Supplementary Table 1. Sulfur-bearing aqueous and solid species and sources of their thermodynamic data, used in the thermodynamic equilibrium calculations of this study.

Species	**Source**
H_2O, H^+, OH^-, $O_{2(aq)}$, $H_{2(aq)}$, $NaCl^0_{(aq)}$, $NaOH^0_{(aq)}$, Cl^-, Na^+, K^+, $KOH^0_{(aq)}$, KSO_4^-, $KHSO_4^0{}_{(aq)}$, $NaHSO_4^0{}_{(aq)}$, $KCl^0_{(aq)}$, HS^-, $H_2S_2O_{3(aq)}$, $HS_2O_3^-$, $S_2O_3^{2-}$, HSO_3^-, SO_3^{2-}, HSO_4^-, SO_4^{2-}, S_{2-5}^{2-}, $H_2S_2O_{4(aq)}$, $HS_2O_4^-$, $S_2O_4^{2-}$, $S_2O_5^{2-}$, $S_{3-5}O_6^{2-}$, $S_{2-3}O_8^{2-}$, $NaCl_{(s)}$	(1)
$NaSO_4^-$	(2)
$HCl^0_{(aq)}$	(3)
$H_2S_{(aq)}$, $SO_{2(aq)}$	(4)
$S_{(s)}$, $S_{(l)}$, $K_2SO_{4(s)}$, $Na_2SO_{4(s)}$	(5)

Notes:

(1) Johnson, J.W., Oelkers, E.H. and Helgeson, H.C. (1992) SUPCRT92: A software package for calculating the standard molal thermodynamic properties of minerals, gases, aqueous species, and reactions from 1 to 5000 bar and 0 to 1000°C. Computers & Geosciences, 18, 899-947, available at http://geopig.asu.edu/?q=tools.

(2) Pokrovski, G.S., Schott, J. and Sergeyev, A.S. (1995) Experimental determination of the stability constants of $NaSO_4^-$ and $NaB(OH)_4^0$ in hydrothermal solutions using a new sodium selective glass electrode. Implications for boron isotopic fractionation. Chemical Geology, 124, 253-265.

(3) Tagirov, B.R., Zotov, A.V. and Akinfiev, N.N. (1997) Experimental study of dissociation of HCl from 350 to 500 °C and from 500 to 2500 bars: Thermodynamic properties of $HCl^0_{(aq)}$. Geochimica et Cosmochimica Acta, 61, 4267-4280.

