Phase transitions in natural C-O-H-N-S fluid inclusions - implications for gas mixtures and the behavior of solid H$_2$S at low temperatures

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C-O-H-N-S-bearing fluids are known as one of the most challenging geochemical systems due to scarcity of available experimental data. H$_2$S-rich fluid systems were recognized in a wide array of world-class mineral deposits and hydrocarbon reservoirs. Here we report on a nature of low-temperature ($T \geq -192 \, ^{\circ}C$) phase transitions observed in natural CH$_4$–H$_2$S–CO$_2$–N$_2$–H$_2$O fluid inclusions, which are modeled as closed thermodynamic systems and thus serve as natural micro-laboratories representative of the C-O-H-N-S system. For the first time, we document solid-solid H$_2$S ($\alpha \leftrightarrow \beta \leftrightarrow \gamma$) transitions, complex clathrates and structural transformations of solid state H$_2$S in natural inclusion gas mixtures. The new data on Raman spectroscopic features and a complete sequence of phase transition temperatures in the gas mixtures contribute to scientific advancements in fluid geochemistry. Enhanced understanding of the phase equilibria in the C-O-H-N-S system is a prerequisite for conscientious estimation of $P$-$T$-$V$-$X$ properties, necessary to model the geologic evolution of hydrocarbon and mineral systems. Our findings are a driver for the future research expeditions to extraterrestrial H$_2$S-rich planetary systems owing to their low temperature environments.

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Hydrogen sulfide (H₂S) is a natural gas of organic or inorganic origin. At shallow crustal levels, it is produced in anaerobic environments by degradation of biomass. As a biological mediator, H₂S plays an important role in the sulfur cycle and the evolution of life on Earth. Recent research has shown that H₂S-bearing gaseous fluid inclusions carry information imperative to understanding the building blocks of the early Archean life. Inorganic H₂S is a common constituent in volcanic gases, active black smoker vents, and carbonate-hosted hydrocarbon reservoirs. Dissolved in water, H₂S or its dissociation products are indispensable for the formation of precious and base metal deposits. Recent discoveries of H₂S-ice on Uranus and Neptune at temperatures ranging between −220°C and −153.7°C, reveal that the low-temperature conditions, which this study focuses on, find clear analogs in the Solar System. Hence, the processes investigated here are of essential importance for understanding the natural terrestrial as well as extraterrestrial environments. In materials science, H₂S is utilized to synthesize superconductive materials in the form of sulfur hydrides, e.g., H₃S, which displays superconductive properties at transition pressure of 155 GPa and temperature of −70.15°C. This finding was an important breakthrough in the development of room-temperature CS₃H₆ superconductor.

Determining fluid properties and understanding the phase relations in the P–T–Vₘ space are paramount in fluid geochemistry and geological sciences. Mineral-hosted natural fluid inclusions, which preserve fluids from various geological records in micrometer-scale cavities, are a powerful tool to characterize fluid properties. Fluid inclusions are modeled as “closed” systems, meaning that they permit heat exchange, whereas their molar volumes (Vₘ) and compositions (Xᵢ) remain constant throughout the geological evolution. Consequently, the P–T conditions of fluid inclusion trapping are deduced from the isochoric trajectories, which are constructed from bulk Vₘ–Xᵢ parameters. Microthermometry allows observation of fluid inclusion phase transition temperatures, which can be converted into Vₘ and Xᵢ by applying equations of state (EoS) or/and quantitative phase diagrams. Laser Raman spectroscopy allows to determine molecular compositions of complex C–O–H–N–S inclusion gas mixtures. Combined microthermometric and Raman spectroscopic analyses coupled with phase diagrams/EoS provide means to reconstruct the spatial and temporal P–T evolution in mineralizing systems and gas reservoirs. The latter are often characterized by multiple episodes of coinciding mineralization and gas/oil re-charge. P–T estimates in such systems rely on the construction of isochores for gaseous and/or aqueous fluid inclusions. This is challenging for CH₄–H₂S–CO₂–N₂ mixtures, which contain elevated H₂S concentrations since the properties of the C–O–H–N–S gas mixtures are poorly constrained by experimental and thermodynamic data.

Natural H₂S-bearing fluid inclusions representing binary CH₄–H₂S and CO₂–H₂S systems have been characterized in terms of molecular compositions and phase changes as phase equilibria of these two systems are well constrained by experimental studies. In contrast, experimental data for ternary system CH₄–CO₂–H₂S are scarce and cover only very limited P–T–X ranges with a focus on the near-critical region of the system. An influence of subordinate amounts of CO₂ on phase equilibria in the CH₄–H₂S system in the low-temperature region remains unclear. Experimental studies on purified H₂S gas have shown that three structurally distinct solid H₂S phases (I-α, I-β, and III-γ) form at low temperatures below −85.5°C. Crystal symmetry of the H₂S-γ phase, which forms at the lowest temperatures below −169.6°C, has been under debate. Laser Raman spectroscopy is one of the most effective techniques in distinguishing structurally distinct solid H₂S molecules. The structure of H₂S solid phases and solid–solid phase transitions have not been recognized in natural fluid inclusions up to date.

In this study, we investigate fluorite-hosted H₂S-bearing fluid inclusions representing the natural CH₄–H₂S–CO₂–N₂–H₂O system. We use combined microthermometric and Raman spectroscopic analyses to record the complete sequence of phase transition temperatures as well as compositions and spectral features of individual phases at low temperatures.

Results and discussion

Fluid inclusion assemblages. Fluid inclusions were analyzed in line with the classic concept of a fluid inclusion assemblage (FIA). Both selected FIA’s (Fig. 1), consisting of low-density gas-rich (V) and aqueous 2-phase inclusions (L+V), evidence precipitation of fluorite in the presence of methane, inorganic gases (H₂S, CO₂, N₂) as well as small proportions of a high salinity brine. The molecular compositions of gas phases in the gas-rich inclusions are shown in Table 1, Supplementary Table 1, and Source Data.

The two biggest gas-rich inclusions (P1-f1A, P1a-f110) in FIA1 contain a visible aqueous film surrounding the gas phase, whereas in the smaller inclusions the aqueous phase is optically invisible. The bimodal distribution, lack of intermediate aqueous fluid/gas ratios, and gas-saturation (in respect of CH₄, CO₂, and H₂S) of the vapor phases of co-existing aqueous brine inclusions imply contemporaneous trapping of immiscible fluids. Fluorite growth from aqueous brine was obstructed by the gas bubbles, which were wet by traces of the aqueous medium during the fluid entrapment. Thus, it is very unlikely to form water-free, pure gas inclusions in such hydrothermal systems. When heating the inclusions to temperatures up to 170°C, Raman spectroscopic analyses of the homogenized inclusion fluid point to the presence of 3 mol% H₂O in all gas-rich inclusions (Table 1, Supplementary Fig. 1 and Source Data). The volume fractions of the aqueous phase (ϕₐ) in two inclusions with optically visible aqueous rim, indicate very similar water contents of 2.2 and 3.5 wt.%. The water vapor or dissolved H₂O was not detected in the gas phase of the gas-rich inclusions at room temperature (Fig. 1a). The gas compositions of six measured inclusions within a single FIA1 (Table 1) are very similar as indicated by very low standard deviation values (σ < 0.02). Median gas compositions for FIA1 are 59 mol% CH₄, 24 mol% H₂S, 10 mol% CO₂, 3 mol% N₂, whereas FIA2 shows a slightly higher H₂S content of 27 mol% (Table 1 and Fig. 1). The aqueous rims of the gas-rich inclusions are H₂S saturated as indicated by the broader Raman peak at 2584 cm⁻¹, which is typical of H₂S dissolved in water at room temperature (Fig. 1b). The origin of low-intensity gas peaks in the latter spectrum is ambiguous, they may be derived from gas species dissolved in water and/or may constitute peak overlaps from a much larger gas phase. The steep band between 3000 and 3700 cm⁻¹, corresponding to the stretching vibrations of H₂O, confirms the high salinity of the aqueous solution coating the gas inclusion (Fig. 1b).

