

1 **A new optical cell for *in situ* Raman spectroscopy, and its application to study**
2 **sulfur-bearing fluids at elevated pressures and temperatures**

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ABSTRACT

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Sulfur is an important component in volcanic gases at the Earth surface but also present in the deep Earth in hydrothermal or magmatic fluids. Little is known about the evolution of such fluids during ascent in the crust. A new optical cell was developed for *in situ* Raman spectroscopic investigations on fluids allowing abrupt or continuous changes of pressure up to 200 MPa at temperatures up to 750 °C. The concept is based on a flexible gold bellow, which separates the sample fluid from the pressure medium water. In order to avoid reactions between aggressive fluids and the pressure cell, steel components in contact with the fluid are shielded by gold foil.

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The cell was tested to study redox reactions in fluids using aqueous ammonium sulfate solutions as a model system. During heating at constant pressure of 130 MPa, sulfate ions transform first to HSO_4^- ions and then to molecular units such as H_2SO_4 . Variation of pressure shows that the stability of sulfate species relies on fluid density, i.e. highly charged species are stable only in high-density fluids. Partial decomposition of ammonium was evident above 550 °C by the occurrence of a nitrogen peak in the Raman spectra. Reduced sulfur species were observed above 700 °C by Raman signals near 2590 cm^{-1} assigned to HS^- and H_2S . No clear evidence for the formation of sulfur dioxide was found in contrary to previous studies on aqueous H_2SO_4 , suggesting very reducing conditions in our experiments. Fluid-mineral interaction was studied by inserting into the cell a small, semi-open capsule filled with a mixture of pyrite and pyrrhotite. Oxidation of the sample assembly was evident by transformation of pyrite to pyrrhotite. As a consequence, sulfide species were observed in the fluid already at temperatures of $\sim 600\text{ °C}$.

39 Keywords: *in situ* Raman spectroscopy, fluids, decompression, optical cell, sulfur speciation,
40 redox reactions

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INTRODUCTION

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Aqueous fluids, especially when containing sulfur, play an important role in the degassing of magmas and in the formation of hydrothermal ore deposits. Large quantities of sulfur are released to the atmosphere by active and passive degassing of magmas, having an important impact on global sulfur budget and hence, on the evolution of climate. Furthermore, the potential of hydrothermal fluids to transport ore-forming metals is affected by sulfur species, which may strongly increase the solubility of metals by formation of complexes (Pokrovski et al. 2008). Sulfur-bearing gases are also of technical interest, e.g., in fining of melts during industrial glass production the temperature-induced decomposition of sulfate in the melt (reaction: $\text{SO}_4^{2-} = \text{SO}_2 + \frac{1}{2} \text{O}_2 + \text{O}^{2-}$) is used to enlarge bubbles and thus to increase their buoyant rise, enhancing the removal of bubbles (Müller-Simon 2011).

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For modeling of melt degassing and formation of magmatic ore deposits, knowledge of the speciation of sulfur in gases and fluids in function of temperature, pressure, oxygen fugacity ($f\text{O}_2$), sulfur fugacity ($f\text{S}_2$, often difficult to constrain) and fluid composition is needed (Burgisser et al. 2010, 2011). The Earth's surface and shallow crust are characterized by a large variation in sulfur speciation, with sulfide ($\text{S}^{\text{II}-}$; as H_2S , HS^- or S^{2-}), sulfur dioxide ($\text{S}^{\text{IV}+}$ as SO_2) and sulfate ($\text{S}^{\text{VI}+}$; as H_2SO_4 , HSO_4^- and SO_4^{2-}) being the most common (e.g. Symonds et al. 1994; Self 2005; Self and Blake 2008; de Moor et al. 2013). Other sulfur species (for instance, elemental sulfur, sulfite, thiosulfate, polysulfides, polythionates, and organic sulfur) form as reaction intermediates in the sulfate-sulfide redox cycle but are relatively minor or thermodynamically metastable at near surface conditions (Pokrovski and Dubrovinsky 2011). The sulfur speciation in deep and hot fluids from hydrothermal magmatic systems and subduction zones hosting the major part of metallic resources on Earth is far less constrained, because such data are difficult to access

64 experimentally. Recent studies of Pokrovski and Dubessy (2015) indicate that intermediate-
65 valence sulfur species such as S_3^- and S_2^- are stable and quite abundant in high temperature
66 hydrothermal fluids.

67 Sulfur-bearing fluids are often not quenchable, and therefore *in situ* observation at high
68 pressure and temperature is required to get insight to the prevailing species in the fluid. Raman
69 spectroscopy has high potential to identify sulfur species, but offers also the option for
70 quantitative analysis of coexisting species (Binder and Keppler 2011). Often, a hydrothermal
71 diamond anvil cell was used for *in situ* observation of fluids at elevated pressures and
72 temperatures (Schmidt 2009; Schmidt and Watenphul 2010; Ni and Keppler 2012). A
73 disadvantage of this method is that the sample volume is fixed and variation in pressure can be
74 initiated only indirectly by changing the temperature or the initial load in the sample chamber.
75 Additionally, low pressures are difficult to adjust properly in such cells, and pressure monitoring
76 relies on the use of pressure sensors, such as quartz or zircon, that are calibrated for both
77 pressure and temperature (Schmidt and Ziemann 2000; Schmidt et al. 2013).

78 First optical cells based on sapphire windows have been developed for *in situ* spectroscopy
79 on fluids at temperatures up to 500°C in the group of Franck in Karlsruhe several decades ago,
80 see review of Buback et al. (1987). Pressurization was achieved with a hydrothermal fluid which
81 was separated from the sample fluid by a flexible bellow. Frantz et al. (1993) presented a
82 miniaturized optical cell for Raman spectroscopy on fluids up to 700 °C and 400 MPa. A
83 disadvantage was that the sample chamber was directly connected to the pressure medium.
84 Another type of high-pressure high-temperature setup for *in situ* Raman spectroscopy of
85 supercritical fluids was reported by Louvel et al. (2015). Sapphire pistons were used for pressure
86 transfer from the pressure medium helium to a hydrothermal fluid. Based on these experiences,

87 we constructed a new cell allowing for abrupt or continuous changes of pressure at constant
88 temperature to mimic degassing processes.

89 The high temperature-high pressure application of the cell was tested using solutions of
90 ammonium sulfate. Ammonium sulfate was selected because of its high solubility in fluids at the
91 P , T conditions of the experiment. Additionally, this solution offers the possibility to study
92 internal redox reactions initiated by decomposition of ammonium. A further advantage is that
93 sapphire windows are basically inert against $(\text{NH}_4)_2\text{SO}_4$ fluids even at the highest P , T conditions
94 applied.

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96 THE SPECTROSCOPIC CELL

97 The set up of the new *in situ* Raman spectroscopy pressure cell is shown in Figure 1. The
98 pressure vessel (1) is machined out of IN 713 LC steel from Doncaster[®]. The material was
99 already successfully used for cold seal pressure vessels working at temperature/pressure
100 conditions of 850 °C/500 MPa and 900 °C/100 MPa. An advantage of this material is its low
101 heat conduction (Zielińska et al. 2010). This minimizes thermal gradients induced by heat
102 transfer to other components of the cell. The dimensions of the cylindrical cell container are
103 60 mm in total lengths with an outer diameter of 11.9 mm and inner diameter of 4.5 mm. At the
104 top, the inner drill hole ends with a conical shape with a total opening angle of 30° over a
105 distance of 2.8 mm, which acts as the seat for the 2 mm thick polished sapphire or diamond
106 window. The windows are shaped to have an exact matching angle. At the bottom, the steel body
107 consists of a screw thread (M16 x 1.5) that fits into a NovaSwiss[®] elbow connector (12). The drill
108 hole in the lower part of the steel container is extended to 6.5 mm in diameter, with a transition
109 total angle of 60°. A double-cone (10) with a central drill hole of 1.6 mm is placed between the

110 conical seats of the cell body and the elbow connector for pressure transmittance. To prevent
111 leakages or any damage (possibly caused by different thermal expansion coefficients of the
112 materials), the same alloy is used for the vessel and the double cone.

113 To provide chemically inert conditions, the sample fluid is separated from the steel
114 components by an inlay (3) made of gold tubing with 4.0 mm inner diameter and 0.2 mm
115 thickness with a tapered top end (30°) and a widened bottom end (60°). A flexible pressure bag
116 (9) separates the sample fluid from the pressure medium. It is machined from gold tubing with
117 2.8 mm inner diameter and 0.2 mm thickness using a welded seam or welded gold foil lid (5)
118 (0.2 mm thickness) as closure on top. The pressure bag is widened with a 60° angle at the bottom
119 end. The inlay is positioned into the vessel first, followed by the sapphire window and the
120 pressure bag. The space between window and pressure bag forms the sample chamber. The
121 pressure vessel is screwed into the NovaSwiss[®] pressure adapter (12) with an open-end wrench
122 matching the spanner flat (11) until the double cone cold-seals at both ends. The bottom end of
123 the double cone towards the NovaSwiss[®] adapter has a slightly smaller angle (59°) than the seat
124 of the connector (60°) to improve sealing.

125

126 **FIGURE 1.** (a) Isometric view of the pressure vessel and heating element. 1 = pressure vessel,
127 2 = sapphire or diamond window, 3 = inlay (Au), 4 = sample chamber, 5 = welded gold foil lid,
128 6 = thermocouple, 7 = heating cartridge (brass), 8 = heating wire, 9 = pressure bag (Au),
129 10 = double-cone, 11 = spanner flat SW11, 12 = NovaSwiss[®] pressure adapter. (b) Technical
130 drawing of the pressure vessel (1) and the double cone (10) with dimensions in mm. (c) View of
131 the cell within in the cooling socket and cylindrical cooling box.

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133 The assembly is mounted on a Carl Zeiss® microscopic adjustment slide, which enables
134 horizontal positioning of the cell. In order to protect the microscope against heat radiation and
135 possible release of hot fluid after rupture of cell components, the cell is inserted in a water-
136 cooled cylindrical box (Fig. 1c). The cooling box is closed with a lid, which contains a 4 mm
137 diameter hole for the laser to pass. A nitrogen-purged gas-cooling collar helps to further protect
138 the objective of the microscope against heating.

