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Close linkage of copper (and uranium) transport to diagenetic reddening of "upstream" basin sediments for sediment-hosted stratiform copper (and roll-type uranium) mineralization

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Abstract

Copper and uranium may be closely associated metals in sedimentary basins in which "upstream" sediments have been diagenetically reddened (e.g., sediment-hosted stratiform copper (SSC) deposits and roll-type uranium deposits) and the immediate hosts of mineralization are adjacent reduced sediments. The timing of leaching is closely linked to the process and timing of reddening, with descending meteoric water providing the oxygen needed for the reddening process. To leach and transport copper, the low-temperature pore solution must evolve to a brine, and importantly, its Eh must decrease to moderately positive levels (0.1 ± 0.1 V). For uranium, a simple oxidized solution is sufficient. Given the parallel Eh paths for copper and uranium and their close associations with diagenetic reddening, the dominant metal in sediment-hosted stratiform copper or roll-type uranium deposits is probably related closely to the source mineral and/or rock constituents of the reddened sediments.

Keywords: Sediment-hosted stratiform copper; Uranium; Sediment diagenesis; Redbeds; Eh–pH

1. Introduction

Redbeds are commonly cited as the source of copper for sediment-hosted stratiform copper (SSC) deposits (e.g., in the Kupferschiefer copperbelt; Oszczepalski, 1999) and of uranium for roll-type deposits (e.g., as found in the Tertiary basins of Wyoming; Adams, 1991). The basic premise is that deeply circulating, low-temperature oxidized pore solutions are capable of leaching trace amounts of metals from large volumes of immature or unstable clastic debris or minerals (e.g., mafic mineral or volcaniclastic constituents) and then those metals may be transported across redox boundaries into reduced sediments where metal deposition occurs (e.g., sediment containing organic matter and/or a sulfide precipitant) (Granger and Warren, 1969; Brown, 1971; Rose, 1976). A re-examination of the probable evolution of pore fluids during the formation of source redbeds sheds more light on the probable circulation and geochemical nature of the metalliferous pore fluids and on the timing of mineralization.

2. Significance of redbed diagenesis

The timing of redbed reddening is crucial to the understanding of metal leaching and transport from redbeds. The spatial and temporal association of reddening with mineralization is well established for uranium in roll-type deposits (Adams, 1991), but

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unfortunately this has not been the case for SSCs. For the formation of SSCs, it has been widely assumed that the prior existence of abundant redbeds in the footwall would assure an environment suitable for the leaching of metals from those redbeds by a circulating brine (Rose, 1976; Boyle et al., 1989). However, the broad Eh–pH stability field of hematite does not usefully constrain or define Eh–pH conditions that should prevail during the transport of copper in a hematite-equilibrated pore solution. Furthermore, little importance is given to the timing of the reddening that produced the hematitic pigment.

A more precise timing can be proposed from independent studies of basin sediment reddening. For example, Walker (1967, 1989) and Zielinski et al. (1983) showed petrographically that basin sediments containing immature, coarse-grained, continental clastic debris were not initially red, but rather became reddened during post-sedimentary diagenesis. The principal cause of reddening was the in situ oxidation of mafic minerals to produce a diagenetic hematitic pigment. Ryan et al. (1989) also noted that, after reddening, hematitic coatings occur on framework grains except at the points of grain-to-grain contact, indicating again that the hematitic pigment of redbeds formed during diagenesis. Walker and colleagues observed that, in their Gulf of California field area, the reddening process spanned millions of years following sedimentation. Because the source of oxygen to produce diagenetic hematitic reddening is presumed to have been the pore water, a pervasive reddening of a large volume of sediments would require an important influx of oxygen-rich water over an extended period of diagenetic time. In the present communication, the preferred footwall pore fluid is oxygen-rich meteoric water (driven, for example, by highland recharge), a concept which implies a post-sedimentary influx of oxygen that is consistent with diagenetic reddening.

