction
Quartz is a common phase in Si-saturated volcanic systems. Quantification of trace elements, such as Na⁺⁺, K⁺⁺, Al³⁺, Ti⁴⁺, B³⁺, P⁵⁺ in quartz from such systems using laser-ablation inductively-coupled plasma mass spectrometry (LA-ICP-MS), secondary-ion mass spectrometry (SIMS), and cathodoluminescence (CL) imaging have become important in recent petrogenetic studies (e.g. Müller et al., 2002, 2003; Stalder & Konzett, 2012). Especially the incorporation of Al³⁺ and Ti⁴⁺ has been studied. Titanium concentration in quartz may be used as a geothermometer (Wark & Watson, 2006; Huang & Audétat, 2012) and allows outlining pre-eruptive thermal histories within the magma chamber (e.g. Shane et al., 2008; Campbell et al., 2009; Matthews et al., 2012). Hydrogen occurs in hydroxyl defects related to the H⁺⁺⁺M⁺⁺ heteroelectronic substitution into silica tetrahedra, as well as molecular water in (nano-)inclusions (Stenina, 2004). Comparative studies on hydroxyl defect-content in quartz samples from various origins have been scarce. Quantitative analysis of structural hydroxyls in clear and smoky natural and synthetic quartz was first performed by Kats (1962) using IR spectrometry. It has been recently experimentally demonstrated that the hydroxyl defect-content of quartz from the Qz–Ab–H₂O and granite–H₂O systems at 5 and 25 kbar ranged from ∼40 to ∼80 wt. ppm (hereafter referred to as ‘ppm’ for short), and from ∼100 to ∼140 ppm respectively (Stalder & Konzett, 2012). Systematic study on the hydroxyl defect concentration of quartz of hydrothermal, metamorphic and plutonic origin revealed generally low values: ∼6–13 ppm.
(Müller & Koch-Müller, 2009). Hydroxyl defect-contents of detrital quartz grains from different origins were also determined (Stalder & Neuser, 2013; Stalder, 2014); they span from 0 to 160 ppm with an average of ~10 ppm in various sandstone formations. Furthermore, the structural hydroxyl-content of quartz was proposed as a good indicator for a crustal-level origin in provenance studies (Stalder, 2014). In spite of this, the hydroxyl-defect concentration of quartz from Si-rich volcanic systems has not yet been investigated systematically.

In this study we present data – to our best knowledge for the first time – on the hydroxyl defect-content of quartz phenocryst fragments produced by Si-rich explosive volcanism. We determined the concentration and the substitution mechanisms of hydroxyl defects in quartz from selected samples of the Bük volatility Volcanic Area in northern Hungary. In addition, trace-element analysis of Ti and Al, which are thought to be the most important trace elements in quartz, was also performed along with cathodoluminescence imaging.

Geological background and sampling sites

In the Bük Volcanic Area, layers of extensive pumice-rich pyroclastic density-current deposits crop out over a ca. 40 × 10 km large area. The ignimbrite-forming eruptions occurred during a 7.5 Ma interval from 21 to 13.5 Ma and produced a voluminous pyroclastic sequence, which exceeds 700 m in thickness (Szakacs et al., 1998; Pelikan, 2005). The identification of the distinct ignimbrite units and correlation between cogenetic layers pose fundamental challenges for volcanologists. To discover the main stratigraphic units, a number of studies have been conducted including stratigraphic log interpretations (Capaccioni et al., 1995; Szakacs et al., 1998; Lukacs et al., 2010), paleomagnetic measurements (Marton, 1990; Marton & Pecskay, 1998; Marton et al., 2007), K/Ar age determinations (Marton & Pecskay, 1998; Lukacs et al., 2007, 2010), major and trace element analyses of minerals (Lukacs et al., 2007) and matrix glass shards (Harangi et al., 2005; Harangi & Lukacs, 2009; Lukacs et al., 2009), and examination of quartz- and feldspar-hosted silicate-melt inclusions (Lukacs et al., 2002, 2005).

The Neogene volcanism within the Carpathian-Pannonian Region started with widespread and voluminous Si-rich volcanism (Szabo et al., 1992). The Bük Foreland Volcanic Area (BFVA) offers an excellent opportunity to study the successions related to this magmatism. In the BFVA three main units (Lower, Middle, and Upper Ignimbrite Units) can be distinguished according to their paleomagnetic, petrographical and geochemical features (Szakacs et al., 1998). Ignimbrites consisting of massive lapilli tuff facies appearance, subordinate plinian fall deposits and phreatomagmatic units characterize the volcanism (Capaccioni et al., 1995). Of these three units the Lower and the Upper one have rhyolitic chemistry, while the Middle Ignimbrite Unit has bimodal composition (rhyolitic–andesitic). According to their silica saturation, the Lower and Upper ignimbrite units consist of layers which bear quartz phenocrysts.

Quartz phenocryst fragments were collected from the following outcrops: Eger, Noszvaj, Tibolddaro, and Harsany (Fig. 1). Ignimbrites at the Eger and Noszvaj outcrops belong to the Lower Ignimbrite Unit according to Pelikan (2005), whereas the Tibolddaro and Harsany formations are related to the Upper Ignimbrite Unit and are attributed to the same eruption (Lukacs et al., 2007).

