

SILICA-CARBONATE HG DEPOSITS (MODEL 27c; Rytuba, 1986)

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INTRODUCTION

Environmental concerns related to mining and processing of silica-carbonate mercury deposits consist primarily of: mercury contamination of soil and water from mine waste rock and tailings (calcine), mercury vapor released during ore processing, and acid mine drainage and toxic metal release into drainage basins. Mercury released into lakes and bogs may become methylated and methylmercury (CH_3Hg^+) may become highly concentrated through biomagnification in fish and animals that consume fish. The mercury concern for humans is primarily related to consumption of contaminated fish.

See Rytuba and others (preceding model, this volume) for a discussion of global mercury budgets, cycling, and processes.

SUMMARY OF RELEVANT GEOLOGIC, GEOENVIRONMENTAL, AND GEOPHYSICAL INFORMATION

Deposit geology

Deposits are generally small (0.1 to 10 million metric tonnes of ore containing 0.2 to 0.8 weight percent mercury) and consist of cinnabar-bearing veins and veinlets and massive cinnabar replacement bodies developed within serpentinite that is hydrothermally altered to a silica-carbonate assemblage. Some orebodies are hosted in argillically altered shale and siltstone adjacent to silica-carbonate altered serpentinite. Orebodies are localized along regional faults, which cut tabular, serpentinitized ophiolite bodies, and along the base of these tabular bodies. Impermeable serpentinite channels focus the flow of hydrothermal fluids resulting in extensive silica-carbonate alteration of serpentinite for several kilometers along contacts with adjacent country rock. Large orebodies are present in hinge regions of anticlinal structures where hydrothermal fluids are trapped below impermeable shale and silica-carbonate altered serpentinite. Mercury vapor derived from organic-rich sedimentary rocks as a result of elevated regional heat flow reacts with H_2S in the gas-rich cap in anticlinal structures to form large silica-carbonate mercury deposits.

Where structural traps are absent, silica-carbonate altered serpentine contains only small mercury deposits or anomalous concentrations of mercury. Because vapor transport is an important process in these deposits, only metals that can be transported in a vapor phase are concentrated in these deposits; exceptions include metals such as nickel and chromium that are remobilized from the serpentinite by hydrothermal fluids. The hydrothermal fluid that forms these deposits is low temperature ($<120^\circ\text{C}$) and characterized by high concentrations of CO_2 - CH_4 - H_2S -petroleum (Peabody and Einaudi, 1992; Sherlock and others, 1993) that reflects its derivation from an evolved connate water (Donnelly-Nolan and others, 1993). This connate water was generated during the early stage of elevated regional heat flow (Rytuba, 1995). Very young deposits, such as those at the Elgin and Turkey Run mercury deposits, Calif., have active associated geothermal gas and hot springs.

Examples

New Almaden (Bailey and Everhart, 1964), Aetna (Yates and Hilpert, 1946), Knoxville (Sherlock and others, 1993), Culver-Baer (Peabody and Einaudi, 1992); Calif.

Spatially and (or) genetically related deposit types

These deposits are present along major structures and form during the early stage of elevated regional heat flow. They may subsequently be overprinted by higher temperature, hot-spring type gold-mercury-antimony deposits as the regional thermal anomaly reaches a maximum and near-surface volcanic activity develops. The McLaughlin, Calif., hot-spring gold-mercury deposit, which overprinted earlier formed silica-carbonate mercury deposits of the Knoxville district (Rytuba, 1995), exemplifies this process.

Potential environmental considerations

The primary geoenvironmental concerns from these deposits are potential acid mine drainage and release of mercury with the result that mercury abundances in soil, water, and (or) vegetation may be elevated above baseline concentrations established by the global atmospheric mercury flux. The potential for acid mine drainage derives from oxidation and dissolution of pyrite and marcasite in silica-carbonate altered rock that hosts the orebodies as well as from extensive areas of silica-carbonate alteration extending beyond ore zones. In some districts, altered rock extends

as much as several kilometers beyond the outer limits of ore. Carbonate minerals in the silica-carbonate alteration zone partially mitigate associated acid generation.

