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An Evaluation of the Inorganic and Organic Geochemistry of the San Vicente Mississippi Valley-Type Zinc-Lead District, Central Peru: Implications for Ore Fluid Composition, Mixing Processes, and Sulfate Reduction

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Abstract

Mississippi Valley-type zinc-lead deposits and ore occurrences in the San Vicente belt are hosted in dolostones of the eastern Upper Triassic to Lower Jurassic Pucará basin, central Peru. Combined inorganic and organic geochemical data from 22 sites, including the main San Vicente deposit, minor ore occurrences, and barren localities, provide better understanding of fluid pathways and composition, ore precipitation mechanisms, Eh-pH changes during mineralization, and relationships between organic matter and ore formation. Ore-stage dark replacement dolomite and white sparry dolomite are Fe and rare earth element (REE) depleted, and Mn enriched, compared to the host dolomite. In the main deposit, they display significant negative Ce and probably Eu anomalies. Mixing of an incoming hot, slightly oxidizing, acidic brine (H_2CO_3 being the dominant dissolved carbon species), probably poor in REE and Fe, with local intraformational, alkaline, reducing waters explains the overall carbon and oxygen isotope variation and the distributions of REE and other trace elements in the different hydrothermal carbonate generations. The incoming ore fluid flowed through major aquifers, probably basal basin detrital units, with limited interaction with the carbonate host rocks. The hydrothermal carbonates show a strong regional chemical homogeneity, indicating access of the ore fluids by interconnected channelways near the ore occurrences. Negative Ce anomalies in the main deposit, that are absent at the district scale, indicate local ore-fluid chemical differences. Oxidation of both migrated and indigenous hydrocarbons by the incoming fluid provided the local reducing conditions necessary for sulfate reduction to H_2S, pyrobitumen precipitation, and reduction of Eu^{3+} to Eu^{2+}. Fe-Mn covariations, combined with the REE contents of the hydrothermal carbonates, are consistent with the mineralizing system shifting from reducing/rock-dominated to oxidizing/fluid-dominated conditions following ore deposition. Sulfate and sulfide sulfur isotopes support sulfide origin from evaporite-derived sulfate by thermochemical organic reduction; further evidence includes the presence of ^{13}C-depleted calcite cements (~–12‰ d^{13}C) as sulfate pseudomorphs, elemental sulfur, altered organic matter in the host dolomite, and isotopically heavier, late, solid bitumen. Significant alteration of the indigenous and extrinsic hydrocarbons, with absent bacterial membrane biomarkers (hopanes) is observed. The lightd^{34}S of sulfides from small mines and occurrences compared to the main deposit reflect a local contribution of isotopically light sulfur, evidence of local differences in the ore-fluid chemistry.