Heavy halogen impact on Raman water bands at high pressure: Implications for salinity estimations in fluid inclusions

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Heavy halogen impact on Raman water bands at high pressure: implications for salinity estimations in fluid inclusions

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Abstract

We present a new experimental dataset on the impact of the heavy halogens chlorine, bromine and iodine on the Raman water bands concerning pressure and their concentration at room temperature. These experiments were conducted at ambient temperature, with variations in halogen concentration and pressure ranging from 0 to 1.4 GPa.

The strength of the Raman water band shift change increases with the ionic size from chlorine, over bromine, to iodine. Our experiments further demonstrate that increased pressure diminishes the impact of the halogen shift change to a varying extent for each of the three halogens. This finding can have significant implications for the salinity calculation of fluid inclusions in minerals such as quartz or olivine. Particularly in the low salinity range, the concentration can be markedly underestimated if the pressure effect is neglected. For experiments in diamond anvil cells involving halogens dissolved in water, the change in Raman water band shifts can serve either as a new tool to monitor pressure, or to monitor the salinity.

Keywords

Raman, water bands, Fluid inclusion, halogens, salinity, high pressure

1. Introduction

Halogens play a pivotal role as volatile elements, significantly impacting geodynamic processes. They constitute essential components of volcanic fumaroles and volcanic ejecta. Upon release into the atmosphere, halogens contribute to ozone destruction. In crustal hydrothermal fluids, halogen complexes (e.g., in saline fluids, brines, or molten salts) serve as major agents for metal transport in ore-forming processes related to hydrothermal systems (e.g., Aiuppa et al., 2009). Samples of such fluids can be found entrapped as inclusions in minerals like quartz (e.g., Brooks et al., 2019; Pankrushina et al., 2020) or olivine (e.g., Kawamoto et al., 2013) in magmatic and metamorphic rocks. Raman spectroscopy has been employed for decades to determine the salinity of fluid inclusions, especially those too small for other common techniques like microthermometry – a method that determines salinity by observing and measuring the freezing temperature of the fluid (cf. e.g., Kawamoto et al., 2013; Moncada and Bodnar, 2012; Brooks et al., 2019).

The Raman spectra of water and aqueous fluids exhibit several peaks closely grouped at 2800-3800 cm^{-1}, resulting in water stretching bands (e.g., Ratcliffe and Irish, 1982; Sun, 2009; Walrafen et al., 1986). In salty solutions or brines, halogen ions interact with the bonds of water molecules. Although ions and ionic bonding cannot be directly detected with Raman spectroscopy, their impact on the network of covalent water bonding is detectable. This effect has been the subject of numerous studies, with a substantial focus on chlorine (e.g., Dubessy et al., 2002; Durickovic et al., 2010; Georgiev et al., 1984; Mernagh and Wilde, 1989; Pankrushina et al., 2020; Sun, 2012; Sun et al., 2010; Tepstra et al., 1990) and, to a lesser extent, on the heavy halogen bromine (e.g., Tepstra et al., 1990). Halogen anions widen the water bonding network, forcing the network to change its bonding structure by favoring a certain type of bonding over others. A shift in water bands can be observed, correlating with the number of dissolved halogens and facilitating the determination of salt concentration in the solution or in mineral fluid inclusions (e.g., Dubessy et al., 2002; Durickovic et al., 2010; Georgiev et al., 1984; Mernagh and Wilde, 1989; Pankrushina et al., 2020; Sun, 2012; Sun et al., 2010; Tepstra et al., 1990).

The heavy halogens bromine and iodine possess a larger ionic size than chlorine. Their anions stretch the water network as much or even more than chlorine, causing a more pronounced alteration of the Raman shift (Tepstra et al., 1990). The impact of the cations (e.g., calcium, magnesium, sodium, potassium) in a salty solution seem to be negligible (Sun et al., 2010).

Two other factors can alter the shape of Raman water bands: (1) temperature (e.g., Krishnamurthy et al., 1983; Ratcliffe and Irish, 1982) and (2) pressure (Romanenko et al., 2018). Increasing temperature has a similar effect to increasing halogen concentrations, enhancing the resulting peak at around 3430 cm^{-1}. Pressure shifts the bands in the opposing direction: It decreases the peak at 3430 cm^{-1} and increases the peak at 3240 cm^{-1}.

While fluid inclusions in minerals are typically studied at ambient temperature and its effect can be ignored, the pressure in mineral fluid inclusions, such as those in quartz, is likely to be elevated, potentially impacting the Raman spectrum. In this study, we present a novel experimental dataset examining the impact of all three heavy halogens — chlorine, bromine, and iodine — on Raman water bands concerning pressure and halogen concentration at room temperature. We further compare our results to some natural fluid inclusion samples from other studies to demonstrate and constrain the impact of our dataset on natural fluid inclusions.

2. Experimental setup and methods

Various concentrations of NaCl, NaBr, or NaI salts were dissolved in water to synthesize salty solutions as starting materials (Table 1). Sodium-halogen salts exhibit excellent solubility in water, and sodium serves as the dominant cation in seawater-related fluids. Despite the seemingly negligible impact of cations (Sun et al., 2010), sodium was selected as the cation for all three halogens to mitigate cation effects and focus on the influence of the three halogen anions.

The experiments were conducted using a Chervin-type hydrothermal diamond anvil cell (HDAC) with a pressure-driving membrane (Chervin et al., 1995). The HDAC was equipped

with 2 mm thick diamonds and culets of 1 mm diameter. The sample chamber, compressed between two diamonds, had a diameter of 500 µm, drilled as a hole into a Re gasket with an initial thickness of 200 µm. Before each experiment, the sample chamber was cleaned with ethanol, dried, and loaded with a salty solution along with a small number of ruby spheres for pressure calibration. Following HDAC closure, the membrane was connected to an inflator with a N_2 gas bottle. The membrane was initially loaded with approximately 10 to 15 bar of gas pressure, sufficient to seal the HDAC but insufficient to observe a fluorescence shift with the ruby spheres.

Ruby fluorescence serves as a widely used pressure monitor for various DAC experiments (e.g., Chervin et al., 2001; Shen et al., 2020). The ruby shift was calibrated with the Raman to ambient pressure and had to be recalibrated for each new sample. After the ruby calibration, the water bands were measured with the Raman at ambient pressure. The pressure was then increased stepwise with an inflator, and pressure increases were monitored on the ruby fluorescence. Pressure steps were approximately 0.2 to 0.3 GPa. Depending on the salt concentration, the solution transformes into ice IV between 1.1 and 1.4 GPa (see below). After each pressure increase, the cell equilibrated the pressure for about 10 minutes before Raman analysis.

Raman measurements were performed with a 514.5 nm Argon laser and a Jobin-Yvon Horiba HR460 spectrometer. A constant grating of 1500 lines/mm, a slit size of 50 µm, and a 50x objective placed in front of the diamond anvil cell were used. The setup was calibrated with a 521 cm^{-1} silicon wafer, and the laser energy was controlled to remain constant at 10 mW between each measurement during the pressure equilibration period. Diamond has no effect on the Raman water bands and is widely used for these types of studies. Test runs for pure water in the DAC and in a glass cylinder showed no difference in the spectra. Measurements in the solution were conducted in the center of the sample chamber by defocusing the laser spot between both surfaces of the two diamonds. Measurements in the solution were set for 10 to 30 seconds with 3 to 5 iterations. Measurements on the ruby spheres were conducted "live" with a repetition rate of 1s.

It is important to note that halogens like iodine can also induce a Raman peak at around 1650 cm^{-1} (Besemer et al., 2016). However, this peak overlaps with the (extremely large) carbon peak from the diamond anvils and cannot be used for hydrothermal DAC experiments or for pressure calibration with HDAC.

The acquisition and processing of the Raman spectra were carried out using the Labspec software. For baseline correction, peak deconvolution, and spectra smoothing (using "adjacent averaging" with a step size of 40), the Origin software was employed. Values for R_D and S_D (both are ratios that can be used to quantify the peak change numerically; see also further below) were calculated prior to spectra smoothing.

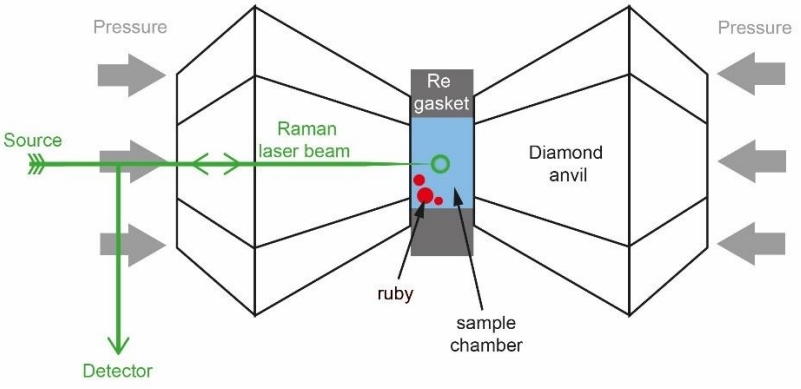

Figure 1 Experimental Setup: The saline solution was loaded into a hydrothermal diamond anvil cell (HDAC). Pressure control was achieved using an external inflator, and pressure levels were monitored via the fluorescence of ruby spheres suspended in the sample chamber. Raman measurements in the solution were performed at the center of the sample chamber by intentionally defocusing the laser spot between the surfaces of the two diamonds.

3. Results

At ambient pressure and temperature, the configuration of the water stretching bands undergoes changes based on halogen concentration:

1. The 3428 cm^{-1} peak increases with rising halogen concentration: from 6660 counts for pure water to 7900 counts for 1.71 mol/l chlorine, 8800 counts for 1.46 mol/l bromine, and 9300 counts for 1.67 mol/l iodine, respectively.
2. The 3428 cm^{-1} peak shifts to higher wavenumbers with specific positions at 3441 cm^{-1} for chlorine, 3450 cm^{-1} for bromine, and 3460 cm^{-1} for iodine at their respective highest concentrations.
3. The minor peak at 3240 cm^{-1} becomes relatively smaller as halogen concentration increases, decreasing from 5060 counts for water to 4400 counts for chlorine, 4190 counts for bromine, and 4430 counts for iodine (Figure 2).

At a constant halogen concentration, the characteristics of the water stretching bands evolve with increasing pressure:

1. The 3428 cm^{-1} peak decreases with rising pressure: from 6975 counts at 0 GPa to 5960 counts at 1.1 GPa for 0.34 mol/l chlorine, from 8800 counts at 0 GPa to 7350 counts at 1.1 GPa for 1.45 mol/l bromine, and from 6315 counts at 0 GPa to 6010 counts at 1.39 GPa for 0.2 mol/l iodine.
2. The 3428 cm^{-1} peak shifts to lower wavenumbers, with new positions at 3390 cm^{-1} for chlorine, from 3450 to 3435 cm^{-1} for bromine, and from 3430 to 3390 cm^{-1} for iodine at their respective highest pressures.
3. The minor peak at 3240 cm^{-1} becomes relatively larger with increasing pressure, exhibiting a slight increase from 4970 to 5140 counts for chlorine, from 4190 to 4590 counts for bromine, and from 4960 to 5255 counts for iodine (Figure 3).

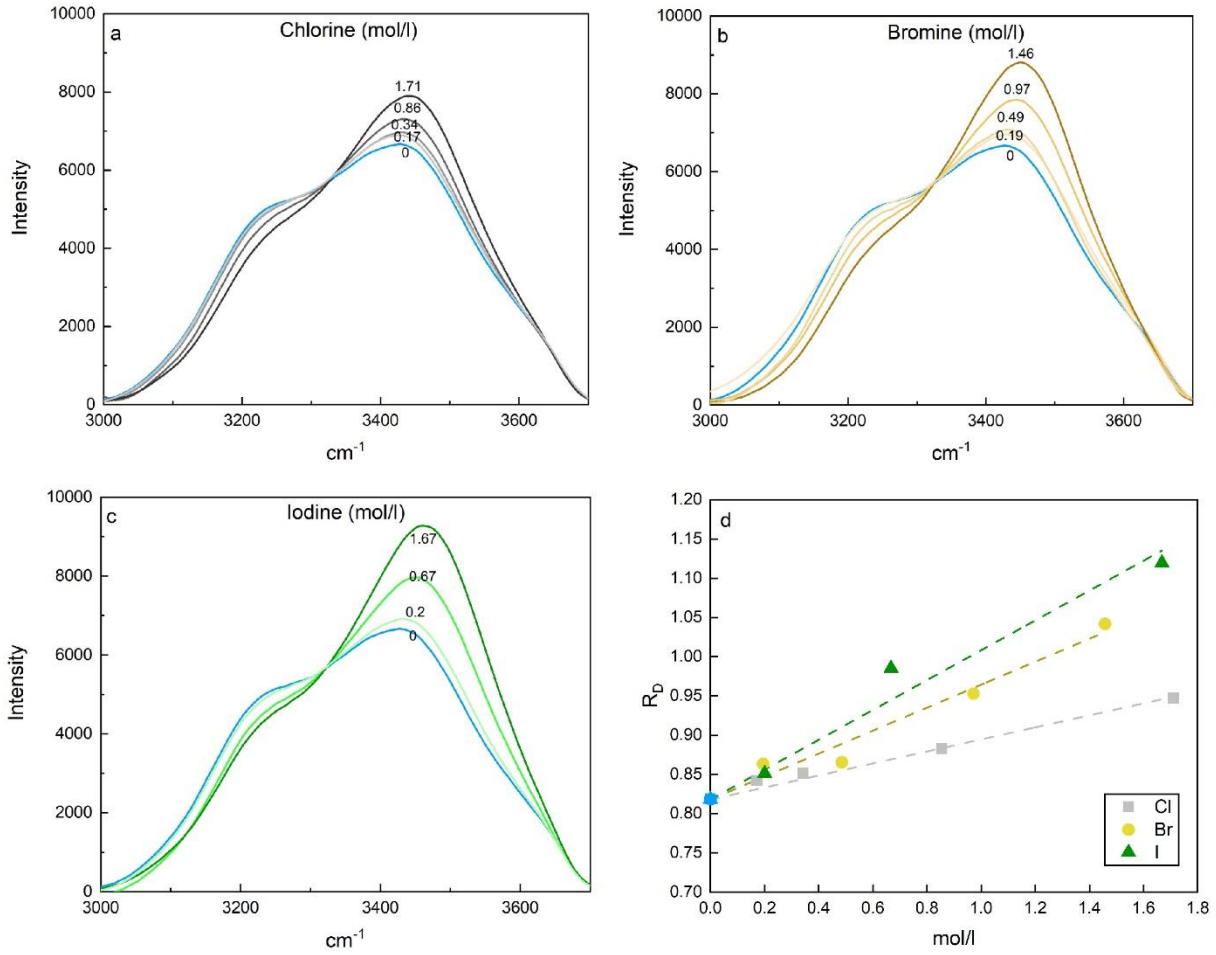

Figure 2 The Raman water bands of saline solutions with varying concentrations of a) chlorine, b) bromine, and c) iodine are depicted. The halogen concentrations are indicated on the spectrum in mol/l. Notably, the resulting peak of the water bands at 3428 cm^{-1} exhibits an increase and shifts further to the right with escalating halogen concentration. The Raman spectrum of pure water is represented in blue. In d), there is a discernible increase in R_D with escalating concentrations of chlorine, bromine, and iodine. This increase is characterized by a larger sum of slopes between 3325 cm^{-1} and 3600 cm^{-1}, and a heightened peak at 3428 cm^{-1}. The observed effects are smallest for chlorine and most pronounced for iodine.

4. Discussion

4.1. Halogen concentration and ionic size

The correlation between the change in the water bands' peak and varying halogen concentration, in addition to ionic size, aligns well with findings from previous studies (Dubessy et al., 2002; Durickovic et al., 2010; Georgiev et al., 1984; Mernagh and Wilde, 1989; Pankrushina et al., 2020; Sun et al., 2010; Tepstra et al., 1990). The observed shift change strength correlates directly with the ionic size of the halogens: Chlorine exhibits the smallest shift, iodine the largest, and bromine falls in between for comparable concentrations (cf. Tepstra et al., 1990 for chlorine and bromine).

Since ionic bonds are not Raman active, NaCl, NaBr, and NaI do not have observable modes of their own, neither as salts nor as dissolved ions in water (Bakker, 2004; Pei et al., 2006; Terpstra et al., 1990). Raman spectroscopy enables the observation of the vibration of chemical bonds, which, in this study, is the chemical vibration of water. The halogen anions are indirectly observed as they modify the vibrations of water bonding. The evolving shape of the Raman spectra in Figure 2 illustrates that different halogens influence the dominant bonding type in the water structure, leading to a reduction in hydrogen bonding in water. Figure 4 presents a deconvolution of the water stretching band into three major Gaussian components representing different bonding types for water molecules:

Peak 1 of the first Gaussian component at 3327 cm^{-1} is attributed to 4 hydrogen bonds per water molecule, involving two electron donors and two acceptors (DDAA). This peak diminishes with increasing halogen content. Peak 2 at 3431 cm^{-1} is attributed to 2 hydrogen bonds (DA) and becomes the predominant bonding type with increasing halogen content. Peak 3 at 3565 cm^{-1} is attributed to 3 hydrogen bonds per water molecule (DDA). It plays a minor role in pure water as well as in salty solutions (e.g., Sun, 2009). With the addition of salt, the increasing presence of cations and anions breaks the hydrogen bonds in the water network, forming ionic bonds.

The deconvolution of the Raman water bands confirms the reduction of hydrogen bonding in water with the addition of various halogens, as well as with their increasing ionic size.