Low-temperature phase transitions—freezing runs. Eight phase transitions were recognized in the studied gas-rich inclusions during freezing (Fig. 2a–i) and heating runs (Fig. 2j–p). The complete temperature sequence of the phase changes is shown in Table 1 and Supplementary Table 2. Two gas-rich inclusions P1-f1A and P4-f1B (hereinafter labeled inclusion A and B) of different molecular compositions (Table 1) were used to document in detail the phase transition sequences (Figs. 2 and 3).
spectrum of the aqueous phase rim surrounding the gas phase. The broad Raman peak between 3000 and 3700 cm$^{-1}$ manifests by two Raman bands at 2593 and 2604 cm$^{-1}$, which is attributed to the doubly degenerate $\nu_2$ mode vibration of CH$_4$ gas$^{49}$. Raman spectrum of the aqueous phase rim surrounding the gas phase. The broad Raman peak between 3000 and 3700 cm$^{-1}$, and weak peak at 2324 and 2323 cm$^{-1}$ correspond to stretching and bending vibrations in H$_2$O, respectively. The low-intensity Raman band at 2584 cm$^{-1}$ is assigned to N$_2$ gas phase.

When cooling the inclusion to temperatures from $\sim$17 to $\sim$28.7 °C, the first solid phase that nucleates at the corners of the inclusion cavities is H$_2$S rich clathrate (Figs. 2b and 3b), which is manifested by two Raman bands at 2593 and 2604 cm$^{-1}$ (Fig. 4). In inclusions, containing a visible water film, the formation of H$_2$S–CH$_4$–CO$_2$–N$_2$ clathrates is observed (Fig. 4). Raman peaks of 1276 and 1380 cm$^{-1}$ are typical for CO$_2$-clathrate, bands at 2903 and 2913 cm$^{-1}$ are assigned to CH$_4$-clathrate, whereas peak splitting to 2324 and 2323 cm$^{-1}$ is attributed to N$_2$-gas hydrate$^{48}$ (Fig. 4a).

During further cooling below $\sim$29.9 °C/$\sim$32.6 °C (inclusions A/B) the H$_2$S–CH$_4$–CO$_2$–N$_2$ gas phase begins to shrink due to volume reduction (Figs. 2c and 3c) and partial separation of H$_2$S-rich liquid. At temperatures of $\sim$58.6 °C/$\sim$58.5 °C (A/B) CH$_4$-rich liquid starts to separate from the gas phase (Fig. 2d). The presence of H$_2$S- and CH$_4$-rich liquids is indicated by the broadening and shift of the Raman bands to 2593 and 2908 cm$^{-1}$, respectively. Raman analyses of the three resulting phases reveal that H$_2$S-rich liquid partitions into the outermost phase, liquid CH$_4$–CO$_2$ into the middle phase, whilst CH$_4$–N$_2$ gases remain in the innermost bubble (Fig. 3d). At $\sim$100 °C, vibrational bands of CH$_4$–N$_2$ gases from the innermost phase show a shift to higher wavenumbers (2915 cm$^{-1}$, 2328 cm$^{-1}$) compared with the gas phase at room temperature (2911 cm$^{-1}$, 2326 cm$^{-1}$) (Fig. 5). Similar peak shifts are observed for CO$_2$ and H$_2$S in the middle and the outermost phases, respectively.

At temperatures of $\sim$125.1 °C/$\sim$117.4 °C (A/B) both H$_2$S and CO$_2$ simultaneously freeze and form a fine-grained mass of bright white (CO$_2$) and yellow-greenish solids (H$_2$S-$\alpha$) of high reflectance (Figs. 2e and 3e, f). In order to investigate the composition and phase behavior of the nucleated solids a cycling heating/freezing method is applied$^{44}$. After melting of solid H$_2$S, the inclusion is heated further on until only one CO$_2$ crystal remains. Subsequent rapid cooling results in crystallization of a pure octahedral CO$_2$ crystal at $\sim$100 °C (Figs. 2f and 3g), which shows Raman peaks at 1280 and 1384 cm$^{-1}$. When cooling the inclusion to about $\sim$112 °C numerous oval solids of H$_2$S-$\alpha$ crystallize. Applying the cycling heating/freezing procedure on H$_2$S-$\alpha$ is difficult due to the very unstable “jelly-like” behavior of solids and rapid melting of the last solid upon approaching the final $T_m$(H$_2$S-$\alpha$). However, when using slow heating rates (4 °C/min) until only some solids remain in the inclusion and then keeping the temperature constant for several minutes, involuntary re-organization of the leftover solids and formation of a single H$_2$S-$\alpha$ solid phase is observed (Figs. 3h and 5d). At $\sim$110 °C solid H$_2$S-$\alpha$ shows a single peak at 2558 cm$^{-1}$ (Fig. 6h). Below $\sim$184 °C solidification of CH$_4$ commences (Fig. 2h, i) and is completed at about $\sim$185.3 °C/$\sim$186.3 °C (A/B). The resulting CH$_4$ solid is characterized by a broad band at a vibrational frequency of 2904.5 cm$^{-1}$. At $\sim$190 °C, Raman peaks of CH$_4$ and N$_2$ in the remaining squeezed gas phase are shifted towards the highest wavenumbers of 2917 and 2329 cm$^{-1}$, respectively.

