

# VOLATILE CONCENTRATION AND DIFFUSIVITY DETERMINED BY VACUUM HOT EXTRACTION

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The concentration and mobility of water or hydrogen, influencing important properties of glasses and ceramics, were measured by vacuum hot extraction coupled with mass spectrometer evolved gas analysis. This method allows simultaneous detection of traces of evolved *water* and *hydrogen* ( $\approx 1$  wt. ppm OH) during heating. While water escapes via diffusive degassing above 350°C, hydrogen shows a more complex behavior. Volatile concentrations were obtained by integration of degassing rates. For water, the use of a low integration limit at  $\approx 400^\circ\text{C}$ , and 40-80  $\mu\text{m}$  powders could minimize the disturbing effects of surface adsorbed water. Diffusion coefficients of water, argon and hydrogen in soda-lime-silica glasses and in fused silica could be measured between  $10^{-5}$  and  $10^{-11}$   $\text{cm}^2 \text{s}^{-1}$ .

Key words: silicate glass, water, hydrogen, degassing, diffusion coefficient

## 1 Introduction

Water and hydrogen can influence important properties of glasses and glass-ceramic materials. Thus, the concentration ( $C_{\text{H}}$ ) and mobility of hydrogen ( $D_{\text{H}}$ ) in fused silica limits the durability of halogen lamps or other optical devices. The concentration of water in silicate glasses ( $C_{\text{W}}$ ) has decisive influence on viscous flow [1]. Both volatile concentrations often depend on glass melting and processing (e.g. hot shaping, joining, sintering), particular for finely grained powders or thin films, or may later vary at high application temperatures.

Water and hydrogen in silicate glasses are most frequently studied by Raman and IR spectroscopy. In some cases, e.g. for un-known extinction coefficients, the simultaneous occurrence of water and hydrogen, or for low volatile concentration [2], however, the complementary use of IR and Raman spectroscopy is necessary. Alternatively, Vacuum Hot Extraction measurements coupled with mass spectrometer detection of evolved gases (VHE-MS) can simultaneously obtain volatile concentration and diffusion coefficients for water and hydrogen. This method is also very advantageous for powdered samples and crystalline materials. The present paper illustrates the use of VHE-MS in measuring water and hydrogen degassing behavior, concentration and mobility in soda-lime-silicate glasses and fused silica.

## 2 Experimental

*Samples:* Soda-lime-silica-glasses, melted in Pt-crucibles and quenched in air, as well as different commercial silica glasses were used for preparation of bulk samples and powders. For selected glass melts, water concentration was enriched by 2h water steam bubbling at 1 bar. Related samples or results are indicated by subscript “w”. In order to compare water release kinetics to that of argon, a physically solved species of similar size, selected powder samples (40 – 50  $\mu\text{m}$ ) were annealed up to 113h at 2000 bar in argon atmosphere, which also contained traces of water. Respective indication is made by subscript “p”. Tab. 1 lists samples, treatments and sample abbreviations.

*VHE-Method and calibration:* The release of volatiles from powdered samples was measured by VHE during heating. Evolved gas detection was made using a quadruple mass spectrometer (BALZERS QMA 400). For the measurement of low temperature mobility, samples were pre-treated in vacuum. Remaining volatile contents were then checked by VHE as illustrated in section 3.2. The VHE water sensitivity,  $K_{\text{W}} = 18 \text{ mol}\cdot\text{A}^{-1}\cdot\text{min}^{-1}$ , was obtained from gypsum ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ) calibration. The minimum water detection rate  $dC_{\text{W}}/dt = 9\cdot 10^{-9}$  mol/min correlates to the signal noise level of the

mass spectrometer current for water,  $I_w^{\min} \approx 10^{-10}$  A, allowing to analyze e.g. soda-lime-silica glass powders of 40-50  $\mu\text{m}$  containing 1 wt. ppm water [3][4].  $\text{H}_2$ -Calibration was based on a reference sample containing 133 wt. ppm OH as proved by infrared spectroscopy and nuclear reaction analysis [2][5] and  $K_{\text{H}_2} \approx 11 \text{ mol A}^{-1} \text{ min}^{-1}$  was found. The VHE signal noise level for hydrogen was about  $5 \cdot 10^{-11}$  A, which allows detection of hydrogen degassing from vitreous silica of  $C_{\text{H}_2}^{\Sigma} > 0.5$  wt. ppm OH.