Direct introduction of mercury into water from these deposits is minimal since the primary ore mineral, cinnabar, is relatively insoluble and is not readily oxidized under ambient, near-surface conditions. Mine water draining deposits that contain native mercury may have elevated mercury concentrations. Introduction of mercury into the environment is primarily from release of mercury into the atmosphere when ore is retorted. When atmospheric mercury concentrations are elevated, plants uptake mercury through their leaves and mercury is concentrated in plant foliage. Wash off from plants and dry deposition of leaf litter to the forest floor is the primary route for introduction of mercury into water and soil. Methylation of mercury in bog and lake environments is enhanced by increased mercury concentrations as well as by sulfate generated during oxidation of pyrite and marcasite.

Exploration geophysics

Remote sensing techniques can identify serpentinite by infra red reflectance, thermal properties, and botanical anomalies. The sparse and unusual vegetation developed on serpentinite and its silica-carbonate altered equivalent is prominent on remote-sensing images. Aeromagnetic highs delineate serpentinite bodies and serpentinite in fault zones, particularly small deposits located along regionally extensive fault zones. Magnetic surveys may have limited utility in identification of serpentinite developed from carbonate rocks, most of which have low initial iron contents. Because cinnabar and native mercury have high specific gravity, large deposits may be detected by detailed gravity surveys. Because mercury is highly conductive, deposits that contain high concentrations of native mercury, may be associated with resistivity lows and induced polarization highs.

References

Geology: Rytuba (1986), and Rytuba and Miller (1994).

Environmental geology, geochemistry: Varekamp and Buseck (1986), Nriagu and Pacyna (1988), Lindberg and others (1992), and Hurley and others (1994).

GEOLOGIC FACTORS THAT INFLUENCE POTENTIAL ENVIRONMENTAL EFFECTS

Deposit size

Deposits are typically small and contain less than 10 million metric tonnes; many deposits are less than 0.1 million metric tonnes. Deposits are clustered along major structures and because silica-carbonate alteration typically extends for several kilometers beyond deposits, areas significantly larger than the ore deposit site may be impacted. Most deposits have been mined by underground methods. Visual impact is relatively limited at rare open pit mines because tailings piles, except those associated with the largest deposits, are small.

Host rocks

Shale and siltstone are locally important host rocks where they form impermeable cap rocks in anticlinal structures.

Surrounding geologic terrane

Deposits are primarily localized along the base of serpentinitized ophiolite bodies, serpentinite diapirs, and serpentinite tectonically emplaced along regional fault zones. Surrounding terranes typically do not contain carbonate rocks nor alteration assemblages with significant acid-buffering capacity. Most deposits are Tertiary, formed near the surface, and have surficial expressions of geothermal activity such as gas vents and hot springs. As a result, elevated abundances of mercury may be present in soil and sediment deposited at the time of ore deposition.

Wall-rock alteration

The silica-carbonate assemblage consists of a central core of quartz + opal + chalcedony + magnesite + dolomite + calcite + marcasite + pyrite that grades outward into a magnesite + magnetite + calcite + dolomite assemblage and then finally into serpentinite + magnetite. Pyrite and marcasite in the sulfidized central core of the alteration assemblage comprise from about 2 to 10 volume percent and are the only important acid generating sulfide minerals present. The carbonate assemblage may partially buffer acid generated by sulfide mineral oxidation. In the upper part of these deposits an advanced argillic alteration zone that consists of kaolinite + alunite + cristobalite + sulfur may be present; most often this alteration assemblage has been removed by erosion. Pyrite and marcasite in this alteration assemblage may be oxidized and contribute to acid mine drainage generation.

Nature of ore

Ore bodies are variable in character. Most consist of tabular to irregular replacement masses but discrete veins and breccia bodies are common; more rarely, stockwork veins are present. Repeated post ore movement along controlling fault zones causes development of blocks (phacoids) of very high grade cinnabar within fault gouge. In vein and breccia ore bodies, marcasite and more rarely stibnite are present. Most replacement ore bodies are monomineralic; they consist of cinnabar and minor native mercury.

