

The role of kinetics in the formation of MVT deposits.

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If it is assumed that ore metal transport cannot reasonably occur in the presence of reduced sulfur at $150\pm50^{\circ}$ C, the chemical aspect of MVT (Mississippi Valley-Type ore deposit) origins is not metal transport but deposition. In other words, what is the source of the reduced sulfur (H₂S) which is required to precipitate the ore minerals, ZnS and PbS? There are two main possibilities, which depend on the timing of the H₂S generation:

- 1. The generation of the H_2S required to precipitate the ores could occur before (possibly long before) the arrival of metal-bearing solutions, in which case it would need to be trapped in some reservoir through which the metal solutions would later travel. The generation of this H_2S could occur by various means, such as bacterial or thermal reduction of sedimentary sulfate (TSR), or by heating of sulfur-bearing petroleum or organic-rich shale. The advent of a metalbearing solution into a reservoir, (possibly a sour gas deposit of the type well known to petroleum geologists) containing H_2S would immediately result in metal sulfide precipitation. This is generally referred to as the mixing hypothesis, and could be referred to as "fast mixing".
- 2. The generation of the H₂S could occur during the formation of the ore deposit. It might be generated from sulfur-bearing organic material, as above, or by thermochemical reduction of sulfate (TSR) in the ore solution itself. Bacterial reduction would not be a possibility in this case, because of the high temperatures. This newly formed H₂S, whether generated in the ore solution or added to it from an external source, then precipitates sulfide minerals at a rate controlled by the rate at which it is produced. Addition of H₂S to an ore solution from an external source in this way is another form of mixing, but must be distinguished

from the previous case. It could be referred to as "slow mixing".

Both possibilities involve a number of problems which have not been completely resolved. However, one important aspect of these two possibilities for H_2S generation is that they are distinguished by the fact that the first (H_2S generation before ore deposition) does not depend on reaction kinetics, while the second (H_2S generation during ore deposition) is highly dependent on kinetics.

Compilation of all available data, including some recent data of our own, shows that at 150° C, the first order rate constant for the overall TSR reaction lies between 10^{0} and 10^{-4} , depending on the reductant and several other factors. Preliminary data on the rate of release of H₂S from organic-rich shale is similar. Although very slow, a simple flow model shows that rates in this range are fast enough to generate relatively small ore bodies. The ores of Central Tennessee are believed to be an example.