Geol. 656 Isotope Geochemistry

Lecture 33 — Spring 2003

HYDROTHERMAL ACTIVITY, METAMORPHISM, AND ORE DEPOSITS II

SULFUR ISOTOPE FRACTIONATION IN LOW-TEMPERATURE SYSTEMS

At temperatures below about 400° C, sulfate (SO_4^{-2}) species becomes the dominant form of oxidized sulfur, and the principal aqueous sulfur species in ore-forming fluids will be H_2S, HS^-, and various sulfate species (SO_4^{-2}, HSO_4^{-}, KSO_4^{-}, $NaSO_4^{-}$, $CaSO_4$ and $MgSO_4$). Neglecting any fractionation between H_2S and HS^-, which will be small, the $\delta^{34}S_{H_2S}$ of the fluid can be expressed as:

$$\delta^{34}S_{H_2S} = \delta^{34}S_{fluid} - \Delta_{SO_4^{2-}} \left[\frac{R'}{R'+1}\right] \qquad 33.1$$

where $\Delta_{SO_4^{2-}}$ is the fractionation between H_2S and SO_4^{-2} and R´ is the molar ratio of sulfide to sulfate:

$$R' = \frac{\Sigma SO_4^{2-}}{\Sigma H_2S} \qquad 33.2$$

In general, R' will be a function of f_{O_2}, pH, fluid composition and temperature. Figure 33.1 shows the difference between $\delta^{34}S$ in sulfide and $\delta^{34}S$ in the total fluid as a function of pH and f_{O_2}. Only under conditions of low pH and low f_{O_2}, will the $\delta^{34}S$ of pyrite (FeS_2) be the same as the $\delta^{34}S$ from which it precipitated. For conditions of relatively high f_{O_2} or high pH, substantial differences between the $\delta^{34}S$ of pyrite and the $\delta^{34}S$ from which it precipitated are possible. Figure 33.2 shows the difference between $\delta^{34}S$ in sulfide and $\delta^{34}S$ in the total fluid as a function of the sulfate/sulfide ratio (R´) and temperature. When the fluid is sulfide dominated, the $\delta^{34}S$ of the sulfide and that of the bulk fluid will necessarily be nearly identical. For conditions where the concentrations of sulfate and sulfide are similar, large fractionations between sulfides and fluids from which they precipitate are possible.

At magmatic temperatures, reactions generally occur rapidly and most systems appear to be close to equilibrium. This will not necessarily be the case at lower temperatures because of the strong dependence of reaction rates on temperature. While isotopic equilibration between various sulfide species and between various sulfate species seems to be readily achieved at moderate and low temperatures, isotopic equilibration between sulfate and sulfide appears to be more difficult

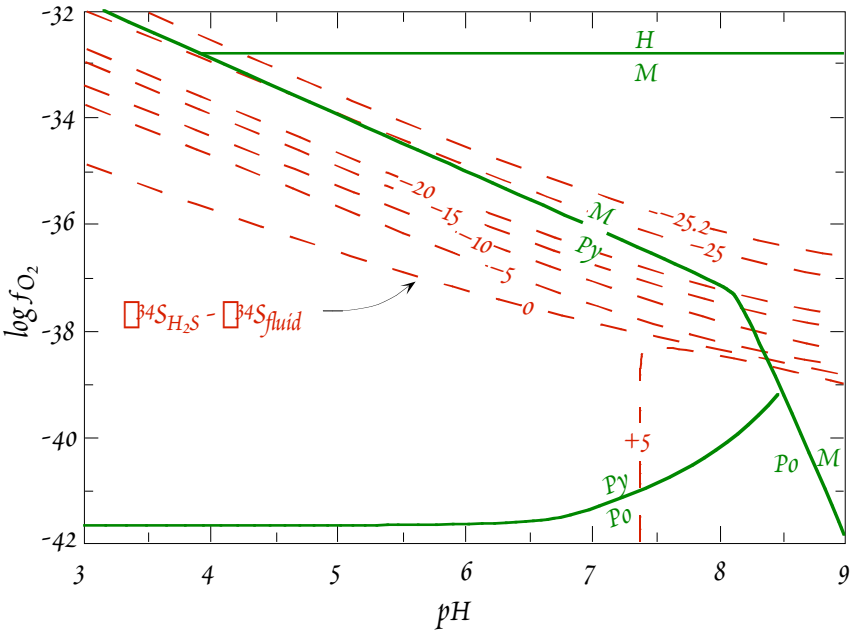


Figure 33.1. Difference in $\delta^{34}S$ between H_2S and bulk fluid as a function of pH and f_{O_2} at 250°C. Equal concentration boundaries are shown for magnetite-hematite (M-H), magnetite-pyrite (M-Py), magnetite-pyrrhotite (M-Po), and pyrite-pyrrhotite (Py-Po). After Ohmoto and Rye (1979).