Deposit trace element geochemistry

Within the ore zone, trace elements, in decreasing order of importance, include 0.1 to 1,000 ppm antimony, 10 to 3,000 ppm nickel, 600 to 5,000 ppm chromium, 2 to 100 ppm tungsten, and 1 to 12 ppm thallium. Arsenic abundances are typically very low, less than 2 ppm, in these deposits. Base metal concentrations, less than 10 ppm lead, less than 100 ppm copper, and less than 50 ppm zinc, are similarly low.

Ore and gangue mineralogy and zonation

Primary ore minerals are cinnabar and native mercury and more rarely in the oxidized, near surface environments more soluble mercury oxychloride, sulfate, and silicate minerals are present. Pyrite and marcasite are the main gangue minerals.

Mineral characteristics

Most cinnabar, about 0.2 mm, is very fine grained in replacement ore bodies but in rare cases is coarser grained in veins. Pyrite and marcasite are coarser grained and typically range from 0.5 to 5 mm.

Secondary mineralogy

Near surface exposures of deposits and alteration zones expose pyrite and marcasite to weathering, which results in formation of limonite and other iron oxide minerals. Cinnabar and native mercury are not typically affected by weathering process because of their low solubilities under ambient conditions. However, under extreme oxidizing and acid pH conditions mercury sulfate and oxychloride minerals may form as coatings on surface exposures. These yellow and green minerals are photosensitive and rapidly turn black when exposed to the sun. As a result, these minerals can be easily misidentified as manganese oxide minerals. Small amounts of mercury silicate and chromate minerals may also be present; these, along with mercury sulfate and oxychloride minerals, are more readily solubilized than cinnabar and native mercury.

Topography, physiography

Ore bodies are associated with large zones of silica-carbonate alteration that typically form resistant ridges with sparse vegetation. Adjacent serpentinite also has sparse vegetation. Altered serpentinite has a distinctive red-brown color due to the presence of iron oxide minerals. Deposits are generally exposed at or near the surface and are along regional structures that may extend for tens of kilometers.

Hydrology

Increased hydrologic head during wet periods results in ground water flow along the regional structures that control the location of silica-carbonate alteration and ore deposits. Adjacent serpentinite bodies serve as impermeable aquitards that focus ground water flow along contacts between altered and fresh serpentinite.

Mining and milling methods

Individual deposits are generally small but in most cases, several deposits are localized along the same regional fault zone. Most mines are underground operations in which high grade pockets and ore shoots have been exploited by open stope mining. Waste rock, only a small fraction of which is brought to the surface, is used to backfill underground workings. High grade ore zones have sharp contacts with low grade ore. Because low grade ore is only rarely mined, stopes tend to follow the outline of high grade ore bodies and are irregular in shape. Near-surface ore bodies have been mined by open pit methods.

See Rytuba and Klein (this volume) for a discussion of methods used to extract mercury from ore.

Mercury has been typically bottled in 76 pound flasks at the retort or furnace site. Inefficiencies in this process have caused mercury contamination of mill sites and calcines. More recently the metric ton flask has been used.

ENVIRONMENTAL SIGNATURES

Drainage signatures

Acid mine water has a pH of 1 to 4 and precipitates amorphous iron hydroxide that selectively absorbs mercury from the water; these precipitates may contain as much as 20 ppm mercury. Elevated concentrations of as much as 670 ppm nickel and 200 ppm chromium, may also be present in these precipitates. Acid mine water may contain 100 to 1,000 mg/l iron and 0.1 to several µg/l mercury. Acid mine water draining deposits that include stibnite may contain 1 to 10 mg/l antimony but base-metal concentrations as well as abundances of chemical precipitates are low.

In active geothermal water associated with recently formed deposits, very high tungsten concentrations range from 1 to 10 mg/l; in stream water as much as several kilometers downstream from deposits, elevated tungsten concentrations range from 260 to 680 µg/l (Rytuba and Miller, 1994). Mercury and iron concentrations, 0.2 to 2.7 µg/l and 0.05 to 1.4 mg/l, respectively, in unfiltered stream water are usually higher than in filtered water. However, these abundances return to baseline concentrations, 0.2 µg/l mercury and 500 µg/l iron, within several kilometers of mercury deposits and (or) geothermal sites (Janik and others, 1994).