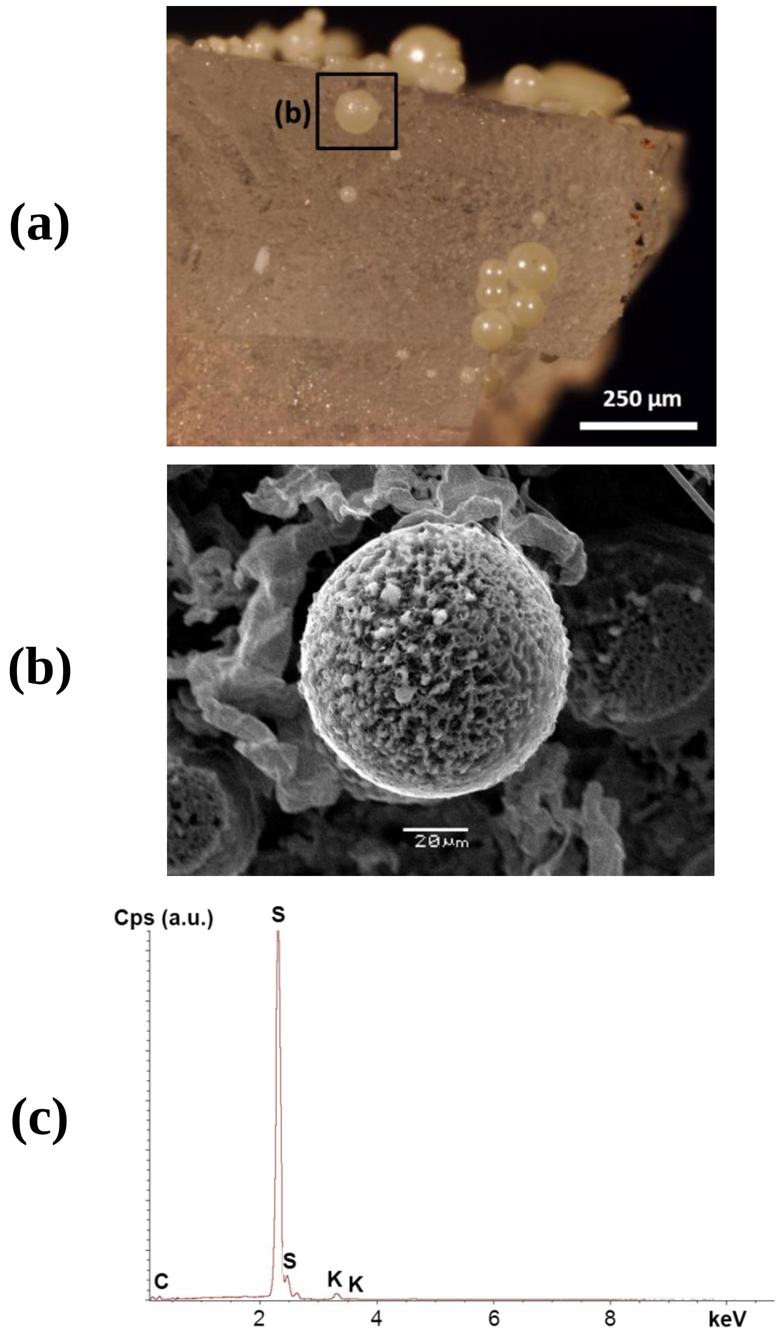
(4) Schulte, M.D., Shock, E.L. and Wood, R.H. (2001) The temperature dependence of the standard-state thermodynamic properties of aqueous nonelectrolytes. Geochimica et Cosmochimica Acta, 65, 3919-3930.

(5) Chase, M.W. Jr. (1998) NIST-JANAF Thermochemical Tables, Fourth Edition. Journal of Physical and Chemical Reference Data, Monograph No. 9.