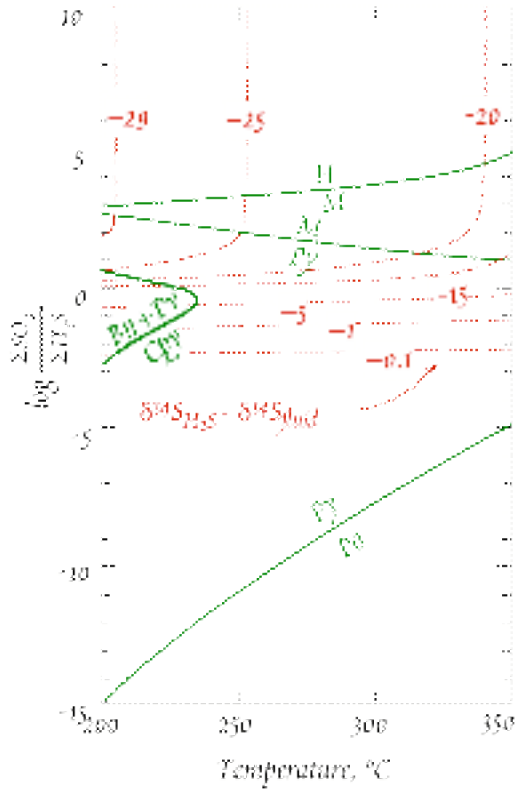


Figure 33.2. Difference in $\delta^{34}S$ between H_2S and bulk fluid as a function of temperature and sulfate/sulfide ratio. Equal concentration boundaries pH neutral M: magnetite, H: hematite, Py: pyrite, Po: pyrrhotite, Bn: bornite (Cu_5FeS_4), Cp: chalcopyrite. After Ohmoto and Rye (1979).

to achieve. Sulfate-sulfide reaction rates have been shown to depend on pH (reaction is more rapid at low pH) and, in particular, on the presence of sulfur species of intermediate valences. Equilibration is much more rapid when such intermediate valence species are present. Presumably, this is because reaction rates between species of adjacent valance states (e.g., sulfate and sulfite) are rapid, but reaction rates between widely differing valence states (e.g., sulfate and sulfide) are much slower.

Low temperatures also lead to kinetic, rather than equilibrium, fractionations. As we saw, kinetic fractionation factors result from different isotopic reaction rates. Interestingly enough, the rates for oxidation of $H_2{}^{32}S$ and $H_2{}^{34}S$ appear to be nearly identical. This leads to the kinetic fractionation factor, α_k, of 1.000±0.003, whereas the equilibrium fractionation between H_2S and SO_4 will be 1.025 at 250° C and 1.075 at 25° C. Thus sulfate produced by oxidation of sulfide can have $\delta^{34}S$ identical to that of the original sulfide. Kinetic fractionations for the reverse reaction, namely reduction of sulfate, are generally larger. The fractionation observed is generally less than the equilibrium fractionation and depends on the overall rate of reduction: the fractionation approaches the equilibrium value when reaction rate is slow. Disequilibrium effects have also been observed in decomposition of sulfide minerals. Figure 33.3 illustrates some interesting possible effects that can arise as a result of disequilibrium.