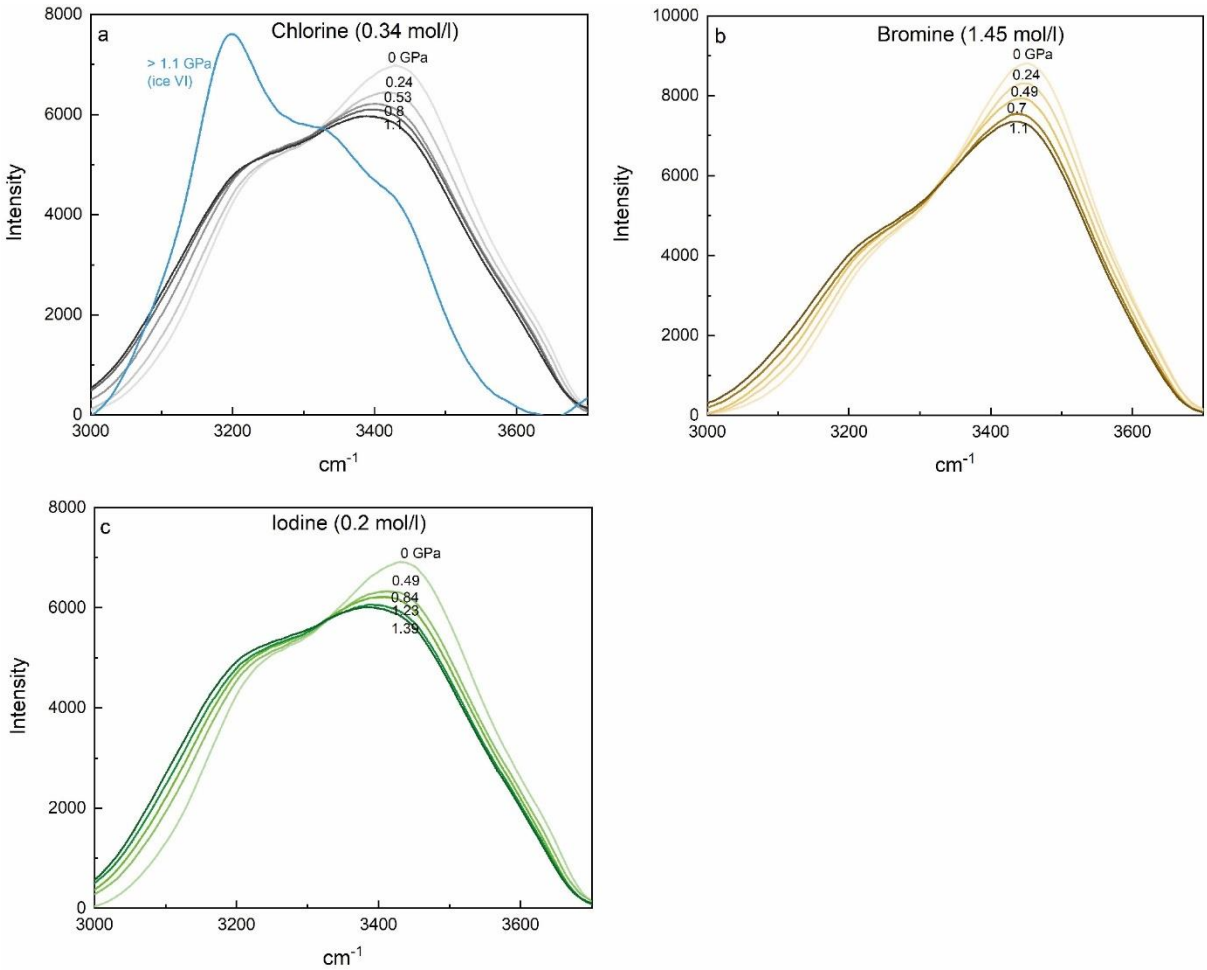

Figure 3 The Raman water bands of saline solutions are presented with fixed halogen concentrations and varying pressure: a) 0.34 mol/l chlorine, b) 1.45 mol/l bromine, and c) 0.2 mol/l iodine. The pressure is indicated in GPa on the spectra. Notably, the resulting peaks exhibit a reduction in intensity with increasing pressure and shift towards lower wavenumbers, indicating a leftward shift in the spectra.

4.2. R_D as numerical value for the changing effect

To quantify the changing shift of the water stretching bands, Durickovic et al. (2010) introduced the ratio S_D, defined by the formula:

$$S_D = \frac{\sum_{i=326}^{650}\left\{\frac{I(i)+I(i-1)}{2} * [n(i)-n(i-1)]\right\}}{\sum_{i=1}^{325}\left\{\frac{I(i)+I(i-1)}{2} * [n(i)-n(i-1)]\right\}}$$

Here, *n(i)* represents the shift at increment (or pixel) *i*, *I(i)* is the intensity at increment (or pixel) *i*, and the range of interest is between 3000 and 3650 cm^{-1} with a total of 650 pixels. This formula establishes the inflection point of the water bands at 3325 cm^{-1} (Figure 4) and divides the water bands into two halves: left and right side from the inflection point. Durickovic et al. (2010) observed that S_D increases linearly with increasing NaCl concentration dissolved in water.

With increasing halogen concentration, the slope increases on both sides of the inflection point, resulting in an increase in both the sum of slopes for the left and right halves (cf., Figure 2). This trend holds for all three studied halogens: chlorine, bromine, and iodine. To avoid division of two values that both correlate positively and increase with higher halogen concentrations, a ratio R_D was calculated, slightly different from S_D. The formula for R_D is as follows:

$$R_D = \frac{\sum_{i=1}^{325}\left\{\frac{I(i)+I(i-1)}{2} * [n(i)-n(i-1)]\right\}}{I_{i=1} * 325}$$

Here again, *n(i)* represents the shift at increment (or pixel) *i*, *I(i)* is the intensity at increment (or pixel) *i*, and the total number of pixels considered is 325, starting from 3325 to 3650 cm^{-1}. This formula reduces some information loss from S_D and steepens the slope, as both the numerator and denominator of the ratio increase with increasing halogen concentration.

However, the applicability of R_D is limited to liquid water. R_D does not account for strong changes in the shape of the slope, making it less suitable for high-pressure or low-temperature polymorphs (e.g., ice VI), which exhibit the dominant peak on the left side of the inflection point (Figure 3).

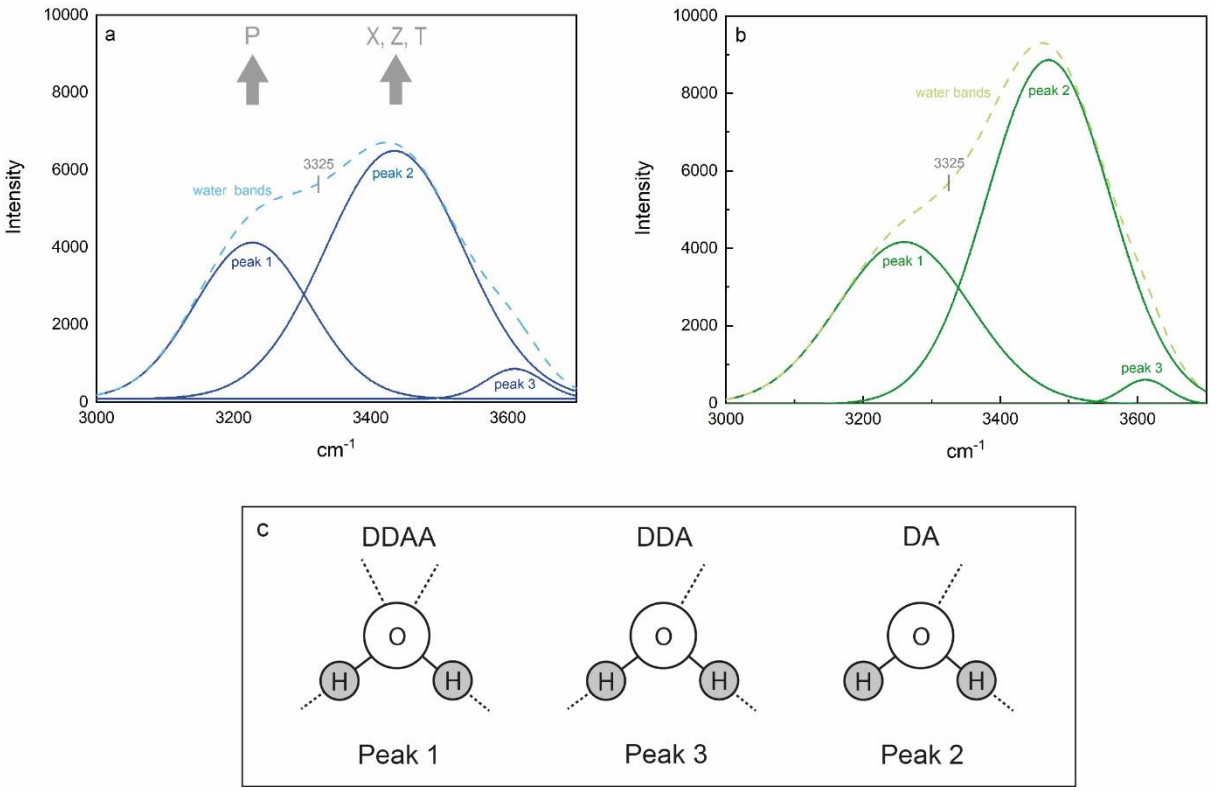

Figure 4 The peak-deconvoluted Raman water bands are presented for a) pure water and b) 1.67 mol/l iodine, resolved into three Gaussian components. The resulting water bands are represented by dashed lines, with the inflection point of the water bands curve identified at 3325 cm^{-1}. Notably, with increasing iodine content (X) halogen ionic size (Z), and temperature (T), peak 2 becomes larger relative to peak 1, while pressure (P) has the opposing effect. In c), the components of the deconvolution are explained: Peak 1 is attributed to 4 hydrogen bonds per water molecule, involving two electron donors and two acceptors (DDAA). Peak 2 is attributed to 2 hydrogen bonds (DA). Peak 3 is attributed to 3 hydrogen bonds per water molecule (DDA) (Sun, 2009). The deconvolution of the Raman water bands confirms a reduction in hydrogen bonding in water with the addition of various halogens and their increasing ionic size. Moreover, increasing pressure correlates with an augmented number of hydrogen bonds.

4.3. Pressure

With increasing pressure, the water stretching band peak at 3428 cm^{-1} undergoes a reduction in intensity and shifts towards the left (e.g., Romanenko et al., 2018), while the smaller peak at 3240 cm^{-1} experiences a slight increase. The observed change stands in contrast to the effects observed during temperature increase (cf., Durickovic et al., 2010) or the addition of halogens (Figure 3). This shift can be interpreted as a transition towards a higher number of hydrogen bonds (from DA to DDAA) in the water molecule network (Sun, 2009, Figure 4). The effect is observable for all three halogens (chlorine, bromine, and iodine) in the saline solutions of this study (Figure 3).

Sun (2012) did not observe the pressure effect in their chlorine data and argue against its existence. However, upon normalizing our data in the same way as Sun (2012), the peak at 3428 cm^{-1} decreases, and the water bands flatten, yet a clear pressure trend remains (Supplementary Figure S1). It remains unclear why the trend was not observed in Sun (2012).

At pressures greater than 1 GPa and ambient temperature, water transforms into ice VI (Figure 3). Notably, with increasing halogen concentrations, the water-ice phase transformation shifts to higher pressures. In this study, liquid water/saline solution was observed at 1.1 GPa and 0.34 mol/l chlorine, 1.37 GPa and 0.97 mol/l bromine, or 1.27 GPa and 0.67 mol/l iodine. The experimental setup does not precisely determine if the phase boundary shifts to higher pressure or if the liquid state is metastable. Journaux et al. (2013) investigated the impact of NaCl on the phase boundary of ice VI and found the boundary at 1.01 GPa for 1 mol/l, 1.09 GPa for 2.5 mol/l, and 1.52 GPa for 4 mol/l at ambient temperature. This boundary shift is much smaller than the observed range, suggesting a metastable liquid phase in our study or other kinetic effects.

As a consequence of the pressure-related shape change of the water stretching bands, R_D decreases with increasing pressure for fixed halogen concentrations (Figure 3). Figure 5 illustrates the R_D values vs. halogen concentration at different pressures (S_D values in Supplementary Figure S2). Despite some outliers, the values follow a linear trend in the studied range, as previously observed for various temperatures (Durickovic et al., 2010). Within the

range of comparable pressures, chlorine exhibits the lowest R_D values, while iodine demonstrates the highest. Comparable trends are also observed for integrated intensities (Supplementary Figure S3) but show larger scatter relative to the R_D trends in Figure 2d and Figure 5.

4.4. Applications

4.4.1. Natural fluid inclusions with one unknown component (P or X)

R_D can be calculated from Raman spectra of natural fluid inclusions in minerals, as demonstrated by Kawamoto et al. (2013). In their study, saline fluid inclusions in spinel-harzburgite xenoliths collected from the 1991 Pinatubo pumice deposits were examined. The salinity of the fluid inclusions was reported as 5.1 ± 1 wt.% NaCl equivalent (0.87 ± 0.17 mol/l), measured with microthermometry. The authors employed Raman spectroscopy for qualitative water measurements.

From the provided Raman spectrum, a R_D value of 0.79 can be calculated. The measured chlorine concentration from microthermometry allows for an estimate of the pressure to be around 0.5 GPa (Figure 5a). This is notably lower than the 2-3 GPa that Kawamoto and colleagues estimated for the formation of the saline fluid inclusions in olivine below the Pinatubo. Given the available information, it can only be speculated whether some (parts) of the olivines formed at a very low pressure of 0.5 GPa, or if the inclusion lost pressure, and it was not fully closed above 0.5 GPa. In this case, the inclusion could at least partially represent the conditions at 0.5 GPa rather than at 2-3 GPa.

It is crucial to note that a fluid inclusion that closes between 810 °C and 1050 °C (Kawamoto et al., 2013) will experience a decrease in pressure when cooling down to ambient temperature. This phenomenon is also well observed in HDAC experiments (e.g., Bureau et al., 2010, 2016; Leroy et al., 2019; Louvel et al., 2020a, 2020b) and argues for a higher pressure than the 0.5 GPa that were obtained from the Raman spectrum. However, this sample

serves as a good illustration of how pressure can be estimated by Raman in saline fluid inclusions with given salinity.

4.4.2. Natural fluid inclusions with two unknown components (P and X)

Difficulties arise when neither pressure nor salinity can be determined with a different method, and only the Raman spectrum is available. This scenario may occur for fluid inclusions that are too small for microthermometry, resulting in a single equation with two unknown parameters that cannot be solved for a distinct value.

Saline fluid inclusions from quartz samples analyzed by Pankrushina et al. (2020) illustrate the pressure dependence in Figure 5d, where R_D values plot as a constant line. For instance, q1 has 1.9 mol/L NaCl at ambient pressure and 2.71 mol/L at 0.16 GPa; q2 has 1.88 mol/L and 2.69 mol/L; and q3 has 1.02 mol/L and 1.75 mol/L at ambient pressure and at 0.16 GPa, respectively. For an unknown pressure, a single salinity value cannot be determined this way. Particularly at lower salinity concentrations, the range of possible salinities can be drastic: for the three natural samples q1-3, a small pressure increase of 0.16 GPa changes the salinity by 42 to 72%. Given the stability field of quartz and saline fluids at room temperature, these are conservative calculations, and a much larger pressure range of > 1 GPa must be considered.

However, fluid inclusions can be saturated in NaCl, and halite crystals do coexist with saline fluids in the inclusion (e.g., Brooks et al., 2019). The solubility of NaCl in water at ambient P-T conditions is 317 g/l or 5.4 mol/l (cf. Figure 5). The pressure effect is diminished at NaCl-saturated conditions: Experiments in this study were conducted up to a salinity of 1.71 mol/L for NaCl, but assuming a continuation of the observed linear trend, the difference between 0 and 0.16 GPa would be only 16 to 18%.

Therefore, the pressure effect in fluid inclusions with high salinity is smaller than in fluid inclusions with low salinity. But as the potential pressure range is large (more than 1 GPa),

ignoring the pressure effect can lead to a huge underestimation of the salinity in the fluid, and Raman spectroscopy alone cannot be used to determine reliable salinities in fluid inclusions.