In each sampling site the exact thickness of the sampled ignimbrites could not be determined, because the lower contact is only observable at Tibolddaro, and the upper boundaries are not exposed in the outcrop. Thus, the exact relative position of the collected pumice clasts within the ignimbrites is unknown, except at Tibolddaro. In the case of Eger and Harsany, the outcrop walls (which expose only a restricted part of the whole deposits) are as high as ~30 m and samples were collected from the middle part of these thick deposits. At Harsany, the minimum thickness of the sampled ignimbrite is 15 m. However the lower and upper contacts are not exposed. Pumice clasts were also collected from the central part of the deposits. At Tibolddaro the samples were collected from ~3 m above the lower contact of the ignimbrite.

In all sites, ignimbrites (pumice-rich pyroclastic density current –PDC deposit–) with block-bearing massive lapilli tuff lithofacies crop out. Internal bedding, gradation or tractional structures are not observed. Pumice clasts range from a few to tens of centimetres in diameter and lapilli-sized clasts are abundant. In addition to main...
geographical and stratigraphical features, basic petrological and chemical data on sampled outcrops are presented in Table 1. In all outcrops the pumices are phenocryst-poor (<5 vol.%), the most abundant mineral is quartz. In all cases complete and intact grains with dihedral shape are scarce, instead fragments of phenocrysts dominate. The maximum size of quartz fragments is 3 mm in Noszvaj and Eger, while in Tibolddaróc and Harsány they range up to 6 mm in diameter. In all outcrops individual quartz grains show pale pink or pale violet colour. All quartz fragments contain needle-like apatite and melt inclusions with bubble. Most of the melt inclusions are rounded, but in some cases negative crystal shape is also present. The largest melt inclusions are 200 μm in diameter. In some cases daughter phases occur in melt inclusions.

Further crushing was performed by using a ceramic crushing mortar. The residual debris was washed under running water and then dried at room temperature until most of the moisture disappeared. Individual phenocryst fragments were handpicked with a plastic tweezer under the microscope. Investigations were carried out on doubly polished crystal sections from individual phenocryst fragments. In order to obtain such sections, fragments were mounted on a glass plate with liquid rapid adhesive, cut, and then polished. This procedure was repeated on the other side of the fragments after dissolving the adhesive with high purity acetone. Doubly polished wafers were then placed in an acetone bath at least three times to dissolve all remaining adhesive. Subsequently, doubly polished wafers were placed in a drying oven for at least 45 min at ~100°C to remove adsorbed water.

### Micro-FTIR spectroscopy

Unpolarised Micro-FTIR measurements have been undertaken at the Hungarian Institute for Forensic Sciences using a Bruker Vertex 70 spectrometer attached to a Bruker Hyperion 1000 infrared microscope. KBr beam splitters and MCT detectors were deployed with a Globar light source. Measurements were conducted by using unpolarised IR light. A rectangular spot size was set at 100 × 100 μm. Nominal spectral resolution of 4 cm⁻¹ was chosen with at least 64 scans usually between 400 and 4000 cm⁻¹ for each measurement.

During each IR measurement the quartz wafers were carefully checked for the presence of visible fluid inclusions. Individual and transect measurements were performed on sites free of mineral, melt or fluid inclusions.

Spectra were processed with the OPUS® software. For the background correction in general the concave rubberband correction including at least two iterations and 64 fitting points was applied, but for spectra with uneven background, manual correction was implemented by using polynomial curve fitting. Manual correction was only used to modify the spectra with sinusoidal background and/or interference fringes. The incorporation of hydroxyl defects in the quartz lattice is strongly anisotropic, while the molecular water in nano-inclusions shows isotropic distribution. In the indicatrix section parallel to c-axis the maximum hydroxyl defect-related linear

### Methods

Hydroxyl defect-contents of 101 quartz phenocryst fragments from Eger, Noszvaj, Tibolddaróc and Harsány localities were measured by unpolarised micro-FTIR spectroscopy. Potential intra-grain variations of hydroxyl defect concentration were checked by measuring four to five points along transects within phenocryst fragments from each locality. The results of the intra-grain variation of hydroxyl defect concentrations are given in the Supplementary Material (freely available online, linked at this article to the GSW website of the journal: http://eurmin.geoscienceworld.org/). To check the relationship between hydroxyl defect-content and quartz chemistry, additional trace-element analysis was carried out by using LA-ICP-MS and scanning-electron-microscope (SEM) cathodoluminescence (CL) imaging.

### Sample preparation

All analyses were performed on doubly polished, ~100–450 μm thick wafers from individual fragments. Quartz phenocryst fragments were selected from pumice clasts which were ~5–8 cm in diameter. Fresh-looking pumice clasts were collected from outcrop walls and then crushed to smaller fragments in the laboratory by hammer.
polarised absorbance can be measured when the electric vector is perpendicular to the c-axis (Ell\(\text{ln}_{\text{c}}\), Stalder & Konzett, 2012). In contrast, hydroxyl defect-related absorbances are negligible when the electric vector is parallel to the c-axis (i.e. Ell\(\text{ln}_{\text{e}}\)). The broad absorption feature associated with molecular water can be observed in all crystallographic directions. The two types of hydrogen incorporation can be further distinguished by other features of their absorbance bands. Hydroxyl defect-related absorbance bands appear as sharp bands, and the molecular water causes a broad absorption feature which is usually centred around 3400 cm\(^{-1}\). Thus, integration of hydroxyl defect-related absorption features was completed using the Integration tool with the B method which includes only the area above the line connecting the intersections of the lower and upper limits of integration with the spectra. Type A method, which includes the whole area below the spectra between the limits of integration, was used to integrate the area between 3500 and 3000 cm\(^{-1}\) to include also the contribution of molecular water in nano-inclusions. This area is the combined contribution of hydroxyl defects and molecular water, thus it could be used as a measure of bulk water content. Figure 2 depicts in detail how the integrations of bulk and hydroxyl defect bands was performed. A comparison of this protocol with the polarized methodology of Stalder & Konzett (2012) is given in the discussion. The area of Si–O-related absorbance bands was determined by using the A integration method between 2110 and 1440 cm\(^{-1}\). More detailed information on baseline correction methods and positions of main absorption bands related to Si–O bonds etc. is presented in the Supplementary Material.