Glass	Sample	Composition	Water enrichment	$C_w$ in wt ppm	$C_{\text{H}_2}$ in wt ppm OH
Fused silica	S1	$\text{SiO}_2$	-	-	133
	S1 <sub>p</sub>		p: 786°C, 17h	442	-
	PE69		-	400	< 1
	PE116		-	411	54
Soda-lime-silica	NCS200	$14\text{Na}_2\text{O} \cdot 10\text{CaO}$	-	138	-
	NCS211 <sub>w</sub>	$\cdot 76\text{SiO}_2^*$	w: 1450°C, 2h	1070	-
	NCS200 <sub>p</sub>		p: 513°C, 90h	1180	-

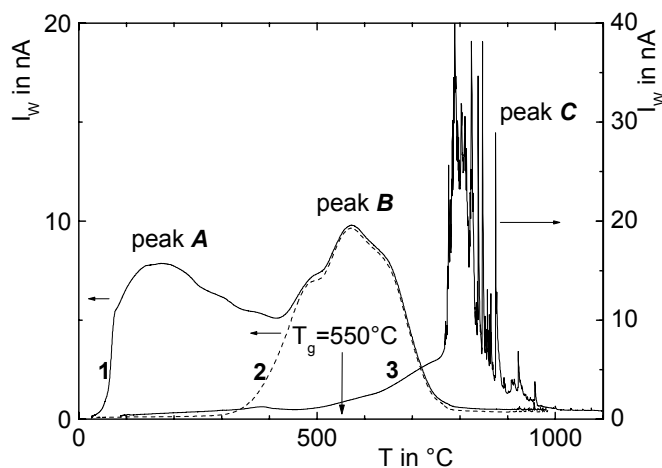
**Tab. 1:** Glass under study. \* = mol %, S1(type V): electrical fusion under  $\text{H}_2$  bearing atmosphere, PE69 and PE116 (type III): pyrolysis of  $\text{SiCl}_4$  in  $\text{O}_2/\text{H}_2$ -flame. Subscripts indicate water enrichment: w = water steam bubbling at 1 bar, p = 2000 bar pressure annealing in wet argon atmosphere. -: Not measured

### 3 Results

#### 3.1 Overall degassing

The VHE method is most traditionally used to study the release and degassing activity of volatiles during constant heating, respective temperature ranges of enhanced degassing or decomposition temperatures.

*Water:* At low concentration, water in silicate glasses is known to form silanol groups according to  $\text{H}_2\text{O} + \equiv\text{Si-O-Si}\equiv \Rightarrow 2 \equiv\text{Si-OH}$  [7]. Nevertheless, VHE degassing studies of soda-lime-silica glass powders [9] showed that water can completely escape above  $\approx 350^\circ\text{C}$  and that its degassing is entirely limited by diffusion. Thus, water can remain within the sample up to high temperature only for small partial pressure difference to the ambience, for long diffusion length (bulk samples), or for fast sample heating. In these cases, intensive bubble bursting (see e.g. Fig.1, curve 3, peak C) or complex interaction with glass crystallization [6] may occur at high temperatures.



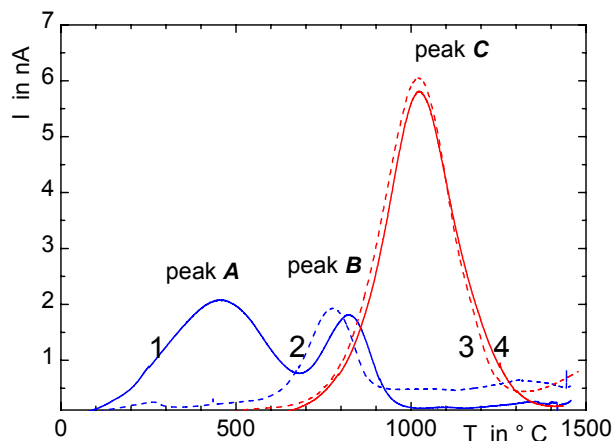
**Fig.1:** Water release from Potters Ballotini soda-lime-silicate glass powders during heating with 20 K/min. Curve 1:  $D = 20 - 40 \mu\text{m}$ , Curve 2:  $D = 20 - 40 \mu\text{m}$ , 3h vacuum pre-treated at  $280^\circ\text{C}$ . Curve 3: 1 - 2 mm. Peak A: release of surface adsorbed water, Peak B: diffusive water release from the bulk. Peak C: water release from the melt via bursting gas bubbles. Sample mass: 67 mg. Arrow: glass transition temperature,  $I_w$ : VHE ion current for water.