The last optically visible phase change is structural re-configuration of H$_2$S at about $\sim$191 °C. Smooth solids rearrange into very fine-grained polycrystalline aggregates (Fig. 3i, j) over a prolonged period of time, meaning the transition is not instantaneous but requires a few minutes of maintaining the temperature constant. Notable is a prismatic H$_2$S-$\gamma$ crystal, tagged with white arrow in Fig. 3i, visible among the fine-grained crystals. This behavior marks the solid H$_2$S ($\beta\rightarrow\gamma$) transition, which actually commences at a higher temperature, however, it is not instantly visible under the
Table 1: Microthermometry data and molecular compositions of fluorite-hosted CH₄–H₂S–CO₂–N₂–H₂O fluid inclusions from two fluid inclusion assemblages (FIA’s).

| Fluid inclusion | Temperature/°C | Chip P1 (FIA1) | Chip P4 (FIA2) |
|----------------|---------------|----------------|---------------|
|                |               | P1-fi1A | P1a-fi10 | gafl2 | flinc3 | flinc4 | flinc5 | Median | σ | P4-fi1B |
| Freezing cycle |               |         |          |        |        |        |        |        |     |        |
| 1              | Clathrate formation | −28.7  | −17      | −20    | n.o.   | n.o.   | n.o.   | −20    | 4.96 | −21   |
| 2              | Partial exsolution of H₂S liquid | −29.9  | −29.5    | −31    | −33    | −32    | −31.9  | −31.5  | 1.22 | −32.6 |
| 3              | Exsolution of liquid CH₄ and gas separation | −58.6  | −57.8    | −59.6  | −59.5  | −59.4  | −59.1  | −59.3  | 0.63 | −58.5 |
| 4              | Simultaneous freezing Tm of H₂S and CO₂ | −125.1 | −124.2   | −120.5 | −114.9 | −125.9 | −114.9 | −122.4 | 4.58 | −117.4 |
| 5              | H₂S freezing in the presence of solid CO₂ | −104   | −105.6   | n.o.   | n.o.   | n.o.   | n.o.   | n.o.   | n.o. |        |
| 6              | Solid H₂S-α → solid H₂S-β transition | −149.6 | n.o.     | n.o.   | n.o.   | n.o.   | n.o.   | n.o.   | n.o. |        |
| 7              | Solid H₂S-β → solid H₂S-γ transition | −176.8a| n.o.     | n.o.   | n.o.   | n.o.   | n.o.   | n.o.   | n.o. |        |
| 8              | CH₄ freezing Tm | −185.3 | −188     | −187   | −186.8 | −185.5 | −185.7 | −186.3 | 0.97 | −186.3 |
| Heating cycle  |               |         |          |        |        |        |        |        |     |        |
| 9              | Final melting Tm (CH₄) | −184.5 | −185    | −184.2 | −184.1 | −184.3 | −184.2 | −184.3 | 0.30 | −185   |
| 10             | Solid H₂S-γ → solid H₂S-β transition | −168.9a| n.o.     | n.o.   | n.o.   | n.o.   | n.o.   | n.o.   | n.o. | −168.1b |
| 11             | Solid H₂S-β → solid H₂S-α transition | −147a  | n.o.     | n.o.   | n.o.   | n.o.   | n.o.   | n.o.   | n.o. | −146.4a |
| 12             | Final melting Tm (H₂S) | −98.8  | −98.8    | −98.9  | −98.9  | −98.8  | −98.9  | −98.9  | 0.05 | −99.2  |
| 13             | Final melting Tm (CO₂) | −91.2  | −91.2    | −94.5  | −91.5  | −92.4  | −92.2  | −91.9  | 1.14 | −92.6  |
| 14             | Partial homogenization Tm1 (L₁L₂V → LV) | −58.4  | −57.6    | −59.5  | −59.8  | −58.7  | −58    | −58.6  | 0.78 | −57.8  |
| 15             | Total homogenization Tm2 (L₂V → V) | −28.6  | −29.1    | −29.2  | −32.5  | −29.2  | −29    | −29.2  | 1.31 | −31    |
| 16             | Final melting Tm (clathrate) | 21.8   | 27.1     | 23.7   | −      | −      | −      | 23.7   | 2.19 | 27.5   |

| Bulk compositions (mole fractions) | X(CH₄) | X(H₂S) | X(CO₂) | X(N₂) | X(H₂O) |
|-----------------------------------|--------|--------|--------|--------|--------|
|                                   | 0.59   | 0.03   | 0.11   | 0.24   | 0.03   |
|                                   | 0.60   | 0.03   | 0.11   | 0.24   | 0.03   |
|                                   | 0.60   | 0.03   | 0.11   | 0.24   | 0.03   |
|                                   | 0.59   | 0.03   | 0.11   | 0.24   | 0.03   |
|                                   | 0.02   | 0.03   | 0.03   | 0.03   | 0.02   |

Temperatures of phase transitions were measured during freezing and heating cycles during coupled microthermometric and Raman spectroscopic analyses without applying the cycling technique (with exception of phase change no. 5 and H₂S solid–solid transitions). See also Source Data file. n.o. - not observed. L₁-L₂V → LV. aAverage from ≥2 measurements. bAverage from ≥15 measurements, also see Supplementary Table 1.
optical microscope. The median temperature range for the H$_2$S ($\beta \rightarrow \gamma$) transition is between $-175.1$ and $-176.1$ °C, which gives an overall median of $-175.6$ °C and $\sigma = 1.27$ (Supplementary Table 2).

The transformation to H$_2$S-$\gamma$ in the studied inclusion is reflected by the appearance of six characteristic peaks at the following wavenumbers: 2523, 2541, 2545, 2547, 2552, and 2556 cm$^{-1}$ (Figs. 6 and 7). The lower intensity five peaks on the high-frequency side of the Raman spectrum (Fig. 7) develop in an expense of the major H$_2$S-$\beta$ peak by decrease in its intensity (Fig. 6). These results are reproducible as H$_2$S ($\gamma \leftrightarrow \beta$) transitions have been observed multiple times during real-time Raman spectroscopic analyses (Supplementary Table 2).
**Low-temperature phase transitions—heating runs.** When heating the inclusion from $-192^\circ C$, eutectic melting of solid CH$_4$ is observed at about $-185.5^\circ C$ until the final $T_m$ of $-184.5^\circ C$/$-185^\circ C$ (A/B) is reached (Fig. 2j-k). At about $-168.1^\circ C$ (B), a rapid decrease in a band number of the H$_2$S solid in the Raman spectrum is observed (Fig. 6). This sharp spectrum change reflects the transition of ordered H$_2$S-$\gamma$ into the disordered H$_2$S-$\beta$ phase. This conversion is detectable using the Raman technique only as the textural change is not instantly optically visible. The latter proceeds gradually over time (Fig. 6) and commences at temperature as low as $-177^\circ C$ (Supplementary Table 2). The median temperature range for the H$_2$S ($\gamma \rightarrow \beta$) transition lies between $-168.9$ and $-167.5^\circ C$, whereas the median from all measurements is $-168.1^\circ C$ ($\sigma = 1.62$, Supplementary Table 2). Upon
Simultaneous crystallization of liquid H2S and liquid CO2. Applying the cycling technique, a white arrow. CH4 intensity Raman bands corresponding to N stretching spectral region, are assigned to a molecular vibration of CH4 occluded in the hydrate lattice and ice, respectively. A green cross. The spectrum was acquired with 100% laser power. (A/B). After CO2 melting the inner CH4 gas-rich inclusion. Symbols: vap-CH4, liq-a-liquid H2S phase, the measurement point is marked with a white arrow. Raman measurement points (see also Fig.6).

(A/B). After CO2 melting the inner CH4 gas-rich inclusion. Symbols: vap-CH4, liq-a-liquid H2S phase, the measurement point is marked with a white arrow. Raman measurement points (see also Fig.6).