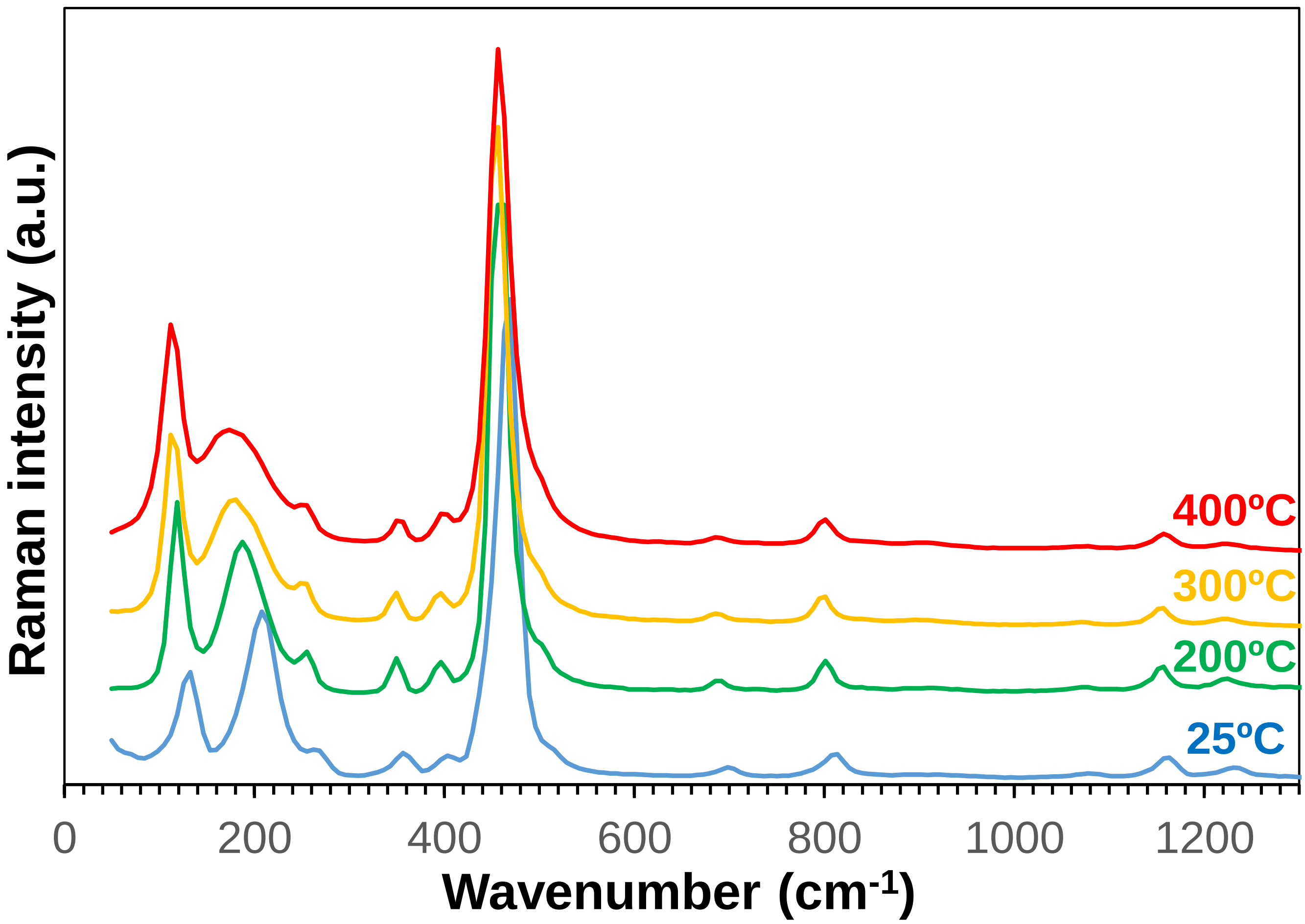
Supplementary Table 2. Normalized integrated intensities of the main Raman peaks of sulfur species detected in the experimental systems. Normalization is accomplished by dividing the area of the band of interest (A) by that of the O-H stretching band of water between 2800 and 3800 cm^{-1} ($A_{2800-3800}$). Note that the spectrometer resolution is about 5-10 cm^{-1}, and uncertainties in determining wavenumber positions for small peaks ($A/A_{2800-3800}$ < 0.005) may attain 10-15 cm^{-1}.

T **(°C)**	***P*** **(bar)**	**Species**	**Vibration mode**	**Wavenumber (cm^{-1})**	**$A/A_{2800-3800}$**
Thiosulfate system					
200	sat	S_3^-	νS-S	537	0.181
		SO_4^{2-}	νS-O	979	0.026
		HS^-+H_2S	νS-H	2585	0.010
300	sat	S_3^-	νS-S	532	0.891
		SO_4^{2-}	νS-O	974	0.018
		S_3^-	2νS-S	1072	0.363
		HS^-+H_2S	νS-H	2585	0.010
400	~500	S_3^-	νS-S	531	0.967
		SO_4^{2-}	νS-O	970	0.017
		S_3^-	2νS-S	1069	0.336
		H_2S	νS-H	2589	0.018
Thiosulfate+HCl system					
200	sat	SO_4^{2-}	νS-O	978	0.006
		HSO_4^{2-}	νS-O	1059	0.008
		H_2S	νS-H	2590	0.003
300	sat	S_3^-	νS-S	540	0.159
		SO_4^{2-}	νS-O	974	0.007
		S_3^-	2νS-S	1065	0.051
		H_2S	νS-H	2592	0.003
400	~500	S_3^-	νS-S	532	0.517
		SO_4^{2-}	νS-O	972	0.002
		S_3^-	2νS-S	1067	0.214
		H_2S	νS-H	2592	0.009
S+NaOH system					
200	sat	S_3^-	νS-S	530	0.025
		SO_4^{2-}	νS-O	971	0.002
		HS^-+H_2S	νS-H	2578	0.009
300	sat	S_3^-	νS-S	529	0.414
		S_3^-	2νS-S	1065	0.251
		H_2S	νS-H	2586	0.007
400	~400	S_3^-	νS-S	531	0.508
		S_3^-	2νS-S	1064	0.286
		H_2S	νS-H	2593	0.016
500	~1000	S_3^-	νS-S	527	0.716
		S_3^-	2νS-S	1062	0.383
		H_2S	νS-H	2590	0.010