Unpolarised measurements on unoriented quartz phenocryst fragments were performed. The indicatrix theory (Kovács et al., 2008; Sambridge et al., 2008) for unpolarised infrared light makes it possible to determine the concentration of hydroxyl defects from a number (\(n > 5\)) of unoriented anisotropic crystals with good accuracy. This method can only be applied for strongly anisotropic minerals (e.g., olivine, calcite, quartz), if the maximum linear unpolarised absorbance is less than 0.15, a criterion that is satisfied by spectra measured in this study. In addition, this method requires that we assume that the concentrations of the analysed hydroxyl defects species are uniform.

Total polarised absorbance (\(A_{\text{tot}}\)) is estimated as three times the average unpolarised absorbance. Note that this factor of three has been determined both theoretically and empirically by Sambridge et al. (2008) and Kovács et al. (2008). The estimation of the average integrated unpolarized absorbance \(A_{\text{tot}}\) is more accurate when the number of measurements on unoriented grains is larger. The \(A_{\text{tot}}\) is then converted to absolute concentration of hydroxyl defect using the calibration factors of Thomas et al. (2009) for natural quartz (HQV, \(\varepsilon = 94\ 000\ \text{l/mol} \cdot \text{cm}^2, k \approx 0.072\)). The approximate amount of molecular water in (nano-)inclusions was estimated following the methodology in Gleason & DeSisto (2008) applying the absorption coefficient of Kats (1962) based on the integrated absorbance \(A_{3500-3000}\) of the broad molecular water band at \(\sim 3300\ \text{cm}^{-1}\).

Thickness of quartz wafers was determined by using a MITUTOYO\textsuperscript{\textregistered} manual micrometer which is accurate to within 10 \(\mu\text{m}\) in the 0–2.5 mm range. The determined thickness of the sample, possible inhomogeneities in hydroxyl defect concentrations and the calibration factors may be all the sources of possible uncertainties. Based on previous experience, however (Kovács et al., 2008, 2012), the overall precision in the absolute concentration of hydroxyl defects usually should not exceed 15%.

**LA-ICP-MS analysis**

Measurements were performed using a New Wave Up 213 laser ablation system coupled to a quadrupole ICP-MS, Perkin Elmer Elan DRCII at the Geological and Geophysical Institute of Hungary. The ablated aerosol was delivered to the ICP torch by a 1/4-inch-wide (~6 mm) tygon tube. Helium, the carrier gas, was mixed with Ar gas as make-up gas via a T-connector. Operating parameters of the ICP-MS and laser ablation system were optimized using NIST612 as the unknown material controlled by NIST610. Conditions of mass spectrometer are characterized by nebulizer gas of 0.9 l/min, auxiliary gas of 1.1 l/min, plasma gas of 15.8 l/min, lens voltage of 7.25 V and RF power of 1450 kW. The He-gas flow was as high as 1.8 l/min. Dwell time was chosen 130 ms for isotopes \(^{27}\text{Al}\) and \(^{40}\text{Ti}\). The laser worked at around 7.3 J/cm\(^2\) energy density and at repetition rate of 5 Hz. The spot size was 100 \(\mu\text{m}\). The acquisition time of background was 40 s while the sample signal was over 60 s. The total integration time of an isotope was 13 s. NIST610 as external, \(^{29}\text{Si}\) as internal standard were applied. The absolute...
concentrations were calculated to SiO$_2$ measured in the same time, on a same spot by LA-ICP-MS after Liu et al. (2008). The concentrations of $^{27}$Al and $^{47}$Ti were measured from individual phenocryst fragments. In addition, measurements along transects were also made to check intra-grain trace-element distribution in representative phenocryst fragments for Eger, Noszvaj and Harsány localities. 

8 SEM-CL imaging 

Digital SEM-CL images from three phenocryst fragments were obtained by using an SEM operating at 10 kV accelerating voltage and 10 nA beam current, and using a Gatan Miniel cathodoluminescence detector at the Eötvös University. Digital images were collected and stored at 1024 × 768 pixels. 

9 Results 

9.1 Micro-FTIR spectroscopy 

Individual IR spectra are presented in Fig. 3, whereas averaged spectra for the four localities are shown in Fig.4. The main absorption features in the 3000–3600 cm$^{-1}$ range are slightly different in the four localities. For the Eger and Noszvaj samples four main sharp absorption bands are identified: a small one at $≈$ 3483 cm$^{-1}$, a main absorption feature at 3378 cm$^{-1}$ with minor bands at 3423 cm$^{-1}$, 3296 cm$^{-1}$ and 3197 cm$^{-1}$. In contrast, IR spectra of quartz from Tibolddaroč and Harsány samples are only characterized by two sharp absorption bands at 3379 and 3197 cm$^{-1}$. Considering the average spectra (Fig.4) the similarity between the Eger and Noszvaj and between the Tibolddaroč and Harsány is evident. The most characteristic absorption feature is the band at 3379 cm$^{-1}$ in all samples. In the Eger and Noszvaj samples a wide absorption feature around 3300 cm$^{-1}$ is also commonly observed. In the case of Tibolddaroč and Harsány this feature is less pronounced or absent. 