Further heating solid H2S (β → α) transition at about −146.4°C (B) is marked by a very slight Raman peak shift from 2549 to 2554 cm⁻¹ and disappearance of the tail at the higher wave-number side. During heating runs the structure of solid H2S phases re-organizes itself by compartmentalization of fine-grained crystals into coarser aggregates (e.g., Fig 3k, l) in order to attain back the disordered form. Solid H2S-α dissolves at −98.8°C/−99.2°C (A/B), whereas CO2 solid remaining in the inclusion does not preserve its octahedral habit but a rounded shape (Fig. 2l) and melts at temperatures of −91.2°C/−92.6°C (A/B). After CO2 melting the inner CH4-N2 gas phase begins to expand continuously (Fig. 2m) and partially homogenizes into a vapor phase at $T_{h1}(L_1V → L_2V) = −58.4°C/−57.8°C$ (A/B, Fig. 2n). The bubble expansion lasts until total homogenization at $T_{h2}(L_2V → V) = −28.6°C/−31°C$ (A/B, Fig. 2o) is reached. The last observed change is the melting of H2S-rich gas hydrate (clathrate) at positive temperatures of 21.8°C/27.5°C (A/B, Fig. 2p).

Gas hydrates. Gas hydrate crystallizes from the aqueous film containing dissolved H2S (Fig. 1b) and it forms a shell surrounding the gas phase (Fig. 2b). As a result, the H2S molecules become encased by the hydrogen-bonded cages in the first place and clathrate cavities are dominated by H2S. This is evidenced by the highest intensity of the 2592 and 2604 cm⁻¹ Raman peaks, which are assigned to the symmetric H–S stretching vibrations ($ν_1$) within large cages (LC) and small cages (SC), respectively, of type I cubic lattice structure (sI). The characteristic clathrate solid (Fig. 4) is achieved by using a heating/freezing cycling technique, which is applied routinely in the experimental studies of gas hydrates. The H2S-dominated clathrate (Fig. 4) dissociates at temperatures between −21.8 and −27.5°C (Table 1), which are lower compared to the quadruple point of the H2O–H2S system ($Q_s = +29.55°C$). The Raman technique has also been used to identify the H2S-clathrate in synthetic H2O–H2S inclinations at −100°C, in natural CO2–H2S–H2O–S inclinations and at −140°C in natural H2S-bearing brine inclusions.

A single measurement of one individual, well-isolated clathrate crystal reveals the presence of CH4 and minor concentrations of CO2 and N2 besides H2S molecules (Fig. 4). This observation suggests crystallization of H2S–CH4–CO2–N2 mixed gas hydrate. The average cage occupancy ratios – $θ_{CH4}/θ_{H2S}$ of CH4 and H2S-hydrates, calculated from deconvoluted Raman spectra, are: 0.81 ($σ = 0.08$) and 0.87 ($σ = 0.05$), respectively. These values deviate from ratios typical of pure CH4 and H2S gas hydrates, probably due to incorporation of minor CO2, and/or N2, which affects relative cage occupancy in the clathrate lattice. The studied clathrate crystal is most likely composed of two clusters of mixed gas hydrates, i.e., the H2S-dominated clathrate, which grew within the aqueous rim, and CH4-dominated, which developed at the water–gas interface. The N2 molecules may occupy both small and large cavities in sI gas hydrates, as indicated by the Raman band splitting (Fig. 4a), whereas CO2 can occupy only large cages due to the absence of a similar peak splitting (Fig. 4).
Nevertheless, the distribution of CO$_2$ and N$_2$ molecules between the clathrates remains ambiguous.

Clathrate crystallization from the aqueous phase, containing the dissolved gas, as well as at the water–gas interface leads to depletion of available water molecules. The nucleation of gas hydrates is known to influence phase equilibria in fluid inclusions, e.g., it may decrease $T_m$ of gas components. Due to the absence of dissolved/vapor H$_2$O in the gas phase, the only process that may affect the gas phase density is the scavenging of gas molecules into the clathrate lattice at the water–gas interface. The water film likely has a negligible impact on the gas phase transitions as they are very consistent within FIA1 (Table 1), e.g., $T_m$’s of H$_2$S ($\sigma = 0.05$) or CH$_4$ ($\sigma = 0.3$). The interaction at the aqueous film-gas phase interface has also some more limitations, e.g., the presence of dissolved H$_2$S and high salinity of an aqueous solution (Fig. 1b), which decreases the chemical potential of H$_2$O resulting in a “salting out” effect. Based on the above, it is apparent that only very low amounts of CO$_2$ and CH$_4$ from the gas phase have been incorporated into the clathrate lattice at low temperatures, and thus the gas phase experienced only a very minor volume change. Thereby the studied CH$_4$–H$_2$S–CO$_2$–N$_2$–H$_2$O system behaves as a gas sub-system below nucleation temperature of clathrate and is interpreted as such in the following section. Applying the isochoric behavior of H$_2$O-free systems to aqueous-multivolatile inclusions at low temperatures is justified as the LCEP (lower critical end-point) coincides with the critical point of the gas mixture. Median compositions of the gas phase in the presence of stable clathrate at $-10 \degree C$ are: 58.9 mol% CH$_4$, 25.5 mol% H$_2$S, 12.6 mol% CO$_2$, 2.9 mol% N$_2$ (FIA1), and 57.1 mol% CH$_4$, 28.2 mol% H$_2$S, 11.9 mol% CO$_2$, 2.9 mol% N$_2$ (FIA2) (Supplementary Table 1 and Source Data).