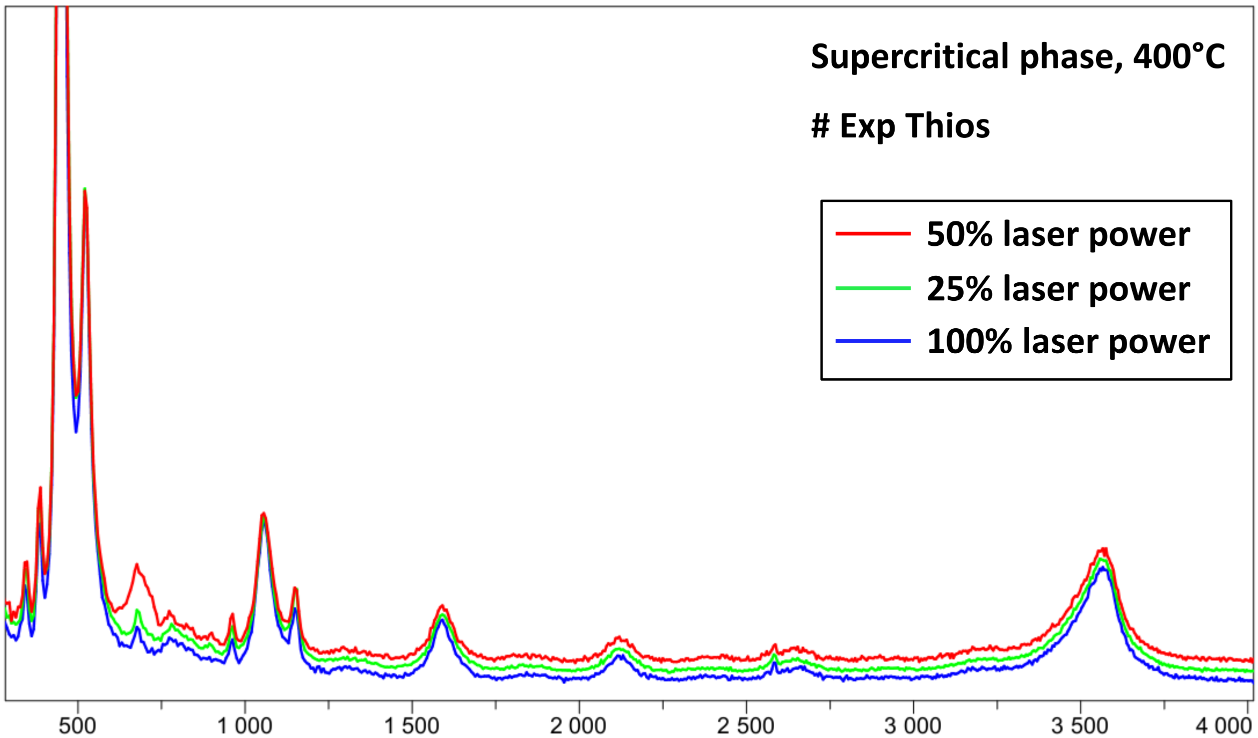
Supplementary Figure 1. Optical (a), scanning electron microscopy (b, detail of a) photographs, and semi-quantitative electron dispersive spectroscopy analysis (c) of sulfur spheres after the experiment Thios-HCl. Carbon (C) and potassium (K) in spectrum (c) stem respectively from the carbon coating of the sample and solution residues.