Diffusive degassing from finely grained powders is disturbed by surface water desorption at low temperature (Fig. 1, curve 1, peak A). The effect of surface water can be reduced by vacuum pretreatments as illustrated by curve 2 in Fig. 1. The diffusive degassing from the bulk (peak B) is not essentially influenced if vacuum pre-treatments do not surpass  $280^\circ\text{C}$ . This lower temperature limit of

water mobility well correlates to DMA studies of silicate glasses which show a maximum of mechanical loss around 200°C attributed to water [10].

*Hydrogen:* Hydrogen in silicate glasses can reversibly form Si-OH and Si-H groups according to  $H_2 + \equiv Si-O-Si \rightleftharpoons \equiv Si-H + \equiv Si-OH$ , whereas the presence of molecular  $H_2$  ( $\varnothing \approx 0.25$  nm) is more likely than that of molecular  $H_2O$  water in technical glasses ( $\varnothing \approx 0.33$  nm) particular for fused silica due to its open structure and due to manufacture technology. Therefore, a more complex degassing behavior as that for water can be expected.

Fig. 2 shows the degassing of hydrogen during heating with 20 K/min from fused silica samples S1 (type V) and PE116 (type III). As illustrated here for the powdered samples (dashed curves, 125-250  $\mu m$ ), almost no degassing occurs at low temperature since hydrogen is practically not adsorbed to the silica glass surface. Instead, degassing occurs between 600°C and 900°C for PE116 (peak **B**), and between 800 and 1200°C for S1 (peak **C**). Peak **B** and **C** are not strongly influenced by the particle size, indicating, that this process is not limited by diffusion but by the thermal stability and recombination of SiH+SiOH. A very strong low temperature degassing process (peak **A**) is evident entirely for the bulk sample of PE116. This process is not detectable for fine powders of that sample and after thermal pre-treatments, what clearly indicates a diffusion limited degassing process as it can be expected for physically solved molecular  $H_2$ . The presence of molecular  $H_2$  in bulk samples of that type of fused silica was confirmed by Raman spectroscopy [11].



**Fig.2:** Degassing of hydrogen from fused silica during heating with 20 K/min. Curve **1**: PE116, 1 - 2 mm. Curve **2** (dashed): PE116, 125 - 250 $\mu m$ , Curve **3** (dashed): S1, 125 - 250 $\mu m$ , Curve **4**: S1, 1 - 2 mm.

Peak **A**: diffusion limited degassing of molecular  $H_2$  from PE116. Peak **B**:  $H_2$  degassing limited by the recombination of SiOH and SiH (bulk and powdered PE 116). Peak **C**: as peak **B** for powdered and bulk S1. Sample mass: 100 mg, Ordinate: VHE ion current for hydrogen.

### 3.2 Concentration

VHE can easily estimate initial volatile concentrations,  $C$ , from integrating the degassing rate  $dC(t)/dt$  with respect to time. This method does not require certain sample shapes, transparency or the knowledge of IR extinction coefficients and is applicable for amorphous and crystal powders or melts of small sample mass (>50 mg) [3][4]. In order to check the completeness of degassing, repeated VHE runs or other methods (e.g. IR, Raman, NRA) can be applied. The latter methods allow calibrating the VHE signal (ion current  $I$ ), as we did for hydrogen. Alternatively, materials of known volatile contents (e.g. gypsum for water calibration) can be used.

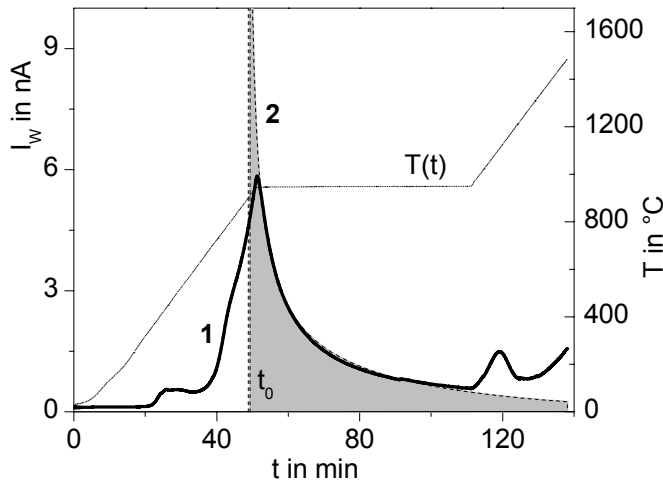
*Water:* VHE measurement of water concentration  $C_w$  of powdered samples is complicated by surface water desorption (Fig.1 curve 1, peak **A**). Therefore, the lower integration limit was set to the water degassing minimum at  $\approx 400^\circ C$ , where surface water desorption is just exhausted. The correctness of this procedure was verified by calculation of  $C_w$  for powders of different grain size ( $R = 20-1000 \mu m$ ), where the effect of surface water strongly varies, and by comparing IR measurements [6]. As an alternative or additional tool, we used vacuum pre-treatments to remove surface water. These studies indicate, that surface water almost fully escapes during 3h pre-treatments at  $280^\circ C$  while diffusive degassing from the bulk at higher temperature is still not significantly influenced (Fig.1, curve 1 and 2, peak **B**).

