Diagenetic H_2S production provides a metal trap in carbonaceous mudstones – In situ microanalysis of $\delta^{34}S$ values in pyrite and barite

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At Macmillan Pass, Selwyn Basin (YT, Canada), Zn-Pb-Ba mineralization is hosted by Late Devonian carbonaceous mudstones at the Tom and Jason deposits. A euxinic water column is widely accepted to form the metal trap for these systems, whereby H_2S is produced during bacterial reduction of seawater sulphate. In this study, isotopic microanalysis (secondary ion mass spectrometry; SIMS) is used to evaluate the $\delta^{34}S$ composition of barite and pyrite and the evidence for euxinia.

Petrographic assessment of drill-core samples from the mineralization at Tom and Jason reveals multiple generations of pre-ore diagenetic barite and pyrite, all of which are overprinted by later hydrothermal sulphides (galena, sphalerite, pyrite). All generations of barite preserve a relatively narrow range of $\delta^{34}S$ values (24‰ to 34‰) and the first generation of pyrite (py-1; framboidal) preserves negative $\delta^{34}S$ values (-23‰ to -28‰); this is consistent with diagenetic precipitation of py-I during open system bacterial sulphate reduction. The isotopic relationship of subsequent stratiform euhedral pyrite (py-II) with barite ($\delta^{34}S_{-pyrite} \cong \delta^{34}S_{-barite}$) can only be explained by sulphate reduction coupled with anaerobic methane oxidation (SR-AOM) at the sulphate-methane transition zone (SMTZ). Methane-rich pore fluids were effective at both mobilizing barium beneath, and reducing sulphate at, the SMTZ. Thus, precipitation of stratiform barite and pyrite occurred when methanic, Ba-rich fluids interacted with the SMTZ, indicating a low temperature, diagenetic origin for this pre-ore assemblage.

Hydrothermal sulphides (pyrite, sphalerite and galena) post-date the diagenetic barite-pyrite assemblage, and so did not precipitate from a euxinic water column. This necessitates an alternative metal trap, and we suggest that H_2S generated during SR-AOM formed an effective mineralization pathway for the metal–bearing hydrothermal fluids.