If there is disequilibrium between sulfate and sulfide in solution, it is likely equilibrium will not be achieved between mineral pairs involving pyrite and chalcopyrite ($CuFeS_2$) even when isotopic equilibrium is attained between other sulfides such as galena (PbS), sphalerite (ZnS), and pyrrhotite (FeS). This is because precipitation of the former involves reactions such as:

$$4Fe^{2+} + 7H_2S + SO_4^{2} \rightleftarrows 4FeS_2 + 4H_2O + 6H^{+} \qquad 33.3$$

whereas the latter involve only simple combinations, e.g.:

$$Zn^{2+} + H_2S + \rightleftarrows ZnS + 2H^{+} \qquad 33.4$$

ISOTOPIC COMPOSITION OF SULFIDE ORES

A number of important sulfide deposits apparently were produced by reduction of sulfate that was ultimately derived from seawater. Their isotopic compositions are shown in Figure 33.4. The isotopic composition of these sulfides depends on the reduction mechanism, temperature, and whether the system was open or closed to sulfate and sulfide. At temperatures less than 50° C, the only mechanism for reduction of sulfate is bacterial. Optimal temperatures for such reduction are around 30 to 50° C. Deep euxinic basins such as the Black Sea are good examples of systems that are open to SO_4 but closed to H_2S and where reduction is bacterial. In these cases, reduction occurs slowly at the bottom, but SO_4 is continuously supplied from the water mass. In such environments, sulfides appear to have a $\delta^{34}S$ of 40 to 60‰ less than that of contemporaneous seawater (the sulfur isotopic composition of sea-

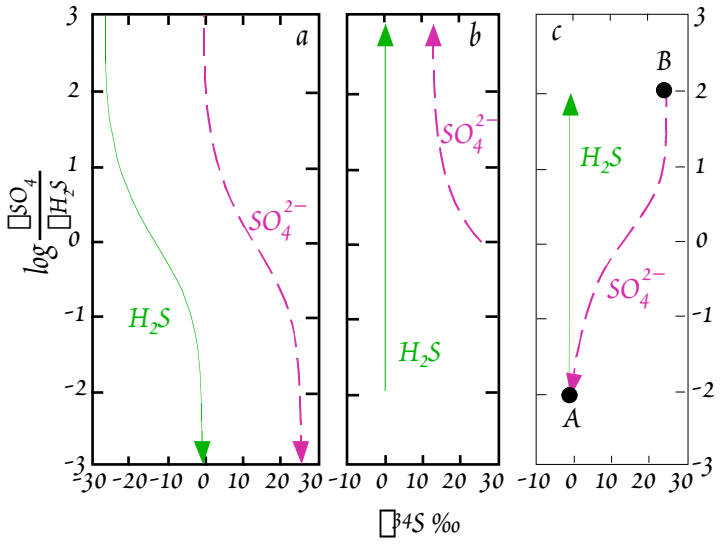


Figure 33.3. Isotopic relationships between coexisting H_2S and SO_4^{2-} as a function of sulfate/sulfide ratio. (a) Equilibrium conditions at 250° C where $\delta^{34}S_{fluid}$ = 0 ‰. (b) Non-equilibrium oxidation of H_2S. Isotopic composition of H_2S remains constant, but that of sulfate changes due to addition of sulfate derived from non-equilibrium oxidation of H_2S. (c) Non-equilibrium mixing of H_2S-rich fluid A and SO_4-rich fluid B. $\delta^{34}S_{H_2S}$ remains constant (equilibrium fractionation is achieved during reduction), but $\delta^{34}S_{SO_4}$ varies due to addition of sulfate derived from oxidation of sulfide. After Ohmoto and Rye (1979).

water has varied through time). A good example of such a deposit is the Kupfershiefer in Germany, where the most common $\delta^{34}S$ is about –40‰, which is about 50‰ less than Permian seawater (+10‰).

In systems closed to SO_4 but open to H_2S, the process is similar to Rayleigh distillation. This would be the case, for example, where sulfate reduction occurs much more rapidly than sulfate is supplied to the system, but sulfide is effectively lost from the system by crystallization of sulfide minerals. The composition of the sulfate, as a function of the fraction of sulfate remaining, f, is given by:

$$\delta^{34}S_{SO_4^{2-}} = \delta^{34}S^{0}_{SO_4^{2-}} + 1000(f^{\alpha-1} - 1) \qquad 33.5$$

The composition of the sulfide at any time, t, is given by:

$$\delta^{34}S^{t}_{H_2S} = \delta^{34}S^{t}_{SO_4^{2-}} - 1000(\alpha - 1) \qquad 33.6$$

where α is the effective sulfate-sulfide fractionation factor. The effective fractionation factor for reduction may be greater than the equilibrium one because of the more rapid reaction of ^{32}S species than ^{34}S ones. A typical value of α under these circumstances might be 1.025.