The integrated absorbances of hydroxyl defects ($A_{\text{tot}}$) and bulk water ($A_{3500-3000}$) are presented in Supplementary Material for each grain. The bulk water includes both hydroxyl defects and molecular water in (nano-)inclusions. In addition, the concentrations of hydroxyl defects for each grain were also determined from the $A_{\text{tot}}$ using the procedure described in the method chapter. Note, however, that this concentration is only indicative as the real concentration could only be deduced precisely from the average unpolarized absorbance of the phenocryst fragments from each subset of samples. Ideally the variation seen in indicative concentrations for each locality reflects the crystallographic anisotropy only (see 'Discussion'). Histograms showing the frequency of quartz phenocryst fragments with respect to their hydroxyl defect-contents are presented in Fig. 5. The water equivalent of hydroxyl defects may imply that there is no interference between two distinct forms of hydrogen. There is a clear difference between the quartz phenocryst fragments from different localities in Fig. 6. While the Eger and Noszvaj samples are characterized by slightly higher hydroxyl defect concentrations and significant amount of bulk water indicated by the integrated area of the wide absorption band around 3300 cm$^{-1}$, the Tibolddaroč and Harsány samples have lower hydroxyl defect concentrations and have generally no molecular water. Usually only the Eger and Noszvaj samples contain appreciable molecular water but always less than 1617 ppm. Just a very few grains from the Tibolddaroč and Harsány show a few ppm of water, with just one grain containing $≈$ 3560 ppm of molecular water. The lack of a positive correlation between the amount of molecular water and the concentration of hydroxyl defects may imply that there is no interference between the two distinct types of hydrogen in quartz. Thus, the presence of molecular water in (nano-) inclusions does not increase or influence the concentration of hydroxyl defects. 

Between 2000 and 1500 cm$^{-1}$, all analyzed samples are characterized by six main absorption bands ($≈$1982, $≈$1986, $≈$1793, $≈$1680, $≈$1610 and $≈$1525 cm$^{-1}$), which are related to the symmetrical and asymmetrical vibrations of the Si–O bonds intrinsic to quartz (Kats, 1962; Shinoda & Aikawa, 1994). The band positions for these Si–O overtones and intensity values are presented in the Supplementary Material. A positive correlation ($R^2 = 0.86$) between the integrated area of these Si–O vibration bands and sample thickness is observed (Fig. 7), which appears to be linear at least to a sample thickness of about 300 μm. 

9.2 Trace-element analysis and SEM-CL imaging 

Figure 8 shows representative Al vs. Ti concentrations of some of quartz phenocryst fragments from different localities. The two groups defined by micro-FTIR results (Eger–Noszvaj; Tibolddaroč–Harsány) are also distinct with respect to their trace-element contents. The Eger and Noszvaj samples have 84–164 ppm Al and 29–69 ppm Ti. In contrast, the Tibolddaroč and Harsány samples have generally lower concentrations of both Al (61–108 ppm) and Ti (24–33 ppm). 

Cathodoluminescence studies revealed that Ti is the principal impurity responsible for the CL characteristics of igneous quartz (Götze et al., 2001; Müller et al.,
This is in accordance with the observed zoning in the CL images, namely that the phenocryst fragments from Eger and Noszvaj show more pronounced zonation in SEM-CL greyscale intensity (Fig. 9a and b). For the quartz grain from Harsány only weak zoning is recognized (Fig. 9c).

Results of micro-FTIR measurements coupled with trace-element analysis along transects on three representative phenocryst fragments are presented in Fig. 10. For the location of transects points see Fig. 9. The hydroxyl defect-content is rather homogenous along the transects. The standard deviation is on the order of \( \sim 0.1 \text{ H/}10^6 \text{ Si} \) for hydroxyl defect concentration in all phenocryst fragments. In contrast, Al and Ti concentrations show more significant variations and inhomogeneity. There is no clear correlation between the hydroxyl defect concentrations...
and trace-element chemistry. While the Al content ranges between 40–400 (Al/10^6 Si), the hydroxyl defect concentrations are low and range between 0.2–0.5 H/10^6 Si. Moreover, the relation between trace-element concentrations and SEM CL intensity is not always straightforward (Fig. 9). Correlation of Ti content with greyscale intensity can be identified on the rim of the quartz phenocryst fragment from the Eger locality.

**Discussion**

**Hydrogen incorporation and hydroxyl defect-content in volcanic quartz**

Individual and average IR spectra (Figs 3 and 4) of the Eger and Noszvaj localities are characterized by four main absorption bands at 3483, 3378 with minor bands at 3423, 3296 and 3197 cm⁻¹. The Tibolddaróc and Harsány samples exhibit only the 3378 cm⁻¹ band with minor bands at 3423 and 3197 cm⁻¹. Most of the observed absorption features are related to structural hydroxyl connected to mono- or trivalent cations. The absorption band at 3483 cm⁻¹ is caused by Li⁺OH⁻ defects (Kats, 1962). Other absorption features at 3378 cm⁻¹, 3423 cm⁻¹, 3296 cm⁻¹ are related to the substitution of H⁺Al³⁺ for Si⁴⁺ (Kats, 1962; Müller & Koch-Müller, 2009; Thomas et al., 2009). The origin of the band at ~3200 cm⁻¹ at 3197 cm⁻¹ in this study – is controversial. It could be an overtone or combination vibration of the Si–O lattice (Kats, 1962). On the contrary, others attributed the band to the symmetric O–H stretching (ν1) of tetrahedrally coordinated water molecules on the quartz surface (Bayly et al., 1963; Ye et al., 2000). Comparing the dependence of the absorption intensity of bands at 3378 cm⁻¹ and at 3197 cm⁻¹ on the sample thickness, a strong dependence for the 3378 cm⁻¹ band is observed. In contrast the intensity of the 3197 cm⁻¹ band does not depend on sample thickness.