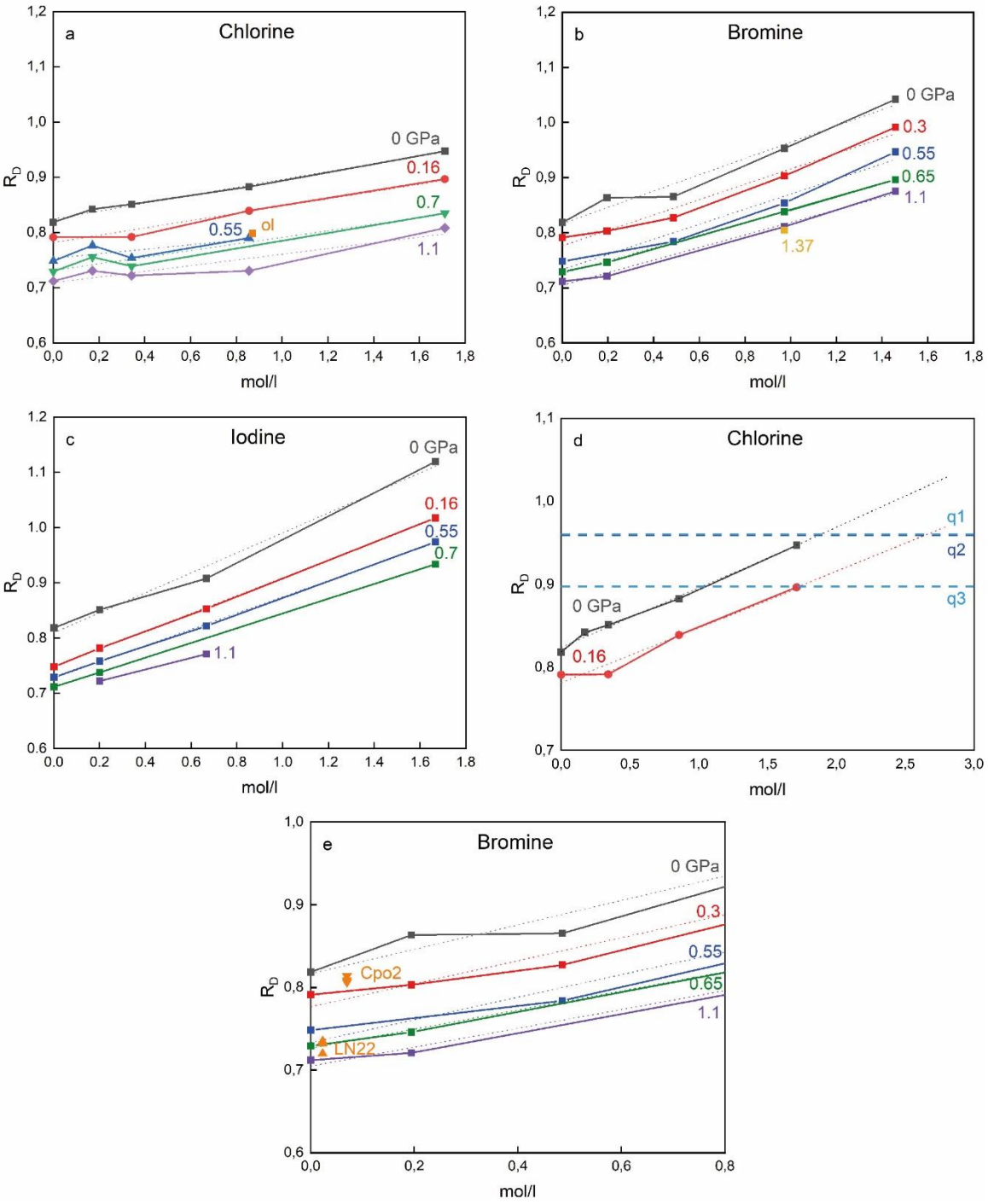

Figure 5 *R_D values vs halogen concentration for (a) chlorine, (b) bromine, and (c) iodine are presented in the figure. The colored lines indicate isobars: the solid lines connect the data points, while the dotted lines represent trend lines. Like the Raman water bands and the R_D*

values, the isobars exhibit the steepest slope for high concentrations of iodine and become flatter with smaller ionic halogen size, but also with increasing pressure. (a) "ol" data are from a natural fluid inclusion in olivine (Kawamoto et al., 2013). (d) Calculated R_D values for natural fluid inclusions in quartz demonstrate the pressure effect: q1 has 1.9 mol/L NaCl equivalent at ambient pressure and 2.71 mol/L at 0.16 GPa; q2 has 1.88 mol/L and 2.69 mol/L; and q3 has 1.02 mol/L and 1.75 mol/L at ambient pressure and at 0.16 GPa, respectively. The fluid inclusions were analyzed by Pankrushina et al. (2020) (sample names are q1 = 672; q2 = 33604; q3 = 20512). (e) Cpo2 and LN22 are experimental HDAC samples. Bromine content was analyzed with X-ray fluorescence following the methods reported in Bureau et al. (2010) and Grützner et al. (2024).

4.4.3. Heavy halogens in HDAC experiments

The heavy halogens bromine and iodine typically play a minor role in natural fluid inclusions. The Cl/Br ratio in seawater is approximately 30, and the Cl/I ratio is around 50 (cf. Shaw and Cooper, 1957 for iodine). Due to enrichment and depletion processes in the Earth's mantle, Cl/Br ratios can vary significantly, ranging, for example, in diamond inclusions from 1 to 500 (Jonson et al., 2000). Despite their low concentration and minor role in fluid inclusions, heavy halogens are highly reactive and serve as important chemical agents in Earth’s atmosphere (Fehn et al., 2012). Particularly for bromine, volcanoes have been recognized as significant contributors (Gerlach et al., 2004), if not the primary controlling factor (Pyle and Mather, 2009), to the current atmospheric content. This recognition is crucial, as bromine can be approximately 60 times more efficient (Sinnhuber et al., 2009) than chlorine in the destruction of stratospheric ozone (Daniel et al., 1999; Gerlach et al., 2004).

Over the past few decades, numerous studies have conducted high-pressure experiments on bromine- and iodine-bearing fluids interacting with silica melts in hydrothermal diamond anvil cells (HDAC). In these studies, the halogen content in the fluid was measured using synchrotron X-ray fluorescence (Bureau et al., 2010, 2016; Kawamoto et al., 2014; Leroy et

al., 2019; Louvel et al., 2020a, 2020b). These experiments provide valuable insights into the behavior of heavy halogens during fluid-magma degassing processes.

However, these experiments entail complex setups and lack reliable and easily adaptable pressure sensors. The fluorescence wavelength shift of ruby is a commonly used pressure sensor (e.g., Chervin et al., 2001; Shen et al., 2020), but it cannot be applied in experiments conducted at elevated temperatures where ruby spheres dissolve. Other pressure indicators, like X-ray diffraction of gold particles, are only reliable at higher temperatures (cf. Grützner et al., 2024; Louvel et al., 2020b). Pressure monitoring in these HDAC experiments is essential to understand the pressure effect on halogen partitioning between silicate melts and aqueous fluids. Moreover, it is crucial to exclude pressure loss processes during the experiment (cf. Bureau et al., 2010, 2016; Leroy et al., 2019; Louvel et al., 2020a, 2020b).

Most HDAC experiments are conducted at high temperatures, reaching several hundred degrees Celsius (e.g., Bureau et al., 2010, 2016; Grützner et al., 2024; Leroy et al., 2019; Louvel et al., 2020a, 2020b). The elevated temperature introduces an additional variable to the shift change of the water bands, as they also change with varying temperature (Krishnamurthy et al., 1983; Ratcliffe and Irish, 1982).

Thus far, residual pressure can be monitored at ambient temperature, for example, before and after the experiment, once the fluid has been cooled down to room temperature. Figure 5e illustrates two samples used for test measurements, following the experimental setup and the analytical methods for bromine concentration reported in Grützner et al. (2024). These samples represent experiments that tested the degassing reaction of a bromine-doped basalt melt into an aqueous fluid. Experiments were conducted at high temperatures (above the basalt solidus) and pressures of up to 1.7 GPa in a hydrothermal diamond anvil cell (cf. Grützner et al., 2024, for a detailed description of the experiments). Bromine concentrations of 0.07 mol/L for sample LN22 and 0.023 mol/L for Cpo2 were measured in the fluid by synchrotron x-ray fluorescence (SXRF) during the experiments. Raman spectra of the aqueous fluids were analyzed after the experiment under room temperature conditions. Bromine

concentrations from SXRF, together with the Raman spectra, allow estimating pressure ranges of 0.7 to 0.9 GPa for LN22 and 0.1 to 0.2 GPa for Cpo2.These promising results show that Raman water bands can be used as pressure or salinity indicators from room to high temperatures, providing additional pressure-concentration-related temperature calibrations are performed.

5. Conclusion

Our new experimental dataset demonstrates that the impact of halogens on the change of Raman water band shifts increases with ionic size from chlorine over bromine to iodine. To address and compare these changes, we calculated the numerical value R_D. Our experiments further show that increased pressure diminishes the impact of the halogen shift change to a different extent for each of the three halogens. This can have drastic consequences for the salinity calculation of fluid inclusions in minerals like quartz or olivine. Especially in the range of low salinity, the concentration can be strongly underestimated if the pressure effect is ignored. Either pressure or salinity needs to be determined by an independent method. For experiments performed in diamond anvil cells with halogens in aqueous fluids, the change of Raman water band shifts can be a beneficial (with some restrictions) tool to monitor the pressure at room temperature, if salinity is known, and inversely this change can be used to monitor the salinity.

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410 Statement: During the preparation of this work the authors used ChatGPT 3.5 to correct
411 errors of spelling, punctuation, grammar and to improve the syntax in several chapters of the
412 manuscript. After using this tool, the authors reviewed and edited the content and take full
413 responsibility for the content of the publication.

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8. Tables

	NaCl				max(NaCl)[a]
g/l	10	20	50	100	*317*
mol/l	0.17	0.34	0.86	1.71	*5.42*
wt.%	0.99	1.96	4.76	9.09	*24.07*

	NaBr				max(NaBr)[a]
g/l	20	50	100	150	*905*
mol/l	0.19	0.49	0.97	1.46	*8.80*
wt.%	1.96	4.76	9.09	13.04	*47.51*

	NaI			max(NaI)[a]
g/l	30	100	250	*1793*
mol/l	0.20	0.67	1.67	*11.96*
wt.%	2.91	9.09	20.00	*64.20*

[a] maximum solubility in H_2O at 20 °C and ambient pressure.

Table 1 Salt concentration in the starting solutions and maximum solubility values.

9. Supplementary material

Supplementary Tables with Raman raw data are stored under https://data.mendeley.com/datasets/tnckfpfjcv/1.

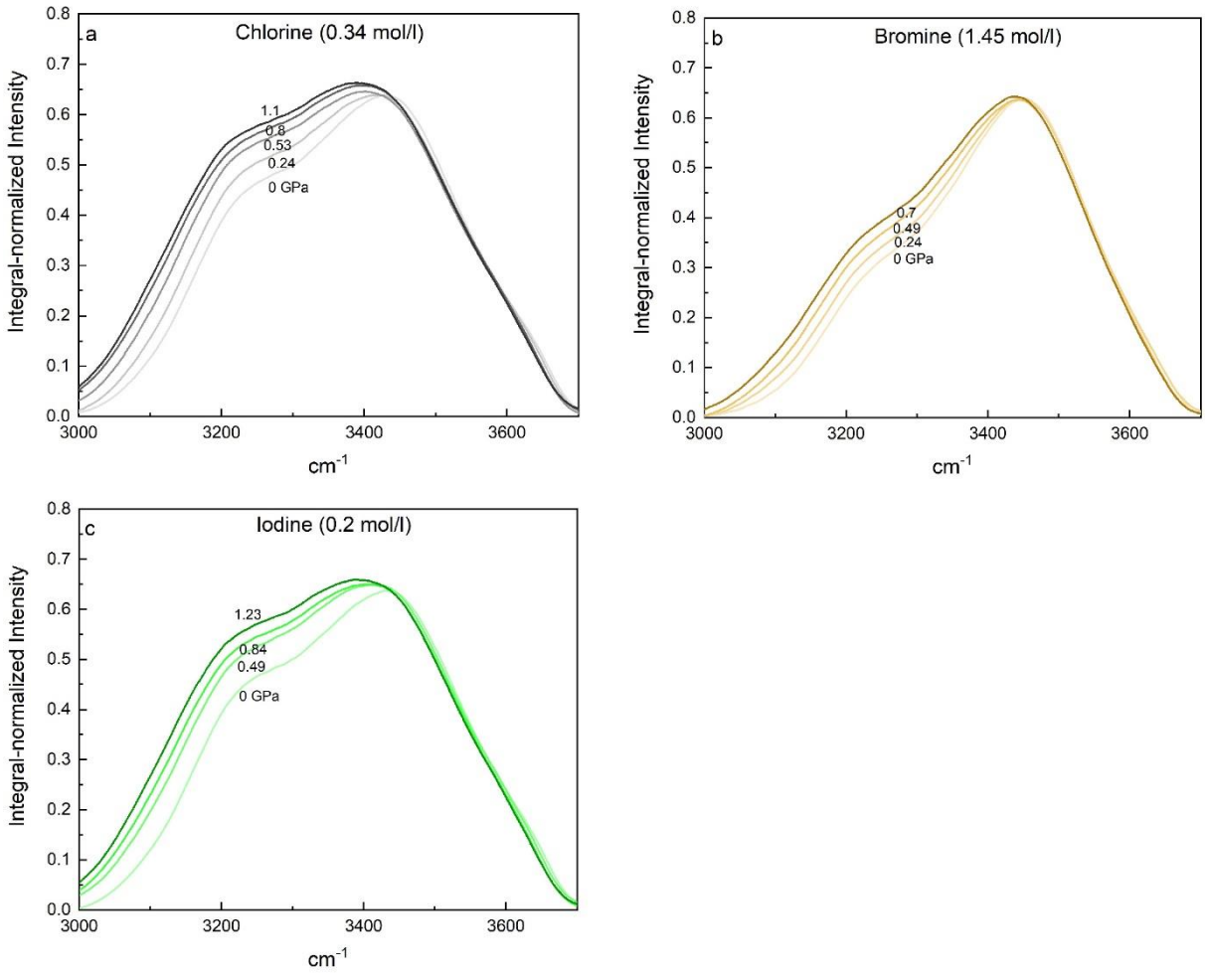
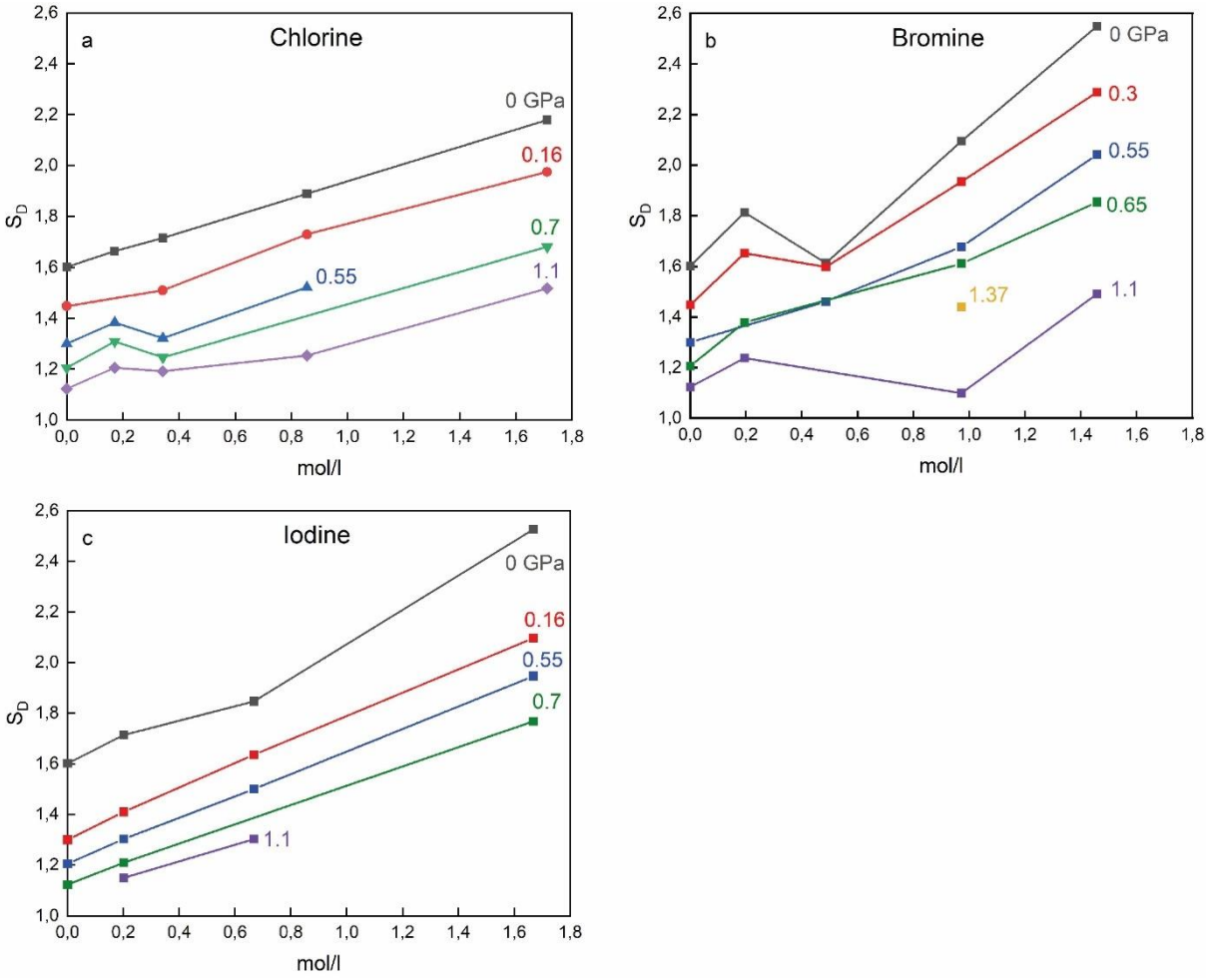


Figure S1 The Raman water bands of saline solutions are presented with fixed halogen concentrations and varying pressure: a) 0.34 mol/l chlorine, b) 1.45 mol/l bromine, and c) 0.2 mol/l iodine. The pressure is indicated in GPa on the spectra. Notably, the intensities are normalized to their integrated intensities for the presented range of 3000 to 3600 cm^{-1}. The resulting peaks exhibit a smaller reduction than the spectra in Figure 3 but a leftward shift in the spectra indicates a clear pressure effect.



