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The possible role of sulfate-reduction kinetics in the

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Abstract

As a sulfate-bearing, hydrothermal solution cools to less than about
200°C, kinetic factors prevent sulfate from entering into oxidation-reduction
reactions. Consequently, the reducing effect of H_2S (and other reduced
species) is not balanced with the oxidizing effect of $SO_4^=$ to the same extent
as at higher temperatures. The result is a lower effective Eh of the
system. This decrease in the effective Eh due to a slowing of the rate of
sulfate reduction with cooling may be the precipitation mechanism for many
types of ore deposits.

The precipitation of hematite in certain hydrothermal deposits suggests
that some hydrothermal solutions are oxidizing with respect to iron. Although
experimental evidence is limited, Rich and others (1977) believed that some
hydrothermal solutions are also oxidizing with respect to uranium and that
uranium in high-temperature solutions is probably transported in the oxidized
state and precipitated in the reduced state just as it is in low-temperature
solutions. Solubility estimates (S. B. Romberger, oral commun., 1978) also
suggest that uranium in hydrothermal solutions is in the oxidized form.
Sulfur in such solutions would be at least partially oxidized and would be
some combination of $SO_4^=$ (the most oxidized form), H_2S (which in this paper
will represent all of the most reduced forms), and possibly some sulfur
species of intermediate oxidation states. Solutions which are sufficiently
oxidizing to precipitate hematite, which are oxidizing with respect to

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uranium, and which contain partially oxidized sulfur may be involved in the transport of hydrothermal uranium.

The Schwartzwalder uranium deposit (Jefferson County, Colo.) is probably of hydrothermal origin. Paragenetic relationships (J. Paschis, oral commun., 1978) indicate that the precipitation of hematite partly preceded and partly overlapped uraninite precipitation, which in turn partly preceded and partly overlapped pyrite precipitation. Rich and others (1977) indicated that this sequence is common to many (but not all) hydrothermal uranium deposits and that this paragenetic sequence could be explained by a progressive change from oxidizing to more reducing conditions. The transport of uranium in an oxidized state followed by its precipitation in a reduced state also suggests a shift to a more reducing environment. This change could be accomplished simply by cooling the mineralizing solution through a temperature range in which sulfate reduction becomes a progressively slower process.

It is well known that, despite thermodynamic favorability, inorganic (that is, nonbiologically catalyzed) sulfate reduction is extremely sluggish at low temperatures. Indeed, the apparent cohabitation of hydrocarbons and sulfate in fluid inclusions formed during the mineralization of some Mississippi Valley-type lead-zinc deposits (Roedder, 1967) attests to the length of time that sulfate can resist reduction. It is also well known that sulfate reduction is rapid at high temperatures. Some insight into the approximate temperature at which inorganic sulfate reduction becomes sluggish is provided by the work of Malinin and Khitarov (1969). In their experiments, they used hydrogen gas to reduce (or attempt to reduce) sulfate from zinc-sulfate solutions at temperatures from 135°C to 450°C. (The pH at which these experiments were conducted is not stated, but calculations based on the initial conditions of the experiments indicate very basic solutions.) They

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showed that sulfate reduction is rapid above 275°C, questionable at 235°C, and not even detectable over a 5-day period at 200°C with hydrogen pressures as high as 185 atmospheres. Their work showed that the rate of sulfate reduction in basic solutions changes abruptly as a function of temperature in the neighborhood of 200°C. They concluded that kinetic factors make inorganic sulfate reduction unlikely under natural conditions at less than 200°C. More recent work (Igumnov, 1976) indicated that a modification of their conclusion is required. Igumnov's experiments showed that the rate of sulfate reduction is influenced by pH along with temperature; as the pH decreases, the rate of sulfate reduction increases. Unfortunately, none of Igumnov's experiments were conducted at less than 228°C and those at or near 228°C were in acidic solutions. Consequently, all of these experiments are at too high a temperature and/or too low a pH to include the effect which Malinin and Khitarov attributed to kinetic factors related to cooling. From these experiments, it appears that kinetic factors affect the rate of sulfate reduction at about 200°C in basic solutions. Under acidic conditions the reaction mechanism and consequently the kinetics of the reaction may change. Nevertheless, at some temperature between 200°C and the earth's surface temperature, $SO_4^=$ reduction becomes notoriously sluggish at any reasonable pH.

The data from Malinin and Khitarov (1969) and the knowledge that inorganic sulfate reduction is extremely sluggish at low temperatures were used to construct figure 1, which schematically presents the relationship of inorganic sulfate reduction to time and temperature in a basic solution. Diagrams like figure 1 but at a lower pH would presumably show a similar abrupt change in the rate of sulfate reduction but at a lower temperature. This change in the rate of sulfate reduction with cooling has some important geological implications which have been previously overlooked.