**Fig. 4.** Baseline corrected average IR spectra from the analysed localities. Hydroxyl defect-contents expressed in water equivalent (wt. ppm) are in brackets. Hydroxyl absorption bands of Eger and Noszvaj samples are comparable, and differ from those of Tibolddaróc and Harsány samples.

**Fig. 5.** Histograms showing the indicative hydroxyl defect concentrations of quartz phenocryst fragments from the investigated localities. All investigated samples are characterized by low indicative hydroxyl defect-contents. Average indicative hydroxyl defect-contents of grains from the Eger and Noszvaj localities are 2.8 ppm, while phenocryst fragments from the Harsány locality are characterized by lower values. Indicative hydroxyl defect-contents of Tibolddaróc grains show transitional values. Note that various indicative structural hydroxyl concentrations are mainly due to anisotropy and probably only subordinately to slight inhomogenity of hydroxyl defect-contents from each locality. Some outlier values are present at Tibolddaróc and Harsány. Average hydroxyl defect concentrations are indicated with dashed lines. See discussion for further explanation.
Moreover, Baron et al. (2015) present spectra of quartz from experimental runs, where this absorption feature is absent. This clearly implies that this band is not a combination vibration of the Si–O lattice, but rather relates to adsorbed hydroxyl or molecular water on the quartz surface. This confirms the observation of Bayly et al. (1963) and Ye et al. (2000). In conclusion, we disregarded the absorption feature at 3197 cm\(^{-1}\) when quantifying intrinsic hydroxyl defects.

In general, the presence of hydrogen as molecular water can be inferred from the broad band centred at \(\sim 3400\) cm\(^{-1}\) (Stenina, 2004). The presence of a broad absorption feature is more common in the Eger and Noszvaj samples and quite rare in the two others. While the molecular-water-related wide absorption band is known to be located at 3400 cm\(^{-1}\) (e.g., Stalder & Konzett, 2012; Stalder & Neuser, 2013; Stalder, 2014), the broad band in our phenocryst fragments appears at \(\sim 3300\) cm\(^{-1}\). This shift may be the result of stronger hydrogen bonding between the hydrogens of the water molecule and the silica framework in nano-inclusions. This stronger hydrogen bonding may cause the shift towards smaller wavenumbers. 

Fig. 6. The amount of molecular water as a function of hydroxyl defect-content. (a) The integrated area between 3500 and 3000 cm\(^{-1}\) as a function of hydroxyl defect-content. The \(A_{3500-3000}\) value represents the amount of molecular water in (nano-)inclusions (Stenina, 2004). (b) Molecular water concentration determined from the integrated area of the wide absorption feature at \(\sim 3300\) cm\(^{-1}\). See text and Supplementary Material for further explanation. Note that the Eger and Noszvaj samples are generally characterized by relatively higher hydroxyl defect-content and higher molecular water content. On the contrary, the Tibolddaróc and Harsány samples generally contain less hydroxyl defect and show smaller \(A_{3500-3000}\) and molecular water values.

Fig. 7. The relationship between \(A_{\text{Si-O}}\) - expressing the integrated area of the overtones of Si–O vibration bands - and thickness. A clear correlation between the two variables can be observed, which is linear up to \(\sim 300\) \(\mu\)m.

Fig. 8. Al vs. Ti (ppm) plots for some representative cores of quartz grains. Note the difference between Eger-Noszvaj and Tibolddaróc-Harsány samples. While Eger and Noszvaj samples exhibit significant scatter in these trace elements, the Tibolddaróc and Harsány exhibit a very narrow range for Ti, and only modest scatter in Al content. This difference is also evident on SEM-CL images, where Eger and Noszvaj samples show more pronounced zonation, while the Harsány sample show only weak zonation (see Fig. 9).
There are several lines of evidence suggesting that the hydroxyl defect concentrations are nearly homogeneous in the studied quartz phenocryst fragments. Several micro-FTIR analyses were carried out along profiles (see Supplementary Material) showing that there are only minor variations in infrared absorbance. There are only a very few concentration spikes. Combined trace element and infrared absorbance profiles (Figs 9 and 10) also indicate that hydroxyl defect-content is commonly found in a narrow range in spite of significant variation in Al along profiles. Thus we can assume that the studied quartz phenocryst fragments have basically homogeneous distribution of hydroxyl defects.

This means that the observed variation in the hydroxyl defect concentration of phenocrysts from the same locality is probably mainly due to anisotropy (Fig. 5; Libowitzky & Rossman, 1996; Kovács et al., 2008). Quartz is an anisotropic mineral, which has two main indicatrix sections. One parallel to the c-axis where there is maximum anisotropy and the isotropic indicatrix section which is perpendicular to the c-axis. While there is always absorption in the isotropic indicatrix section, there is no or only FTIR analyses were carried out along profiles (see Supplementary Material) showing that there are only minor variations in infrared absorbance. There are only a very few concentration spikes. Combined trace element and infrared absorbance profiles (Figs 9 and 10) also indicate that hydroxyl defect-content is commonly found in a narrow range in spite of significant variation in Al along profiles. Thus we can assume that the studied quartz phenocryst fragments have basically homogeneous distribution of hydroxyl defects.