Systems closed to both species are analogous to equilibrium crystallization. In either case, the $\delta^{34}S$ of both sulfide and sulfate increases during the reduction process. Systems closed to SO_4 characteristically show a spread in $\delta^{34}S$ that is skewed toward positive values, have $\delta^{34}S$ that increases in the later stages, and have both minimum and modal values that are approximately 25‰ lower than the original sulfate (e.g., contemporaneous seawater). Examples are

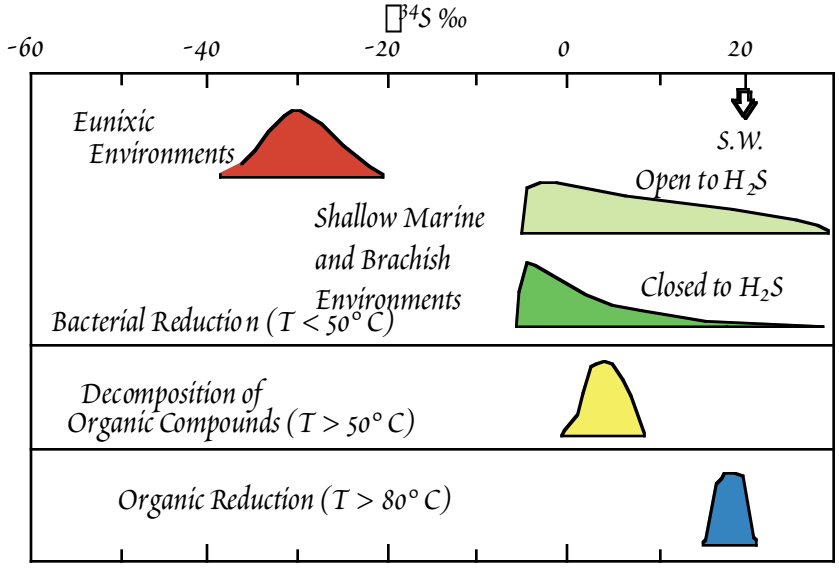


Figure 33.4. Expected distribution of $\delta^{34}S$ values for sulfide ores produced by sulfate reduction of seawater having an isotopic composition of $\delta^{34}S$ = +20‰. After Ohmoto and Rye (1979).

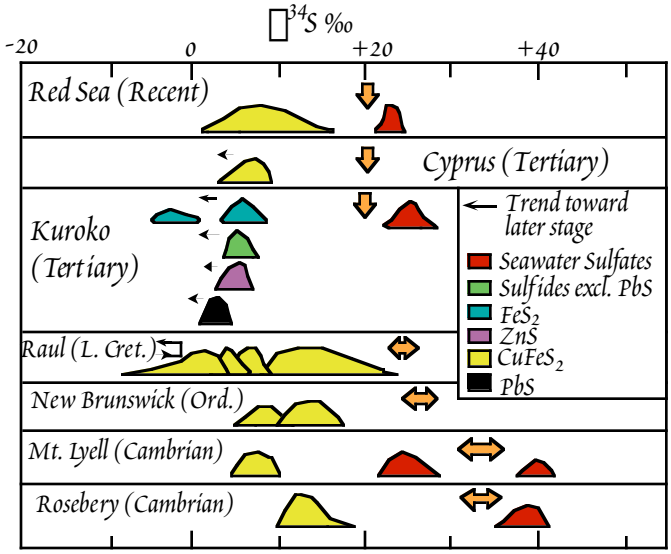


Figure 33.5. $\delta^{34}S$ in volcanogenic massive sulfide deposits. Arrows show the isotopic composition of contemporaneous seawater sulfate. After Ohmoto and Rye (1979).

the White Pine and Zambian copper deposits, which apparently formed in shallow marine or brackish environments.

At temperatures above 50° C, thermal decomposition of sulfur-bearing organic compounds produces H_2S. The $\delta^{34}S$ values of such H_2S are typically 15‰ less than that of seawater. This reduction is accelerated by the presence of S species of intermediate valence. The extent of isotopic fractionation in this process will depend on temperature.