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Fig. 5 Raman spectra of symmetric stretching ($\nu_1$) region of CH$_4$ gas in a natural CH$_4$–H$_2$S–CO$_2$–N$_2$–H$_2$O fluid inclusion gas mixture (no. P1-f1A) at low temperatures. a–e Microphotographs of measured individual phases in analyzed gas-rich inclusion. f Sequence of Raman spectra showing that with decreasing temperature Raman peak positions of the exsolved liquid and gas methane shift to lower and higher wavenumbers, respectively. This is a result of relative density increase/decrease during differential partitioning between co-existing phases. The FWHM of the Raman peaks also decrease with decreasing temperatures. Symbols: I: CH$_4$–H$_2$S–CO$_2$–N$_2$, Ib: CH$_4$–N$_2$, II-clathrate, III-liquid phases: IIIa: H$_2$S, IIIb: CH$_4$–CO$_2$, IIIc: CH$_4$, IV-solid phases: IVa: CO$_2$, IVa,γ: H$_2$S, IVc: CH$_4$, measurement points of different phases are marked with large and small crosses.
The CH$_4$–H$_2$S–CO$_2$–N$_2$ gas system. A phase diagram defining phase transitions in the multicomponent CH$_4$–H$_2$S–CO$_2$–N$_2$ system has neither been experimentally nor numerically developed so far. The behavior of CH$_4$–H$_2$S–CO$_2$ mixtures, previously observed in fluid inclusions$^{30,57}$, was interpreted in the frame of the CH$_4$–H$_2$S system$^{31}$ under the assumption that 10–20 mol% CO$_2$ should not significantly affect the phase boundaries. In our study the available P–T projections of phase boundaries of the CH$_4$–H$_2$S–CO$_2$, CH$_4$–H$_2$S, and H$_2$S systems are used to discuss the phase transitions in natural fluid inclusions. The CH$_4$–H$_2$S binary diagram$^{32}$ is utilized to interpret the phase behavior to $-100 \degree$C, whereas for lower temperatures, the numerically derived CH$_4$–H$_2$S phase diagram$^{35}$ and the phase boundaries for pure H$_2$S system in the low-pressure region$^{40}$ are used (Fig. 8). Fluid inclusion behavior above $-60 \degree$C cannot be explained by the CH$_4$–H$_2$S system alone, therefore for this temperature region we use partial ternary CH$_4$–H$_2$S–CO$_2$ phase diagram$^{58}$. Experimentally derived phase boundaries for a CH$_4$–H$_2$S–CO$_2$ system were defined only for a gas mixture with H$_2$S content of 40.2 mol%$^{58}$, which is higher than that in studied inclusions (25–28 mol%, Table 1 and Source Data), and CO$_2$ content of 9.87 mol%, which is close to CO$_2$ concentrations in the inclusions (11.9–13.3 mol%, Supplementary Table 1). This P–T phase diagram, based on the experimentally studied gas mixture, is, therefore, the best available approximation of the studied system at $T > -83 \degree$C. Notable are three critical points in the CH$_4$–H$_2$S–CO$_2$ system: C$_1$ and C$_2$ lying along the 2-phase boundary curves, and C$_3$ situated on the 3-phase envelope$^{58}$. The presence of additional gases, e.g., N$_2$ or CH$_4$, is well known to depress the melting points in fluid inclusion gas mixtures$^{59}$, however, we assume that N$_2$ quantities as low as 3 mol% would likely have a negligible effect on the phase equilibria. The trajectories followed by studied fluid inclusions (blue) during heating are shown schematically in the P–T space, in the considered diagrams (Fig. 8). The phase transition points (9–15) are indicated by black circles and correspond to numbers given in Table 1.

Cooling of fluid inclusions triggers separation of two phases at temperatures between $-33$ and $-29.5 \degree$C ($\sigma = 1.22$), therefore they follow the trajectory intersecting the dew-point locus and thus enter the L$_2$V 2-phase field (L$_2$—liquid H$_2$S, Fig. 8a). This phase behavior is characteristic for the retrograde system as with decreasing pressure exsolution of the liquid phase takes place instead of the vapor phase. The first appearance of the liquid droplet is difficult to spot meaning that the temperature of condensation may be slightly underestimated. The P–T pathway should intersect the dew curve above the critical point C$_1$, however, the temperature of the V $\rightarrow$ L$_2$V transition is located below this point in the diagram. This discrepancy stems from the fact that the used phase boundaries were constructed for 40.2 mol% H$_2$S. For lower H$_2$S contents, alike in the studied inclusions...
(25–28 mol%), the dew curve would extend to lower temperatures.

At temperatures between $-59.6$ and $-57.8 \, ^\circ C$ ($\sigma = 0.63$), closely below the critical point $C_3$ ($-57.5 \, ^\circ C$, where $V = L_1$), the fluid inclusion trajectory intersects the 3-phase $L_1L_2V$ boundary emanating from the $C_3$ point ($L_1$—liquid CH$_4$, Fig. 8a). It is manifested by the separation of a third phase in the inclusion and marks the exsolution of a first drop of methane condensate. Under the optical microscope the newly formed phase appears vapor-like (Figs. 2d and 3d), probably due to the very close proximity of the $C_3$. Since fluid inclusions contain two immiscible liquid phases and a vapor they follow the path along the $L_1L_2V$ phase boundary and at about $-122 \, ^\circ C$ reach the invariant point: $QP_1$ (Fig. 8a). At the $QP_1$, in the CH$_4$–H$_2$S system four phases co-exist: solid H$_2$S-$\alpha$, liquid H$_2$S, liquid CH$_4$ and a vapor$^{31}$. In the analyzed system, the simultaneous and instant solidification of H$_2$S and CO$_2$ (Figs. 2e and 3e) is observed, thus in the 3-component CH$_4$–H$_2$S–CO$_2$ system five phases co-exist in equilibrium at the invariant quintuple point-$QP_3$: H$_2$S solid, CO$_2$ solid, CH$_4$ liquid, H$_2$S + CO$_2$ liquid, and a vapor. If N$_2$ component is considered the number of phases at equilibrium remains the same, however, the $QP_1$ is converted into a
univariant curve in the P–T space. The solidification of H$_2$S–CO$_2$ is subject to metastability as the measurements of the same inclusion yield a range of temperatures, and similar variability is also reflected by measured FIA1 ($\sigma = 4.58$, Table 1). The freezing temperatures ($T_n$) are relatively lower compared to melting temperatures ($T_m$) of H$_2$S or CO$_2$ (Table 1), which requires supercooling to nucleate solids. Precipitation of pure solid H$_2$S—a in the presence of pure solid CO$_2$ increases the temperature of the QP$_1$ to between $-107$ and $-104 \degree C$ (Table 1), when the cycling technique is applied.

Contemporaneous freezing of H$_2$S and CO$_2$ is typically observed in binary H$_2$S–CO$_2$ systems at an eutectic temperature of $-95.6 \degree C$, where the SCO$_2$LV and S$_{H2S}$LV triple-point loci converge at the quadruple point$^{32}$. The phase behavior, observed in the studied fluid inclusions, can thus be explained by an overlap of quadruple points of the binary CH$_4$–H$_2$S and H$_2$S–CO$_2$ systems. Moreover, the H$_2$S–CO$_2$ freezing point temperatures between $-125.9$ and $-114.9 \degree C$ (Table 1), measured in the CH$_4$–H$_2$S–CO$_2$–N$_2$ inclusion gas phase with 11.9–13.3 mol % CO$_2$ (in the presence of clathrate, Source Data), are much lower compared to the eutectic temperature for binary H$_2$S–CO$_2$ gas mixtures. According to experimental studies, the latter gas mixtures with $12.5$ mol % CO$_2$ follow triple point equilibria with solid H$_2$S in the binary systems and do not represent eutectic mixtures$^{32}$. Therefore, our study shows that the presence of CH$_4$ gas has a significant impact on the phase behavior of H$_2$S–CO$_2$ gases in studied natural fluid inclusions.