Metal mobility from solid mine wastes

Sulfide minerals in ore are oxidized during roasting, which causes calcines to have a distinctive red color attributable to contained iron oxide minerals. In this high Eh environment iron is readily leachable and associated metals such as antimony, arsenic, and thallium may be mobilized as well. Mercury in calcine is native mercury and a variety of mercury oxychloride and sulfate minerals that are readily solubilized.

Soil, sediment signatures prior to mining

Mercury abundances in soil range from 10 to 100 ppb and may reach several ppm directly over exposed orebodies. Stream sediment samples from drainages in mineralized areas contain 2 to 200 ppm mercury. Stream sediment samples from drainage basins with young deposits and active geothermal systems contain 0.3 to 141 ppm mercury, 1.2 to 17.4 ppm antimony, and 8.3 to 20.3 ppm arsenic (Janik and others, 1994). Heavy mineral concentrates from streams that drain areas near deposits contain elevated metal concentrations, including as much as 4,400 ppm mercury, 10,000 ppm barium, 7,000 ppm chromium, 150 ppm copper, 500 ppm nickel, 200 ppm lead, 300 ppm tin, and 500 ppm zinc.

Potential environmental concerns associated with mineral processing

In tailings and waste dumps pyrite and marcasite are susceptible to oxidation and acid water may develop.

Mine tailings, commonly termed calcine, consist of the rock aggregate generated after mercury ore has been processed by roasting in a retort or furnace to remove mercury. Mercury recovery during retorting ranges from 90 to 95 percent, which results in calcine that may contain from 5 to 10 percent of the mercury originally present in the ore. During roasting, pyrite and marcasite are oxidized to iron oxide minerals, which gives calcine dumps their characteristic red color. The amount of mercury removed from small mines is extremely variable so that calcines associated with these operations may contain significant mercury.

Mercury abundances in calcine range from 10 to 1,500 ppm depending on the efficiency of the retorts used. Abundances of other trace metals, such as nickel and chromium, originally present in elevated concentration in ore, range from 100 to 5,000 ppm. Calcine adjacent to condensing pipes where mercury was recovered and bottled in flasks may have mercury contents of as much as several thousand ppm because mercury was commonly spilled in this area and absorbed by iron oxide coatings on calcine fragments.

Calcine was commonly used as road metal on unpaved roads surrounding mercury districts. This may be a problem in the case of calcine that was contaminated by mercury during the recovery process. Introduction of tailings particles into creeks is a concern because native mercury and mercury oxychloride and sulfate minerals can be methylated in aqueous environments. The fine grained nature of the calcine also increases water turbidity.

Smelter signatures

Several different types of retorts and condensing pipes have been used to recover mercury. These range from relatively small, inefficient single and double pipe retorts at small mines to very efficient Herschhoff type retorts at larger mines. In most cases prior to the 1970s, significant amounts of elemental mercury vapor and ionic mercury complexed as a chloride or sulfate were vented to the atmosphere. Elevated ambient air concentrations of mercury result in increased leaf uptake of mercury by plants downwind from retort sites and in elevated mercury concentrations in soil through wash off and litter fall to the forest floor. SO₂ was also released to the atmosphere from less efficient mine operations. These releases may increase sulfate and acid concentrations in water, which in

turn enhance mercury methylation.

Climate effects on environmental signatures

In wet climates oxidation and dissolution of pyrite and marcasite increase the possibility of acid mine drainage. Formation of sulfate minerals and derivation of organic carbon from plants enhances mercury methylation by sulfate reducing bacteria in wet climates. In high temperature, dry climates, soil gas emission of elemental mercury is important; this process may increase the area affected by elevated mercury if adjacent plant communities uptake mercury in their leaves.

Geoenvironmental geophysics

Geophysical methods can be used to identify contaminated water and soil around mining operations. Electromagnetic, direct current resistivity, and induced polarization surveys can detect and monitor conductive acidic groundwater plumes resulting from oxidation and dissolution of pyrite and marcasite in altered rocks that host mercury deposits. Hot spots in tailing piles that result from ongoing redox reactions can be monitored using self potential methods. Ground penetrating radar can detect near-surface acidic water.

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