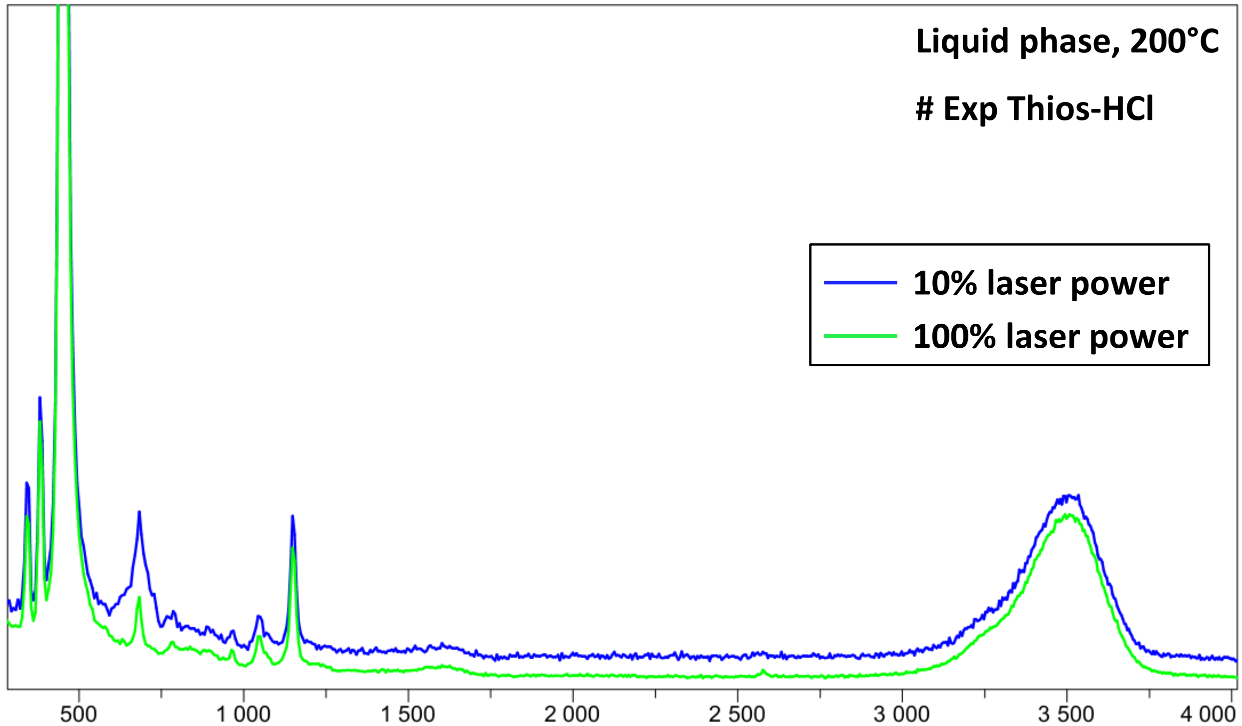


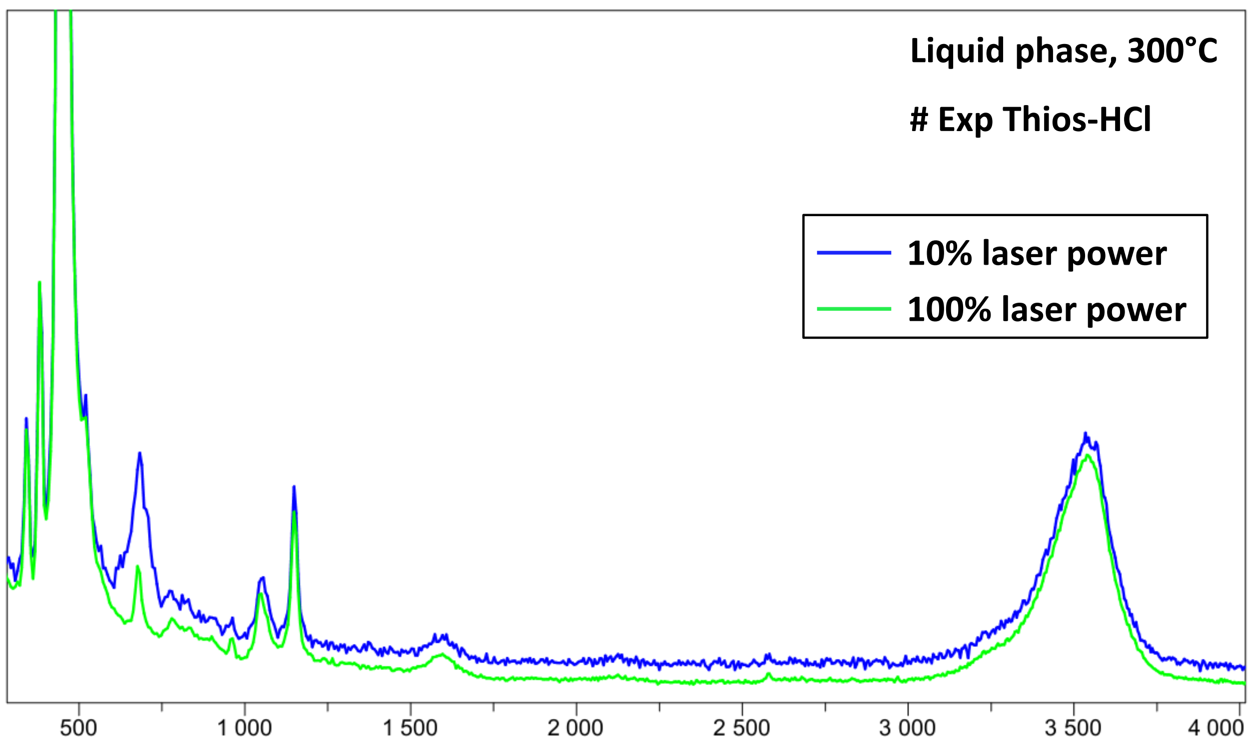
Supplementary Figure 2. Raman spectra of the host quartz at indicated temperatures.