From the QP$_1$ point onwards fluid inclusions follow the S$_{H2S}$L$_1$V phase boundary and after intersecting the second quintuple point-QP$_2$ at temperatures between $-188$ and $-185.3 \degree C$ ($\sigma = 0.97$), the S$_{H2S}$V curve becomes a path (Fig. 8b). At the QP$_2$ two solids: CH$_4$ (S$_1$) and H$_2$S (S$_2$), liquid CH$_4$ and vapor phases are co-existing in equilibrium in the CH$_4$–H$_2$S system. The position of the QP$_2$ point in this binary system is determined by SLV equation of state since experimental data are lacking$^{35}$. In the CH$_4$–H$_2$S–CO$_2$ system, five phases co-exist at QP$_2$: H$_2$S solid, CO$_2$ solid, CH$_4$ solid, CH$_4$ liquid, and a vapor. Our study shows that both solidification and melting of methane progress gradually over a temperature interval as the liquid/solid methane phase boundary has been clearly observed (Fig. 2h, j). During the latter phase transition five phases: S$_1$S$_2$L$_1$V$_2$, where S$_2$ stands for both H$_2$S and CO$_2$ solids, are co-existing (Fig. 2h, j). Comparison of $T_m$ and $T_n$ values of CH$_4$, measured in the inclusion gas mixtures (Table 1), reveals that only slight supercooling is required to nucleate solid CH$_4$ and it is achievable using liquid N$_2$ coolant during microthermometry runs. Melting of methane (point 9 in Fig. 8b) occurs at $T_m$ between $-186.3$ and $-184.1 \degree C$, which are very consistent ($\sigma = 0.3$, Table 1) and lie slightly below the triple point of a pure CH$_4$ system ($-182.48 \degree C$ and a quadruple point-QP$_2$ of the CH$_4$–H$_2$S system ($-182.4 \degree C$)$^{35}$. The melting temperatures of H$_2$S–a solid (point 12 in Fig. 8a) within FIA1 (from $-98.9$ to $-98.8 \degree C$) show extremely low variability ($\sigma = 0.05$), which corresponds to stable H$_2$S contents in the inclusions (Table 1). Solid CO$_2$ melts (point 13 in Fig. 8a) at temperatures $-91.2 \degree C$/$-92.6 \degree C$ (A/B). Elevated standard deviation ($\sigma = 1.14$) for $T_m$(CO$_2$) may be due to slight compositional variation in the inclusions (11.9–13.3 mol % CO$_2$) or due to difficulties in $T_m$ observations, which stem from a small difference in refractive indices between the liquid phase and very small CO$_2$ crystals. Melting of all three solids: CH$_4$, H$_2$S, and CO$_2$ proceeds over temperature intervals, which is characteristic of multicomponent gas systems$^{17,60}$. The median $T_m$ values (FIA1): $-184.3 \degree C$ (CH$_4$), $-98.9 \degree C$ (H$_2$S) and $-91.9 \degree C$ (CO$_2$) are depressed compared to temperatures of melting points of the relative unary systems, i.e., $-182.5 \degree C$ (CH$_4$), $-85.5 \degree C$ (H$_2$S), and $-56.6 \degree C$ (CO$_2$). This implies that such melting behavior is not only typical for multivolatile H$_2$S-free systems$^{17}$, but also for H$_2$S-rich gas mixtures.

At the point, where the last solid-phase melts, the fluid inclusions follow back the L$_1$L$_2$V curve (point 13 in Fig. 8a). The first partial homogenization $T_h$(L$_1$L$_2$V $\rightarrow$ L$_2$V) takes place in a similar temperature interval from $-59.8$ to $-57.6 \degree C$ ($\sigma = 0.78$, point 14 in Fig. 8a) as the relative opposite phase transition during cooling (no. 3 in Table 1). This enforces the inclusions to enter the 2-phase L$_2$V field (Fig. 8a) until the homogenization to the vapor (L$_2$V $\rightarrow$ V), through a dew-point transition, takes place at temperatures between $-32.5$ and $-28.6 \degree C$ ($\sigma = 1.31$). During the latter transition 2-phase fluid inclusions (L$_2$V) follow back the trajectory intersecting the dew-point locus (point 15 in Fig. 8) and enter the vapor 1-phase field (Fig. 8a).

H$_2$S solid–solid transitions in fluid inclusions. The observation of low-temperature H$_2$S solid–solid transitions ($\alpha \leftrightarrow \beta \leftrightarrow \gamma$) in natural fluid inclusions requires consideration of new phase boundaries: $S_\alpha$S$_\beta$L$_1$V and S$_\beta$S$_\gamma$L$_1$V, and their influence on the CH$_4$–H$_2$S–CO$_2$–N$_2$ system. The experimentally determined solid–solid transitions of pure H$_2$S occur at temperatures of $-169.55$ and $-146.95 \degree C$ and are the latter the QP$_2$ point of the CH$_4$–H$_2$S system (Fig. 8b). The temperature range of H$_2$S $(\beta \leftrightarrow \gamma)$ transformations measured in the studied inclusions indicate that the above expected equilibrium temperatures are not sustained along the cooling pathway. In order to nucleate H$_2$S–$\gamma$ undercooling or maintaining a constant temperature for a period of time is required, which indicates metastable behavior or kinetics problems. The measured temperatures of the H$_2$S($\gamma \rightarrow \beta$) transition in the studied inclusion are oscillating around an average of $-168.1 \degree C$ (point 10 in Fig. 8b, Supplementary Table 2), which is slightly higher compared to the corresponding value for a pure H$_2$S system ($-169.55 \degree C$). This may be related to pressure as the P–T diagram for phase transitions of pure (99.5%) solid H$_2$S, at low pressures, shows that temperatures of solid–solid transitions increase with increasing pressures$^{40}$. The H$_2$S ($\gamma \rightarrow \beta$) transition is peculiar as after commencement it gradually proceeds even without temperature increase (on hold) with only the laser on, irrespectively of the laser power used. The temperatures of $-147$ and $-146.4 \degree C$ for the solid H$_2$S($\beta \rightarrow \alpha$) transitions in the studied fluid inclusion (point 11 in Fig. 8b) are in a very good agreement with the experimentally derived temperature of $-146.95 \degree C$ (Fig. 8b). According to numerical modeling$^{35}$ allotropic behavior of solid H$_2$S does not affect significantly the overall solid-fluid equilibria of the CH$_4$–H$_2$S mixture. Instead, the modeling has shown that in the CH$_4$–H$_2$S system the temperatures of solid–solid H$_2$S transitions are depressed relative to corresponding temperatures in pure H$_2$S system$^{35}$. This hypothesis is not consistent with H$_2$S($\gamma \leftrightarrow \beta \leftrightarrow \alpha$) transitions temperatures in the natural fluid inclusions studied here and shows that the presence of CH$_4$–CO$_2$ gas affects solid–solid H$_2$S phase equilibria in gas mixtures. Experimental studies of laboratory-grown H$_2$S crystals has shown that the solid H$_2$S($\gamma \rightarrow \beta$) transition is attributed to a decrease in the dielectric constant, whereas the H$_2$S($\beta \rightarrow \alpha$) transition is ascribed to orientational ordering relative to the rotational vibrations of the hydrogen atoms$^{61}$. During the higher temperature transition, the crystal structure of both phases ($\alpha$, $\beta$) of fluid inclusion H$_2$S remains disordered, which is expressed by broad bands observed in the stretching region of the Raman spectrum (Fig. 6) and “bloppy” appearance under the optical microscope (Figs. 2g and 3e, f, h, l). The number of peaks and their bandwidths shifts, at the point of the lowest temperature transformation (Fig. 6), imply structural modifications of solid H$_2$S (Fig. 3i). The crystalline H$_2$S–$\gamma$ solid, which nucleates in
natural fluid inclusions, shows peaks at wavenumbers (Fig. 7) very similar to those detected by an experimental study of purified H$_2$S gas\textsuperscript{39}. Microscopic observations during low-temperature runs unambiguously show a structural change to a polycrystalline aggregate with in-situ growing prismatic crystals (Fig. 3) and confirm the crystalline nature of the studied H$_2$S-$\gamma$ phase. Two crystal systems, orthorhombic or tetragonal, were proposed for solid H$_2$S-$\gamma$ phase\textsuperscript{30,41}. Our study clearly shows that the protracted structural transformations do not immediately follow up the low-temperature phase transitions detected by Raman spectroscopic analyses.

