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B3

Re-thinking the role of redox in clastic-dominant Zn-Pb deposits

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The largest and highest value Zn reserves are hosted in carbonaceous mudstones. For many years it was considered that these mudstones (“shales”) formed by pelagic settling of organic matter in deep water settings over long time periods, in basins that were restricted from the global oceans. Basin stagnation and the development of a stratified, sulfidic (euxinic) water column then formed the trap for exhaling hydrothermal fluids. Recent geochemical and isotopic studies, however, have shown these sub-basins are more dynamic than previously thought, prompting a re-think of redox in these systems. In sub-basins that host the ore deposits in Palaeozoic (Selwyn Basin, Canada; Kuna Basin, U.S.A) and Proterozoic (McArthur Basin, Australia) systems, the spatial and paragenetic relationship between highly sulfidic conditions and mineralization is more nuanced. In these sub-basins, the water column during sedimentation was generally anoxic, but may have had oxic, sub-oxic and euxinic periods. Water column redox was controlled by changes in regional sea-level, supply of nutrients and biological activity (i.e. both global and local effects), which will have changed through time. For example, in the Proterozoic Teena sub-basin (Australia) a unit with high concentrations of diagenetic pyrite formed during a relatively short-lived period of euxinia and is found stratigraphically above the hydrothermal system; this unit can be recognised as a regional feature across the McArthur basin. Major redox boundaries can also develop during diagenesis in the pre-ore environment of major CD-type deposits. For example, recent work at the Anarraaq (Red Dog) and Macmillan Pass deposits has shown that the sulphide ore zones overprinted a diagenetic assemblage of barite and pyrite ± calcite. These phases formed when methane, generated in the sediment pile, mixed with downward diffusing seawater sulphate, resulting in the anaerobic oxidation of methane (AOM). This process is biologically mediated, and can be associated with the genesis of H₂S, which can ultimately result in stratiform pyrite formation. AOM has been suggested to be an important process in the formation of thick sequences of diagenetic, hanging-wall pyrite at Macmillan Pass, Howards Pass and in the Anarraaq deposit. At Macmillan Pass and in the Anarraaq deposit, diagenetic barite dissolution released SO₄, which was then reduced and the S was incorporated into the ore minerals. In summary, these deposits formed in sub-basins that are characterised by 1) fluctuating sea-level, 2) high biological productivity and fluxes of organic material to the seafloor and 3) high, but variable, rates of sedimentation. Such conditions are found near continental margins or in epicontinental basins with relatively shallow water. These are optimal settings for processes that generate abundant reduced S as a “trap” for the hydrothermal system, but which can also result in the formation of stratiform, barren, diagenetic pyrite; the latter poses a challenge for exploration programs. There are no known modern analogues for these mineral systems but areas like the Guaymas Basin, Baltic Sea and the South China Sea may be appropriate modern analogues for the ore deposit “trap” environment.