139 Sapphire was chosen as window material because of good experience in previous *in situ*
140 spectroscopic studies (e.g. Frantz et al. 1993; Nowak et al. 1996). The window was prepared
141 from a 2 mm thick disc of a synthetic sapphire crystal orientated parallel to the (001) plane,
142 which was polished on both sides to finally 0.25 µm. Cylinders with a diameter of 3.9 mm were
143 drilled from the polished disc, and grinded to a conical shape with a taper of 30°. Sharp edges on
144 both ends were removed using a diamond file. Finally, the flanks of the cone were polished with
145 diamond paste down to 1 µm.

146

147 **Pressure control and variation**

148 The pressure is applied by a NovaSwiss® hand pump with a spindle drive using water as
149 pressure medium. The pump is connected with a flexible pressure tubing (KGT®) to the
150 spectroscopic cell. Soldered connectors of this tubing limit the pressure to a maximum of
151 200 MPa. Pressure is measured with a digital WIKA® HP-2 USB pressure transducer with an
152 uncertainty of 0.25 % in the pressure range of 0 to 200 MPa. The transducer is connected to a PC
153 and enables to record pressures using the WIKA® communication software EasyCom® 2011.

154 A change in temperature from room temperature to 750 °C at constant pressure of
155 200 MPa increases the fluid volume by a factor of 2.3, calculated on the basis of pure H₂O

156 (Wagner and Pruß 2002). Assuming a completely expanded pressure bag at room temperature,
157 the free fluid volume in the cell is about 70 μl . Thus, the maximum pressure reduction at 750 $^{\circ}\text{C}$
158 is from 200 MPa to ca. 80 MPa after complete compression of the gold bag. The minimum
159 pressure, which can be achieved at high temperature, is determined by the initial amount of fluid
160 and the size of the gold bag. Assuming an initial fluid amount of 35 μl and a corresponding
161 increase in volume of the pressure bag, the minimum pressure at 750 $^{\circ}\text{C}$ will be 50 MPa. This
162 simple estimation demonstrates the limits in application of the presented assembly, i.e. pressures
163 below 50 MPa are extremely difficult to adjust at magmatic temperatures.

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165 **Temperature control and calibration**

166 A standard heating element (HotSet[®] hotslot[®] coil heater, WRP 7803107, 230 V, 225 W,
167 235 Ohms) mounted on a brass tube was used, limiting the operation temperature to 750 $^{\circ}\text{C}$. The
168 heating element is powered by two coupled Delta[®] ES30 (300 V DC, 450 mA, 135 W) current
169 supplies (regulated in Master/Slave configuration) using a Eurotherm[®] PID controller type 2704f
170 connected to TC1.

171 Since the temperature inside the cell cannot be directly measured with a thermocouple, the
172 temperature distribution is externally characterized by (type K) thermocouples in notches on the
173 micro-vessel at four different distances from the top (TC1 = 5 mm, TC2 = 10 mm, TC3 = 15 mm
174 and TC4 = 20 mm, compare to Fig. 1b). Temperatures are recorded during the experimental run
175 with a Mod-Mux module MM8TC combined with the SpecView SCADA Software.

176 The temperature distribution along the cell is shown in Fig. 2a. The difference between
177 TC1 (Set point temperature of the controller) and TC4 increases from 1 $^{\circ}\text{C}$ at 100 $^{\circ}\text{C}$ (as set
178 point temperature) to 15 $^{\circ}\text{C}$ at 650 $^{\circ}\text{C}$. Convection of the fluid is assumed to homogenize

179 efficiently the temperature inside the cell, and thus variation in fluid temperature is expected to
180 be smaller than measured with the thermocouples. Temperature distribution within the fluid was
181 determined in a calibration experiment using the Raman shift of the anti-symmetric stretching
182 mode of zircon $\nu_3(\text{SiO}_4)$, which shifts with pressure towards higher wavenumber and with
183 temperature towards lower wavenumber (Schmidt et al. 2013). The shift of the $\nu_3(\text{SiO}_4)$ Raman
184 band at 19 °C induced by a pressure increase from 0.1 MPa to 100 MPa was determined within
185 the cell to be $0.73 \pm 0.06 \text{ cm}^{-1}$. The measured shift is similar to the value of $0.58 \pm 0.01 \text{ cm}^{-1}/100$
186 MPa given by Schmidt et al. (2013) for the $\nu_3(\text{SiO}_4)$ band. Since the pressure range applied in
187 our study is rather small compared to Schmidt et al. (2013), their determination is considered to
188 be more precise and, therefore, we applied this value for correcting Raman spectra with respect
189 to pressure. The corresponding temperatures T_{Zr} were iteratively determined using the pressure-
190 corrected values and equation 1 reported in Schmidt et al. (2013):

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$$192 \quad \nu(\text{cm}^{-1}) = 7.5488 \cdot 10^{-9} \cdot T^3 - 1.6113 \cdot 10^{-5} \cdot T^2 - 2.895 \cdot 10^{-2} \cdot T + 1008.9 \quad (1)$$

193

194 **FIGURE 2.** (a) Temperature distribution in the pressure vessel at 100 °C and 650 °C. TC1-4 refer
195 to the positions of the thermocouple tips, TC1 represents the set point of the controller. (b)
196 Comparison of the temperatures measured with thermocouples TC1 and TC2 with T_{Zr} based on
197 the Raman shift of the zircon mode $\nu_3(\text{SiO}_4)$.

198

199 The precision of equation 1 in terms of wavenumber is better than $\pm 0.12 \text{ cm}^{-1}$, depending
200 on temperature (Schmidt et al. 2013). The uncertainty of the pressure correction is $\pm 0.01 \text{ cm}^{-1}$
201 $/100 \text{ MPa}$ (Schmidt et al. 2013). Considering an uncertainty in the determination of the peak

202 position of $\pm 0.06 \text{ cm}^{-1}$ for the $\nu_3(\text{SiO}_4)$ band, error propagation leads to a total error of $\Delta\nu$ of 0.14
203 cm^{-1} resulting in an error of the sample temperature of about 4 °C in the range 100 to 700 °C. As
204 shown in Fig. 2b, the temperature determined using the zircon is lower by 2 °C at 100 °C and by
205 15 °C at 700 °C than TC1 measured by the thermocouple on top of the cell which was used for
206 temperature control. On the other hand, temperatures TC2 and TC3 measured in the center of the
207 cell are in very good agreement with T_{Zr} . Temperatures given below for the spectra always
208 represent the corrected temperatures according to T_{Zr} of this calibration run.

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210

EXPERIMENTAL AND ANALYTICS

211 **Experimental conditions**

212 A perfect alignment of the sapphire window to the gold plated cone seat (inlay in Fig. 1) of
213 the pressure vessel is crucial to achieve a good sealing as well as to eliminate any stress on the
214 window. Even a very small shear stress may produce fractures in the sapphire. Sealing of the
215 sapphire window is achieved by stepwise “pressure-shooting” at room temperature without a
216 pressure bag in the cell. In a first step, a pressure of 50 MPa is adjusted in the pressure line
217 before opening the valve to the vessel. Afterwards, the pressure is progressively increased in
218 50 MPa steps to 150 MPa. Then, the cell is slowly heated up to 200 °C at a rate of 1 °C/s at
219 constant volume, means slightly increasing pressure. Finally, the temperature is reduced by 100
220 °C at a rate of 0.5 °C/s at constant pressure before heating was switched off. This procedure
221 assured that the window stayed in position while the vessel was shrinking upon cooling. As a
222 consequence the flanks of the window are pressed into the gold, eliminating any leakage
223 pathways.

224 After this sealing procedure of the window, the sample chamber was filled with 150 - 200
225 μl of a 3 molar ammonium sulfate solution ($(\text{NH}_4)_2\text{SO}_4$ for analysis, EMSURE[®]). The pressure
226 bag was inserted, pushing out the air and replacing excessive solution. The system is closed by
227 the double-cone when the pressure vessel is screwed into the pressure adapter. After adjusting
228 the target pressure, the temperature was increased in steps of 50 °C using a ramp of 1 °C·s⁻¹.
229 Pressure was manually adopted using the spindle drive. Minor changes in the spectra were
230 observed within the first 5 minutes after adjusting new P , T conditions, probably due to vertical
231 drifting of the window pushed by thermal expansion of the cell body.

232 The sample chamber volume of the new cell is large compared to diamond anvil cells and
233 offers sufficient space for placing a capsule next to the pressure bag. The capsule can be used to
234 add an oxygen or sulfur buffer to the system or to host material for chemical reactions. The setup
235 of the reaction capsule is illustrated in Fig. 3. Gold tubing of 1.0 mm inner diameter with a wall
236 thickness of 0.1 mm and a length of 6 - 12 mm was used to prepare the capsule. A mixture of
237 pyrite and pyrrhotite in mass ratio of 1:1 was used as reactant to test the possible applicability of
238 the technique to control sulfur fugacity. Corundum was added as a getter to capture iron released
239 from the reactants.

240 The capsule was welded shut and then pressurized in a cold seal pressure vessel to 30
241 MPa to compact the assembly. Then, the capsule was pierced at both ends, evacuated and floated
242 with H₂O shortly before the experiment. The piercings on top and bottom are large enough to
243 enable fluid transfer but small enough to prevent transfer of solids into the fluid chamber.

244

245 **FIGURE 3.** Schematic cross section of the reaction capsule. The capsule length is typically ca. 10
246 mm.

247

248 **Raman spectroscopy**

249 Spectra were recorded on a HORIBA Jobin Yvon LabRAM HR 800 UV-Vis Raman
250 spectrometer using a COBOLT Blues™ DPSS laser with 473 nm wavelengths for excitation.
251 The CCD-detector offers a resolution of 1024 x 256 pixel and is cooled by a Peltier element.
252 Unpolarized spectra were acquired in backscattering geometry typically 1000 μm beneath the
253 window/fluid transition (about 100 μm in the case of window etching) using a 20x magnification
254 objective with long working distance (N. A. =0.25), a grating of 1800 lines/mm, a focal length of
255 800 mm and a pinhole of 1000 μm. The measured laser power at the objective was 13 mW.
256 Accuracy of wavenumber is $\pm 0.2 \text{ cm}^{-1}$ as determined frequently using a Neon lamp. Spectral
257 resolution was typically 0.28 cm^{-1} . The time for recording a full range spectrum (150 to 3900 cm^{-1})
258 was 120 s and 320 s depending on accumulation conditions (2 repetitions, 5 s / 10 s
259 accumulation time).