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555 *Figure S2* *S_D values vs halogen concentration for a) chlorine, b) bromine, and c) iodine*

556 *calculated after Durickovic et al. (2010).*

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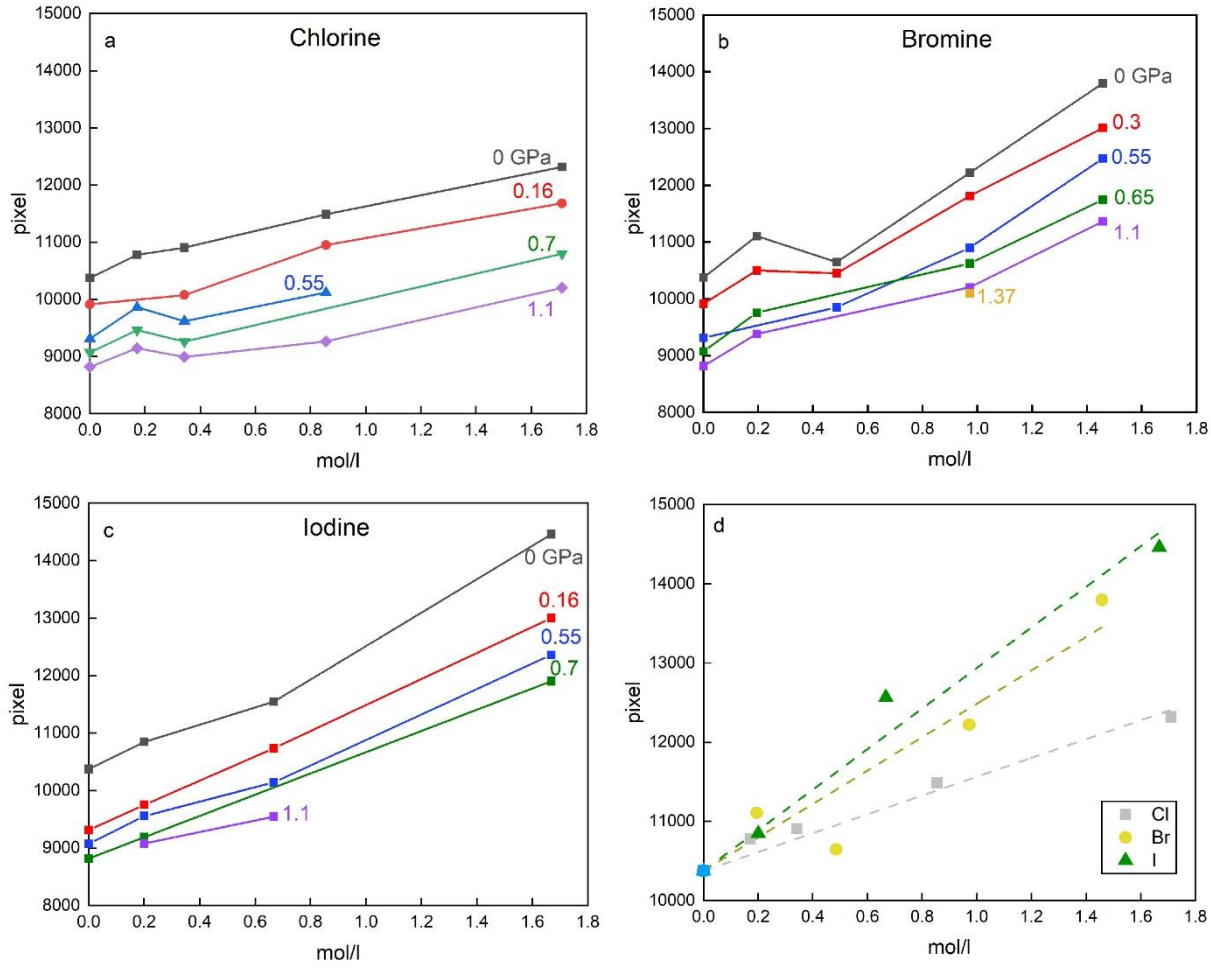

Figure S3 Integrated intensities vs halogen concentration for (a) chlorine, (b) bromine, (c) iodine, and (d) all three elements at ambient pressure show comparable trends but large scatter relative to the R_D values. The intensities were integrated over the range of 3000 to 3600 cm^{-1}.

Heavy halogen impact on Raman water bands at high pressure: implications for salinity estimations in fluid inclusions

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Abstract

We present a new experimental dataset on the impact of the heavy halogens chlorine, bromine and iodine on the Raman water bands concerning pressure and their concentration at room temperature. These experiments were conducted at ambient temperature, with variations in halogen concentration and pressure ranging from 0 to 1.4 GPa.

The strength of the Raman water band shift change increases with the ionic size from chlorine, over bromine, to iodine. Our experiments further demonstrate that increased pressure diminishes the impact of the halogen shift change to a varying extent for each of the three halogens. This finding can have significant implications for the salinity calculation of fluid inclusions in minerals such as quartz or olivine. Particularly in the low salinity range, the concentration can be markedly underestimated if the pressure effect is neglected. For experiments in diamond anvil cells involving halogens dissolved in water, the change in Raman water band shifts can serve either as a new tool to monitor pressure, or to monitor the salinity.

Keywords

Raman, water bands, Fluid inclusion, halogens, salinity, high pressure

1. Introduction

Halogens play a pivotal role as volatile elements, significantly impacting geodynamic processes. They constitute essential components of volcanic fumaroles and volcanic ejecta. Upon release into the atmosphere, halogens contribute to ozone destruction. In crustal hydrothermal fluids, halogen complexes (e.g., in saline fluids, brines, or molten salts) serve as major agents for metal transport in ore-forming processes related to hydrothermal systems (e.g., Aiuppa et al., 2009). Samples of such fluids can be found entrapped as inclusions in minerals like quartz (e.g., Brooks et al., 2019; Pankrushina et al., 2020) or olivine (e.g., Kawamoto et al., 2013) in magmatic and metamorphic rocks. Raman spectroscopy has been employed for decades to determine the salinity of fluid inclusions, especially those too small for other common techniques like microthermometry – a method that determines salinity by observing and measuring the freezing temperature of the fluid (cf. e.g., Kawamoto et al., 2013; Moncada and Bodnar, 2012; Brooks et al., 2019).

The Raman spectra of water and aqueous fluids exhibit several peaks closely grouped at 2800-3800 cm^{-1}, resulting in water stretching bands (e.g., Ratcliffe and Irish, 1982; Sun, 2009; Walrafen et al., 1986). In salty solutions or brines, halogen ions interact with the bonds of water molecules. Although ions and ionic bonding cannot be directly detected with Raman spectroscopy, their impact on the network of covalent water bonding is detectable. This effect has been the subject of numerous studies, with a substantial focus on chlorine (e.g., Dubessy et al., 2002; Durickovic et al., 2010; Georgiev et al., 1984; Mernagh and Wilde, 1989; Pankrushina et al., 2020; Sun, 2012; Sun et al., 2010; Tepstra et al., 1990) and, to a lesser extent, on the heavy halogen bromine (e.g., Tepstra et al., 1990). Halogen anions widen the water bonding network, forcing the network to change its bonding structure by favoring a certain type of bonding over others. A shift in water bands can be observed, correlating with the number of dissolved halogens and facilitating the determination of salt concentration in the solution or in mineral fluid inclusions (e.g., Dubessy et al., 2002; Durickovic et al., 2010; Georgiev et al., 1984; Mernagh and Wilde, 1989; Pankrushina et al., 2020; Sun, 2012; Sun et al., 2010; Tepstra et al., 1990).

The heavy halogens bromine and iodine possess a larger ionic size than chlorine. Their anions stretch the water network as much or even more than chlorine, causing a more pronounced alteration of the Raman shift (Tepstra et al., 1990). The impact of the cations (e.g., calcium, magnesium, sodium, potassium) in a salty solution seem to be negligible (Sun et al., 2010).

Two other factors can alter the shape of Raman water bands: (1) temperature (e.g., Krishnamurthy et al., 1983; Ratcliffe and Irish, 1982) and (2) pressure (Romanenko et al., 2018). Increasing temperature has a similar effect to increasing halogen concentrations, enhancing the resulting peak at around 3430 cm^{-1}. Pressure shifts the bands in the opposing direction: It decreases the peak at 3430 cm^{-1} and increases the peak at 3240 cm^{-1}.

While fluid inclusions in minerals are typically studied at ambient temperature and its effect can be ignored, the pressure in mineral fluid inclusions, such as those in quartz, is likely to be elevated, potentially impacting the Raman spectrum. In this study, we present a novel experimental dataset examining the impact of all three heavy halogens — chlorine, bromine, and iodine — on Raman water bands concerning pressure and halogen concentration at room temperature. We further compare our results to some natural fluid inclusion samples from other studies to demonstrate and constrain the impact of our dataset on natural fluid inclusions.

2. Experimental setup and methods

Various concentrations of NaCl, NaBr, or NaI salts were dissolved in water to synthesize salty solutions as starting materials (Table 1). Sodium-halogen salts exhibit excellent solubility in water, and sodium serves as the dominant cation in seawater-related fluids. Despite the seemingly negligible impact of cations (Sun et al., 2010), sodium was selected as the cation for all three halogens to mitigate cation effects and focus on the influence of the three halogen anions.

The experiments were conducted using a Chervin-type hydrothermal diamond anvil cell (HDAC) with a pressure-driving membrane (Chervin et al., 1995). The HDAC was equipped

with 2 mm thick diamonds and culets of 1 mm diameter. The sample chamber, compressed between two diamonds, had a diameter of 500 µm, drilled as a hole into a Re gasket with an initial thickness of 200 µm. Before each experiment, the sample chamber was cleaned with ethanol, dried, and loaded with a salty solution along with a small number of ruby spheres for pressure calibration. Following HDAC closure, the membrane was connected to an inflator with a N_2 gas bottle. The membrane was initially loaded with approximately 10 to 15 bar of gas pressure, sufficient to seal the HDAC but insufficient to observe a fluorescence shift with the ruby spheres.

Ruby fluorescence serves as a widely used pressure monitor for various DAC experiments (e.g., Chervin et al., 2001; Shen et al., 2020). The ruby shift was calibrated with the Raman to ambient pressure and had to be recalibrated for each new sample. After the ruby calibration, the water bands were measured with the Raman at ambient pressure. The pressure was then increased stepwise with an inflator, and pressure increases were monitored on the ruby fluorescence. Pressure steps were approximately 0.2 to 0.3 GPa. Depending on the salt concentration, the solution transformes into ice IV between 1.1 and 1.4 GPa (see below). After each pressure increase, the cell equilibrated the pressure for about 10 minutes before Raman analysis.

Raman measurements were performed with a 514.5 nm Argon laser and a Jobin-Yvon Horiba HR460 spectrometer. A constant grating of 1500 lines/mm, a slit size of 50 µm, and a 50x objective placed in front of the diamond anvil cell were used. The setup was calibrated with a 521 cm^{-1} silicon wafer, and the laser energy was controlled to remain constant at 10 mW between each measurement during the pressure equilibration period. Diamond has no effect on the Raman water bands and is widely used for these types of studies. Test runs for pure water in the DAC and in a glass cylinder showed no difference in the spectra. Measurements in the solution were conducted in the center of the sample chamber by defocusing the laser spot between both surfaces of the two diamonds. Measurements in the solution were set for 10 to 30 seconds with 3 to 5 iterations. Measurements on the ruby spheres were conducted "live" with a repetition rate of 1s.

It is important to note that halogens like iodine can also induce a Raman peak at around 1650 cm^{-1} (Besemer et al., 2016). However, this peak overlaps with the (extremely large) carbon peak from the diamond anvils and cannot be used for hydrothermal DAC experiments or for pressure calibration with HDAC.

The acquisition and processing of the Raman spectra were carried out using the Labspec software. For baseline correction, peak deconvolution, and spectra smoothing (using "adjacent averaging" with a step size of 40), the Origin software was employed. Values for R_D and S_D (both are ratios that can be used to quantify the peak change numerically; see also further below) were calculated prior to spectra smoothing.

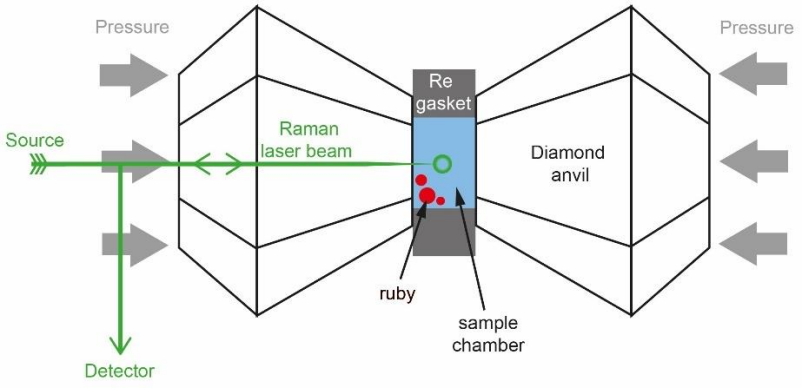

Figure 1 Experimental Setup: The saline solution was loaded into a hydrothermal diamond anvil cell (HDAC). Pressure control was achieved using an external inflator, and pressure levels were monitored via the fluorescence of ruby spheres suspended in the sample chamber. Raman measurements in the solution were performed at the center of the sample chamber by intentionally defocusing the laser spot between the surfaces of the two diamonds.

3. Results

At ambient pressure and temperature, the configuration of the water stretching bands undergoes changes based on halogen concentration:

1. The 3428 cm^{-1} peak increases with rising halogen concentration: from 6660 counts for pure water to 7900 counts for 1.71 mol/l chlorine, 8800 counts for 1.46 mol/l bromine, and 9300 counts for 1.67 mol/l iodine, respectively.
2. The 3428 cm^{-1} peak shifts to higher wavenumbers with specific positions at 3441 cm^{-1} for chlorine, 3450 cm^{-1} for bromine, and 3460 cm^{-1} for iodine at their respective highest concentrations.
3. The minor peak at 3240 cm^{-1} becomes relatively smaller as halogen concentration increases, decreasing from 5060 counts for water to 4400 counts for chlorine, 4190 counts for bromine, and 4430 counts for iodine (Figure 2).

At a constant halogen concentration, the characteristics of the water stretching bands evolve with increasing pressure:

1. The 3428 cm^{-1} peak decreases with rising pressure: from 6975 counts at 0 GPa to 5960 counts at 1.1 GPa for 0.34 mol/l chlorine, from 8800 counts at 0 GPa to 7350 counts at 1.1 GPa for 1.45 mol/l bromine, and from 6315 counts at 0 GPa to 6010 counts at 1.39 GPa for 0.2 mol/l iodine.
2. The 3428 cm^{-1} peak shifts to lower wavenumbers, with new positions at 3390 cm^{-1} for chlorine, from 3450 to 3435 cm^{-1} for bromine, and from 3430 to 3390 cm^{-1} for iodine at their respective highest pressures.
3. The minor peak at 3240 cm^{-1} becomes relatively larger with increasing pressure, exhibiting a slight increase from 4970 to 5140 counts for chlorine, from 4190 to 4590 counts for bromine, and from 4960 to 5255 counts for iodine (Figure 3).

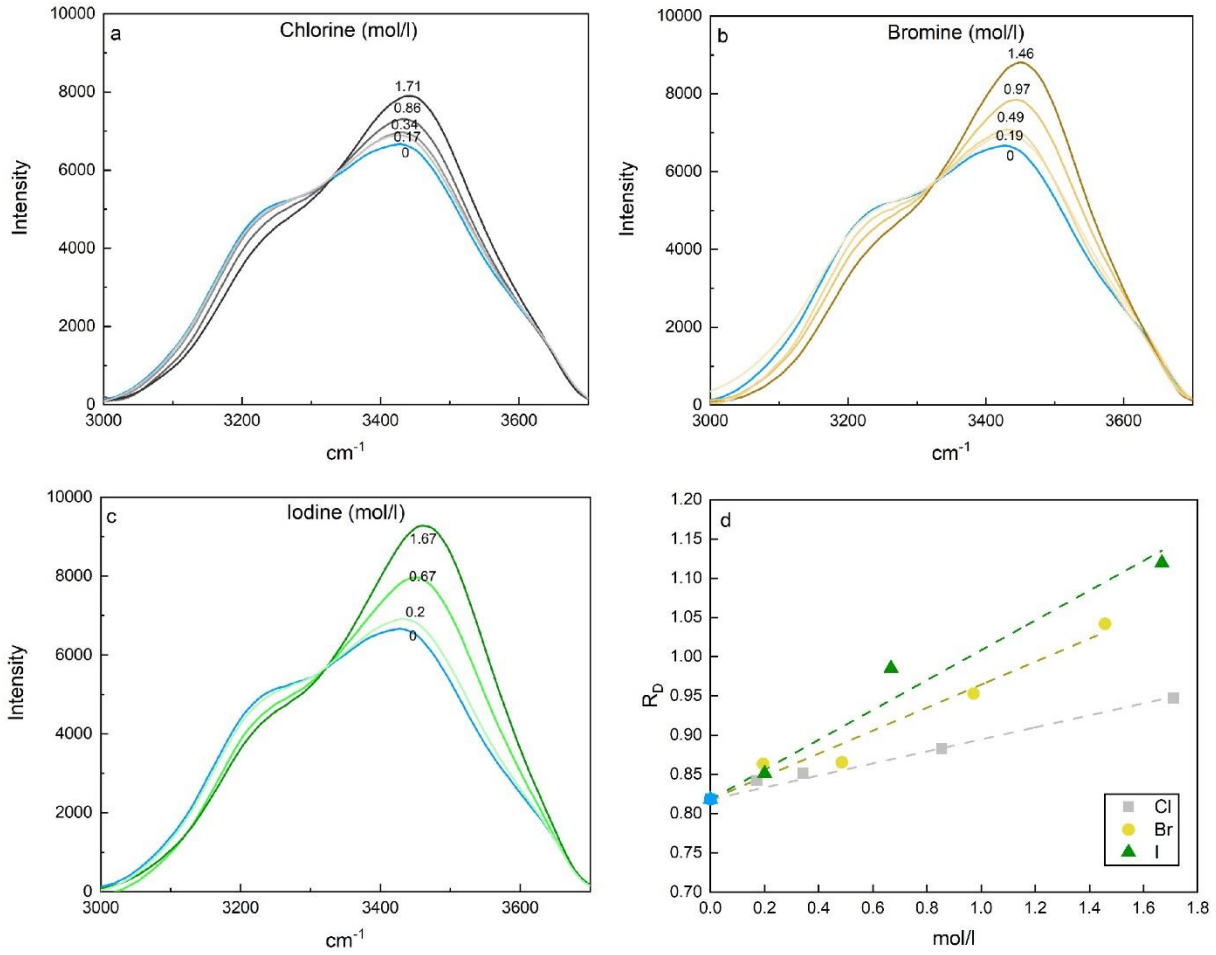

Figure 2 The Raman water bands of saline solutions with varying concentrations of a) chlorine, b) bromine, and c) iodine are depicted. The halogen concentrations are indicated on the spectrum in mol/l. Notably, the resulting peak of the water bands at 3428 cm^{-1} exhibits an increase and shifts further to the right with escalating halogen concentration. The Raman spectrum of pure water is represented in blue. In d), there is a discernible increase in R_D with escalating concentrations of chlorine, bromine, and iodine. This increase is characterized by a larger sum of slopes between 3325 cm^{-1} and 3600 cm^{-1}, and a heightened peak at 3428 cm^{-1}. The observed effects are smallest for chlorine and most pronounced for iodine.