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negligible absorption in the anisotropic section when the electric vector is parallel to the c-axis. (i.e. Stalder & Konzett, 2012). Consequently, if different indicatrix sections are analysed the absorbance will vary between a maximum value (in the isotropic section) and a minimum value (perpendicular to the c-axis), which is supposed to be half of the maximum value if linear absorbance is low (<0.15; Kovács et al., 2008; Sambridge et al., 2008). This is because the unpolarised absorbance, for perfectly unpolarised light, is thought to be the average of the principal polarised absorbances in each indicatrix section (Kovács et al., 2008). From the distributions shown in Fig.5 it becomes clear that the maximum hydroxyl defect-contents for the Eger and Noszvaj samples are, indeed, almost twice the minimum values. For the Tibolddaro and Harsány localities the maximum concentrations are more than twice the minimum concentrations. This indicates that among partial polarization of the unpolarized radiation slight inhomogeneity in hydroxyl defect-content could also exist. The distribution of Tibolddaro and Harsány samples with respect to their hydroxyl defect-content show a few ‘outlier’ values. These values may be due to the incorporation of xenocrysts in the syn-eruptive pyroclastic material, possibly from the underlying older quartz-bearing pyroclasts. If we consider the effect of partial polarization, the relatively few indicatrix sections (≤30) and the presence of minor inhomogeneity of hydroxyl defect-content, the measured difference between minimum and maximum unpolarised absorbance is close to the factor of two in Eger and Noszvaj samples, as theoretically expected. We can conclude, therefore, that the distribution and variation of absorbance in different phenocryst fragments is mainly due to anisotropy in these samples. In the case of Tibolddaro and Harsány samples minor inhomogeneity possibly due to xenocryst incorporation is possible. The broad band centred around 3300 cm⁻¹, which is associated with the isotropically distributed molecular water (e.g. Stalder & Konzett, 2012) shows more significant variation in each samples (Figs 3 and 6).

Stalder & Konzett (2012) developed a polarised infrared methodology for the quantitative evaluation of hydroxyl defects in quartz by excluding the spectral contribution of molecular water in nano-inclusions. The method requires oriented quartz phenocryst fragments (parallel to c-axis) and two polarised spectra that need to be taken with the electric vector parallel and perpendicular to the c-axis. Since the broad band typical for molecular water is isotropic it appears uniformly in the two spectra, whereas the narrow bands of hydroxyl defects only show up when the electric vector is perpendicular to the c-axis. Thus, if the former spectrum is subtracted from the latter the contribution of molecular water could be effectively removed. While this methodology provides more accurate quantitative estimations it requires the preparation of oriented quartz phenocryst fragments and the spectra may be noisier due to the lower intensity of polarised infrared radiation. In addition, it may not be fully evaluated whether all phenocryst fragments in the sample suite have the same absolute water concentration, as usually only a few phenocryst fragments have suitable orientations. Our methodology, on the other hand, provides better signal strength of the unpolarised IR radiation, does not require oriented phenocryst fragments, in fact the phenocryst fragments should be unoriented. Furthermore, the unpolarised measurements of several unoriented phenocryst fragments also reveals whether the absolute hydroxyl defect concentration in phenocryst fragments is homogeneous (Sambridge et al., 2008). Nevertheless, the spectral contribution of molecular water could not be eliminated as perfectly as for the polarized methodology. This is because the broad band of molecular water could only be reduced by background subtraction and setting the integration limits to include only the narrow bands of hydroxyl defects. The limits of integration may be appropriately set by observing the main absorption bands in the average spectrum.

The apparent hydroxyl defect-contents of individual phenocrysts based on hydroxyl bands measured for different phenocryst fragments ranges between ~0.5 and ~3.9 ppm (Fig. 5). The average concentration of hydroxyl defect is 2.8 ppm for Eger and Noszvaj, 1.6 for Tibolddaro, 0.9 for Harsány. Thus, our results indicate that the hydroxyl defect-content of quartz from rhyolitic ignimbrites is quite low, compared to values from other rock types: on the basis of 433 quartz grains from different sedimentary sources the hydroxyl defect-contents of crustal quartz are known to vary between 0 and 160 ppm, and the crustal average is ~10 ppm (Stalder, 2014). Systematic investigation of hydroxyl defect-contents in quartz of different origin was performed by Müller & Koch-Müller (2009). The hydroxyl defect concentration of hydrothermal quartz varies between 6 and 8 ppm, in granites and pegmatites from 6 to 45 ppm and in metamorphic rocks from 4 to 12 ppm. The hydroxyl defect-content of experimentally crystallized quartz in the system quartz–albite–water and granite–H₂O between 5 and 25 kbar have been measured by Stalder & Konzett (2012). Hydroxyl defect-contents from the Qz–Ab–H₂O experiments ranged from ~40 to ~80 ppm, and those from the granite–H₂O experiments from ~100 to ~140 ppm.