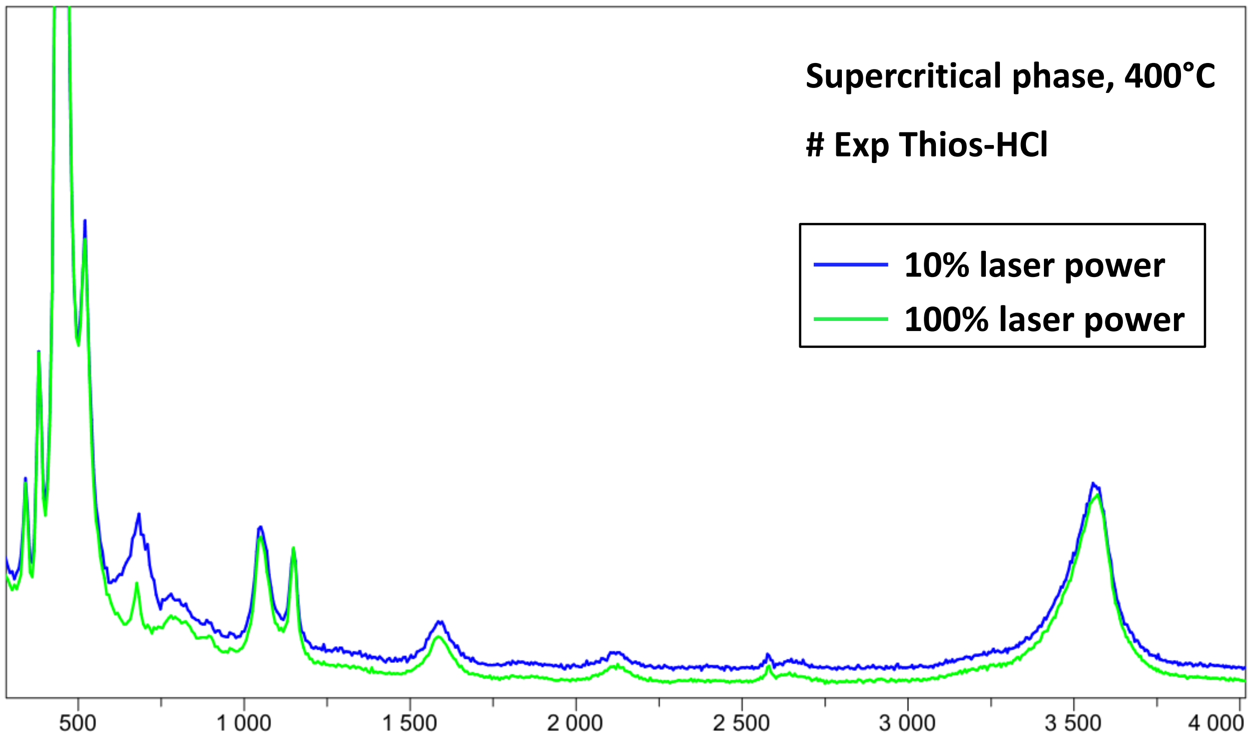


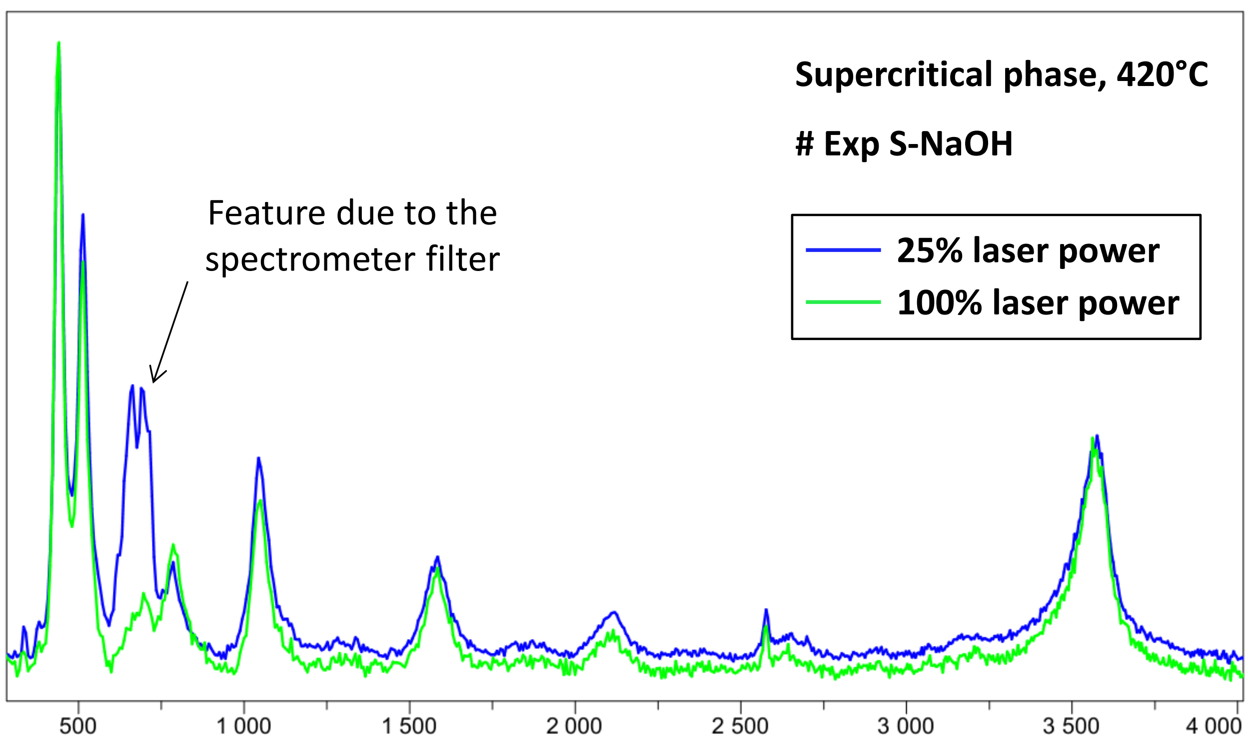
Supplementary Figure 3. The effect of the laser power on the liquid and supercritical-phase spectra in the three systems at indicated temperatures (see main text for discussion). The feature at ~700 cm^{-1} is an artifact due to the spectrometer filter used for ≤ 25 % power.




Liquid phase, 200°C
Exp Thios-HCl
10% laser power
100% laser power
500
1 000
1 500
2 000
2 500
3 000
3 500
4 000


Liquid phase, 300°C
Exp Thios-HCl
10% laser power
100% laser power
500
1 000
1 500
2 000
2 500
3 000
3 500
4 000


Supercritical phase, 400°C
Exp Thios-HCl
10% laser power
100% laser power
500
1 000
1 500
2 000
2 500
3 000
3 500
4 000


Supercritical phase, 420°C
Exp S-NaOH
Feature due to the spectrometer filter
25% laser power
100% laser power
500
1 000
1 500
2 000
2 500
3 000
3 500
4 000

Supplementary Figure 4. The effect of the laser wavelength on selected spectra in the Thios system at 400°C. Spectra were acquired with the red (637.7 nm) and green (532.1 nm) lasers on the same fluid inclusion with identical focusing and acquisition parameters and were normalized to the water stretching band to facilitate comparison.