4. Discussion

4.1. Halogen concentration and ionic size

The correlation between the change in the water bands' peak and varying halogen concentration, in addition to ionic size, aligns well with findings from previous studies (Dubessy et al., 2002; Durickovic et al., 2010; Georgiev et al., 1984; Mernagh and Wilde, 1989; Pankrushina et al., 2020; Sun et al., 2010; Tepstra et al., 1990). The observed shift change strength correlates directly with the ionic size of the halogens: Chlorine exhibits the smallest shift, iodine the largest, and bromine falls in between for comparable concentrations (cf. Tepstra et al., 1990 for chlorine and bromine).

Since ionic bonds are not Raman active, NaCl, NaBr, and NaI do not have observable modes of their own, neither as salts nor as dissolved ions in water (Bakker, 2004; Pei et al., 2006; Terpstra et al., 1990). Raman spectroscopy enables the observation of the vibration of chemical bonds, which, in this study, is the chemical vibration of water. The halogen anions are indirectly observed as they modify the vibrations of water bonding. The evolving shape of the Raman spectra in Figure 2 illustrates that different halogens influence the dominant bonding type in the water structure, leading to a reduction in hydrogen bonding in water. Figure 4 presents a deconvolution of the water stretching band into three major Gaussian components representing different bonding types for water molecules:

Peak 1 of the first Gaussian component at 3327 cm^{-1} is attributed to 4 hydrogen bonds per water molecule, involving two electron donors and two acceptors (DDAA). This peak diminishes with increasing halogen content. Peak 2 at 3431 cm^{-1} is attributed to 2 hydrogen bonds (DA) and becomes the predominant bonding type with increasing halogen content. Peak 3 at 3565 cm^{-1} is attributed to 3 hydrogen bonds per water molecule (DDA). It plays a minor role in pure water as well as in salty solutions (e.g., Sun, 2009). With the addition of salt, the increasing presence of cations and anions breaks the hydrogen bonds in the water network, forming ionic bonds.

The deconvolution of the Raman water bands confirms the reduction of hydrogen bonding in water with the addition of various halogens, as well as with their increasing ionic size.

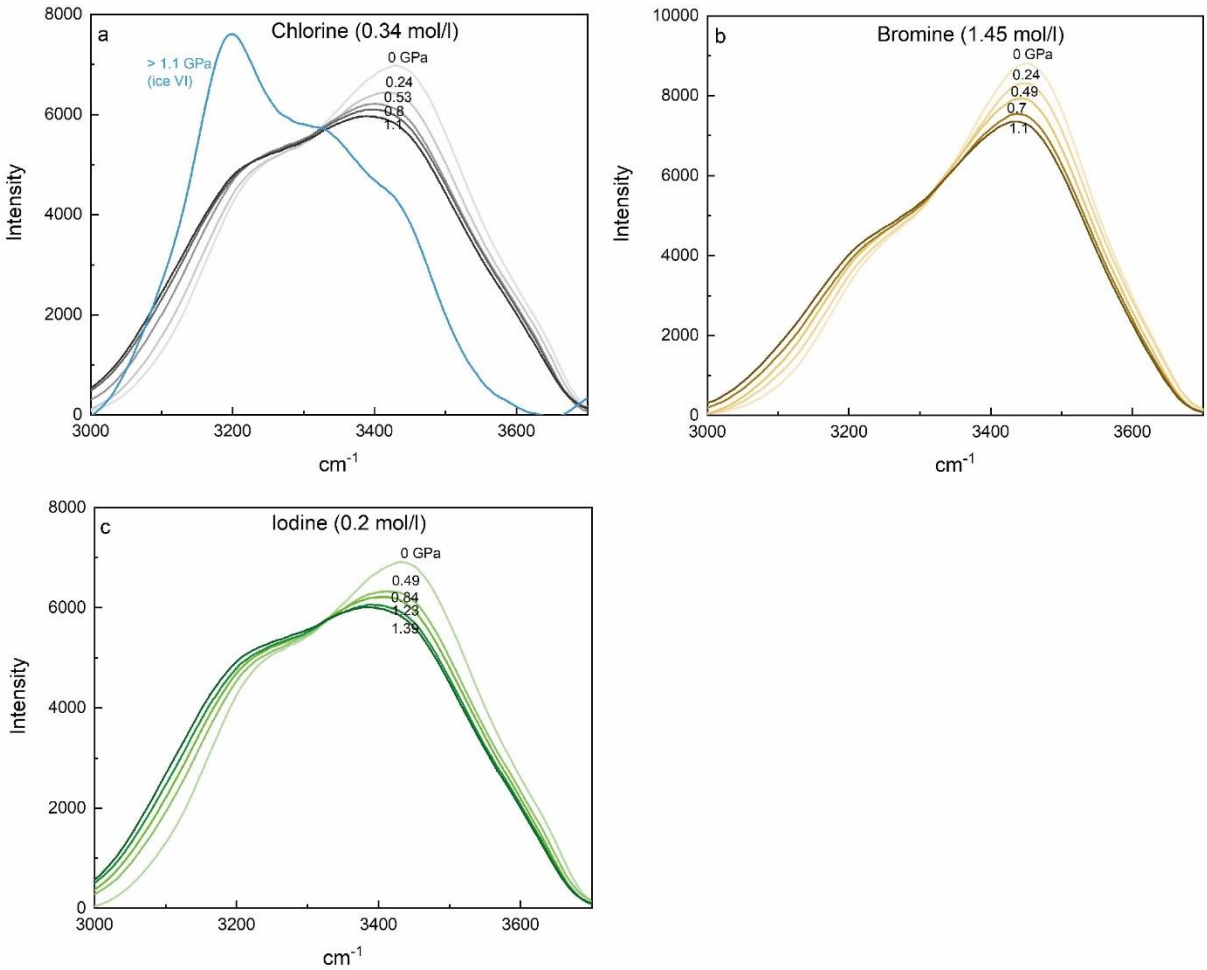

Figure 3 The Raman water bands of saline solutions are presented with fixed halogen concentrations and varying pressure: a) 0.34 mol/l chlorine, b) 1.45 mol/l bromine, and c) 0.2 mol/l iodine. The pressure is indicated in GPa on the spectra. Notably, the resulting peaks exhibit a reduction in intensity with increasing pressure and shift towards lower wavenumbers, indicating a leftward shift in the spectra.

4.2. R_D as numerical value for the changing effect

To quantify the changing shift of the water stretching bands, Durickovic et al. (2010) introduced the ratio S_D, defined by the formula:

$$S_D = \frac{\sum_{i=326}^{650}\left\{\frac{I(i)+I(i-1)}{2} * [n(i)-n(i-1)]\right\}}{\sum_{i=1}^{325}\left\{\frac{I(i)+I(i-1)}{2} * [n(i)-n(i-1)]\right\}}$$

Here, *n(i)* represents the shift at increment (or pixel) *i*, *I(i)* is the intensity at increment (or pixel) *i*, and the range of interest is between 3000 and 3650 cm^{-1} with a total of 650 pixels. This formula establishes the inflection point of the water bands at 3325 cm^{-1} (Figure 4) and divides the water bands into two halves: left and right side from the inflection point. Durickovic et al. (2010) observed that S_D increases linearly with increasing NaCl concentration dissolved in water.

With increasing halogen concentration, the slope increases on both sides of the inflection point, resulting in an increase in both the sum of slopes for the left and right halves (cf., Figure 2). This trend holds for all three studied halogens: chlorine, bromine, and iodine. To avoid division of two values that both correlate positively and increase with higher halogen concentrations, a ratio R_D was calculated, slightly different from S_D. The formula for R_D is as follows:

$$R_D = \frac{\sum_{i=1}^{325}\left\{\frac{I(i)+I(i-1)}{2} * [n(i)-n(i-1)]\right\}}{I_{i=1} * 325}$$

Here again, *n(i)* represents the shift at increment (or pixel) *i*, *I(i)* is the intensity at increment (or pixel) *i*, and the total number of pixels considered is 325, starting from 3325 to 3650 cm^{-1}. This formula reduces some information loss from S_D and steepens the slope, as both the numerator and denominator of the ratio increase with increasing halogen concentration.

However, the applicability of R_D is limited to liquid water. R_D does not account for strong changes in the shape of the slope, making it less suitable for high-pressure or low-temperature polymorphs (e.g., ice VI), which exhibit the dominant peak on the left side of the inflection point (Figure 3).

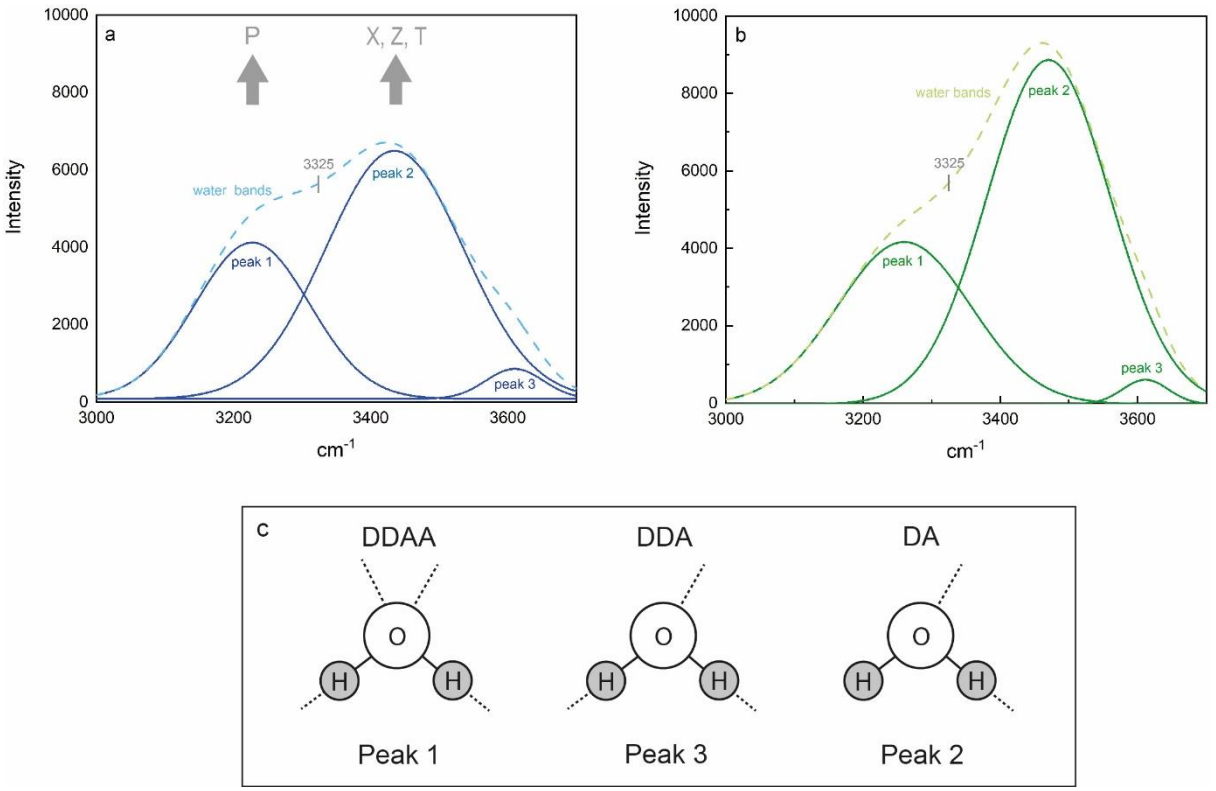

Figure 4 The peak-deconvoluted Raman water bands are presented for a) pure water and b) 1.67 mol/l iodine, resolved into three Gaussian components. The resulting water bands are represented by dashed lines, with the inflection point of the water bands curve identified at 3325 cm^{-1}. Notably, with increasing iodine content (X) halogen ionic size (Z), and temperature (T), peak 2 becomes larger relative to peak 1, while pressure (P) has the opposing effect. In c), the components of the deconvolution are explained: Peak 1 is attributed to 4 hydrogen bonds per water molecule, involving two electron donors and two acceptors (DDAA). Peak 2 is attributed to 2 hydrogen bonds (DA). Peak 3 is attributed to 3 hydrogen bonds per water molecule (DDA) (Sun, 2009). The deconvolution of the Raman water bands confirms a reduction in hydrogen bonding in water with the addition of various halogens and their increasing ionic size. Moreover, increasing pressure correlates with an augmented number of hydrogen bonds.

4.3. Pressure

With increasing pressure, the water stretching band peak at 3428 cm^{-1} undergoes a reduction in intensity and shifts towards the left (e.g., Romanenko et al., 2018), while the smaller peak at 3240 cm^{-1} experiences a slight increase. The observed change stands in contrast to the effects observed during temperature increase (cf., Durickovic et al., 2010) or the addition of halogens (Figure 3). This shift can be interpreted as a transition towards a higher number of hydrogen bonds (from DA to DDAA) in the water molecule network (Sun, 2009, Figure 4). The effect is observable for all three halogens (chlorine, bromine, and iodine) in the saline solutions of this study (Figure 3).

Sun (2012) did not observe the pressure effect in their chlorine data and argue against its existence. However, upon normalizing our data in the same way as Sun (2012), the peak at 3428 cm^{-1} decreases, and the water bands flatten, yet a clear pressure trend remains (Supplementary Figure S1). It remains unclear why the trend was not observed in Sun (2012).

At pressures greater than 1 GPa and ambient temperature, water transforms into ice VI (Figure 3). Notably, with increasing halogen concentrations, the water-ice phase transformation shifts to higher pressures. In this study, liquid water/saline solution was observed at 1.1 GPa and 0.34 mol/l chlorine, 1.37 GPa and 0.97 mol/l bromine, or 1.27 GPa and 0.67 mol/l iodine. The experimental setup does not precisely determine if the phase boundary shifts to higher pressure or if the liquid state is metastable. Journaux et al. (2013) investigated the impact of NaCl on the phase boundary of ice VI and found the boundary at 1.01 GPa for 1 mol/l, 1.09 GPa for 2.5 mol/l, and 1.52 GPa for 4 mol/l at ambient temperature. This boundary shift is much smaller than the observed range, suggesting a metastable liquid phase in our study or other kinetic effects.

As a consequence of the pressure-related shape change of the water stretching bands, R_D decreases with increasing pressure for fixed halogen concentrations (Figure 3). Figure 5 illustrates the R_D values vs. halogen concentration at different pressures (S_D values in Supplementary Figure S2). Despite some outliers, the values follow a linear trend in the studied range, as previously observed for various temperatures (Durickovic et al., 2010). Within the

range of comparable pressures, chlorine exhibits the lowest R_D values, while iodine demonstrates the highest. Comparable trends are also observed for integrated intensities (Supplementary Figure S3) but show larger scatter relative to the R_D trends in Figure 2d and Figure 5.

4.4. Applications

4.4.1. Natural fluid inclusions with one unknown component (P or X)

R_D can be calculated from Raman spectra of natural fluid inclusions in minerals, as demonstrated by Kawamoto et al. (2013). In their study, saline fluid inclusions in spinel-harzburgite xenoliths collected from the 1991 Pinatubo pumice deposits were examined. The salinity of the fluid inclusions was reported as 5.1 ± 1 wt.% NaCl equivalent (0.87 ± 0.17 mol/l), measured with microthermometry. The authors employed Raman spectroscopy for qualitative water measurements.

From the provided Raman spectrum, a R_D value of 0.79 can be calculated. The measured chlorine concentration from microthermometry allows for an estimate of the pressure to be around 0.5 GPa (Figure 5a). This is notably lower than the 2-3 GPa that Kawamoto and colleagues estimated for the formation of the saline fluid inclusions in olivine below the Pinatubo. Given the available information, it can only be speculated whether some (parts) of the olivines formed at a very low pressure of 0.5 GPa, or if the inclusion lost pressure, and it was not fully closed above 0.5 GPa. In this case, the inclusion could at least partially represent the conditions at 0.5 GPa rather than at 2-3 GPa.

It is crucial to note that a fluid inclusion that closes between 810 °C and 1050 °C (Kawamoto et al., 2013) will experience a decrease in pressure when cooling down to ambient temperature. This phenomenon is also well observed in HDAC experiments (e.g., Bureau et al., 2010, 2016; Leroy et al., 2019; Louvel et al., 2020a, 2020b) and argues for a higher pressure than the 0.5 GPa that were obtained from the Raman spectrum. However, this sample

serves as a good illustration of how pressure can be estimated by Raman in saline fluid inclusions with given salinity.

4.4.2. Natural fluid inclusions with two unknown components (P and X)

Difficulties arise when neither pressure nor salinity can be determined with a different method, and only the Raman spectrum is available. This scenario may occur for fluid inclusions that are too small for microthermometry, resulting in a single equation with two unknown parameters that cannot be solved for a distinct value.

Saline fluid inclusions from quartz samples analyzed by Pankrushina et al. (2020) illustrate the pressure dependence in Figure 5d, where R_D values plot as a constant line. For instance, q1 has 1.9 mol/L NaCl at ambient pressure and 2.71 mol/L at 0.16 GPa; q2 has 1.88 mol/L and 2.69 mol/L; and q3 has 1.02 mol/L and 1.75 mol/L at ambient pressure and at 0.16 GPa, respectively. For an unknown pressure, a single salinity value cannot be determined this way. Particularly at lower salinity concentrations, the range of possible salinities can be drastic: for the three natural samples q1-3, a small pressure increase of 0.16 GPa changes the salinity by 42 to 72%. Given the stability field of quartz and saline fluids at room temperature, these are conservative calculations, and a much larger pressure range of > 1 GPa must be considered.

However, fluid inclusions can be saturated in NaCl, and halite crystals do coexist with saline fluids in the inclusion (e.g., Brooks et al., 2019). The solubility of NaCl in water at ambient P-T conditions is 317 g/l or 5.4 mol/l (cf. Figure 5). The pressure effect is diminished at NaCl-saturated conditions: Experiments in this study were conducted up to a salinity of 1.71 mol/L for NaCl, but assuming a continuation of the observed linear trend, the difference between 0 and 0.16 GPa would be only 16 to 18%.