Spectral features of complex gas mixtures. Systematic shifts of Raman peak positions are observed for all inclusion gas species during the measurements. They are most pronounced for H$_2$S and CH$_4$ due to their high concentrations in the studied gas-rich inclusions (Figs. 5 and 6). Experimental studies have shown that changes in pressure, temperature and density of a single gas component as well as CH$_4$-CO$_2$ gas mixtures have an influence on the Raman peak positions\textsuperscript{62-64}. Modifications of gas peak positions in H$_2$S-bearing ternary, as well as any more complex gas mixtures, have not been studied so far.

Our results show that the Raman band positions are shifted to higher wavenumbers for more volatile components and to lower wavenumbers for less volatile components, relative to the original peak positions of the gas mixture at room temperature (Fig. 5). This tendency is also marked by systematic trends in diagrams illustrating H$_2$S and CH$_4$ band positions (cm$^{-1}$) versus temperature (Fig. 9 and Source Data). It is observed that the FWHM (full width at half maximum) of the peaks of gaseous, liquid, and solid CH$_4$ phases, which exsolved from the CH$_4$-H$_2$S-CO$_2$-N$_2$ gas mixture, consistently decrease with decreasing temperatures (Fig. 5). The above-mentioned features reflect well differential partitioning between the co-existing phases in an individual inclusion upon cooling, which is the strongest at the lowest recorded temperatures of about $-190^\circ$C (Fig. 9). The observations also reveal that gases of the highest volatility, i.e., N$_2$ and CH$_4$, partition into the inner vapor phase, whereas CO$_2$ and H$_2$S partition into the outer liquid phases. Similar distribution of gaseous components between the phases has been described for binary gas mixtures\textsuperscript{17}. Our study shows that the composition of the gas mixture affects the wavenumbers of its gas components, e.g., CH$_4$ peak measured in the gas mixture at room temperature is positioned at 2911 cm$^{-1}$, whereas at $-190^\circ$C it shifts to 2917 cm$^{-1}$ (Fig. 9), which is the wavenumber typical of pure CH$_4$ gas. The band position downshifts can also be indirectly related to the density difference between gas, liquid, and solid physical states of the inclusion components, i.e., solid H$_2$S or CH$_4$ show shifts to the lowest wavenumbers: 2522 and 2904 cm$^{-1}$, respectively (Fig. 9).

Applications

Experimental models and databases. We report on new fluid inclusion-derived temperature, compositional and spectroscopic data on a multicomponent CH$_4$-H$_2$S-CO$_2$-N$_2$-H$_2$O system. The results of our study are helpful not only for the interpretation of phase equilibria observed in fluid inclusion gas mixtures but also can be used as a guide for future experimental studies of fluids utilizing, e.g., synthetic fluid inclusions, fused-silica optical cells, or silica capillary tubes. Such studies are necessary to construct the unified complete topology of the C-O-H-N-S chemical system, which is required to improve understanding of the phase equilibria\textsuperscript{29}. Such purely experimental results cannot ideally reproduce natural systems, hence data from natural fluid inclusion gas--H$_2$O mixtures are complementary and can be used for validation and models refinement. Detailed characterization of phase transition ($\alpha \rightarrow \beta \rightarrow \gamma$) temperatures, structural transformations and spectral features of different solid H$_2$S phases, in natural fluid inclusions, contribute to the advancement of scientific knowledge about the nature of the H$_2$S solid--solid-phase equilibria.

Our study shows that the band wavenumbers of gas components in the natural CH$_4$-H$_2$S-CO$_2$-N$_2$ gas mixtures differ from the standard Raman shifts ($\Delta \nu$ in cm$^{-1}$) known from the Raman databases, and thus have a substantial impact on interpretation of literature data. It has been shown here that gas

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**Fig. 9** Diagrams showing the relationship between temperature and Raman band wavenumbers. **a** Shifts in peak positions of H$_2$S vapor, liquid, and solid ($\alpha$, $\beta$, $\gamma$) phases with decreasing temperature. The measurements were recorded in 10 °C increments. **b** Shifts in band positions of vapor, liquid and solid CH$_4$ with decreasing temperature. The measurements were recorded in 30 °C increments. Both H$_2$S and CH$_4$ show similar trends, namely Raman peak positions of volatile phases shift towards higher wavenumbers, whereas less volatile components reveal opposite tendency. This discrepancy reflects differential partitioning between co-existing phases. The data were collected from one individual fluid inclusion (no. P1a-f10) during the heating run. The peak positions were calibrated using neon emission lines. See also Source Data file.
peak modifications in ternary H$_2$S-bearing and more complex gas mixtures depend on their compositions as well as on relative density differences arising from differential partitioning of the gas mixture components in a closed system. These findings constitute new and valuable insights into the behavior of individual gases in multi-gas mixtures in natural fluid systems.

**Hydrocarbon and mineral systems.** The improved understanding of complex gas-H$_2$O systems is a prerequisite for more accurate reconstruction of the P–T conditions in hydrocarbon and mineralizing fluid systems in the geological record. The P–T information obtained from studies of fluid inclusions hosted in cements and fracture-filling minerals provide means for the reconstruction of multiphase fluid and gas migration events in hydrocarbon reservoirs and contribute, e.g., to enhancement of gas accumulation models. The migration of geological fluids, carrying reduced sulfur species (e.g. H$_2$S, HS$^-$), has a paramount control on the deposition of hydrothermal ore deposits. In evaporitic diagenetic environments of sedimentary basins, hydrocarbon and ore mineral systems are often closely linked. In poritic diagenetic environments of sedimentary basins, hydrocarbon exploration and environmental hazards. Constraining the geological time frames and depth intervals of thermonchemical sulfate reduction (TSR) is also of high importance as it produces H$_2$S and CO$_2$, which contaminate hydrocarbon reservoirs.

Microthermometric studies of CH$_4$–H$_2$S–CO$_2$–N$_2$ fluid inclusions allow the prediction of freezing points of H$_2$S and CO$_2$. Our study indicates that at low temperatures of about $-122 \, ^\circ C$ (Table 1), the H$_2$S–CO$_2$ gases in analyzed gas inclusions show very unique behavior of contemporaneous freezing, which is likely linked to the subordinate amounts of CO$_2$ (11.9–13.3 mol %). Therefore, CH$_4$–rich gas mixtures have a potential for relatively efficient purification to commercial quality grades by using, e.g., low-temperature distillation process. However, the disposal of resulting by-products (H$_2$S, CO$_2$) rises substantial environmental concerns as geochemical behavior of these gases in various deep geological formations is not yet well constrained.