3. Evolving Eh-pH conditions in deep-circulating meteoric water

If the above concepts of diagenetic reddening are combined with the observed surface and subsurface Eh–pH conditions in natural waters (e.g., Garrels, 1960), it is clear that deeply circulating oxygen-rich, meteoric water with highly positive Eh values approximating "stream" water should evolve toward low-Eh "groundwater" conditions (Fig. 1); the principal cause of this decrease in Eh would be the consumption of dissolved oxygen in the formation of iron oxyhydroxides and oxides during diagenetic reddening. At the same time, the initial slight

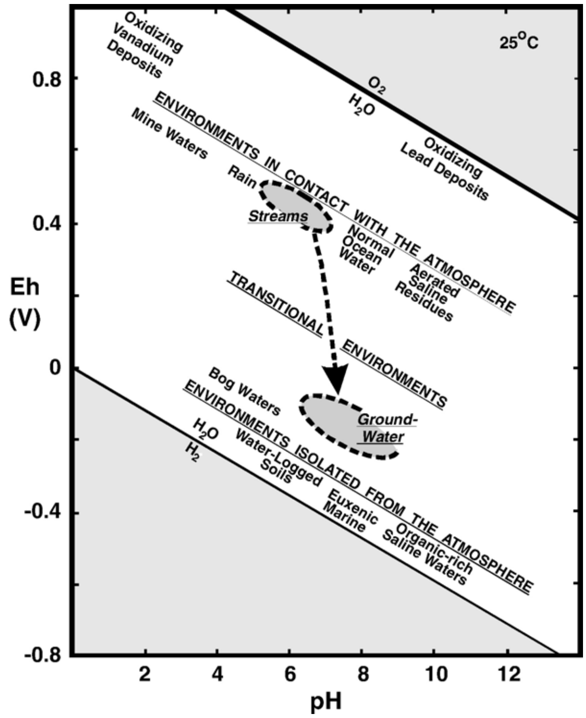

Fig. 1. Natural aqueous environments in Eh–pH space, according to Garrels (1960). As interpreted in the current communication, the upper dashed ellipse represents typical Eh–pH conditions (oxidizing and slightly acidic) of surface water ("streams") before their descent as meteoric water into basin sediments; the lower ellipse represents probable Eh–pH conditions (strongly reducing and neutral in pH) for "ground water", representative of deeply circulating meteoric water which has become oxygen-depleted as a result of reddening of the deep sediments encountered. The dashed arrow indicates the evolution of Eh–pH conditions between those two environments as a result of the diagenetic buffering of the meteoric water by the infiltrated sediment.

acidity of the "stream" water would be neutralized by reactions with silicate and/or carbonate constituents in the basin sediments. The dashed arrow of Fig. 1 illustrates the expected evolution of the meteoric water as it slowly circulates and reddens the basin sediments.

Simultaneously, this arrow, transferred to Fig. 2, defines the rather precise (and not broadly general, as once assumed) Eh–pH conditions needed to leach and transport copper deep within the basin. With this figure, Rose (1976, 1989) demonstrated that copper becomes significantly soluble as copper chloride complexes in low-temperature brines only if Eh conditions are near 0.1 ± 0.1 V, for near-neutral pH values. Importantly, those restricted conditions favorable for copper transport lie midway along the dashed arrow, i.e., where the pore brine is losing oxygen, i.e., where reddening is actively in progress. The meteoric water could become saline by encountering basin evaporates or by mixing