*Hydrogen:* Measurement of hydrogen concentration  $C_H$  is more difficult due to the strong low temperature mobility of molecular hydrogen (peak *A* in Fig. 2). This effect may even result in slow decreasing hydrogen contents for samples of short diffusion length at room temperature. Nevertheless, the actual hydrogen content of a sample could be obtained by integration of degassing rate during heating between  $\approx 25^\circ\text{C}$  and  $1600^\circ\text{C}$ . Completeness of degassing was checked by repeated VHE and for the sample S1 by comparison with other methods (IR and Raman spectroscopy) [2].

### 3.3 Diffusion coefficient

*Theory:* Isothermal degassing experiments can be utilized to obtain the coefficient of diffusion,  $D$ , according to Eq. (1) [12] where  $t$  is the degassing time,  $C^0$  the initial volatile concentration, and  $2R$  the particle diameter.  $D$  can be obtained directly from (non-calibrated) ion current  $I(t)$ , since only  $C(t)/C^0$  appears in Eq.1. In order to apply this method, we heated the sample to a temperature, where heating was stopped (curve  $T(t)$  in Fig.3) and  $I(t)$  was measured (Fig. 3, decaying part of curve 1). The second heating is convenient to shorten the time of complete degassing, needed to measure  $C^0$  or  $\int I(t)dt$  (A·min). Numerical fitting (Fig. 3, curve 2) then yields the diffusion coefficient. A virtual starting temperature  $t_0$  simulates the degassing during the first heating stage. Two different methods were applied: (I) the isothermal degassing rate was directly measured by VHE and (II) the residual concentration after vacuum pre-treatments was measured by VHE according to section 3.2 and then fitted with Eq.1. A detailed discussion of these methods is given in [3], where we also show their applicability to crystal powders.

$$\frac{C(t)}{C^0} = 1 - \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} \exp\left[-\frac{n^2 \pi^2 D t}{R^2}\right] \quad (1)$$