In our samples hydroxyl defect concentrations show reasonable homogeneity within phenocryst fragments (see Supplementary Material) and the absent or very poor correlation with Al and Ti zonation (Fig. 10) is evident. Our observations are in accordance with the results of former studies, namely that the incorporation of structural hydroxyl into quartz in a Qz–Ab–water system at 900°C at 5–25 kbar is not proportional to the Al³⁺ incorporation (Stalder & Konzett, 2012). The amount of hydroxyl defects deviates from the theoretical 1:1 molar ratio of Al/H (Stalder & Konzett, 2012). The Al³⁺ substitutions can be charge-compensated by other monovalent cations such as by K⁺, Na⁺, Li⁺ or by the coupled substitution of Al³⁺ with P⁵⁺ (e.g. Müller & Koch-Müller, 2009). Even if the measurement of these trace elements was not performed in this study, it is reasonable to assume that most of the Al³⁺ impurities are charge-compensated via these cations, because the rhyolitic melt can contain significant amount of alkalis and phosphorus (Bowen, 1922).
Possible pre- and post-eruptive processes affecting the hydroxyl defect-content in quartz from ignimbrites: preliminary implications

Our results indicate that quartz in rhyolitic ignimbrites appear to be generally poor in hydroxyl defects and the contribution of molecular water in (nano-)inclusions is also in the order of a few hundreds of ppm. In addition, it appears that the more hydroxyl defect-rich phenocryst fragments from Eger and Noszvaj contain more molecular water. A remarkable observation is that hydroxyl defects are almost homogeneously distributed within the quartz phenocryst fragments, whereas the Al content shows distinct variations. Two main processes which may be responsible for the low and homogeneous hydroxyl defect-contents are proposed: 1) diffusive re-equilibration of hydrogen between silica framework and silicate melt/fluid before the eruption, and 2) post-eruptive hydrogen loss during hot emplacement and slow cooling of the pyroclastic material.

(1) The hydroxyl defect-contents of experimentally crystallized quartz phenocryst from Qz–Ab–H2O and granite-H2O runs at crustal pressures, which are considered as a good approximation of the typical conditions in silicic magma chambers, are higher by one or two order of magnitude than in our phenocryst fragments (Stalder & Konzett, 2012). Müller & Koch-Müller (2009) report 6–13 ppm of hydroxyl defect concentrations in granite-hosted quartz phenocrysts. According to the robust dataset of Thomas & Davidson (2012), the frequency distribution of H2O concentrations in granite melts is characterized by three main peaks at: 4.0 ± 1.3, 5.9 ± 1.2, and 8.1 ± 1.1 wt.% on the basis of 4600 melt inclusions, mainly quartz-hosted. The typical concentration of H2O in quartz-hosted melt inclusions from the rhyolitic pyroclastites of the Bishop Tuff can be also as high as 6 wt.% (Table 2 in Skirius et al., 1999; Table 2 in Wallace et al., 2003). The Bishop Tuff is considered to be a good analogue to the pyroclastites of the Bükkalja Volcanic Field based on the high SiO2-content and the physical volcanological features of the deposits. This suggests that low hydroxyl defect concentrations in quartz phenocryst fragments of this study may not be related to the lower concentration of H2O in rhyolitic melt with respect to granite melts. Instead, the measured low concentrations suggest diffusive loss of hydrogen presumably coupled with the incorporation of other monovalent cations (i.e. Na+, K+) to maintain charge balance. Consequently, diffusive re-equilibration just before the eruption may be responsible – in part – for overprinting of possible former zonation of hydroxyl defects (due to Al3+ zonation) and recording the latest equilibrium hydroxyl defect-content.

Indeed the injection of hot, primitive melts into the magma chamber shortly before the eruption is commonly reported from silicic volcanic systems with the application of Ti-in-Q geothermometry (Wark & Watson, 2006; Shane et al., 2008; Campbell et al., 2009; Czuppon et al., 2012; Matthews et al., 2012). This can potentially also enhance the hydrogen and alkali diffusion in quartz. This temperature rise (in the order of ~150°C) shortly before the eruption may cause the complete re-equilibration of hydroxyl defect-content. Data on hydrogen diffusion (e.g. Kronenberg & Kirby, 1987) in natural and synthetic quartz imply an increase of the diffusivity (D [m2/s]) from ~10^-12 (T = 700°C) to ~10^-10 (T = 900°C). Using the equation (t = x^2/2D), where t is the elapsed time since diffusion began, x is the mean distance travelled by the diffusing species in one direction along one axis and D is the diffusion coefficient of hydrogen in quartz) and the above mentioned parameters (Kronenberg & Kirby, 1987) at 800°C and over ~3.5 hours, the hydrogen can diffuse over 500 µm. An increase in diffusion velocity due to temperature rise is supported by the bright luminescent and Ti-rich margins observed in some phenocryst fragments (Figs 9 and 10). The temperature rise can cause a nearly complete diffusive loss of hydrogen in quartz of which charge defects may be compensated by the incorporation of alkali cations. Thus, the pre-eruptive diffusive re-equilibration may alter the initial hydroxyl defect distribution.

(2) The hydroxyl defect-content may be further modified during post-eruption hot deposition and slow cooling. This is due to the effective diffusive loss of hydrogen from the quartz lattice generated by long-lasting high temperature coupled with the presumably much lower concentration of hydrogen (i.e. activity of hydrogen) outside of the quartz crystals in the pyroclastic material, especially during the eruption and the initial phase of deposition. We can model the potential impact of the cooling ignimbrite deposits on diffusive loss of hydrogen from quartz phenocryst fragments by model calculations. The Lower Merihuca non-welded ignimbrite around the Cerro Galán caldera is characterized by a depositional temperature of 580–610°C (Lesi et al., 2011). Considering a 600°C initial depositional temperature, using the heat-conduction formulae of Wallace et al. (2003) the temperature can stay above 550°C in the middle part of a 20 m thick ignimbrite for more than 500 days. At this temperature hydrogen diffusion is still relatively fast (ln D = 10^-13 m^2/s Kronenberg & Kirby, 1987). Using Equation 3 in Ingrin et al. (1995) the complete removal of hydroxyl defect-related absorption bands (i.e. when C_HO/C_O ~ 0) is predicted even for large quartz phenocrysts up to 3 mm at T > 550°C for 500 days. The fact that a...
A significantly lower initial temperature of deposition is the most probable factor according to several volcanological and sedimentological features, which imply strong phreatomagmatic character and shallow-marinal paleoenvironment and, thus, relatively low temperatures at the site of deposition. The presence of ash aggregates (accretionary lapilli) is characteristic for both the Lower and the Upper Ignimbrite Unit (Szakács et al., 1998). Sedimentation in partly underwater conditions is apparent from the following sedimentological fingerprints: 1) we observed water-settled clay and sand deposits beneath the lower contact of the sampled ignimbrite at Tibolddaroć; 2) coal beds from near-shore environment are significant between thick ignimbrite deposits at the Bükkalja area (Szakács et al., 1998); 3) the Lower Ignimbrite Unit covers marine sediments (Capaccioni et al., 1995).