260 Intensities of recorded Raman spectra were corrected for the response function of the
261 spectrometer (Frantz et al. 1993). This function was determined by the manufacturer using a
262 calibrated white light source and corrects for the used excitation wavelength λ_0 of the laser and
263 the grating applied in the measurement.

264

265

RESULTS

266 **Redox reactions in ammonium sulfate-bearing fluids**

267 The ability to control temperature and pressure independently offers new possibilities for
268 *in situ* observations of isobaric or isothermal evolution of fluids using Raman spectroscopy. In
269 the following sections experiments are presented using 3 molar ammonium sulfate solutions

270 under various conditions. First the sample was heated up to 737 °C while a pressure of 130 MPa
271 was kept constant. Second the pressure was lowered to 80 MPa while the temperature of 737 °C
272 was kept constant. At the end the experiment was cooled at 80 MPa pressure to room
273 temperature. The time span for the experiment was 8 hours in total. Dwells at each step for
274 measuring spectra were about 10 min.

275 Total intensities of the acquired spectra depend strongly on the parameters used for data
276 acquisition as well as the position of the volume, which is probed by confocal Raman
277 spectroscopy. For better comparison of spectral features in Fig. 4, the peak height of the OH
278 stretching band around 3600 cm⁻¹ was normalized to 1.

279

280 **FIGURE 4.** Scaled raw data Raman spectra of the isobar heating path in full range and zoomed on
281 900-1200 cm⁻¹ and 2200-2700 cm⁻¹ (a), isothermal decompression path in full range and zoomed
282 on 1050-1200 cm⁻¹ and 2200-2700 cm⁻¹ (b) and isobaric quench path in full range and zoomed on
283 900-1200 cm⁻¹ and 2200-2700 cm⁻¹ (c). Signals at 416 cm⁻¹ (strong), 576 cm⁻¹ (medium) and 749
284 cm⁻¹ (medium) are caused by the sapphire window.

285

286 **TABLE 1.** Raman frequencies above 900 cm⁻¹ and species assignments.

287

288 **Isobaric heating.** Raman spectra recorded during heating at 130 MPa fluid pressure are
289 shown in Figure 4a. Detailed band assignment is given in Table 1. Dominating features at 22 °C
290 are the very intensive and narrow peak at 980 cm⁻¹ assigned to SO₄²⁻ (Rudolph 1996; Schmidt
291 2009) and the broad, asymmetric OH stretching vibration band of water molecules with
292 maximum at 3443 cm⁻¹ (Schmidt and Watenphul 2010; Schmidt and Manning 2017).

293 Superimposed on the low-wavenumber tail of this band at 3000-3200 cm⁻¹ are bands of the NH
294 stretching-vibration of ammonium ions (Schmidt and Watenphul 2010; Schmidt and Manning
295 2017). The OH-NH band system is strongly affected by hydrogen bonding. With increasing
296 temperature at constant pressure, fluid density decreases and, as a consequence, hydrogen
297 bonding is reduced (e.g. Soper 2000; Sahle et al. 2013). Thus, the OH and NH related peaks are
298 getting narrower and shift towards higher wavenumber. At temperatures above 191 °C up to 489
299 °C, spectra were strongly affected by fluorescence superimposing the Raman signal, probably
300 due to contamination by organic material during set-up of the cell. An indication for such
301 contamination is the additional small signal at 2830 cm⁻¹, possibly originating from CH -
302 vibrations. Within this temperature region the signal of SO₄²⁻ decreases and a new band forms at
303 1050 cm⁻¹, assigned to HSO₄⁻ (Rudolph 1996). While the shape of the SO₄²⁻ band appears
304 symmetric the HSO₄⁻ band has an asymmetry towards lower wavenumber. At 489 °C, SO₄²⁻ is
305 still observed in the fluid while the intensity of HSO₄⁻ increases. At 1140 cm⁻¹, a new peak
306 appears, which has been interpreted as overlapping signals of H₂SO₄ (~1140 cm⁻¹) and SO₂
307 (1145 cm⁻¹) in previous studies (Walrafen 1964; Maillard et al. 1975; Ni and Keppler 2012). The
308 HSO₄⁻ signal vanished at 685 °C, and the band system near 1140 cm⁻¹ represents the only
309 remaining sulfate species.

310 Two narrow peaks at 3233 and 3314 cm⁻¹ are firstly observed at 339 °C during heating.
311 The peaks are assigned to NH₃ (Buback and Schulz 1976) formed by the dissociation reaction
312
$$\text{NH}_4^+_{\text{aq}} = \text{NH}_3 + \text{H}^+_{\text{aq}} \quad (2)$$

313 where the subscript *aq* indicates that these species are stabilized in aqueous complexes. The
314 dissociation is a consequence of decreasing hydrogen bonding with increasing temperature. At
315 the highest temperature of 737 °C NH and OH related peaks are well separated in the spectra.

316 A sharp signal at 2323 cm^{-1} appears at $591\text{ }^{\circ}\text{C}$, increasing with temperature. This signal
317 was assigned to N_2 (Schroetter and Kloeckner 1979), formed by decomposition of NH_3 . At 737
318 $^{\circ}\text{C}$, the 1140 cm^{-1} band system decreases in intensity, and a new signal around 2580 cm^{-1} is
319 visible, which is composed by a weak signal at 2578 cm^{-1} assigned to HS^- and a stronger signal at
320 2590 cm^{-1} assigned to H_2S (Rosasco and Roedder 1979; Bény et al. 1982; Chazallon et al. 2007).

321

322 **Isothermal decompression.** Fig. 4b illustrates the evolution of the Raman spectra upon
323 decompression from 130 MPa to 80 MPa at $737\text{ }^{\circ}\text{C}$. In this pressure range, in the case of pure
324 water, the density is supposed to decrease by a factor of 1.6 from 0.34 g/cm^3 to 0.21 g/cm^3
325 (Wagner and Pruß 2002). The response of Raman spectra to pressure changes is very fast, i.e.
326 stable conditions were achieved two minutes after pressure drop.

327 There are not many changes in the spectra after decompression. The sulfate-related bands
328 near 1140 cm^{-1} and NH_3 -related signals near 3200 cm^{-1} slightly decrease in intensity compared to
329 the OH bands, whereas the peaks assigned to N_2 and $\text{HS}^-/\text{H}_2\text{S}$ slightly increase. The latter trend
330 suggests continuation of the internal reduction reaction in the fluid during decompression.

331

332 **Isobaric cooling.** To test the reversibility of effects observed during heating, Raman
333 spectra were collected during isobaric cooling at 80 MPa (Fig. 4c). Below $343\text{ }^{\circ}\text{C}$ spectra were
334 very noisy and the background increased, i.e. in the low and in the high wavenumber range, and
335 even qualitative statements about peak evolutions were not possible. Thus, we could not re-
336 measure the fluid after the run at ambient temperature.

337 Towards low temperatures, intensities of all signals are slightly increasing. Sulfate-related
338 peaks show the same trend as observed during heating, i.e. an increasing stability of ionic species

339 towards lower temperature from H_2SO_4 to HSO_4^- to SO_4^{2-} . HSO_4^- was firstly observed at 489 °C
340 and SO_4^{2-} at 388 °C (see inlet in Fig. 4c). These temperatures are roughly consistent with the
341 heating path although confining pressure was different. The signals of $\text{HS}^-/\text{H}_2\text{S}$ and N_2 are
342 visible in all spectra (see inlet in Fig. 4c). While the intensity of the $\text{HS}^-/\text{H}_2\text{S}$ remains roughly
343 constant over the whole temperature range, the intensity of the N_2 peak is continuously
344 increasing. The NH_3 bands decrease during cooling but re-formation of the NH_4^+ -related bands
345 during cooling cannot be approved due to the increase in background. Although a final proof is
346 missing, a reversibility of reaction (2) is very likely on the basis of the observations. On the other
347 hand, it is evident that the reduction of sulfate species to sulfide species is irreversible.

348

349 **Fluid-Solid interaction**

350 The experiment with 3 molar ammonium sulfate solution and a reaction capsule
351 containing a pyrrhotite/pyrite mixture was also affected by fluorescence at low temperatures, and
352 Raman spectra could be recorded during heating only above 500 °C (Fig. 5a). During cooling the
353 whole temperature range was accessible down to room temperature (Fig. 5b).

354

355 **FIGURE 5.** (a) Raman spectra recorded on ammonium sulfate solutions in contact with
356 pyrite/pyrrhotite mixture at constant pressure of 130 MPa and temperatures of 592-685 °C during
357 heating. For comparison the spectrum of the experiment without pyrite/pyrrhotite at 685 °C is
358 shown. (b) Evolution of spectra during cooling to room pressure at same pressure.

359

360 The evolution of spectra during heating is similar as in the experiment without reaction
361 capsule except that the $\text{HS}^-/\text{H}_2\text{S}$ band system was firstly observed at much lower temperature of

362 592 °C (Fig. 5a). Additionally, the high temperature spectra in presence of pyrite/pyrrhotite show
363 a pronounced peak at 567 cm⁻¹, which appears to be correlated in intensity to the HS⁻/H₂S band
364 system. Duration of the heating path was similar in both experiments.

365 During cooling, the evolution of sulfate-related bands is similar to the experiment without
366 sulfur-bearing minerals (Fig. 5b). The H₂SO₄ band system near 1140 cm⁻¹ disappeared at 400 °C;
367 HSO₄⁻ was firstly observed at 489 °C and disappeared at 191 °C; SO₄²⁻ was firstly visible in the
368 spectrum recorded at 391 °C. The N₂ peak is much more pronounced than in the
369 pyrrhotite/pyrite-free experiments, and the HS⁻/H₂S band system is visible even at room
370 temperature after cooling. Below 200 °C the H₂S component systematically decreases and in the
371 r.t. spectrum only HS⁻ is present. Again, this observation is in line with stabilization of ionic
372 species by aqua complexes at low *T* and high fluid density.