Therefore, the pressure effect in fluid inclusions with high salinity is smaller than in fluid inclusions with low salinity. But as the potential pressure range is large (more than 1 GPa),

ignoring the pressure effect can lead to a huge underestimation of the salinity in the fluid, and Raman spectroscopy alone cannot be used to determine reliable salinities in fluid inclusions.

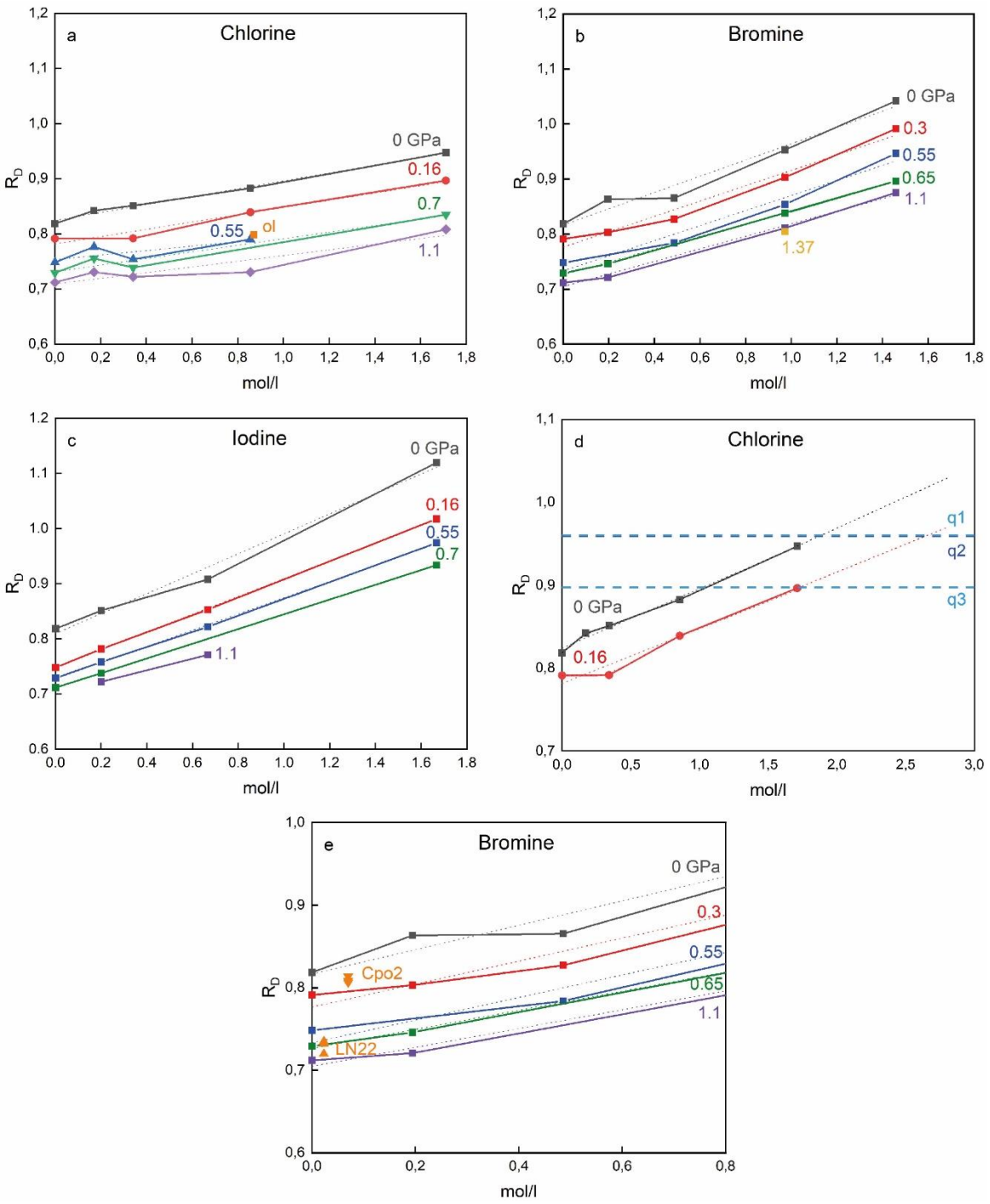

Figure 5 *R_D values vs halogen concentration for (a) chlorine, (b) bromine, and (c) iodine are presented in the figure. The colored lines indicate isobars: the solid lines connect the data points, while the dotted lines represent trend lines. Like the Raman water bands and the R_D*

values, the isobars exhibit the steepest slope for high concentrations of iodine and become flatter with smaller ionic halogen size, but also with increasing pressure. (a) "ol" data are from a natural fluid inclusion in olivine (Kawamoto et al., 2013). (d) Calculated R_D values for natural fluid inclusions in quartz demonstrate the pressure effect: q1 has 1.9 mol/L NaCl equivalent at ambient pressure and 2.71 mol/L at 0.16 GPa; q2 has 1.88 mol/L and 2.69 mol/L; and q3 has 1.02 mol/L and 1.75 mol/L at ambient pressure and at 0.16 GPa, respectively. The fluid inclusions were analyzed by Pankrushina et al. (2020) (sample names are q1 = 672; q2 = 33604; q3 = 20512). (e) Cpo2 and LN22 are experimental HDAC samples. Bromine content was analyzed with X-ray fluorescence following the methods reported in Bureau et al. (2010) and Grützner et al. (2024).

4.4.3. Heavy halogens in HDAC experiments

The heavy halogens bromine and iodine typically play a minor role in natural fluid inclusions. The Cl/Br ratio in seawater is approximately 30, and the Cl/I ratio is around 50 (cf. Shaw and Cooper, 1957 for iodine). Due to enrichment and depletion processes in the Earth's mantle, Cl/Br ratios can vary significantly, ranging, for example, in diamond inclusions from 1 to 500 (Jonson et al., 2000). Despite their low concentration and minor role in fluid inclusions, heavy halogens are highly reactive and serve as important chemical agents in Earth’s atmosphere (Fehn et al., 2012). Particularly for bromine, volcanoes have been recognized as significant contributors (Gerlach et al., 2004), if not the primary controlling factor (Pyle and Mather, 2009), to the current atmospheric content. This recognition is crucial, as bromine can be approximately 60 times more efficient (Sinnhuber et al., 2009) than chlorine in the destruction of stratospheric ozone (Daniel et al., 1999; Gerlach et al., 2004).

Over the past few decades, numerous studies have conducted high-pressure experiments on bromine- and iodine-bearing fluids interacting with silica melts in hydrothermal diamond anvil cells (HDAC). In these studies, the halogen content in the fluid was measured using synchrotron X-ray fluorescence (Bureau et al., 2010, 2016; Kawamoto et al., 2014; Leroy et

al., 2019; Louvel et al., 2020a, 2020b). These experiments provide valuable insights into the behavior of heavy halogens during fluid-magma degassing processes.

However, these experiments entail complex setups and lack reliable and easily adaptable pressure sensors. The fluorescence wavelength shift of ruby is a commonly used pressure sensor (e.g., Chervin et al., 2001; Shen et al., 2020), but it cannot be applied in experiments conducted at elevated temperatures where ruby spheres dissolve. Other pressure indicators, like X-ray diffraction of gold particles, are only reliable at higher temperatures (cf. Grützner et al., 2024; Louvel et al., 2020b). Pressure monitoring in these HDAC experiments is essential to understand the pressure effect on halogen partitioning between silicate melts and aqueous fluids. Moreover, it is crucial to exclude pressure loss processes during the experiment (cf. Bureau et al., 2010, 2016; Leroy et al., 2019; Louvel et al., 2020a, 2020b).

Most HDAC experiments are conducted at high temperatures, reaching several hundred degrees Celsius (e.g., Bureau et al., 2010, 2016; Grützner et al., 2024; Leroy et al., 2019; Louvel et al., 2020a, 2020b). The elevated temperature introduces an additional variable to the shift change of the water bands, as they also change with varying temperature (Krishnamurthy et al., 1983; Ratcliffe and Irish, 1982).

Thus far, residual pressure can be monitored at ambient temperature, for example, before and after the experiment, once the fluid has been cooled down to room temperature. Figure 5e illustrates two samples used for test measurements, following the experimental setup and the analytical methods for bromine concentration reported in Grützner et al. (2024). These samples represent experiments that tested the degassing reaction of a bromine-doped basalt melt into an aqueous fluid. Experiments were conducted at high temperatures (above the basalt solidus) and pressures of up to 1.7 GPa in a hydrothermal diamond anvil cell (cf. Grützner et al., 2024, for a detailed description of the experiments). Bromine concentrations of 0.07 mol/L for sample LN22 and 0.023 mol/L for Cpo2 were measured in the fluid by synchrotron x-ray fluorescence (SXRF) during the experiments. Raman spectra of the aqueous fluids were analyzed after the experiment under room temperature conditions. Bromine

concentrations from SXRF, together with the Raman spectra, allow estimating pressure ranges of 0.7 to 0.9 GPa for LN22 and 0.1 to 0.2 GPa for Cpo2.These promising results show that Raman water bands can be used as pressure or salinity indicators from room to high temperatures, providing additional pressure-concentration-related temperature calibrations are performed.

5. Conclusion

Our new experimental dataset demonstrates that the impact of halogens on the change of Raman water band shifts increases with ionic size from chlorine over bromine to iodine. To address and compare these changes, we calculated the numerical value R_D. Our experiments further show that increased pressure diminishes the impact of the halogen shift change to a different extent for each of the three halogens. This can have drastic consequences for the salinity calculation of fluid inclusions in minerals like quartz or olivine. Especially in the range of low salinity, the concentration can be strongly underestimated if the pressure effect is ignored. Either pressure or salinity needs to be determined by an independent method. For experiments performed in diamond anvil cells with halogens in aqueous fluids, the change of Raman water band shifts can be a beneficial (with some restrictions) tool to monitor the pressure at room temperature, if salinity is known, and inversely this change can be used to monitor the salinity.

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410 Statement: During the preparation of this work the authors used ChatGPT 3.5 to correct
411 errors of spelling, punctuation, grammar and to improve the syntax in several chapters of the
412 manuscript. After using this tool, the authors reviewed and edited the content and take full
413 responsibility for the content of the publication.

414

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536

8. Tables

	NaCl				max(NaCl)[a]
g/l	10	20	50	100	*317*
mol/l	0.17	0.34	0.86	1.71	*5.42*
wt.%	0.99	1.96	4.76	9.09	*24.07*

	NaBr				max(NaBr)[a]
g/l	20	50	100	150	*905*
mol/l	0.19	0.49	0.97	1.46	*8.80*
wt.%	1.96	4.76	9.09	13.04	*47.51*

	NaI			max(NaI)[a]
g/l	30	100	250	*1793*
mol/l	0.20	0.67	1.67	*11.96*
wt.%	2.91	9.09	20.00	*64.20*

[a] maximum solubility in H_2O at 20 °C and ambient pressure.

Table 1 Salt concentration in the starting solutions and maximum solubility values.

9. Supplementary material

Supplementary Tables with Raman raw data are stored under https://data.mendeley.com/datasets/tnckfpfjcv/1.

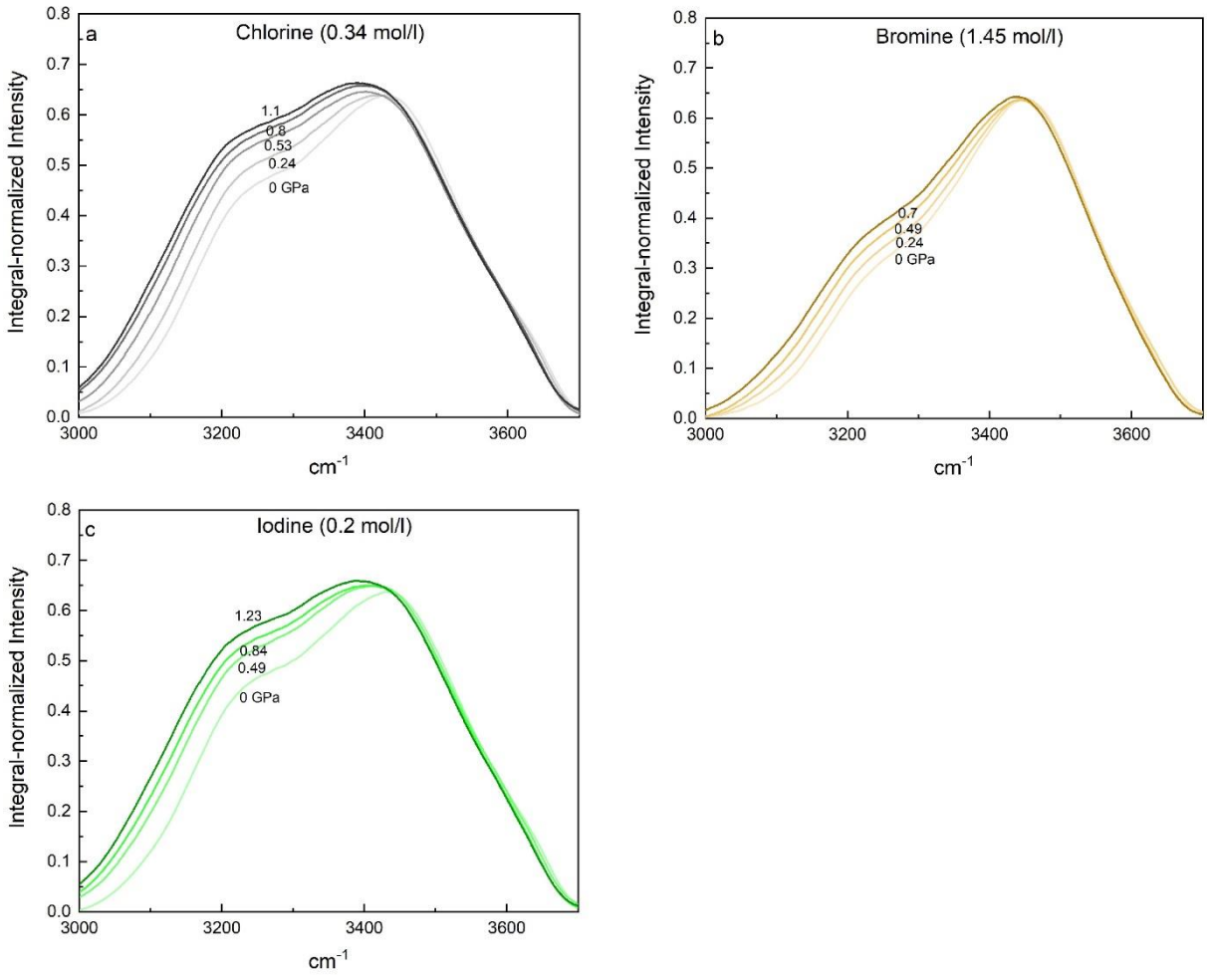
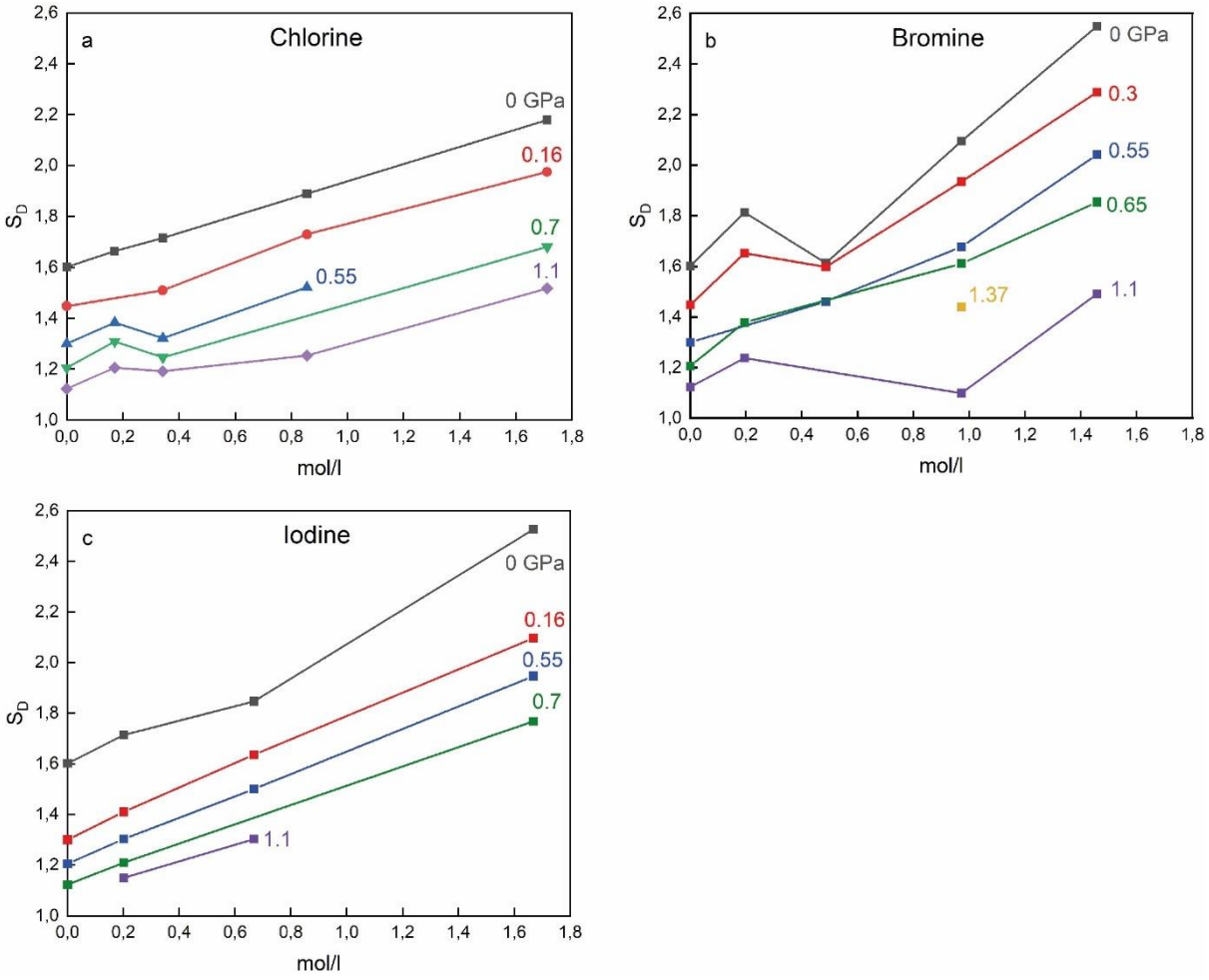


Figure S1 The Raman water bands of saline solutions are presented with fixed halogen concentrations and varying pressure: a) 0.34 mol/l chlorine, b) 1.45 mol/l bromine, and c) 0.2 mol/l iodine. The pressure is indicated in GPa on the spectra. Notably, the intensities are normalized to their integrated intensities for the presented range of 3000 to 3600 cm^{-1}. The resulting peaks exhibit a smaller reduction than the spectra in Figure 3 but a leftward shift in the spectra indicates a clear pressure effect.



