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An Experimental Investigation of the Role of Liquid Hydrocarbons in the Formation of Ore Deposits

Jethro Sanz-Robinson,* AE Williams-Jones, and Ichiko Sugiyama

McGill University, Montreal, QC, Canada, *e-mail, jethro.sanz-robinson@mail.mcgill.ca

Organic matter and liquid hydrocarbons are known to coexist with ore minerals in a number of major deposits around the world, including the Zunyi black shale-hosted Ni-Mo-Au-PGE deposit in Southern China and the Pine Point Pb-Zn Mississippi Valley-type deposit in the Northwest Territories of Canada. The role of liquid hydrocarbons in the genesis of ore deposits, however, has been relatively unexplored. Here we consider their role as ore fluids.

In order to test the potential of liquid hydrocarbons to act as palladium ore-fluids, palladium metal wires were dissolved in three different natural crude oils at temperatures representative of the oil window (150°, 200° and 250°C). Palladium was selected for the experiments because it is present in elevated concentrations in the organic-rich ore horizon of the Zunyi Deposit. It is also a metal of considerable economic interest that is rarely concentrated by hydrothermal processes. The measured solubility of palladium was highest in the most viscous of the three oils. Somewhat unexpectedly, however, the solubility decreased with increasing temperature. In the case of the most viscous oil, the palladium concentrations were 128, 50, and 26 ppb at 150°, 200°, and 250 °C, respectively. The palladium wires were analysed with X-ray Photoelectron Spectroscopy (XPS) after reacting them with oil in order to gain some insight into the nature of the functional groups that likely control the dissolution of palladium in liquid hydrocarbons. The XPS spectrum displays a well-defined sulfur peak at a binding energy of 163eV, which shows that palladium has an affinity for thiol complexes in liquid hydrocarbons.

An important issue for the formation of Mississippi Valley-type deposits is the mechanism responsible for the deposition of the Pb-Zn ore minerals (galena, sphalerite). In the case of the Pine Point deposit, it has been proposed that ore mineral precipitation was driven by thermochemical sulfate reduction (TSR), in which sulfate-bearing minerals reacted with hydrocarbons to produce hydrogen sulfide gas, carbonate minerals, and water. The H_2S so-produced is interpreted to have reacted with the dissolved Pb and Zn species in the ore fluid, thereby causing deposition of galena and sphalerite. We have evaluated this process experimentally for the case in which the ore fluid is a hydrocarbon liquid rather than a brine by bringing a 1,000 ppm zinc oil, composed of long-chain Zn-sulfonates, into contact with a calcite-equilibrated, 15 wt % NaCl brine. The fluid assemblage was purged with hydrogen sulfide gas so as to imitate the geochemical conditions imposed by TSR and precipitated sphalerite crystals (determined by XRD) from the Zn-rich oil, even at room temperature. The results of this experiment show that TSR is potentially a very effective means of producing Zn ore deposits from both Zn brines and oils.