373 In the low wavenumber range, some distinct differences to Fig. 4 need to be
374 acknowledged. At 685 °C an intense peak occurs at 567 cm⁻¹ concomitant with growth of the HS⁻
375 /H₂S band (Fig. 5a). Upon cooling, this band is dramatically reduced in intensity already at 591
376 °C (Fig. 5b), indicating that the responsible species is highly *P*, *T* dependent. The absence of this
377 peak in the system without reaction capsule (Fig. 4) suggests that the 567 cm⁻¹ peak relies on
378 specific conditions induced by the pyrrhotite/pyrite assemblage. It is very likely that this band is
379 caused by S²⁻ ions in the fluid (Pokrovski and Dubessy 2015; Schmidt and Seward 2017).

380 Another intense peak is formed at 527 cm⁻¹ at intermediate temperatures and disappeared
381 below 200 °C. According to Pokrovski and Dubessy (2015), this band can be assigned to the
382 symmetric stretching vibration of the S₃⁻ ion that forms in solutions in which sulfate and sulfide
383 coexist. The large shoulder at the HSO₄⁻ peak at 1060 cm⁻¹ is due to the 2nd order harmonics of
384 the S₃⁻ that exhibits a resonance phenomenon at the applied laser wavelength (Pokrovski, pers.

385 communication). The large and multiple peak feature clearly apparent in the 295 °C spectrum
386 around 450 cm⁻¹ in Fig. 5b is likely to be polymeric molecular sulfur in solution (Pokrovski and
387 Dubessy 2015; Barré et al. 2017).

388 Microscopic investigation on a polished cross section of the reaction capsule after the run
389 gives evidence for proceeding reactions in the mineral assemblage. A porous layer was formed
390 around large pyrrhotite grains. The newly formed phase was identified as pyrite by Raman
391 spectroscopy. Thus, oxidation of sulfide is evident in the powder, most likely by sulfate from the
392 fluid. Outside the reaction capsule, sulfate was still present in large concentration and sulfide was
393 formed by homogeneous redox reaction in the fluid. These findings suggest that the capsule
394 interior and the fluid outside the capsule were not in chemical equilibrium.

395

396

DISCUSSION

397 Fitting of band components and intensity corrections

398 In order to analyze changes in abundance of species during the experiment, we
399 deconvoluted the Raman spectra. Spectra were fitted with a minimum number of Pseudo-Voigt
400 functions required to reproduce the measured spectrum in the respective ranges of interest. All
401 bands are consistent with band assignments for given species as outlined above. The Pseudo-
402 Voigt function was based on the normalized sum of a Gaussian and a Lorentzian. The Gauss-
403 Lorentz ratio was constrained to be the same for all fitted peaks within a given subrange. Broad
404 and asymmetric band systems like the OH band system were fitted by several peaks to describe
405 the envelope of the band system. Individual peaks have no direct meaning and are only used to
406 determine the intensity of the band system. During the fit of these individual spectral regions of
407 interest, we used linear baselines for simplicity. Ranges of particular interests are at 950 - 1200

408 cm^{-1} , where different sulfate species and possibly SO_2 occur, at $2300 - 2600 \text{ cm}^{-1}$, where
409 vibrations of N_2 and $\text{HS}^-/\text{H}_2\text{S}$ are excited, and $2600 - 3800 \text{ cm}^{-1}$, which is the range of OH and
410 NH stretching vibrations.

411

412 **FIGURE 6.** Deconvolution of Raman signals in selected spectral regions for the experiment with 3
413 molar ammonium sulfate solution at different P, T conditions. For band assignment see Table 1.
414 (a) - (c) Regime of OH and NH stretching vibrations. (d) - (f) Regime of H_2SO_4 stretching
415 vibrations. (g) - (h) Regime of SH stretching vibrations.

416

417 The broad band system of the ammonium sulfate solution at $2600 - 3800 \text{ cm}^{-1}$ measured at
418 $20 \text{ }^\circ\text{C}$, 130 MPa can be reproduced well using five components, the three high frequency bands
419 are assigned to OH stretching vibration bands of water molecules and the two bands at lower
420 frequency (2930 and 3073 cm^{-1}) are assigned to NH stretching vibrations of NH_4^+ ions (Fig. 6a).
421 Ammonium ions are only a minor species at $600 \text{ }^\circ\text{C}$ and are absent at $734 \text{ }^\circ\text{C}$ (Fig. 6b,c). Instead
422 of that, well-resolved bands of NH_3 occur in the high temperature spectra at 3232 and 3322 cm^{-1} .

423 Simultaneously with the disappearance of the NH_4^+ species, sulfate groups are transformed
424 first to HSO_4^- and then to H_2SO_4 units. The evolution of the latter band system located around
425 1140 cm^{-1} is shown in Figure 6d-f. Three band components are sufficient to fit the spectra in this
426 region, the broad additional component in Figure 6f can be considered as being part of the
427 background. A key question is whether the narrow band component at 1145 cm^{-1} is caused by
428 symmetrical stretching vibration of SO_2 molecules (Maillard et al. 1975; Ni and Keppler 2012).
429 Ni and Keppler (2012) made such assignment in their *in situ* Raman study on sulfuric acid at
430 temperatures up to $700 \text{ }^\circ\text{C}$. A possible explanation given by the authors is that the solution

431 reacted with rhenium metal from the gasket of the diamond anvil cell, as indicated by the
432 observation of rhenium oxide in the assembly after experiment.

433 We have several reasons inferring that this is not the case in our experiments: (i) The
434 intensity ratio of sub-bands in this region depends only weakly on temperature and pressure, and
435 we do not observe a systematic relative increase of the 1145 cm^{-1} component with dwell time at
436 high temperature. Such trend would be expected for a progressing reduction reaction in the fluid
437 that produces sulfur dioxide. (ii) The 1145 cm^{-1} band completely vanished during cooling
438 together with the other band components in this spectral region. In the study of Ni and Keppler
439 (2012) the SO_2 peak was still present in the post-experimental spectra recorded at room
440 temperature. (iii) The degradation of the band system at 1140 cm^{-1} and the formation of the band
441 system at 1040 cm^{-1} during cooling occurs very fast (Fig. 4c). This trend is consistent with rapid
442 protonation/deprotonation processes but not with complex redox reactions, which are typically
443 slow. Thus, we assign the band at 1145 cm^{-1} to a symmetrical SO_2 stretching vibration in H_2SO_4
444 molecules, denoted in following as $^*\text{H}_2\text{SO}_4$.

445 A major difference of our spectra above $600\text{ }^\circ\text{C}$ to those of sulfuric acid shown in Ni and
446 Keppler (2012) is the absence of the band at 1200 cm^{-1} , assigned to the ν_1 mode of H_2SO_4 by
447 these authors. We attribute the different findings to the composition of the fluid, i.e. the presence
448 of ammonium. A strong change in fluid properties after addition of ammonium can be inferred
449 from experiments of Schmidt and Watenphul (2010). They observed a drastic decrease of silica
450 solubility for NH_4Cl -bearing solutions compared to a pure H_2O fluid, e.g. by a factor of 2 at
451 500°C , 500 MPa for a $6.6\text{ m NH}_4\text{Cl}$ solution. These observations indicate that dissolved
452 ammonium reduces the capability of fluids to form solvation complexes. Thus, $^*\text{H}_2\text{SO}_4$ most

453 likely represents a state with very weak to negligible interaction with neighboring fluid
454 constituents.

455 The band system at 2580 cm^{-1} can be fitted by three components. The two components at
456 higher wavenumber are assigned to H_2S molecules and the broader one at lower wavenumber to
457 HS^- ions (Table 1). Both species coexist down to temperatures of $200\text{ }^\circ\text{C}$ (Fig. 5b), at lower
458 temperatures the high-wavenumber components systematically decrease in abundance, and HS^-
459 appears to be the only sulfide species in solution at room temperature.

460

461 **Evolution of species abundance with temperature and pressure**

462 Peak areas determined by fitting the spectra as described above were used to monitor the
463 evolution of species abundance during the experiments. Using the position of peak maxima, peak
464 areas were corrected for the temperature dependence of Stoke's scattering cross section
465 according to (Long 1977; Rudolph and Irmer 2007):

$$466 \quad F_{BE} = \frac{1}{1 - \exp\left(\frac{-hc\omega_j}{k_B T}\right)} \quad (3)$$

467 where h is Planck's constant, c the speed of light, ω_j the Raman shift (peak position), k_B the
468 Boltzmann constant and T the absolute temperature. The wavenumber dependence of the Raman
469 scattering intensity was considered according to (Rudolph and Irmer 2007) by dividing with a
470 factor

$$471 \quad F_s = (\omega_0 - \omega_j)^3 \omega_j^{-1} \quad (4)$$

472 where ω_0 is the wavenumber of the exciting light. Scaling of the intensity of a given species to
473 the total peak area of the OH vibration bands was used to reduce effects induced by changing
474 temperature and pressure of the fluid (Schmidt 2009; Schmidt and Manning 2017). Thus, a

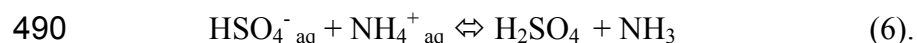
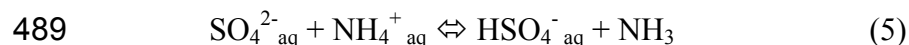
475 qualitative description of species evolution during the experiment was achieved. Quantification
476 suffers from missing knowledge of Raman cross section for the bands. Raman cross sections
477 may strongly change from band to band, and are expected to be highly dependent on fluid
478 properties. Errors in normalized intensities were estimated from counting statistics.