554

555 *Figure S2 S_D values vs halogen concentration for a) chlorine, b) bromine, and c) iodine*

556 *calculated after Durickovic et al. (2010).*

557

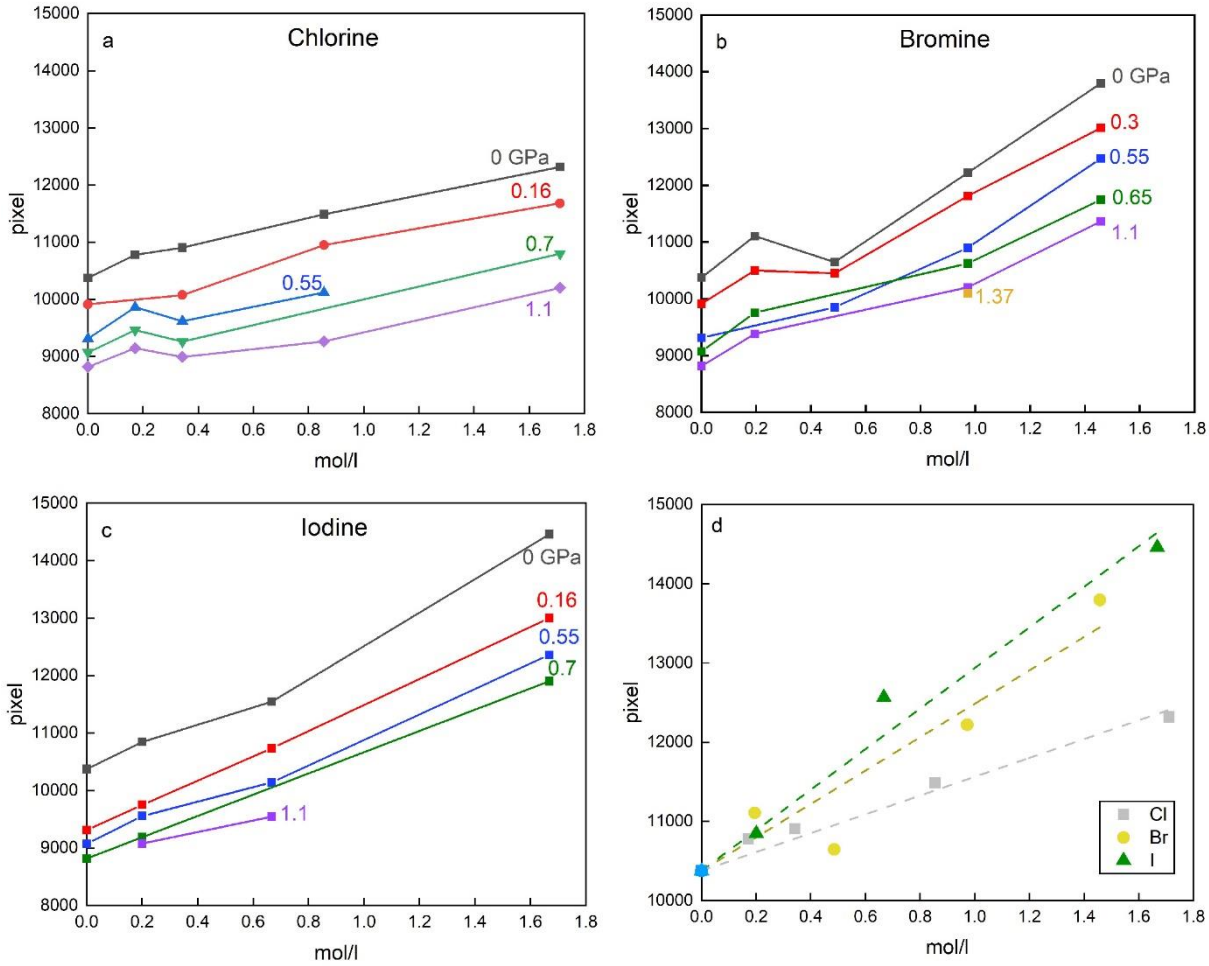


Figure S3 Integrated intensities vs halogen concentration for (a) chlorine, (b) bromine, (c) iodine, and (d) all three elements at ambient pressure show comparable trends but large scatter relative to the R_D values. The intensities were integrated over the range of 3000 to 3600 cm^{-1}.

