

ALMADEN HG DEPOSITS (MODEL 27b; Rytuba, 1986)

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INTRODUCTION

Environmental concerns related to mining and processing Almaden-type mercury deposits consist primarily of: mercury contamination of soil and plants from mine smelters because of mercury vapor and dust released during ore processing, mercury degassing from contaminated soil at mine sites and from undisturbed deposits, and potential for acid mine drainage and toxic metal release into drainage basins. These deposits typically are extremely high grade; central parts of deposits can contain more than 20 weight percent mercury. As a result, extremely high concentrations of mercury are present in residual soil where these deposits are exposed at the surface. Mercury released into creeks and rivers may contaminate lakes, estuaries, and bogs; subsequently methylmercury (CH_3Hg^+) may form and become highly concentrated through biomagnification in fish, and eventually in any animals that consume fish. For humans, most toxicity concerns related to mercury pertain to consumption of contaminated fish. However, ambient mercury vapor pressure in underground mercury mines may allow direct mercury ingestion through breathing. Also, direct ingestion of mercury contaminated soil can pose a health threat among children.

The global atmospheric mercury cycle contributes mercury to drainage basins and lakes through both wet and dry depositional processes that are mediated by leaf uptake of mercury by plants (Mason and others, 1994). The potential flux of mercury to the environment from mercury deposits and mine sites must be evaluated in the context of its flux from the global mercury atmospheric cycle. The primary natural sources of mercury to the atmosphere include the oceans, soil degassing, volcanoes, and geothermal systems (Varekamp and Buseck, 1986; Mason and others, 1994). Anthropogenic sources of mercury to the atmosphere are primarily from coal combustion, waste incineration, and smelters (Nriagu and Pacyna, 1988). Since the beginning of industrialization in about 1850, the atmospheric mercury concentration increased until about 1970, and then has decreased moderately. The mercury increase is reflected in the sedimentary record of lakes, estuaries, and bogs; recently deposited sediment from all these environments record an increase in mercury concentration of about two to five times over baseline mercury concentrations established prior to industrialization (for example see, Verta and others, 1990; and Hurley and others, 1994).

Mercury concentrations in soil associated with Almaden-type deposits can be extremely high and elevated summer temperatures can increase rock and soil degassing rates. Native mercury contained in ore also enhances degassing. Plants on or adjacent to these deposits may play an important role in mediating mercury vapor flux. Mercury is taken up by plants primarily through leaves, rather than through the root system, and fixed at the site of plant uptake. Thus, high ambient-air mercury concentrations cause plants to uptake and concentrate mercury in their leaves, and conversely, low ambient air mercury concentrations cause plants to give off mercury through their leaves (Lindberg and others, 1992). In mine areas where ambient air concentrations of mercury are elevated, due either to roasting mercury ore or from natural degassing of mercury from either contaminated (see Lindberg and others, 1995) or naturally anomalous soil (Lindberg and others, 1979), plant communities concentrate mercury in their leaves. Wash off and litter fall from these plant communities may redistribute mercury into creeks and lakes.

The formation of methylmercury is favored by the presence of ionic mercury, low pH, and high dissolved organic carbon and sulfate. Mercury methylation is a co-metabolic reaction; sulfate reducing bacteria are the most important mediators in the biotic methylation process (Campeau and Bartha, 1985; Summers, 1986). Acid mine water that has a high sulfate concentration may develop at a mercury mine site or at a naturally oxidizing mercury ore deposit. Introduction of acid water to a bog or lake may enhance methylation. Nearly all methylmercury is formed in lakes where most of it resides in fish. In lakes and estuaries, detrital particles such as clays capture Hg^{++} from the water by absorption; sedimentation of these particles inhibits methylation. Similarly, tailings that enter surface water may aid methylmercury removal from the water column and enhance sequestration in sediment.