479

480 **FIGURE 7.** Evolution of species abundance during (a) heating, (b) decompression and (c)
481 cooling. Peak areas are normalized to the area of the total OH signals. *H₂SO₄ refers to the band
482 at 1145 cm⁻¹, which has been assigned to SO₂ molecules in previous study. Error bars are not
483 shown for clarity. Errors are smaller than the symbols for values ≥ 0.0005 .

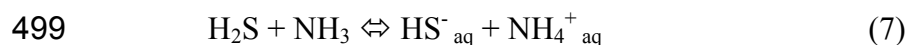
484

485 **Homogeneous reaction.** Fig. 7 shows the results obtained for the experiment with the
486 ammonium sulfate solution. As a general trend highly charged ions are stable only in high
487 density fluids while in low-density fluids molecular species are predominant. In the case of the
488 ammonium sulfate solution, these trends can be described by the following reactions



491 During cooling the backwards reaction, i.e. formation of ionic species, is shifted to lower
492 temperatures (Fig. 7c) due to lower pressure and hence lower fluid density. For instance, at 500
493 °C and 80 MPa, when HSO₄⁻ re-appears during cooling, the density of pure H₂O fluid would be
494 0.46 g/cm³ at these conditions (Wagner and Pruß 2002). The same density at 130 MPa would be
495 reached at 600 °C.

496 The appearance of the N₂ signal at 586 °C indicates the onset of redox reactions in the
497 fluid. Evidence for reduction of sulfate is given by occurrence of the band system at 2580 cm⁻¹ at
498 high temperature. H₂S coexists with HS⁻, which may be described by



500 Neither decompression nor quench leads to a re-oxidation of HS⁻/H₂S. Thus, it seems, once
501 formed, sulfide species remain stable under prevalent conditions. As noted above, despite of the
502 occurrence of a peak at 1145 cm⁻¹, we don't see an indication for the formation of SO₂, in
503 contrary to Ni and Keppler (2012). Roughly parallel trends for H₂SO₄ (sum of areas of sub-bands
504 at 1131 and 1138 cm⁻¹) and *H₂SO₄ (areas of sub-band at 1145 cm⁻¹) also support this statement.
505 The reason for the different findings in Ni and Keppler (2012) is probably the oxygen fugacity in
506 the experiments. Ni and Keppler (2012) detected rhenium oxide in the sample after experiment
507 and suggest that conditions were probably close to the Re-ReO₂ oxygen buffer. Using
508 thermodynamic data of Pownceby and O'Neill (1994) and assuming for simplicity ideal mixing
509 in the fluid, the corresponding hydrogen fugacity at 700 °C/130 MPa is about 0.05 MPa.
510 Decomposition of 0.2% of the loaded ammonium sulfate would be sufficient to generate such
511 hydrogen pressure, if hydrogen is not consumed by subsequent reactions. Comparing the area of
512 NH₃-related bands of the heating path with the cooling path implies that 20% of NH₃ was
513 converted to nitrogen and hydrogen, supporting the hypothesis of a much lower oxygen fugacity
514 in our system compared to Ni and Keppler (2012). However, pressures were different during
515 heating and cooling and Raman cross-sections of the bands are not known so that we cannot
516 make quantitative statements about the extent of the redox reaction.

517 Due to experimental failure we could not collect spectra at the end of the experiment and,
518 hence, the degree of the dissociation of ammonium could not be determined. Comparing NH₃-

519 related peaks at 489 °C during heating and cooling implies that more than 90% of NH₃ survived
520 the high temperature treatment (Fig. 7a,c). But due to different pressures and probably different
521 NH₃/NH₄⁺ ratios this value is not more than a rough estimate.

522

523 **FIGURE 8.** Species evolution during (a) heating and (b) cooling in presence of a pyrrhotite/pyrite
524 assembly. Peak areas are normalized to the area of the total OH signals. *H₂SO₄ refers to the
525 band at 1145 cm⁻¹, which has been assigned to SO₂ molecules in previous study. Error bars are
526 not shown for clarity.

527

528 **Heterogeneous reaction.** For the experiment with the pyrrhotite/pyrite capsule,
529 comparison of NH₄⁺-related bands at room temperature before and after experiment indicate that
530 50% of the ammonium has reacted (Fig. 8a,b). H₂S formation in the fluid was negligible below
531 592 °C. In the interval 592 °C → 685 °C → 592 °C the area ratio for the sum of HS⁻ + H₂S peaks
532 increases by a factor of four from 0.0021 to 0.0092. An even larger increase from 0.0003 to
533 0.0037 occurs for the N₂ band during this cycle. This implies that a large fraction of the sulfide
534 species in the fluid was formed by reduction of sulfate with hydrogen originating from
535 decomposition of NH₃. However, we cannot completely exclude some contribution by
536 dissolution of pyrrhotite inside the reaction capsule and transport of dissolved species outwards.
537 On the other hand, Figure 6 shows that pyrrhotite is covered by pyrite and release of FeS is
538 increasingly hindered with progressing reaction. The reaction products are highly porous, which
539 may indicate a volume reduction of solids during reaction.

540 The apparent disequilibrium between the fluid phase inside and outside the reaction
541 capsule points to kinetic barriers in the system. Limiting parameters are the reaction kinetics of

542 transformation of pyrrhotite to pyrite as well as fluid transport in the pore system within the
543 capsule but possibly also reactions between fluid components (e.g. iron released from the sulfur-
544 bearing minerals) and corundum of the window. Such kinetic problems will also limit the
545 possibility to use a reaction capsule to control oxygen fugacity in the spectroscopic cell. Only if
546 the initial conditions in the fluid are close to the equilibrium conditions imposed by the solid
547 buffer system, the exchange between capsule interior and outside fluid will be sufficient to
548 maintain equilibrium on the time scale of hours, which is the accessible working time for the
549 spectroscopic cell.

550

551

IMPLICATIONS

552 The new spectroscopic cell developed in this study allows observation of hydrothermal
553 and magmatic fluids at temperatures up to 750 °C and pressures up to 200 MPa. Pressure and
554 temperature can be independently varied and thus, enables simulation of decompression of fluids
555 during ascent in the Earth's crust. The cell has sufficient space inside to add a small capsule to
556 study interaction of fluids with solid materials. This assembly may be used to control sulfur
557 and/or oxygen fugacity in the fluid. However, mass transfer between the capsule and duration of
558 the high T experiments is limited so that equilibrium conditions can be adjusted only for specific
559 conditions.

560 Combining the cell with Raman spectroscopy is a powerful method to study
561 homogeneous reactions in fluids with high temporal resolution, depending mainly on the
562 available Raman spectrometer. Tests on 3 molar ammonium sulfate solutions demonstrate the
563 importance of fluid density for stabilization of ionic species. Ammonium was found to have high

564 thermal stability under conditions of the Earth's crust. Even at temperatures of 700 °C in
565 presence of an oxidant, the lifetime of NH₃ is at least several hours.

566 The experiments performed in our studies have also implications concerning the
567 evolution of sulfur species during degassing of magmas and subsequent ascent of fluids to the
568 Earth's surface. Formation of SO₂ in sulfate-bearing fluids, as observed in the study of Ni and
569 Keppler (2012), seems to depend strongly on the prevailing redox conditions in the system. In
570 presence of strongly reducing agents (such as ammonium) sulfide species will be formed while at
571 moderate redox conditions, SO₂ is the reaction product. Confining pressure will also play a
572 crucial role for the reaction.

573

574

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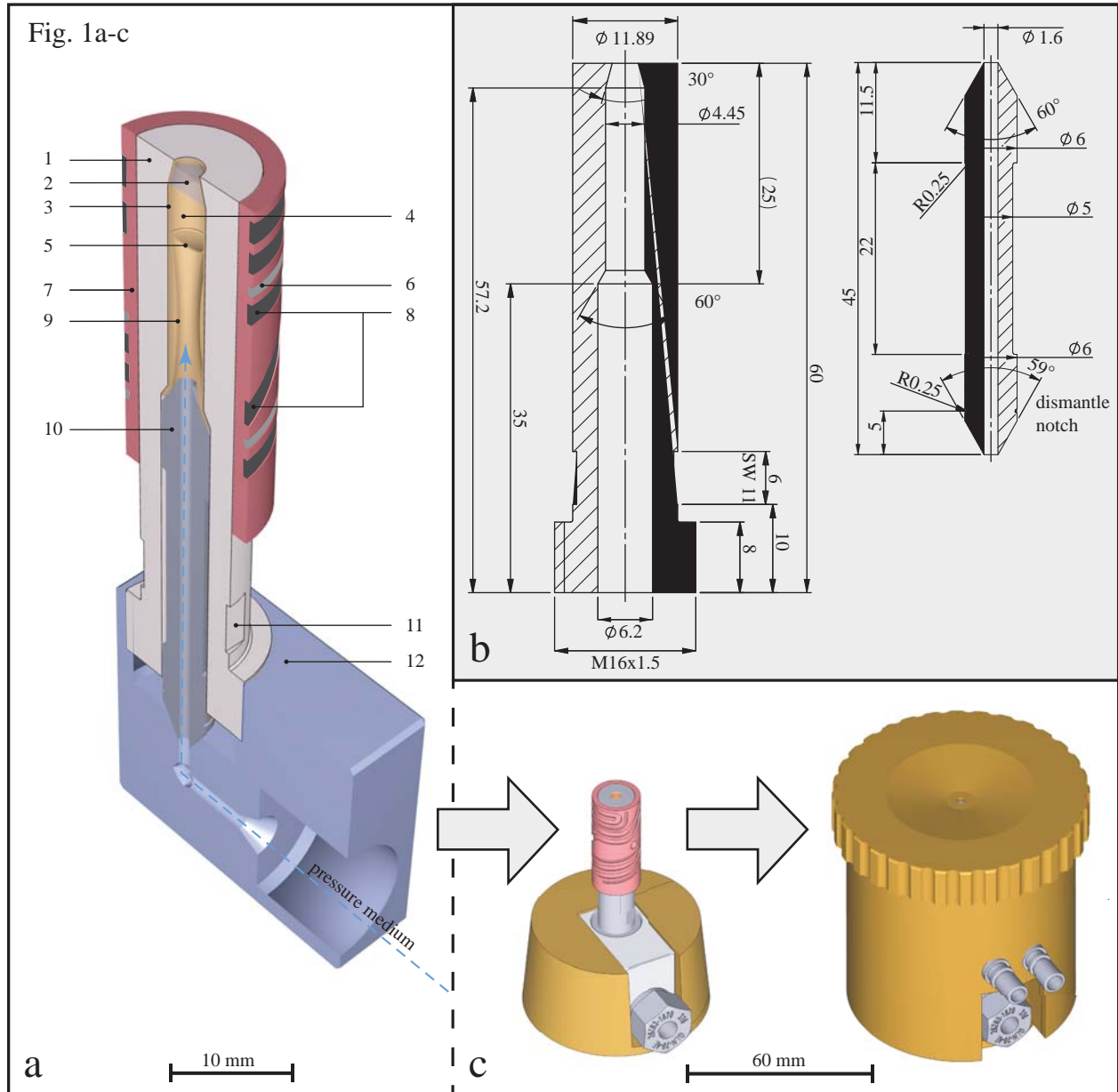
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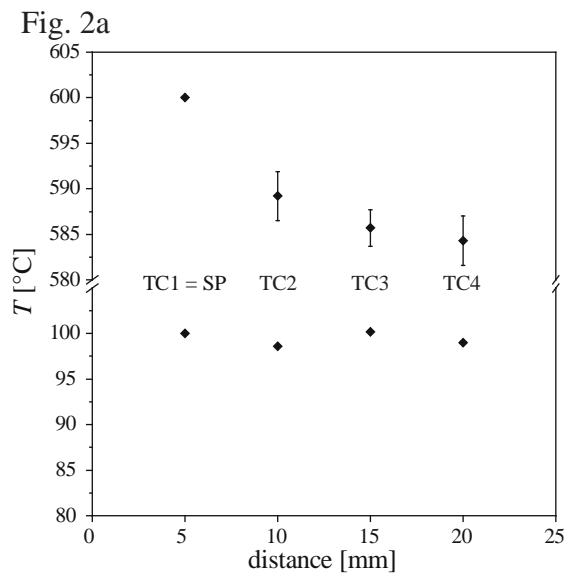


