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Geochemical factors influencing cyclical precipitation of sphalerite and galena in low temperature Mississippi Valley Type ore deposits

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Mississippi Valley Type (MVT) lead and zinc deposits provide a significant source of economically valuable, sedimentary galena (PbS) and sphalerite (ZnS). Several field and laboratory studies have characterized important aspects of MVT ores, such as brine composition and transportation mechanisms. However, geochemical characteristics and genesis required for galena and sphalerite ore formation and the reasoning for quick, episodic mineralization are not fully understood. Specifically, differentiating between the sources of reduced sulfur and the potential microbial role in the mineralization process needs further attention. By simulating regional MVT brines, the input and effect of microbial by-products during the development of these ores, as well as the cause of cyclicity within MVT deposits were investigated in this study. Regional MVT fluid inclusions were tested in autoclaves with dolomite as the substrate mineral at different temperatures over two-week period. Variables during the experiments included CO_2, sulfide, lead and zinc. Control experiments were run at 120 $^{\circ}$C to account for the temperature at which galena and sphalerite formation occurs in the measured regional brine, while all other reactions were run at 70 $^{\circ}$C.

Experiments where sulfide was removed from the test brine solution at 70^{o}C did not allow galena or sphalerite precipitation, indicating that at this temperature, thermochemical reduction of sulfur did not occur. Sphalerite did not precipitate when Zinc was present, suggesting that change in fluid chemistry could be responsible for the cyclicity. Sulfur isotope measurements of the galena precipitates revealed large decreases in heavy sulfur. The lower δ^{34}S values, however, could not be attributed to biogenically derived hydrogen sulfur, and the isotopic signatures were largely dependent on the source of sulfur used in the experiments. Conclusions of this study are that fluid mixing or in-situ sulfur reduction by thermochemical or biogenic means are the primary mechanisms of MVT deposition, while at low temperatures biogenic sulfur reduction is the main driver.