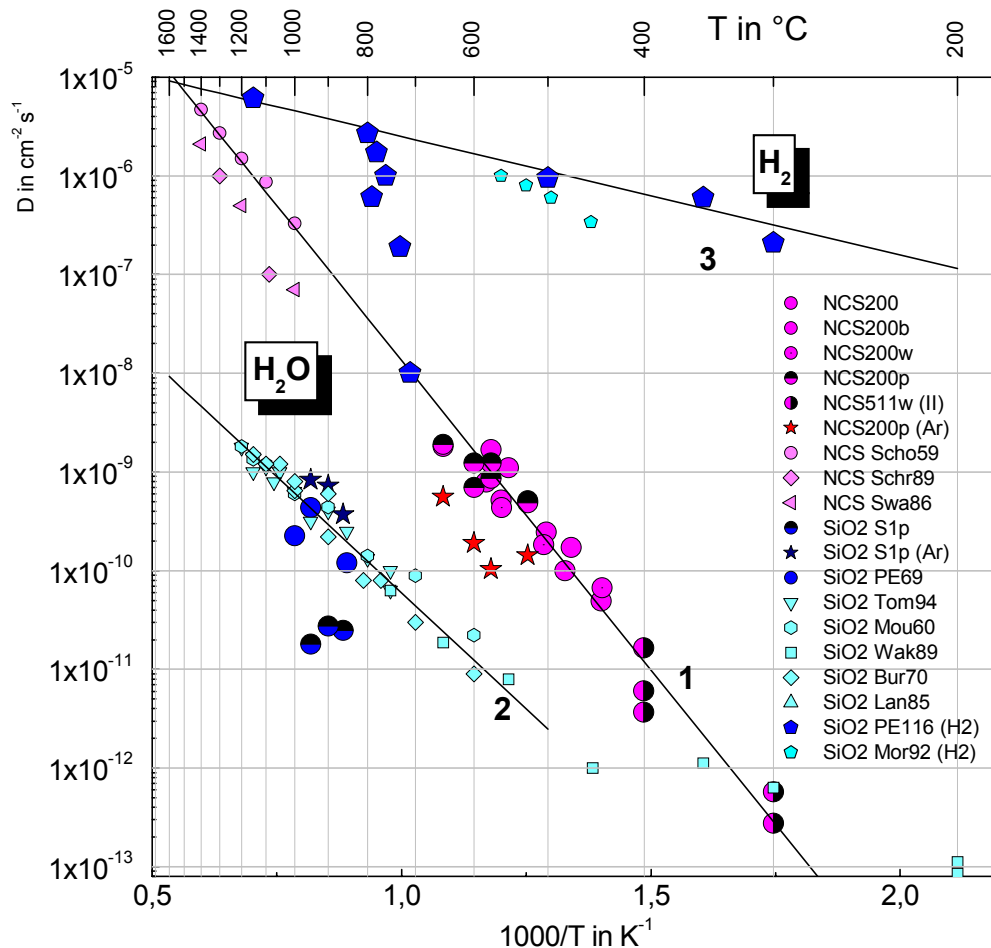


**Fig. 3:** Estimation of the diffusion coefficient for water in fused silica in terms of the respective VHE ion current  $I_W$ . Curve 1: measured degassing rate. Curve 2: fitted isothermal degassing rate according to Eq. 1. The applied time-temperature schedule is shown by dotted line and the right ordinate. The dotted vertical line indicates the virtual starting time of the numerical fitting procedure  $t_0$ . Sample: fused silica PE69 (type III), 53 mg,  $2R = 40\text{-}50 \mu\text{m}$ ,  $D_W = 4.36 \cdot 10^{-10} \text{ cm}^2\text{s}^{-1}$  at  $950^\circ\text{C}$ . Heating: 20 K/min. See Tab. 1 for sample details.

For all materials and volatiles under study, Eq. 1 fits well the observed diffusive degassing. Diffusion coefficients for water ( $D_W$ ), argon ( $D_{Ar}$ ) and hydrogen ( $D_H$ ), obtained this way, are summarized in Fig. 4 backed up by literature values.

*Water:* Obtained  $D_W$  values for soda-lime-silica glass well agree with literature data at higher temperature (Fig. 4, line 1). One should note that  $\log D_W(T)$  versus  $1/T$  follows a straight line within the very broad temperature range  $200\text{-}1600^\circ\text{C}$ , indicating a uniform energy of activation ( $E_{AW} = 116 \text{ kJ/mol}$ ) and similar structural processes of water diffusion. (In contrast,  $E_{AW}$  of the water diffusion in fused silica changes at  $\approx 500\text{-}600^\circ\text{C}$  as illustrated in Fig.4, lower right cyan scales). Furthermore,  $D_W$  does not depend on the applied water enrichment procedures for the range of  $C_W$  under study (see central pointed magenta circles for water steam bubbling and half top filled magenta circles for high-pressure annealing). At the average,  $D_W$  is about  $5 \cdot 10^{-10} \text{ cm}^2 \text{ s}^{-1}$  at  $T_g \approx 520 - 540^\circ\text{C}$ . Lines in Fig. 4 are calculated from  $D_W(T) = D_W^0 \exp[-E_{AW}/RT]$  with  $R$  as the gas constant.  $D_W^0$  and  $E_{AW}$  are listed in the caption of Fig. 4 (see [3][4] for  $D_W(T)$  of other glasses).

Confirming literature data, obtained  $D_W$  values for fused silica of type III (PE69) are much lower than those for soda-lime-silica glass, particular above 400°C (Fig. 4, line 2). This difference in  $D_W$  increases with temperature due to its moderate temperature dependency ( $E_A \approx 90 \text{ kJ mol}^{-1}$ ). In terms of the relative temperature ( $T/T_g$  were  $T_g$  is the glass transition temperature, which is 545, 521 and  $\approx 1190^\circ\text{C}$  for NCS200, NCS200<sub>w</sub> and PE69, respectively), however, water mobility is rather similar for both glasses. Compared to sample PE69,  $D_W$  for the high-pressure annealed silica glass S1<sub>p</sub> (type V), is substantial lowered ( $\approx \times 10\text{-}20$ , see half top shadowed blue circles).