Fig. 2b

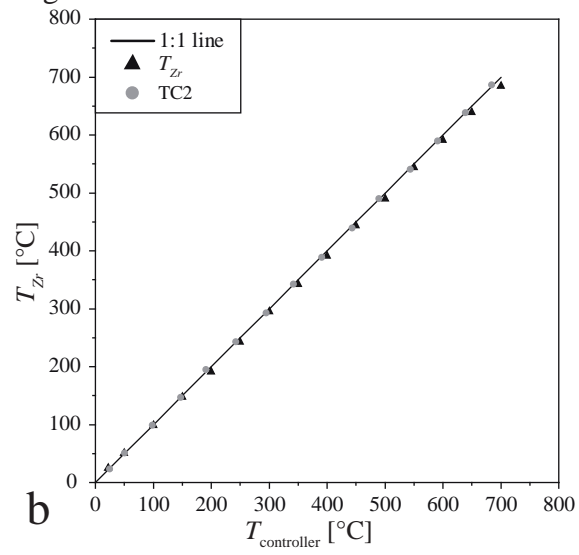


Fig. 3

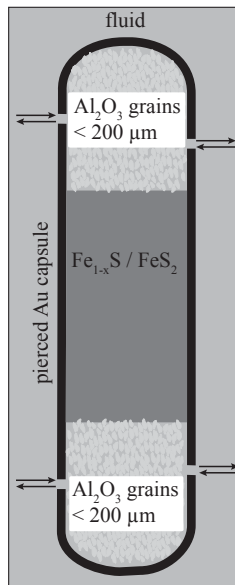


Fig. 4a

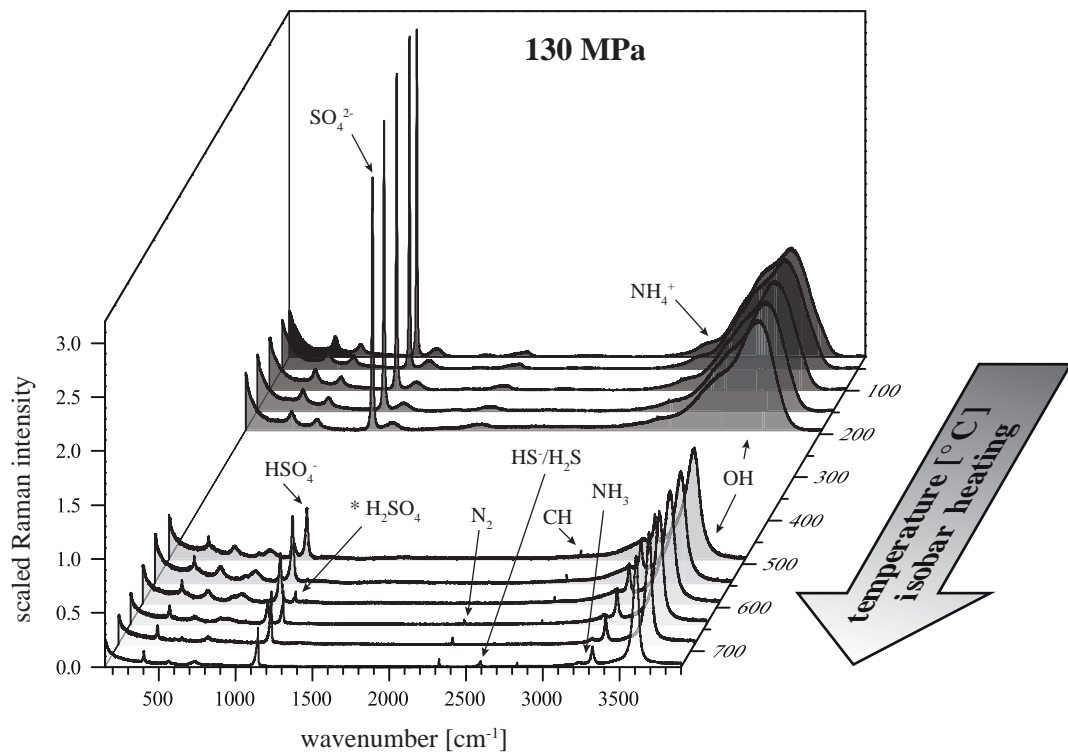


Fig. 4b

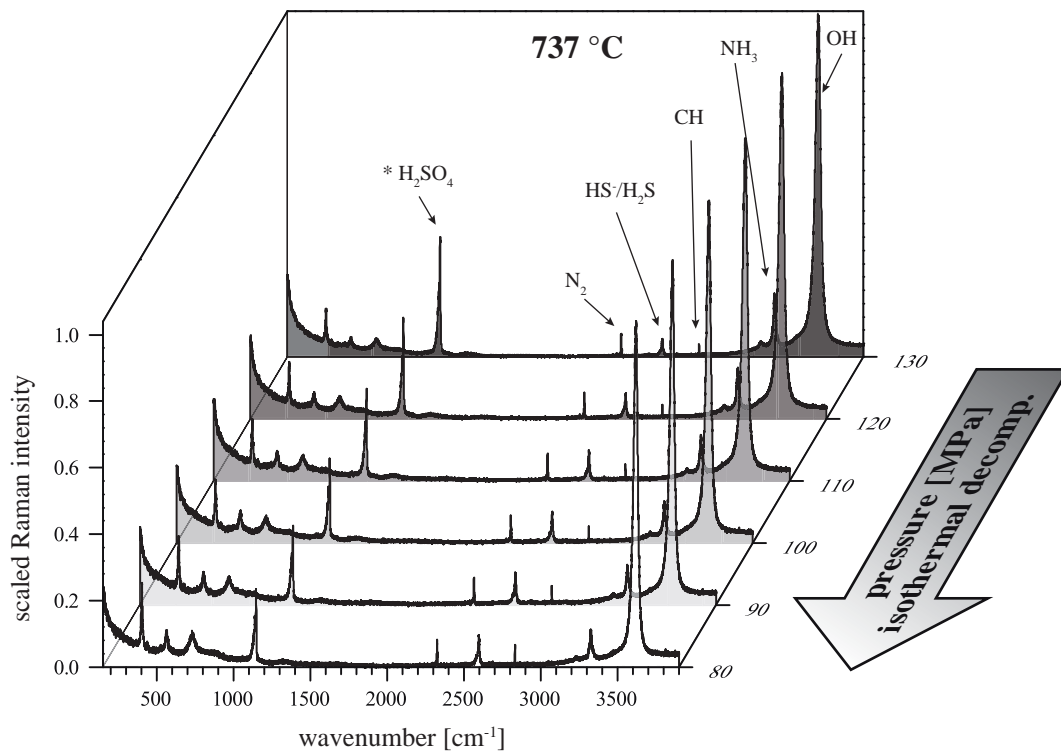


Fig. 4c

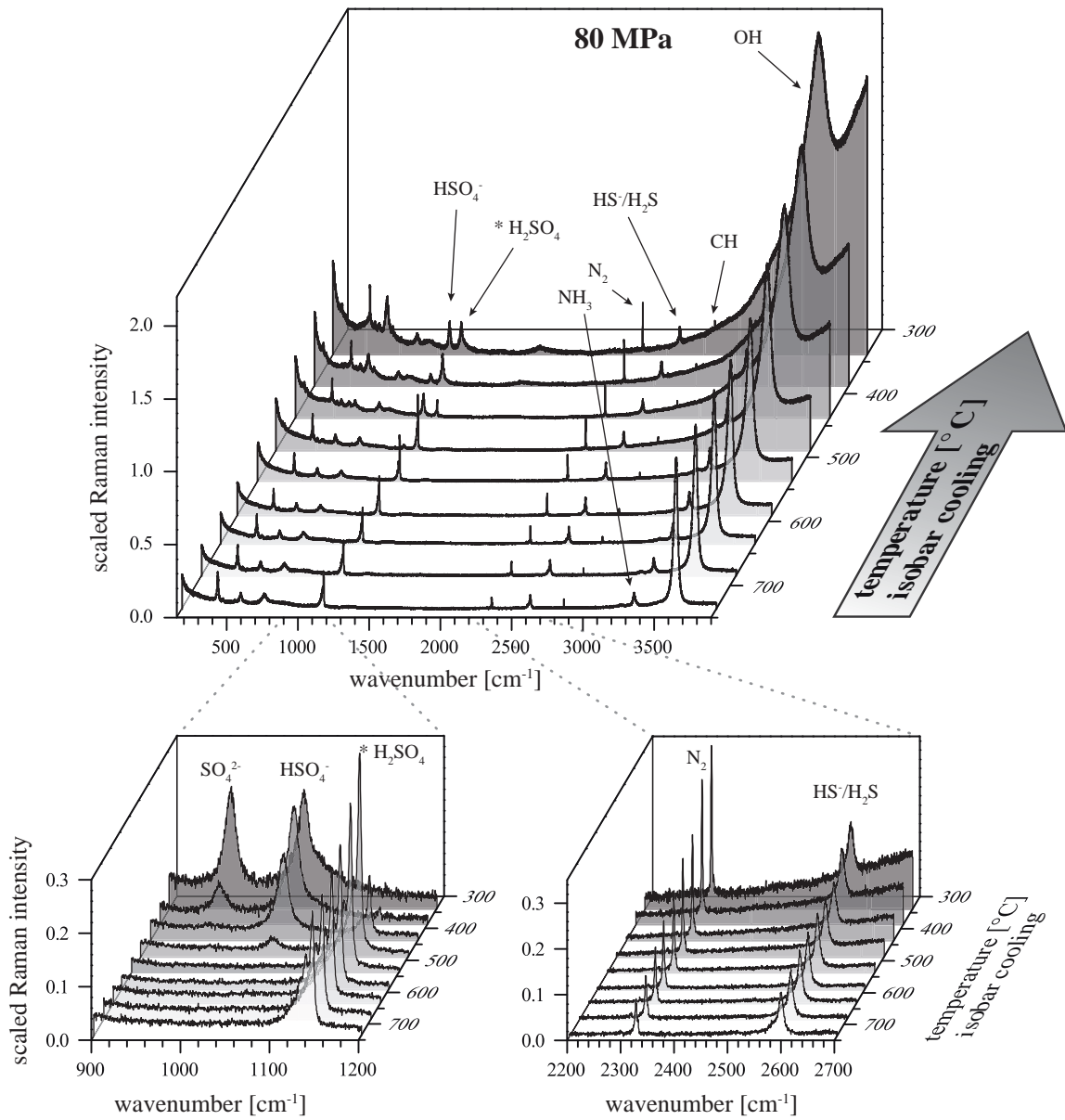


Fig. 5a

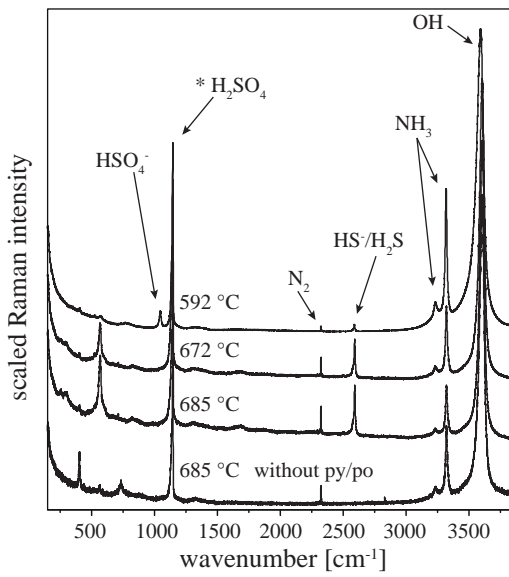


Fig. 5b

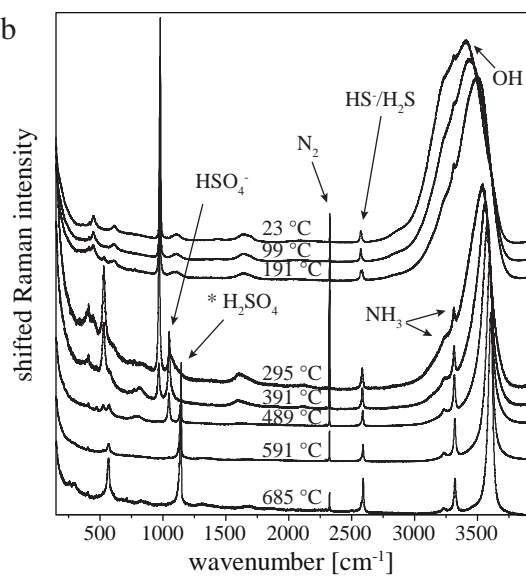


Fig. 6 a-h

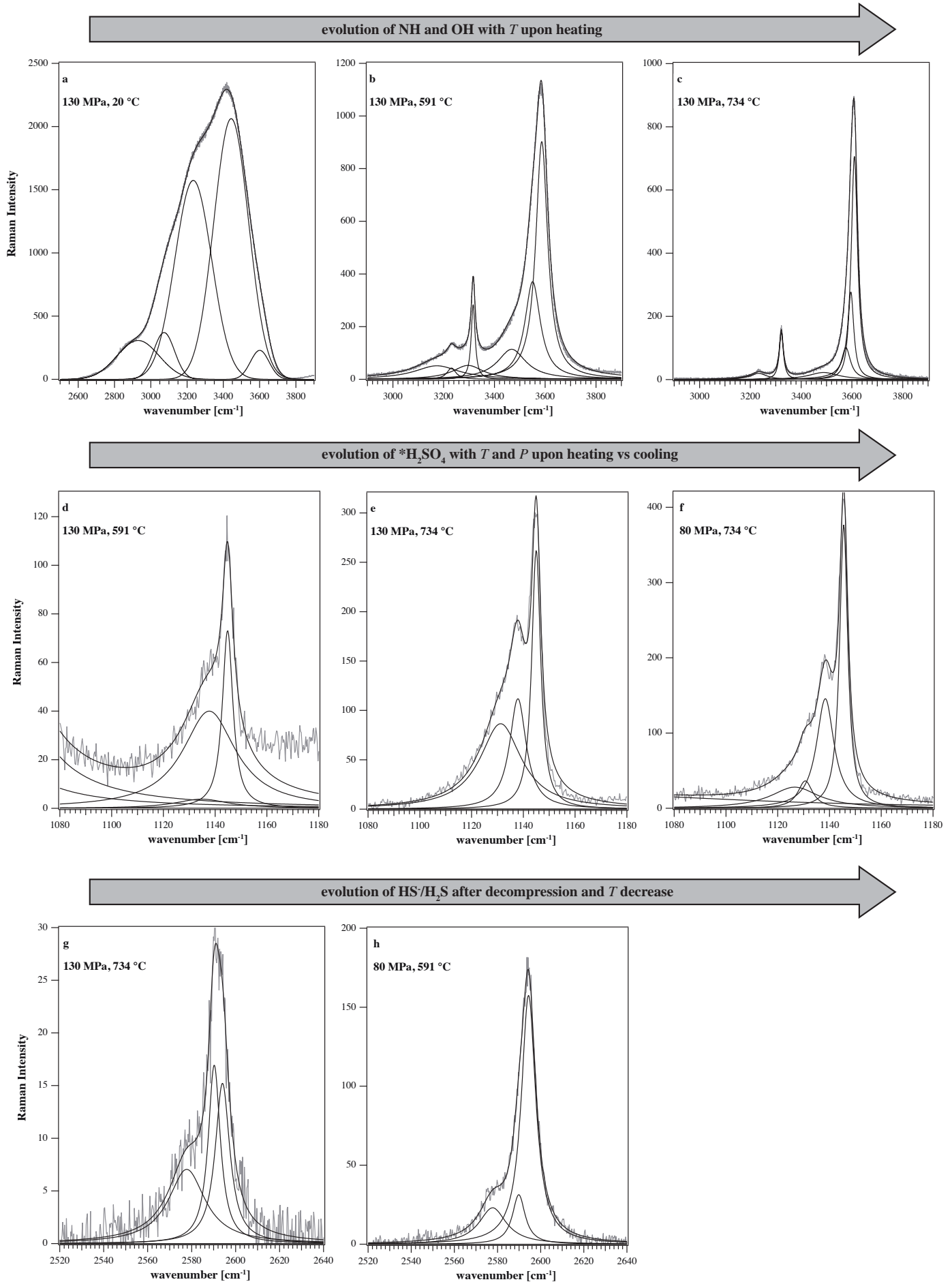


Fig. 7a
130 MPa

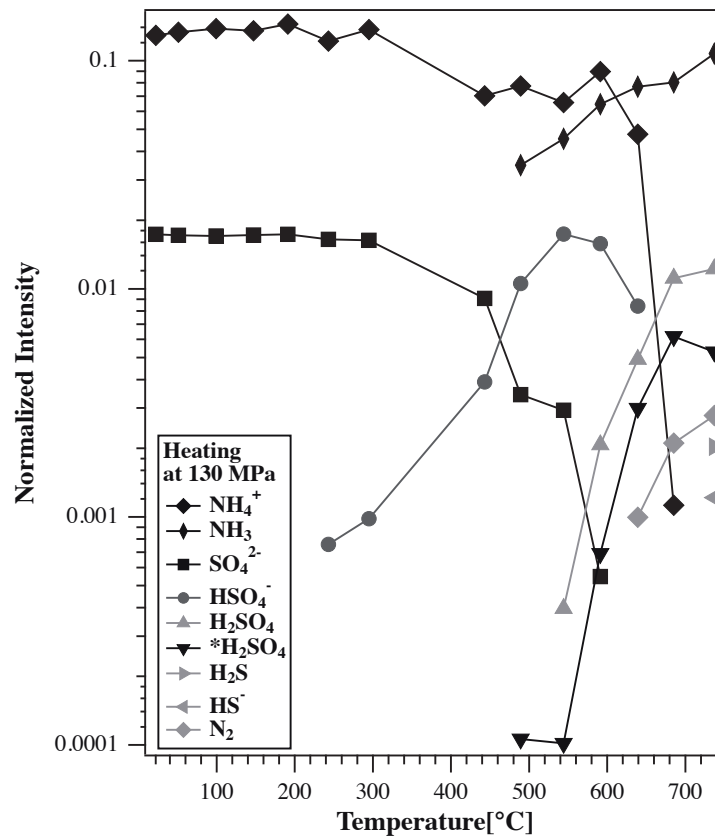


Fig. 7b
734 °C

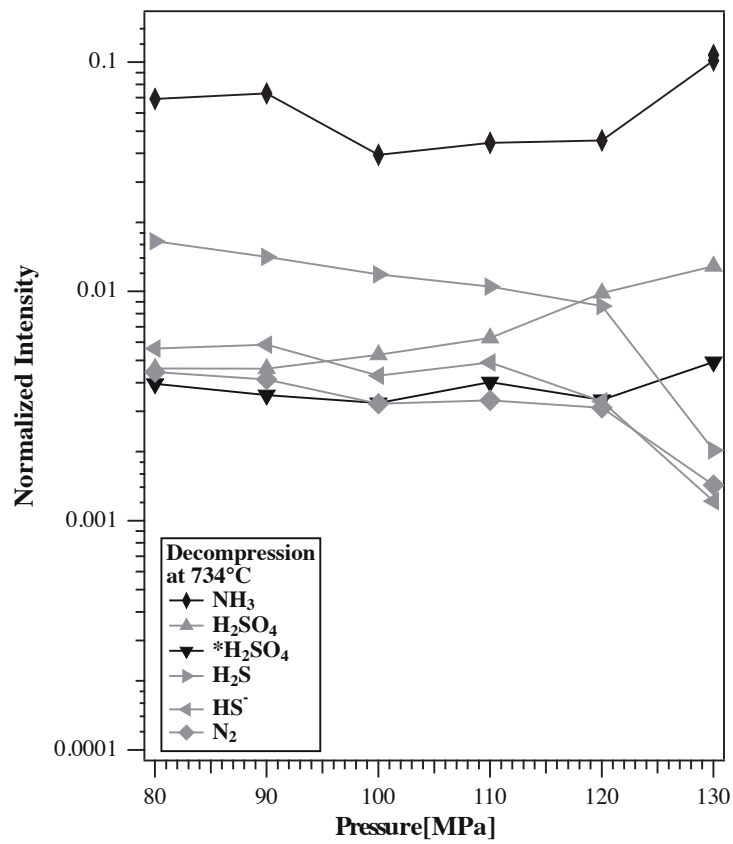