It has been recently reported for olivine that different hydroxyl defects show different diffusion rates (Padrón-Navarta et al., 2014). Thus, it is possible that the dominance of the heteroelectronic H⁺⁺⁺Al⁺⁺ substitution for Si⁺⁺⁺ in quartz phenocryst fragments and the subordinate nature or lack of defects (i.e., hydrogarnet or Li-related defect) may imply that even if these hydroxyl defects were present before eruption, they may have been completely removed owing to their higher diffusivity. It may well be that a portion of hydroxyl defects could have been recombined into molecular water during post-eruptive cooling, like molecular water in volcanic glass during slow cooling (Zhang & Behrens 2000). However, even if this process can take place it is also in line with the more considerable hydrogen loss for the Harsány and Tibolddaroć quartz phenocryst fragments, where both molecular water and defect hydroxyl-contents are smaller.

In summary, it seems that both pre-eruptive and post-eruptive processes can effectively decrease both the hydroxyl defect and molecular water-content of quartz phenocryst fragments from rhyolite pyroclast deposits. The concentration levels and proportions of different hydrogen species in quartz, nevertheless, may bear fingerprints of both pre- and post-eruptive processes, which may help in correlating different pyroclastic horizons and reveal the position and cooling history of quartz phenocryst fragments in ignimbrite deposits. Furthermore, the investigation of hydroxyl defects and molecular water in quartz may be a viable complementary or alternative tool to the methodology of Wallace et al. (2003) to estimate cooling rates in pyroclastites. The authors used the water speciation in glass inclusions from quartz phenocryst fragments to estimate the cooling rates by considering the proportion of molecular water and hydroxyl in glass.

**Determination of effective sample ‘thickness’ of quartz by using micro-FTIR spectrometry**

The main absorption features between ~ 2010 and ~ 1440 cm⁻¹ are related to the symmetrical and asymmetrical vibrations of the Si–O bonds in quartz (Shinoda & Aikawa, 1994). The good (R² = 0.86) correlation between sample thickness and A_{Si–O}, which expresses the integrated area between 2110 and 1440 cm⁻¹, can be observed in Fig. 7. The linear relationship holds up to ~300 μm, but at larger thickness it becomes non-linear. This is because at large wafer thicknesses (~300 μm), the unpolarized absorbance is no longer a linear function of thickness (i.e., Libowitzky & Rossman, 1996; Kovács et al., 2008; Withers, 2013). This means that above ~300 μm thickness unpolared absorbance cannot be used to estimate the effective thickness of quartz. Given this limitation, the thickness of any quartz phenocryst fragments can be determined with the application of micro-FTIR spectrometry using the following equation: y = 3.3089 × ± 15%, where x is sample thickness in micrometres and y = A_{Si–O} (integrated area of Si–O bands).

![Fig. 11. Si–O-related absorbances of reference quartz sections for light propagating parallel and perpendicular to e-axis. Note the small differences between the different orientations: the first main absorption feature is observed at 1982 cm⁻¹ when the light propagates perpendicular to the e-axis (black curve) and at 1997 cm⁻¹ when light propagates parallel to the e-axis (grey curve). Furthermore, the sixth main overtone appears to split up into two well-resolvable bands at 1525 cm⁻¹ and 1471 cm⁻¹ when light propagates parallel to the e-axis. Splits of these bands is less pronounced when light propagates perpendicular to the e-axis. However, the A_{Si–O}/T (Thickness) values are nearly similar: 2.53 and 2.38 respectively.](image-url)
Although the observed correlation is not as strong as for polarised measurements and linear absorbances (Shinoda & Aikwa, 1994), a good estimation of effective sample ‘thickness’ can be achieved by using the suggested protocol. If this is applied to clean, transparent and unprepared phenocryst fragments, it gives an ‘effective thickness’ which is believed to be proportional to the volume sampled by the infrared light. This methodology has been routinely used for olivines in the diamond industry (Matveev & Stachel, 2007). The main advantage of this unpolarised method is that the preparation of oriented sections is not required and the ‘thicknesses’ of any randomly oriented quartz grain up to 300 μm can be constrained using these Si–O bands.

The minor uncertainty involved in this methodology is attributed to the moderate anisotropy of Si–O bonds and the partially polarized nature of unpolarised light. Only subordinate anisotropy was observed using unpolarised infrared radiation in two principal indicatrix sections of quartz which were parallel and perpendicular to the c-axis, respectively (Fig. 11). Both sections are characterized by six main absorption bands between 2110 and 1440 cm⁻¹.

## Conclusion

The presented micro-FTIR study of quartz wafers with different thickness shows linear relationship between sample thickness and the integrated area of Si–O bonds between 2110 and 1440 cm⁻¹. This offers a fast and accurate method of determining the effective ‘thickness’ of separated quartz phenocryst fragments without the need for orienting crystals.

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