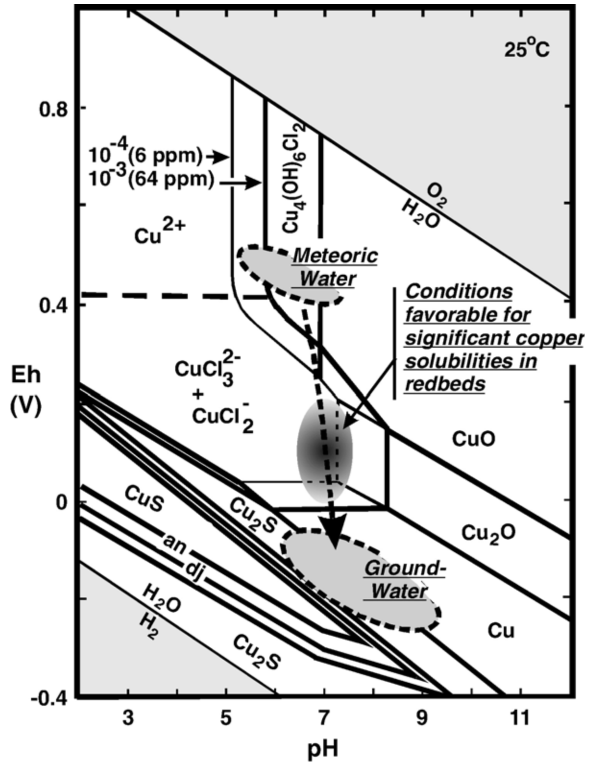

Fig. 2. Solubility of copper as cuprous chloride complexes in a low-temperature brine. The central elliptical gray area outlines Eh–pH conditions most favorable for the leaching and transport of copper (>64 ppm for Eh = +0.1 ± 0.1 V and near-neutral pH) as chloride complexes. Modified after Rose (1976, 1989) and Brown (2003).

with brines draining downward from contemporaneous surface evaporite pans.

The solubility of uranium for the formation of roll-type deposits is also dependent largely on oxidizing conditions that favor the formation of the highly soluble uranyl (U^{6+}) complexes (e.g., uranyl carbonates or oxides). Such complexes assure an important solubility for uranium for Eh values above about 0.1 ± 0.1 V at near-neutral pH. Under low-Eh conditions, uranium precipitates as uranous (U^{4+}) oxides such as pitchblende, normally in the presence of a reductant such as plant fragments. Note also that the uranyl ion does not need to form chloride complexes and it is highly soluble over a broad range of oxidizing Eh values, whereas the solubility of copper requires the formation of chloride complexes in a brine.

4. Linkage between the formation of SSC mineralization and diagenetic reddening

Copper-dominant deposits of the Kupferschiefer type are classic examples of the diagenetic overprint of cupriferous sulfides on the reduced side of redox boundaries represented by greybeds overlying redbeds. The position of the mineralization immediately adjacent to the redbeds, textures showing the replacement of syndiagenetic pyrite by cupriferous sulfides, and the zoning of sulfides with the most sulfophile metals adjacent to the redbeds are among the strong pieces of evidence for an influx of copper from the redbeds during sediment diagenesis. Fig. 2 supports a refinement of that general concept in that it indicates that copper is most soluble in a pore brine if its Eh is not highly oxidizing, but is in fact midway between the initial Eh of meteoric water and the Eh of that meteoric water after it has been partially depleted in oxygen during the diagenetic reddening of the footwall basin sediments. Thus, the timing of formation of SSC mineralization may be directly linked to the active diagenetic reddening process.

Uranium could be leached during the reddening process as well, given that it would be soluble for the high-Eh conditions characteristic of meteoric water before it loses oxygen in the reddening process. Some SSCs are in fact known for their associated uranium (e.g., the Kupferschiefer and the central African Copperbelt). Of course, if the reddened basin sediments were initially uranium-poor and copper-rich, uranium-poor SSCs should be expected.

5. Concluding comments

Once oxidizing pore waters enter an initially unoxidized sediment and reddening begins, both metals (Cu and U) could be leached and transported from the reddened portions of the basin to form “downstream” sediment-hosted stratiform copper deposits or roll-type uranium deposits where suitably reduced sediments are present. Interestingly, the delay between sedimentation and pervasive diagenetic reddening is consistent with the independently interpreted diagenetic timing of copper emplacement determined in detailed studies of most SSCs (see, for example, Boyle et al., 1989) and with the diagenetic timing of roll-type uranium deposits (Granger and Warren, 1969; Adams, 1991).

On the other hand, the diagenetic timing of reddening and metal transport is inconsistent with the proposal that the emplacement of copper results from burial compaction of the basin sediments (for details, see Garven and Freeze, 1984; Garven and Raffensperger, 1997; Swenson et al., 2004). That concept does not recognize that the footwall sediments are not initially red or that the footwall sediments cannot become redbeds until compaction abates sufficiently to allow oxidizing waters to enter and redden those sediments (Brown, 2005).

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