Fig. 7c
80 MPa

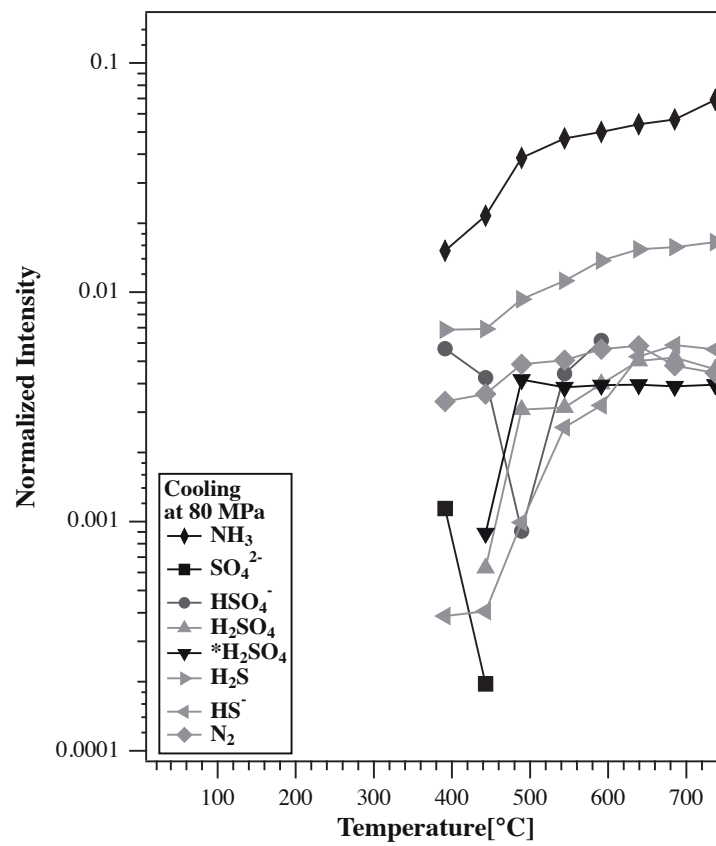


Fig. 8a
pyrite, pyrrhotite
130 MPa

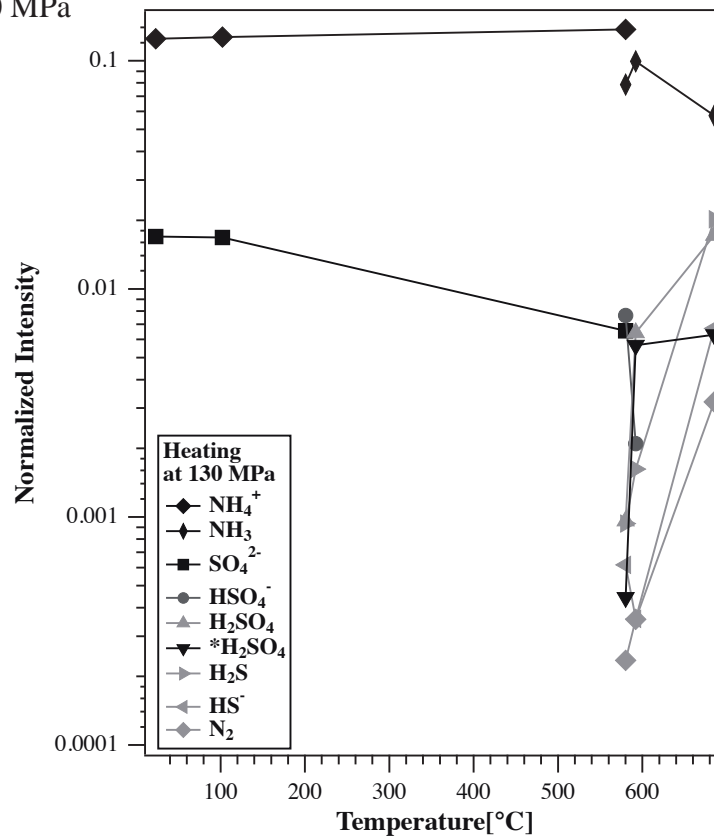


Fig 8b
pyrite, pyrrhotite
130 MPa

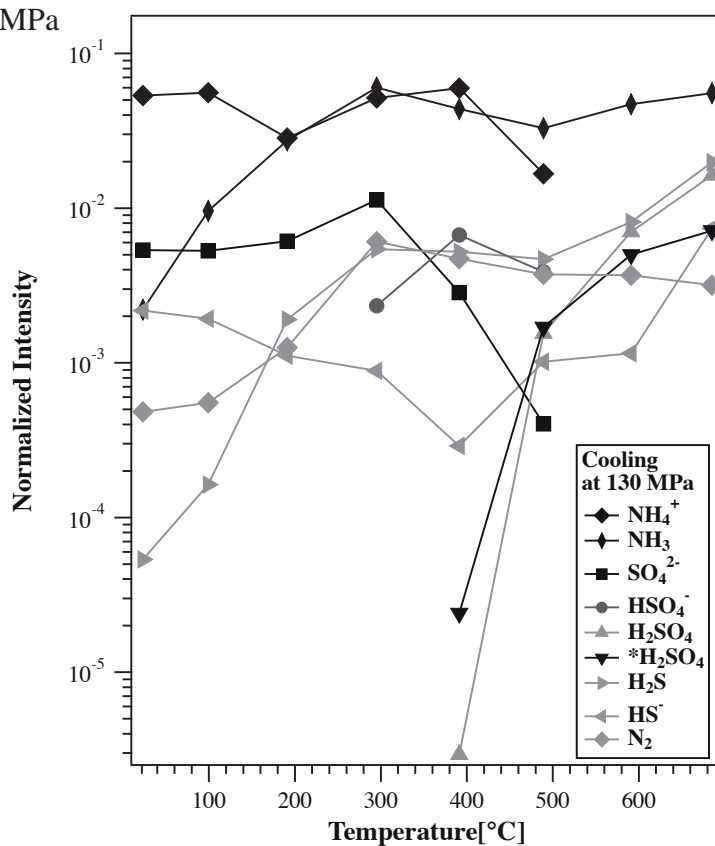


Table 1. Raman frequencies above 900 cm⁻¹ and species assignments at three temperatures

Position (cm ⁻¹)	Species	Ref.	Position (cm ⁻¹)	Species	Ref.	Position (cm ⁻¹)	Species	Ref.
19°C			544°C			737°C		
980	SO ₄ ²⁻	1,2	964	SO ₄ ²⁻	1,2	1047	HSO ₄ ⁻	1
2930	NH ₄ ⁺	8	1039	HSO ₄ ⁻	1	1131	H ₂ SO ₄	3
3073	NH ₄ ⁺	8,9	1047	HSO ₄ ⁻	1	1138	H ₂ SO ₄	3
3234	H ₂ O	8,9	1138	H ₂ SO ₄	3	1145	SO ₂ , *H ₂ SO ₄	3, 11
3443	H ₂ O	8,9	1145	SO ₂ , *H ₂ SO ₄	3, 11	2323	N ₂	7
3601	H ₂ O	8,9	3165	NH ₄ ⁺	10	2578	HS ⁻	4,5,6
			3231	NH ₃	10	2594	H ₂ S	4,5,6
			3314	NH ₃	8,9	3232	NH ₃	10
			3270	H ₂ O	8,9	3322	NH ₃	10
			3436	H ₂ O	8,9	3488	H ₂ O	8,9
			3576	H ₂ O	8,9	3576	H ₂ O	8,9
						3596	H ₂ O	8,9
						3610	H ₂ O	8,9

Notes. Positions represent the band maxima from fitting as shown in Figures 7, except for 1

different temperatures α

α_2 where peak positions we