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As a sulfate-bearing, hydrothermal solution cools, sulfate reduction becomes progressively slower; and more oxidized sulfur in the form of sulfate is barred, due to kinetic factors, from entering into oxidation-reduction reactions. This is not to suggest that sulfate becomes less abundant or that it is unavailable for other types of reactions; only its reduction is inhibited by cooling. The increasing sluggishness of sulfate reduction with decreasing temperature prevents the maintenance of equilibrium among the sulfur species in the cooling solution. This lack of equilibrium has an important, and previously ignored, effect on the Eh of the solution. Above the time-temperature line for H_2S-$SO_4^=$ equilibrium (figure 1), the Eh of the solution is a balance of $SO_4^=$ and H_2S (along with other oxidized and reduced species) and the standard equation for the calculation of Eh applies. Below the line, equilibrium between H_2S and $SO_4^=$ is not maintained. Therefore, the standard equation, which assumes that the oxidation-reduction reactions between the species involved are reversible in the time alloted, does not apply. Below the time temperature line (figure 1), H_2S is still an active reductant, but sulfate is not completely available for oxidation due to the sluggishness at which sulfate enters oxidation-reduction reactions at these temperatures. Consequently, reduction by H_2S (and other reduced species) is not balanced with oxidation by $SO_4^=$ to the same extent as at higher temperatures. Thus, the inability of the solution to maintain equilibrium among oxidized and reduced species lowers the effective Eh of the solution. The effective Eh, after the solution cools to approximately 200°C (possibly lower in acidic solutions), is less than the equilibrium Eh. Furthermore, as cooling proceeds, sulfate reduction becomes progressively slower and the effective Eh continues to drop.
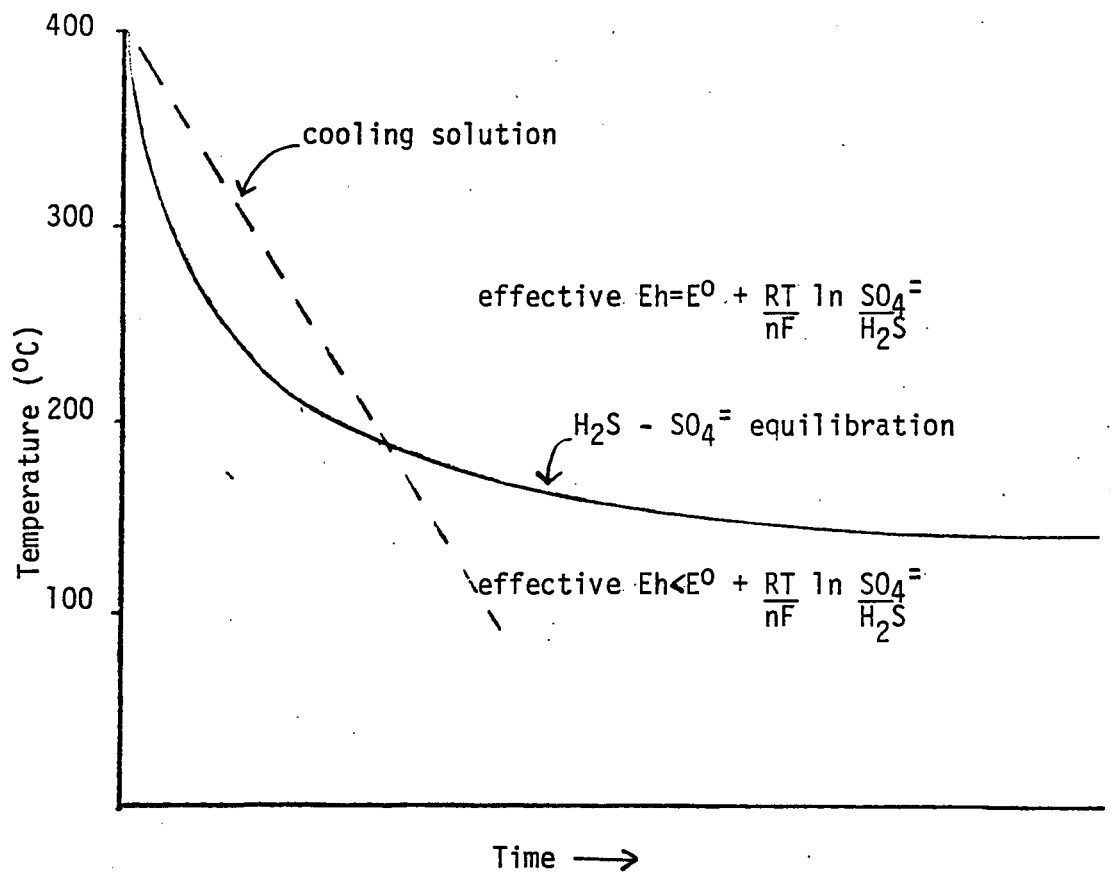
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Figure 1.--Sulfate reduction as a function of time and temperature in a basic solution.