Our study demonstrates that gas-rich CH$_4$–H$_2$S–CO$_2$–N$_2$–H$_2$O fluid inclusions offer an excellent opportunity to study the formation of complex natural gas hydrates in a closed system. Due to global warming, there is an increasing interest in understanding the behavior of natural gas hydrates that were discovered in deep-sea environments and permafrost regions. The formation mechanisms, as well as structural and compositional heterogeneities of the complex/mixed natural clathrate crystals, are not yet fully understood. Comparison of experimental simulations of synthetic gas hydrates with systematic studies of natural gas–H$_2$O inclusions mixtures provides means for a better understanding of the kinetics and thermodynamics of clathrates formation and dissociation. Such knowledge is relevant to investigations of synergies between CH$_4$–gas hydrates and climate change on a global scale.

**Extraterrestrial systems.** Low-temperature systems, which are a prerequisite for solid–solid H$_2$S transitions do not exist in terrestrial environments, but they persist on ice planets such as Uranus and Neptune. Recent studies evidenced the presence of gaseous H$_2$S above the cloud deck of Uranus, which led to the conclusion that H$_2$S ice is a major constituent of main clouds at 1.2–3 bar. Similarly, the H$_2$S ice is considered to be a prime constituent of Neptune’s main clouds at pressures of 2.5–3.5 bar.

At extremely low temperatures (from ca. $-220 \, ^\circ C$ to 153.7 $^\circ C$), at various depth levels in the ice giants atmosphere(s), there is a thus a high likelihood that H$_2$S ice cloud decks exist in different temperature-dependent solid states. This, in turn, may potentially have an influence on the atmospheric dynamics of the ice planets. Recent studies point also towards differences in the distribution of H$_2$S ice and CH$_4$, between polar and equatorial regions of the Uranus’s atmosphere, which yet require explanation. The latter could provide valuable insights into the atmospheric dynamics of the enigmatic ice giants. Possible future exploratory missions to the ice planets would benefit from having a Raman spectrometer on board, which allows identification of possible perturbations caused by distinct H$_2$S solid states and constraining distribution of H$_2$S ice and associated gases at low temperatures. A miniaturized Raman spectrometer has been used, e.g., in a mission to Mars.

**Methods**

**Microthermometry.** For this study, we used fracture-filling fluorite mineralization, hosted by Upper Permian Zechstein C$_3$X carbonate from the Southern Permian Basin, as a primary source for the CH$_4$–H$_2$S–CO$_2$–N$_2$–H$_2$O fluid inclusions. The drill core sample originates from the well PB–20 situated at the border of the Pompecký Block and the northern flank of the Lower Saxony Basin. The translucent coarse fluorite crystals, selected for analyses, host abundant CH$_4$–H$_2$S–CO$_2$–N$_2$–H$_2$O fluid inclusions (Fig. 1 and Table 1). Doubly-polished fluorite chips (~8 x 8 mm) with a thickness of 180 μm were used for analyses.

Microthermometric and laser Raman spectroscopic measurements were performed at the GFZ Potsdam, Germany. Microthermometry and observations of phase changes in gas-rich inclusions were conducted using a Linkam heating–freezing stage (THMS600 system) that allows observations of phase transitions in fluid inclusions in the temperature range between $-195$ and $600 \, ^\circ C$. The heating/freezing system was calibrated using SynFlinc synthetic fluid inclusion standards: CO$_2$ and pure H$_2$O for melting temperatures of CO$_2$ and ice, respectively as well as critical homogenization temperature of pure H$_2$O. Temperature were recorded using Linksys 32 software with reproducibility of $0.1 \, ^\circ C$. Imaging during the microthermometry runs was performed using a digital QICAM FAST1394 camera attached to an Olympus BX53M microscope and the Q-Capture Pro 7 software was used for image acquisition.

**Raman spectroscopy combined with microthermometry.** Laser Raman spectroscopy coupled with microthermometric experiments was utilized to examine phase changes and solid phases formed at low temperatures. Measurements were performed using the Linkam THMS600 system equipped with LNP95 nitrogen flow system, a 785 μm Nd:YAG laser, a Papst temperature controller, and a stage for isotherm measurements. Laser heating/freezing stage was calibrated using SynFlinc synthetic fluid inclusion standards: CO$_2$ and pure H$_2$O for melting temperatures of CO$_2$ and ice, respectively as well as critical homogenization temperature of pure H$_2$O. Temperature were recorded, in a range between $-192$ and $+352 \, ^\circ C$, using a Linksys 32 software with reproducibility of $0.1 \, ^\circ C$. Heating/freezing rates during measurements were 4 °C/min or/and 10 °C/min, whereas in between the phase transitions the rates were 20–30 °C/min.

The vibrational spectra of phases in gas-rich inclusions during freezing-heating runs were measured using a LabRAM HR Evolution Raman micro-probe supplied by Horiba Scientific. The system is equipped with a dispersive Raman spectrometer with focal length of 800 mm, the frequency-doubled Nd:YAG solid-state green laser source with an excitation radiation of 532 nm and output power of 100 mW (max. $\pm 48 $mW at the sample surface), edge filters, and a CCD detector. A grating of 1800 grooves/mm and confocal hole of 100 μm were used, and the spectral resolution was $<1 \, \text{cm}^{-1}$. Most measurements (when not indicated otherwise) were performed using a neutral density filter, which reduces the output laser power at the sample to 50% ($\pm 24\,\text{mW}$) to avoid frequent “out of range” high intensity CH$_4$ peaks with artificially cut tops. Internal calibration has been performed using a silicon standard (520 cm$^{-1}$). A neon lamp attached to the Linkam stage was used for a wavenumber calibration. The spectra of Ne emission lines were collected simultaneously with each peak position measurement. The reference Ne emission lines used for the wavenumber calibration of H$_2$S were: 2389, 2708 cm$^{-1}$, and of CH$_4$: 2835, 3006 cm$^{-1}$. The peak positions, corrected for instrumental drift, were calculated using the measured wavenumbers of CH$_4$ and Ne lines, and applying the linear interpolation equation. The average standard error for peak position measurements at room temperature, based on 8 measurements (2 inclusions measured 4x), was 0.02 cm$^{-1}$ for CH$_4$ and 0.01 cm$^{-1}$ for H$_2$S. The uncertainty of the peak wavenumber measurements was $\pm 1 \, \text{cm}^{-1}$ for all gas components.

The Raman spectrometer is adapted to an Olympus BXFM optical microscope, which is equipped with 50× (NA = 0.5) long working distance objective, reflected and transmitted light sources, and a VIS Camera. This setup enables optical
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**Author contributions** V.L. studied phase transitions in numerous C–O–H–N–S fluid inclusions microscopically for a pre-selection of fluid inclusions used in this study. M.S. carried out microthermometry and Raman spectroscopy of selected fluid inclusions, interpreted the results, and wrote the manuscript. V.L. contributed to writing and the discussion of the results. Both authors contributed to the concept and design of the experiments.

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