In ridge crest hydrothermal systems, seawater sulfate is reduced by reactions with Fe^{2+} such as:

$$8Fe^{2+} + 10H^+ + SO_4^{2-} \rightleftarrows H_2S + 8Fe^{3+} + 4H_2O \qquad 33.7$$

Reduction most likely occurs at temperatures above 250° C (sulfide was not produced in basalt-seawater experiments below this temperature), and it is likely that equilibrium is achieved in this process. Modern seawater has a $\delta^{34}S$ of +20, and values of H_2S between –5‰ and +20‰ (the latter value is a result of complete reduction of sulfate) are expected. Consistent with this prediction, sulfide in active seafloor hydrothermal vents has a $\delta^{34}S$ of +3.5. This process produces the class of ores referred to either as stratabound sulfides or volcanogenic massive sulfides. Isotopic compositions of some example deposits are shown in Figure 33.5, along with the composition of contemporaneous seawater. They typically have $\delta^{34}S$ approximately 17‰ lower than contemporaneous seawater.

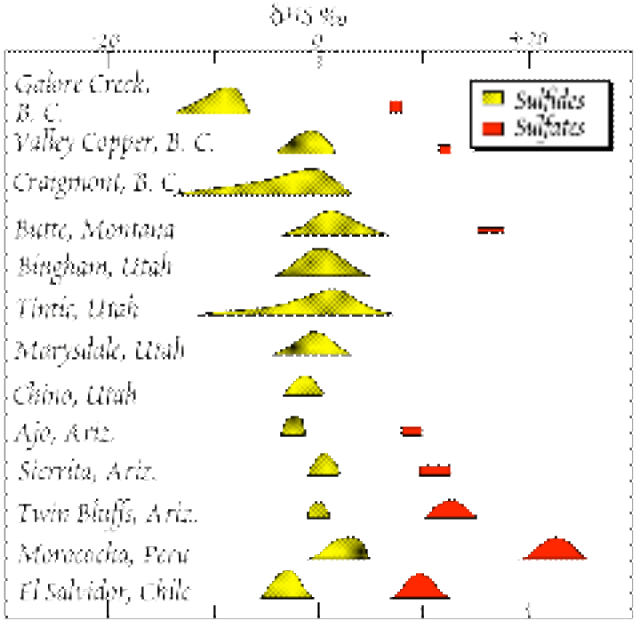


Figure 33.6. $\delta^{34}S$ in porphyry copper sulfides and sulfates. After Ohmoto and Rye (1979).

The isotopic compositions of example porphyry copper deposits are shown in Figure 33.6. The sulfides in these generally have $\delta^{34}S$ between –3 and +1‰, which is close to the mantle value, and the fractionation between sulfides and coexisting sulfates suggest equilibration temperatures between 450° C and 650° C, which is generally in good agreement with other temperature estimates. The isotopic compositions indicate the sulfur was derived from igneous sources, either as magmatic fluids or by dissolution of igneous sulfides. The low $\delta^{34}S$ of Galore Creek suggests the oxidation state of the magma was high or that some sedimentary sulfide was incorporated. The high $\delta^{34}S$ of Morococha suggests some sulfur was derived from the evaporites found in the surrounding country rock. H and O isotopic compositions in these deposits are generally inconsistent with water being of magmatic derivation. It is possible these isotope ratios reflect overprint of meteoric water

circulation after mineralization.

Mississippi Valley type deposits are carbonate-hosted lead and zinc sulfides formed under relatively low temperature conditions. Figure 33.7 shows the sulfur isotope ratios of some examples. They can be subdivided into Zn-rich and Pb-rich classes. The Pb-rich and most of the Zn-rich deposits were formed between 70 and 120° C, while some of the Zn-rich deposits, such as those of the Upper Mississippi Valley, were formed at temperatures up to 200° C. Coexisting sulfides of the Pb-poor Upper Mississippi Valley deposits are in isotopic equilibrium, whereas sulfur isotope equilibrium was most often not achieved in Pb-rich deposits. In the former, $\delta^{34}S$ values are quite uniform over a large area, suggesting the ore-forming fluid supplied both metals and sulfides and transported them over long distances. The high positive $\delta^{34}S$ suggests the sulfur was ultimately derived from ancient seawater, perhaps from formation water or evaporites in deep sedimentary basins, and reduced by reaction with organic compounds.