**Fig. 4:** Obtained diffusion coefficients  $D$ , calculated from isothermal VHE degassing experiments (method I, not indicated) and from the VHE  $C_W$  measurement of vacuum pre-treated samples (method II). **Small symbols** and light color: literature data. **Big symbols** and deep color: this study. Water in soda-lime-silica is shown by magenta points. Circles: NCS200, central dotted circles: NCS211<sub>w</sub>, half top shadowed circles: NCS200<sub>p</sub>, half right shadowed circles: NCS511<sub>w</sub> (method II), small open circles: [7], left turned triangles: [17], diamonds: [18]. Water in fused silica: Half top shadowed blue circles: S1<sub>p</sub>, blue circles: PE69, downward cyan triangles: [20], cyan hexagons: [21], cyan squares: [22], cyan diamonds: [23]. Argon in soda-lime-silica: red stars: NCS200<sub>p</sub>, Argon in fused silica: blue stars: S1<sub>p</sub>. Hydrogen in fused silica: blue pentagon: PE116, cyan pentagon: [24]. **Lines:** calculated with  $D = D^0 \exp(-E_A/RT)$ , **1** (water in soda-lime-silica glass):  $D^0 = 2 \cdot 10^{-2} \text{ cm}^2 \text{ s}^{-1}$ ,  $E_A = 116 \text{ kJ/mol}$ , **2** (water in fused silica):  $D^0 = 3 \cdot 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ ,  $E_A = 90 \text{ kJ/mol}$ , **3** (hydrogen in fused silica):  $D^0 = 4 \cdot 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ ,  $E_A = 26 \text{ kJ/mol}$ .

Argon: Some samples were annealed at 2 kbar in argon atmosphere in order to compare the mobility of water to that of a physically solved species of similar size ( $\varnothing_{\text{Ar}} = 0.32 \text{ nm}$ ,  $\varnothing_{\text{H}_2\text{O}} = 0.33 \text{ nm}$ ). Diffusion coefficients of argon in these samples are shown in Fig.4 by blue and red stars.

Compared to the large data range shown in Fig. 4, the mobility of argon and its temperature dependence are rather similar to that of water for both glasses. Nevertheless, Ar mobility in NCS200<sub>p</sub> (soda-lime-silica glass, which was high-pressure treated close to  $T_g$  at 513°C) is  $\approx 10$  times less than that of water, whereas the mobility of water was not reduced by the high-pressure treatment. This observation indicates that the diffusion of water, which is partially present as SiOH interacting with NBO in technical soda-lime silica glass, is even relieved by this interaction. In contrast to that, high-pressure treated fused silica does not show this behavior. In this case, water mobility is strongly reduced, whereas Ar mobility is better ( $\approx \times 10$ ), being comparable to that of water in not pressure-treated fused silica samples. This interesting effect, which we do not understand so far, may reflect the low concentration of NBO and the lower relative temperature of the applied pressure treatment ( $T=786^\circ\text{C} < T_g \approx 1120^\circ\text{C}$ ).

*Hydrogen:* Isothermal  $\text{H}_2$  degassing studies for sample PE 116 conducted so far show that Eq.1 is formally applicable. Our fittings show better  $\text{H}_2$  mobility (pentagons in Fig.4) and a lower activation energy (29 KJ/mol) as found for water diffusion in fused silica. Unfortunately,  $D_{\text{H}_2}$  values between 700°C and 800°C, obtained by method I, strongly deviate from the general trend (line 3 in Fig.4). We believe that, in these cases, the recombination kinetics of SiH and SiOH (peak B in Fig.2) additionally limit the degassing process and that Eq. 1 (which assumes fully mobile species) is therefore not applicable. This effect decreases with increasing temperature, as all hydrogen is fully mobile. On the other hand,  $D_{\text{H}_2}$  at 300°C, 350°C and 1150°C was obtained by dropping bulk pieces of the sample (PE116) into the hot VHE recipient. During this very fast heating, mobile molecular hydrogen (peak A in Fig.2) remains within the sample and Eq. 1 is applicable. We are aware, however, that more and more systematic measurements are necessary to understand these interesting degassing phenomena.

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#### 5 Acknowledgements

The authors grateful acknowledge financial support from the DFG and thank Dr. H. Behrens from the University of Hannover for the high-pressure treatments, OSRAM GmbH and HERAUS Quarzglas GmbH & Co. KG for providing testing material and Mrs. A. Buchholz for technical help.