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Reply to Comment on "Formation of abnormally high density H_2S fluid in sedimentary basins" by Liu *et al.*, 2025

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Reply to Comment

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We acknowledge, with appreciation, the comments from Cui (2025) and his effort in evaluating our recent publication on Raman spectroscopic and microthermometric identification of high density, high purity H_2S fluid inclusions in sedimentary basins (Liu *et al.*, 2025). We are also grateful to the editor for the opportunity to clarify aspects of our manuscript requiring further explanation. Below we respond to the questions raised by Cui (2025).

1. Mississippi Valley-Type (MVT) Pb-Zn Ore Deposits. In Liu *et al.* (2025), we pointed out the major goal of this work as "...to test whether high density H_2S fluids can be formed in sedimentary basins and to evaluate the validity of the proposed mineralising mechanisms for MVT deposits". Our fluid inclusion observations provide direct evidence confirming the potential for high density H_2S fluid formation. Therefore, in the discussion, we emphasised that such a finding provides critical implications for research on the mineralisation models of MVT Pb-Zn deposits. We acknowledge the point raised by Cui (2025) that sections like Caojunba do not host MVT Pb-Zn mineralisation, which was not the primary focus of Liu *et al.* (2025). The formation of ore deposits is the result of convergence of multiple factors. For the fluid mixing model, formation of an H_2S reservoir is only a prerequisite. In the "Samples and Methods" section, we stated: "The nodular pore-filling quartz-calcite cements are common in the upper Z_1d and the lower to middle Z_2dn dolomites hosting MVT deposits (*e.g.*, Yangjiaping, Zhongling, Caojunba, Nanbeizhen, and Zouma sections)". This statement plausibly led to the misunderstanding by Cui (2025). Our intended meaning was that the upper Z_1d and lower to middle Z_2dn dolomite represent host rocks for MVT Pb-Zn deposits, and the aforementioned sections are typical Z_1d-Z_2dn outcrops. In fact, several large MVT Pb-Zn deposits, such as Bingdongshan, Dongjiahe, and Muyuhe, have been discovered within Z_1d dolomite in South China (see Supplementary Information in Liu *et al.*, 2025).

2. Calcite Purification Model. Cui (2025) argues that H_2S cannot coexist with calcite, as high H_2S concentrations indicate strongly acidic fluids, which would lead to calcite dissolution. Consequently, he dismisses the proposed calcite purification model—where calcite precipitation consumes CO_2 and enriches H_2S—as unfeasible. However, this interpretation overlooks well documented evidence that TSR-derived CO_2 can be sequestered by secondary carbonate minerals (Worden *et al.*, 1996; Bildstein *et al.*, 2001; Zhu *et al.*, 2005). Notably, the negative carbon isotope values of such carbonates (*e.g.*, <−5 ‰, VPDB) serve as a key indicator of TSR involvement (Krouse *et al.*, 1988; Jiang *et al.*, 2014; Jenden *et al.*, 2015). For example, in Sichuan (South China) and Southern Permian basins (Poland), TSR significantly alters hydrocarbon compositions, with H_2S concentrations exceeding those of CO_2, while carbonate cements are common (Liu *et al.*, 2014; Li *et al.*, 2016; Kotarba *et al.*, 2017, 2020).

To evaluate the feasibility of calcite purification, we simulated the TSR reaction using HCh software under conditions relevant to deep burial diagenetic environments (150–200 °C, 100 MPa). For the $CaSO_4$-CH_4-H_2O system, it comprised 0.5 mol CH_4 and 1 kg H_2O, with stepwise additions of anhydrite (0.01 mol/step) to emulate progressive sulfate availability. The simulations confirmed the redox reaction:

$$CaSO_4\,(s) + CH_4\,(aq) \rightarrow CaCO_3\,(s) + H_2S\,(aq) + H_2O\,(aq)$$

where anhydrite dissolution drives methane oxidation, yielding calcite and H_2S as dominant products (Fig. 1a, b). At 150 °C, the system produced 0.465 mol calcite with residual 0.0338 mol/kg CO_2 and 0.423 mol/kg H_2S (plus 0.0721 mol/kg HS^-; Fig. 1c); at 200 °C, calcite precipitation increased to 0.472 mol, while CO_2 declined to 0.0277 mol/kg and H_2S rose to 0.437 mol/kg (Fig. 1d). H_2S concentration consistently exceeded CO_2 by an order of magnitude, underscoring the efficiency of CO_2 sequestration *via* calcite formation.

To address natural brine chemistry, we incorporated 7.6 wt. % $CaCl_2$ and tested pH conditions (neutral to slightly alkaline: $\Delta pH = 0$–0.2) to account for TSR's hydrogen demand (Truche *et al.*, 2014) and carbonate buffering (Machel, 2001) (Fig. 1e, f). Under these constraints, calcite precipitation further