A cooling sulfate-bearing, hydrothermal solution, as depicted by the dashed line in figure 1, would initially have an Eh determined by the relative abundance of its oxidized and reduced species. One of the reactions that would influence the Eh of such a solution is

$$H_2S + 2O_{2(g)} = SO_4^= + 2H^+ \quad K_{200°C} = 10^{67}.$$
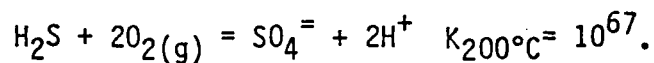
(The equilibrium constant is from Helgeson, 1969). This reaction would not be affected by the change in the kinetics of sulfate reduction with cooling until the solution cooled to a point below the $H_2S-SO_4^=$ equilibration line. (That is any point on the dashed line but below the solid line on figure 1.) Then, as the solution continues to cool at a rate faster than the rate of sulfate reduction, the above reaction proceeds to the right and sulfate is produced while H_2S and O_2 are consumed. The early precipitation of hematite in these deposits suggests that initially the oxygen fugacity of the mineralizing solutions was above the stability boundary between hematite and magnetite. Using the data in Helgeson, (1969), the hematite-magnetite boundary at 200°C can be calculated to be at an oxygen fugacity of $10^{-37.9}$. If the initial f_{O_2} is slightly above this level, then for any possible pH and $SO_4^=$ concentration, the H_2S concentration would be many orders of magnitude greater than the oxygen fugacity. Consequently, essentially all of the oxygen could be consumed without significantly changing the concentration of H_2S. By tying up oxygen in the form of $SO_4^=$, which is inactive or only partially active with respect to reduction, a drop in both the oxygen fugacity and the effective Eh is achieved. The role of sulfate in the high-temperature oxidation of uranium may be expressed by the equation

$$H_2S + 4H_2O = 4UO_2^{++} = SO_4^= + \underline{4UO_2} + 10H^+ \quad K_{200°C} = 10^{-4.5}.$$
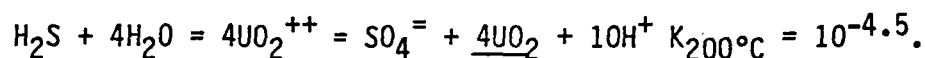
(The equilibrium constant for this reaction was calculated using the methods described in Helgeson, 1969, with free-energy data for the aqueous species from Criss and Cobble, 1964; for uraninite from Robie and others, 1978.)

Although this equation does not consider the effects of complexing or other factors on the solubility of uranium, it does show that, in an acid environment at 200°C, sulfate may oxidize uraninite. Iron in the solution may also enter into oxidation-reduction reactions with uranium; the ratio of ferrous to ferric ions, however, is dependent on the oxygen fugacity. Thus when kinetic factors inhibit sulfate reduction, the effects of three oxidizing agents, O_2, $SO_4^=$, and Fe^{+++}, are diminished while the concentration of reduced sulfur decreases only slightly and the concentration of ferrous iron increases. The progressive drop in the effective Eh concomitant with the decrease in the rate of sulfate reduction is precisely what is needed to form hydrothermal uranium deposits, and it is consistent with the drop in Eh (or effective Eh) indicated by the paragenetic sequence observed in these deposits.

Preliminary fluid-inclusion data from the Schwartzwalder mine (Rich and Barabas, 1976) indicate that the uranium minerals precipitated at a temperature at which the kinetics of sulfate reduction would affect the Eh of the solution. According to Rich and others (1977), the uranium minerals in most hydrothermal uranium deposits precipitate at less than 200°C. Only a few of the fluid-inclusion studies, which are summarized in Rich and others (1977), include temperature data for the pre-uranium stage of mineralization. Where the data are available, they suggest that the fluids did indeed cool from a temperature at which sulfate is active in oxidation-reduction reactions to a temperature at which sulfate reduction is sluggish. Thus a change of the effective Eh of these systems due to a slowing of sulfate reduction because of cooling appears inevitable.

Any solution which contains sulfate and which cools to less than about 200°C (possibly less in acidic solutions) will experience a drop in effective

Eh. Such a drop could cause the precipitation of many minerals. Thus, the hypothesis presented here may have application in the genesis of many types of mineral deposits.

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