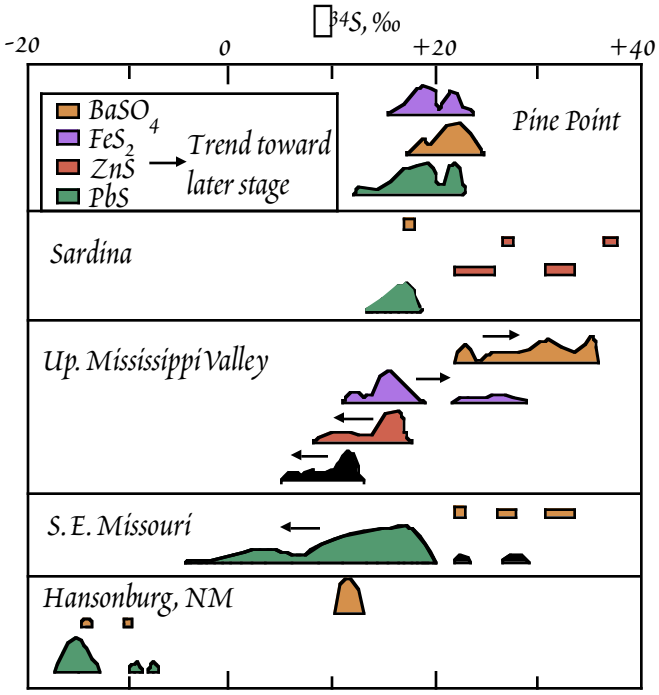


Figure 33.7. Sulfur isotope ratios in some Mississippi Valley-type Pb and Zn deposits. After Ohmoto and Rye (1979).

$\delta^{34}S$ is correlated with Pb isotope ratios in galenas of the S. E. Missouri district. This, and the variability of $\delta^{34}S$, suggests there was more than one source of the sulfur and lead. Isotopically heavy sulfur was apparently carried with the metal by the ore forming fluid while the isotopically light sulfur was derived from pyrite in the host rock. In Pine Point, sulfide may have been locally produced by reaction between sulfate-bearing fluids and organic matter in sediment. Local production of sulfide shortly before ore deposition may help to account for the lack of isotopic equilibrium in this deposit,

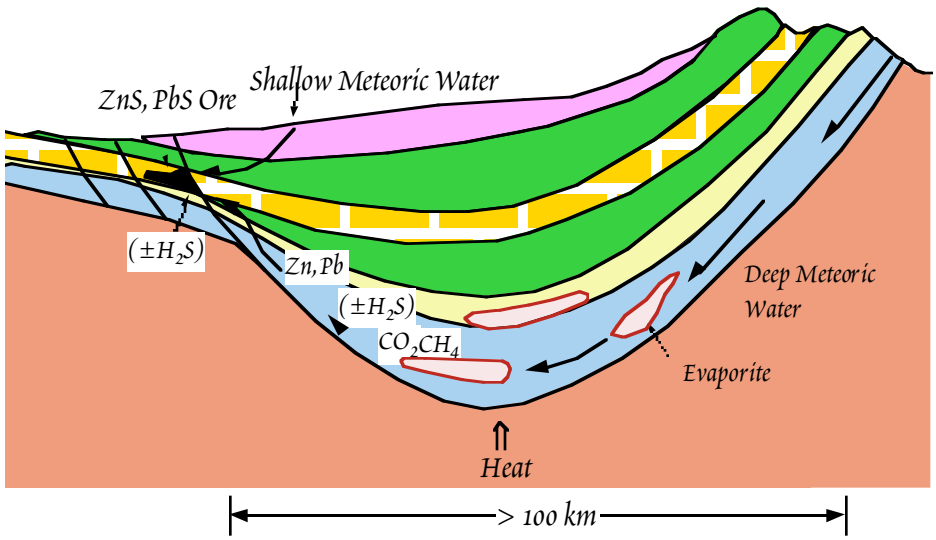


Figure 33.8. Cartoon illustrating the essential features of the genesis of Mississippi Valley sulfide ores. After Ohmoto (1986).

since time is an element in the attainment of isotopic equilibrium.

Figure 33.8 illustrates a generalized model for the genesis of Mississippi Valley type deposits. In most instances, metals and sulfur appear to have been derived distant from sedimentary units, perhaps particularly from evaporites, by hot, deep-circulating meteoric water. In North America, most of these seem to have formed during or shortly after the late Paleozoic Appalachian-Ouchita-Marathon Orogeny. Mixing of the hot saline fluids with low salinity ground water was probably the immediate cause of metal precipitation in most instances. In others, such as Pine-Point, local reduction of sulfate in the fluids to sulfide may have cause precipitation.

REFERENCES AND SUGGESTIONS FOR FURTHER READING

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