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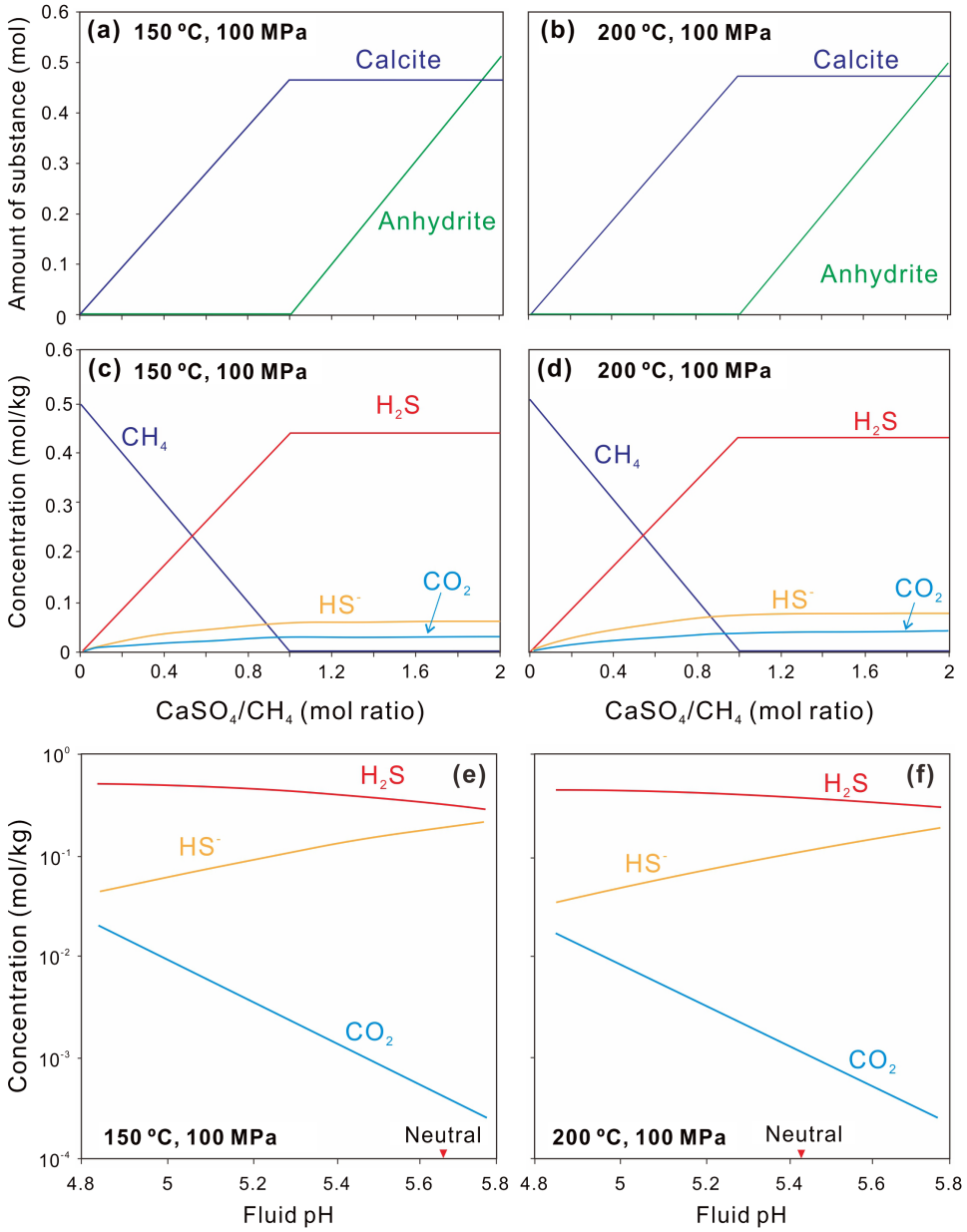

Figure 1 HCh simulation results of the TSR reactions. **(a–d)** CH_4-$CaSO_4$-H_2O system; **(e–f)** CH_4-$CaSO_4$-$CaCl_2$-H_2O system.

suppresses CO_2 concentrations to <0.001 mol/kg, while H_2S dominates the fluid phase (0.3–0.34 mol/kg). The resultant H_2S/CO_2 ratios (~660:1) demonstrate that calcite acts as a CO_2 sink, enabling H_2S enrichment. If phase separation occurs, the volatile H_2S may partition into a gas phase, generating high purity H_2S fluids—a plausible mechanism for the observed H_2S predominance in TSR-altered reservoirs.

Cui (2025) proposed that the formation of large scale MVT Pb-Zn deposits requires external sulfur sources, which constitutes the essence of the fluid mixing model (*e.g.*, Leach *et al.*, 2010). However, we emphasise that potential sulfur sources are not limited to microbial sulfate reduction, as TSR also represents a significant source of reduced sulfur. Regarding paragenetic sequence, while Cui (2025) suggested quartz cementation might predate calcite formation, our petrographic observations revealed no quartz rims lining the nodule. Instead, H_2S-rich fluid inclusions were exclusively found in quartz cements located within the nodules (Fig. 1b in Liu *et al.*, 2025), whereas only aqueous inclusions were identified in adjacent calcite cements, with no high density, H_2S-bearing inclusions detected. These observations lead us to conclude that the high density H_2S fluids were generated subsequent to calcite precipitation.

3. Complex Diagenetic and Burial Histories. Cui (2025) highlighted the complexity of the diagenetic history of the Neoproterozoic strata in South China. We have no disagreement with this understanding. We appreciate the recognition of our fluid inclusion observations. In comparison with calcite and dolomite, quartz has greater hardness and, generally, does not develop cleavage. As a result, fluid inclusions within quartz can often retain primary information even after undergoing complex diagenetic alteration. Nevertheless, further studies are still necessary to better reconstruct the diagenetic history.

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Additional Information

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