Figure 1

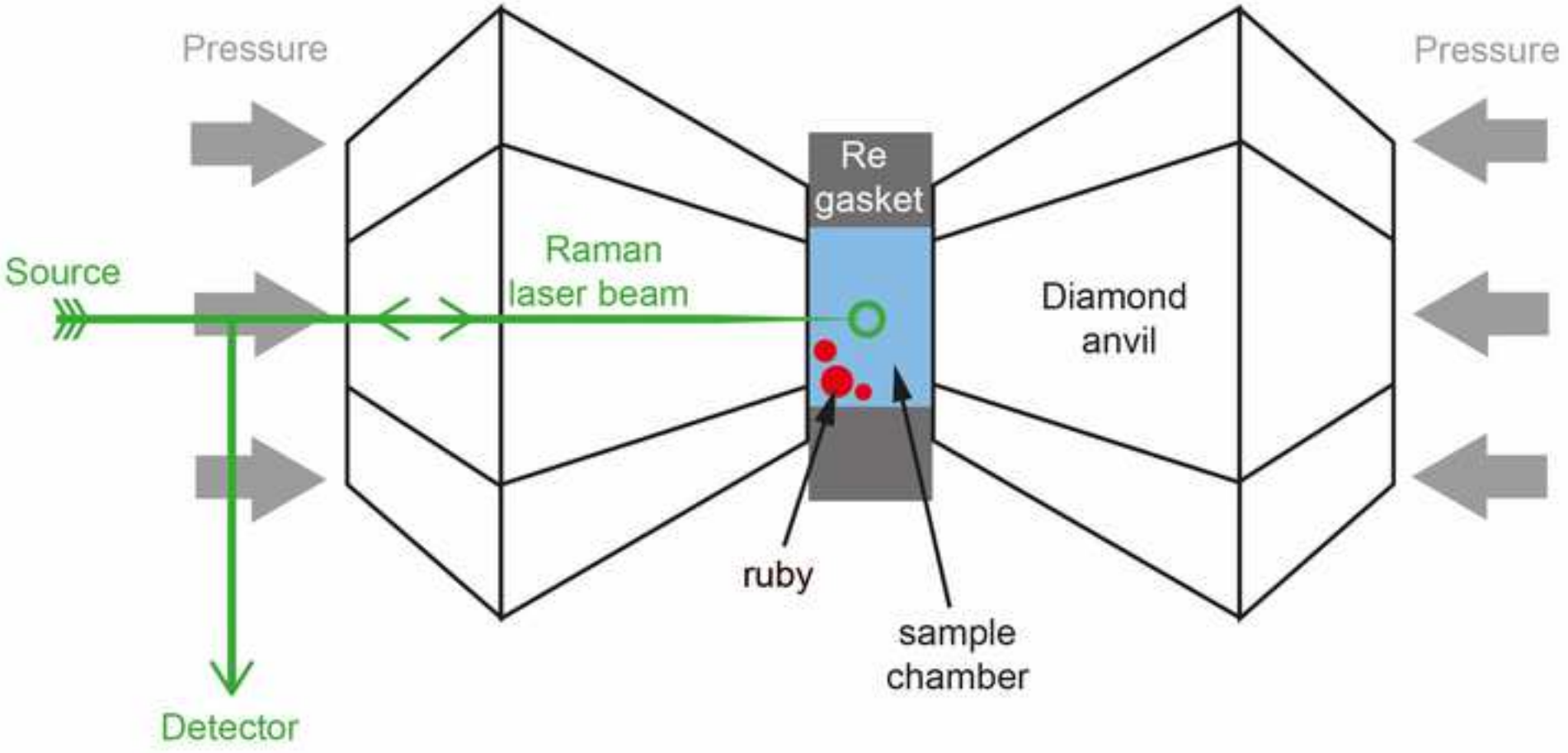


Figure 2

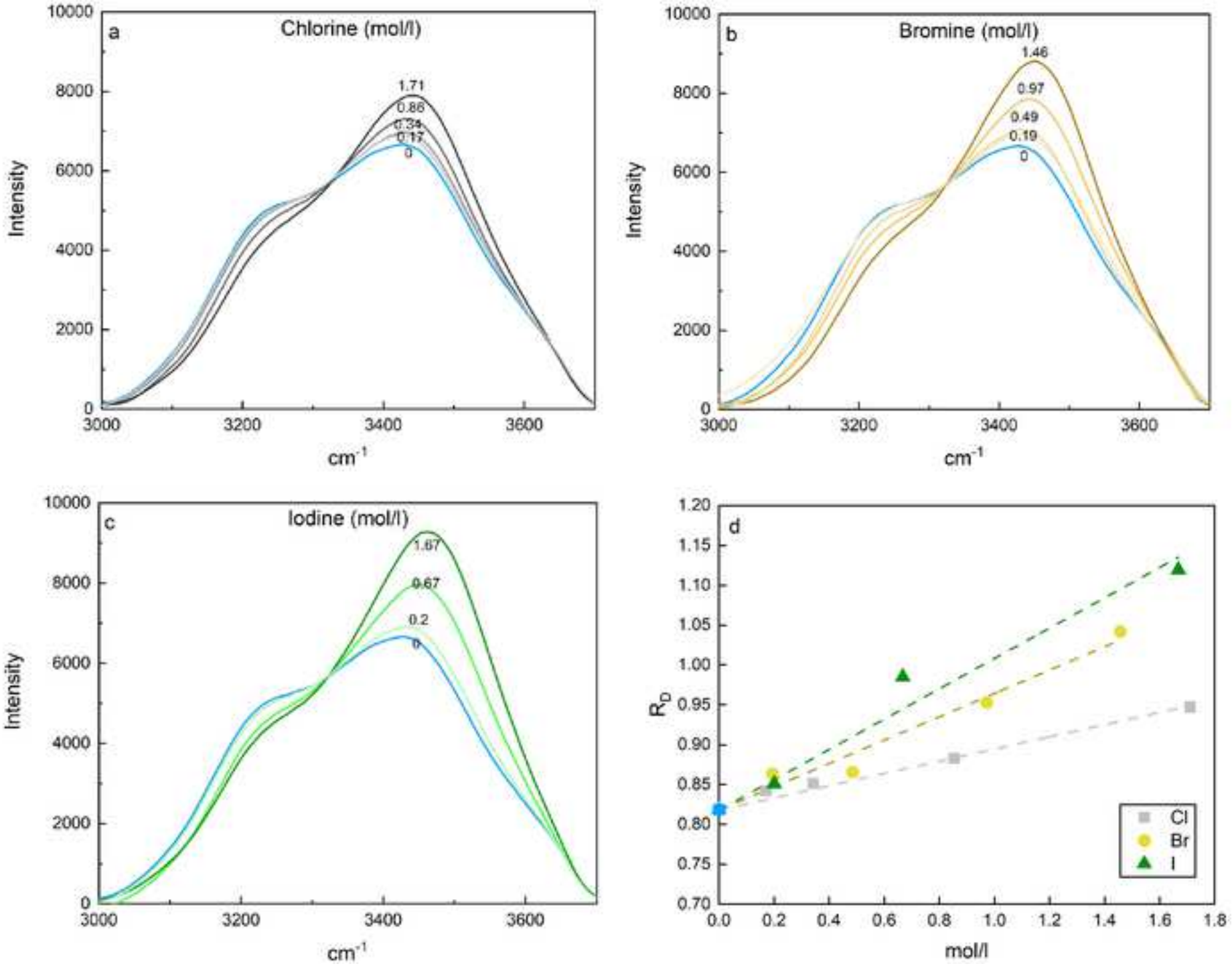


Figure 3

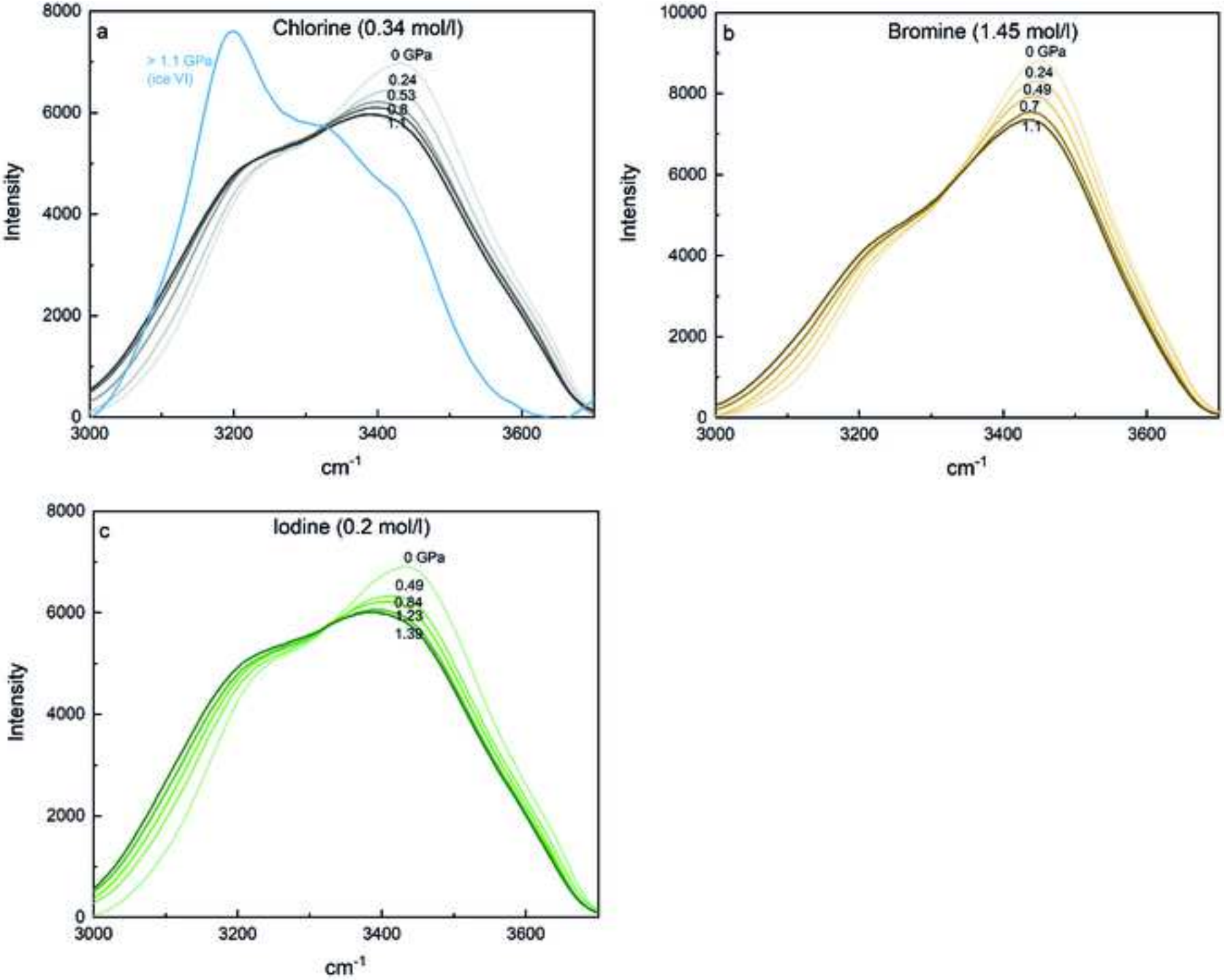


Figure 4

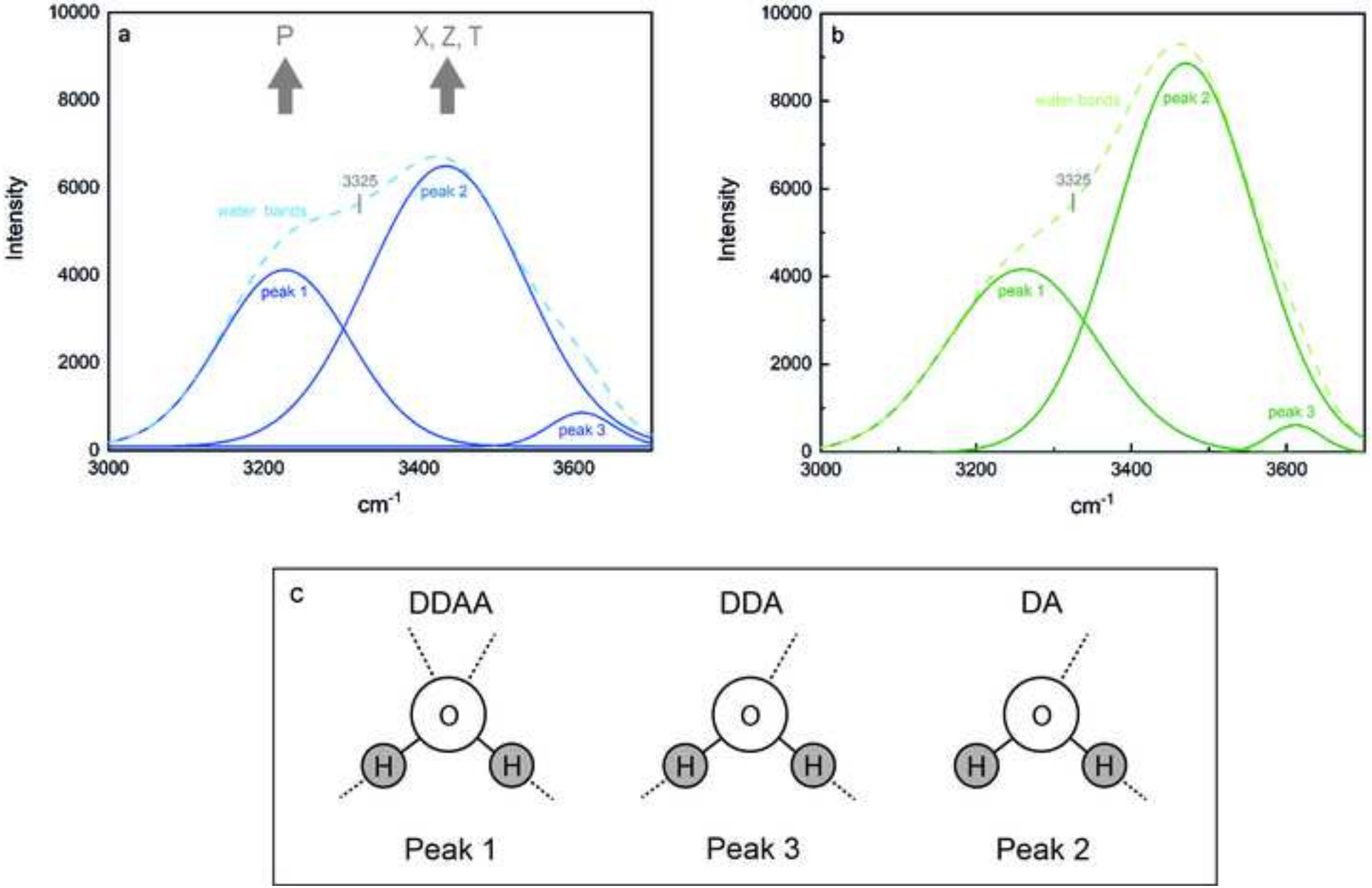
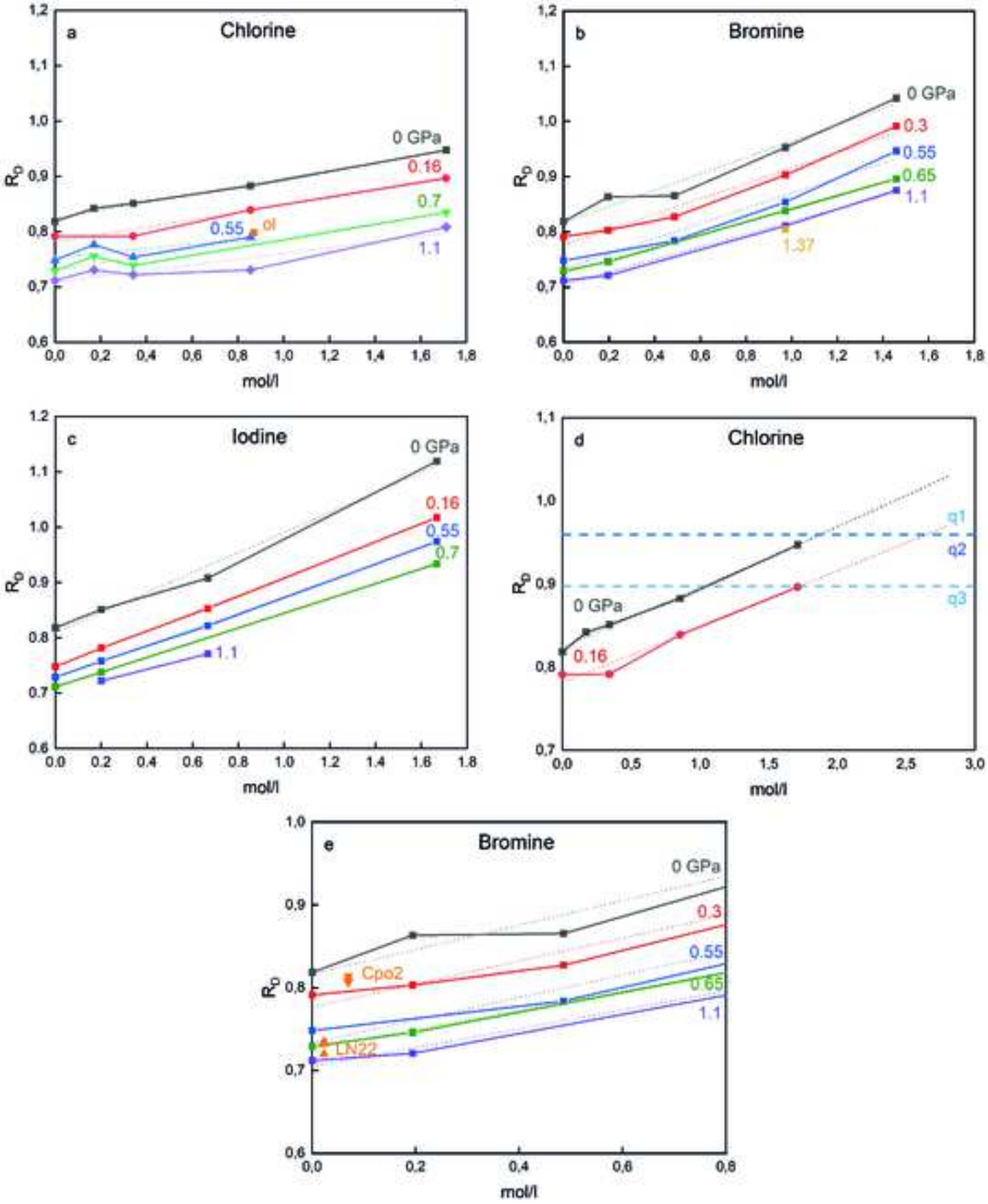


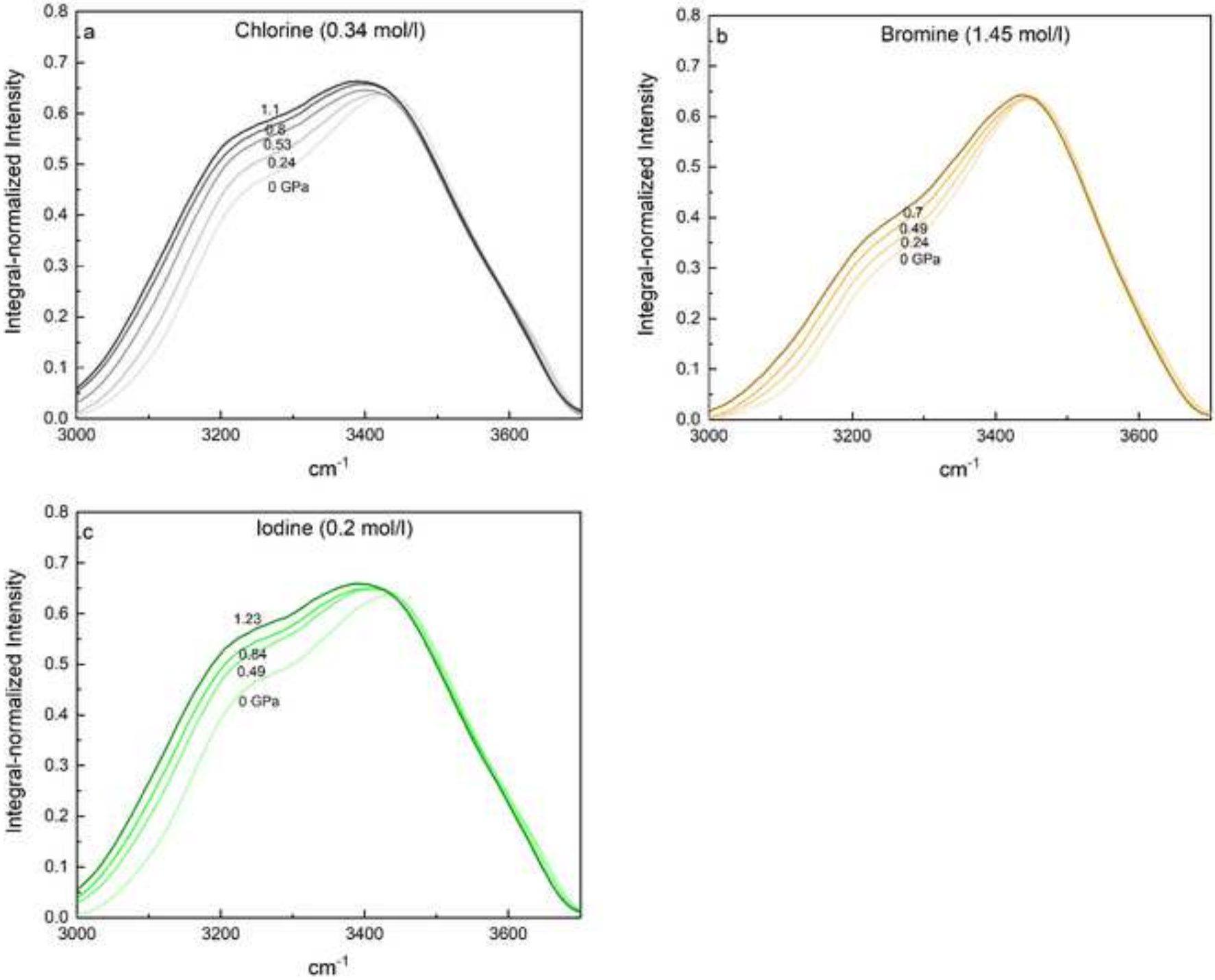
Figure 5

Click here to access/download;Figure;Figure 5.jpg



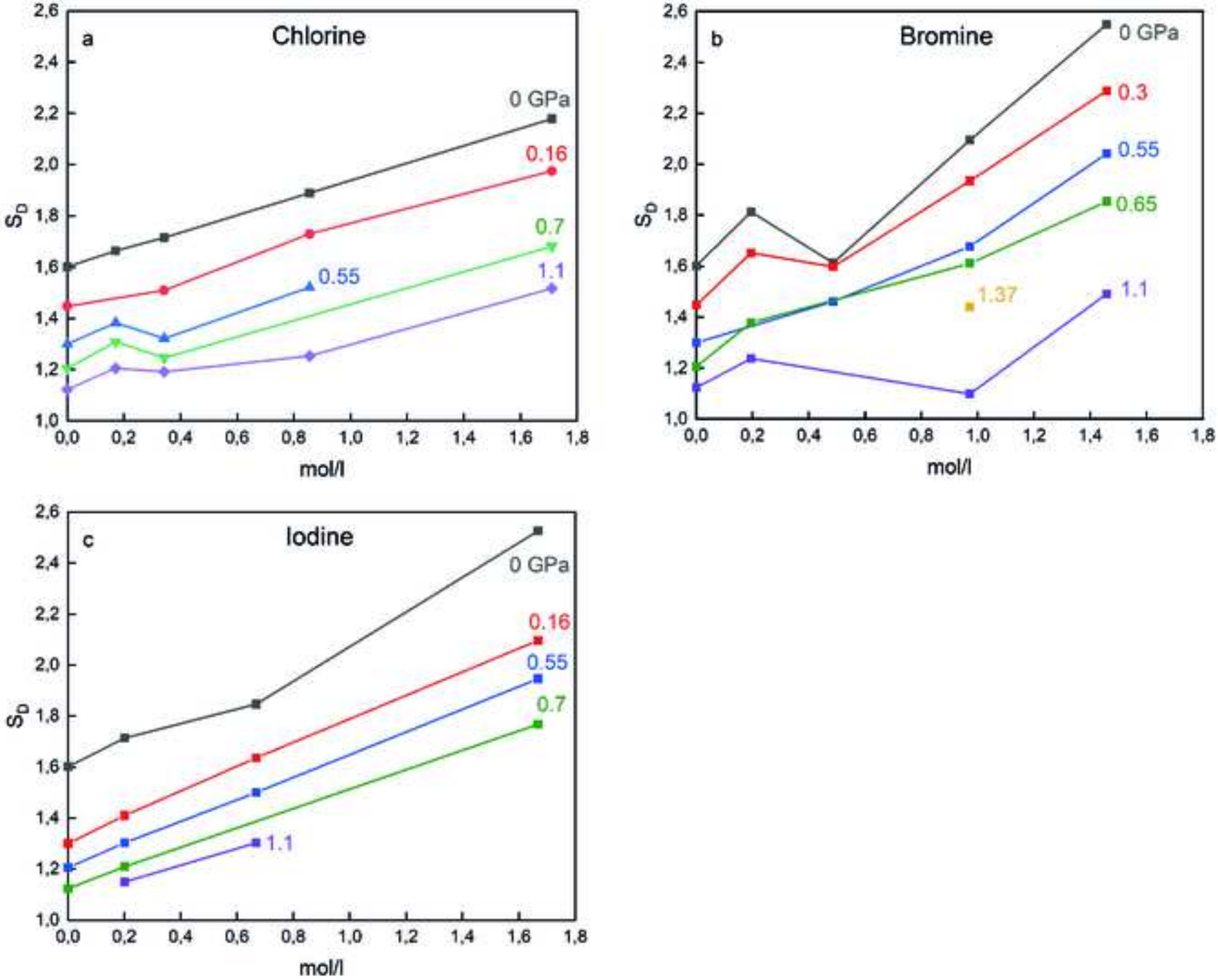
Supplementary Figure S1

Click here to access/download;Figure;Figure S1.jpg



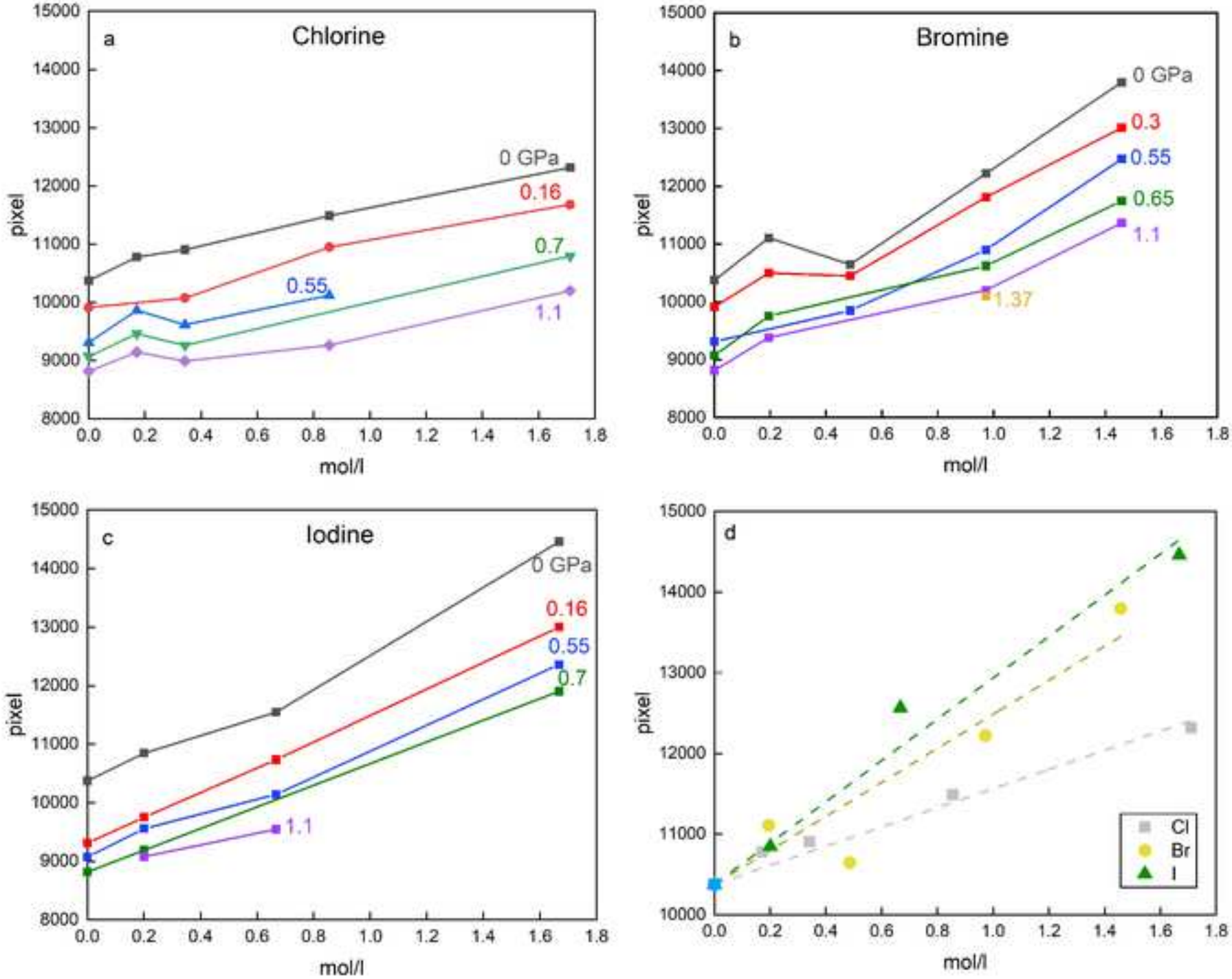
Supplementary Figure S2

Click here to access/download;Figure;Figure S2.jpg



Supplementary Figure S3

Click here to access/download;Figure;Figure S3.jpg



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[a] maximum solubility in H_2O at 20 °C and ambient pressure.

Declaration of interests

☐The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

☒The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

Tobias Grutzner reports financial support was provided by European Commission. Helene Bureau reports financial support was provided by French National Research Agency. If there are other authors, they declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Raw data Raman

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