SUMMARY OF RELEVANT GEOLOGIC, GEOENVIRONMENTAL, AND GEOPHYSICAL INFORMATION

Deposit geology

Deposits are generally large (10 to 100 million metric tonnes of ore containing about 2 to 20 weight percent Hg); the Almaden, Spain, deposit is the single largest mercury deposit in the world and it has been mined continuously for more than 2,000 years. The deposits essentially contain only mercury as an economically recoverable metal, and consist of massive cinnabar and native mercury replacement bodies hosted in quartzite and tuff breccias, submarine

mafic to intermediate composition pyroclastic flows, mafic dikes, and organic-rich black shales. Cinnabar-bearing veins and veinlets are present primarily as gash fractures developed during regional metamorphism of these deposits (Rytuba and others, 1988). Native mercury is present in all deposits and is the primary mineral in deposits, such as in the Las Cuevas deposit, hosted in submarine tuffs. All of these deposits are spatially associated with mafic submarine vent complexes that consist of mafic dikes and sills, oval craters typically with dimensions of 300 m by 150 m (Hernandez, 1985), and submarine calderas, such as at the Las Cuevas deposit (Rytuba and others, 1988). Megabreccia composed of black shale blocks, as much as 100 m in maximum dimension and contained in a tuff matrix, are interstratified with caldera filling lithic tuffs. Tuff breccias that fill the craters consist primarily of sedimentary wall rocks with lesser amounts of ultramafic and plutonic igneous clasts. Juvenile magma clasts within the craters are typically alkali basalt. Replacement deposits hosted in quartzite consist of stratiform zones of cross cutting mineralized rock composed of cinnabar, native mercury, pyrite, calcite, and quartz. Ore zone grades and thicknesses are highest near crater margins and decrease systematically away from crater margins.

Examples

Almaden, El Entredicho, Nueva Concepcion, Las Cuevas; Spain (Hernandez, 1985; Saupe, 1990).

Spatially and (or) genetically related deposit types

These deposits form in the early phase of near-craton, submarine basin rifting; they are closely associated with mafic, submarine vent complexes. Although back-arc volcanogenic massive sulfide deposits form in this geologic environment, none have been identified in areas adjacent to these deposits.

Potential environmental considerations

The primary geoenvironmental concerns associated with these deposits are the potential for mercury vapor release from furnaces and retorts as well as from soil and rock degassing; mercury abundances in soil, water, and vegetation may be elevated above baseline concentrations established by the global atmospheric mercury flux. Acid mine drainage may result from oxidation and dissolution of pyrite in altered shale and pyroclastic rocks that host ore. Carbonate minerals are minor gash fracture fillings and have limited acid drainage buffering capacity.

Direct introduction of mercury from these deposits into ground water may result from native mercury oxidation and dissolution but mercury from cinnabar is minor because of cinnabar's low solubility and weak oxidation under ambient conditions. Introduction of mercury into the environment primarily results from its release into the atmosphere during ore roasting and from soil and rock degassing at mine sites and undisturbed deposits. When high mercury concentrations prevail, it is efficiently absorbed from the atmosphere by plants through their leaves; mercury is concentrated in plant foliage and root uptake is minor. Wash off from plants and dry deposition of leaf litter to the forest floor are the primary routes for mercury introduction into water and soil. Methylation of mercury in bog and lake environments is enhanced by increased mercury concentrations as well as by sulfate that may be generated during pyrite oxidation.

Exploration geophysics

No geophysical investigations of this deposit type are known, however certain inferences may be drawn from surveys of deposits with similar geologic relations. Aeromagnetic anomalies may delineate mafic vent complexes with which these deposits are spatially associated. Remote sensing images can be used to identify limonite and iron oxide minerals that develop due to pyrite oxidation. Cinnabar is resistive but native mercury is highly conductive; both have very high specific gravity, near 8 gm/cm³. Almaden type deposits can probably be identified by detailed gravity surveys because they are large and contain elevated abundances of high density mercury minerals. Resistivity lows and induced polarization highs are probably associated with these deposits because of their elevated native mercury abundances. Resistivity surveys may aid identification of cinnabar deposits because of the association between conductive carbonaceous rock (black shale) and these deposits. Regional airborne or ground electrical surveys may help delineate the extent of conductive, shallow-marine-basin black shale and altered volcanic rocks that host these deposits. Induced polarization traverses may further refine the distribution of rocks that contain abundant pyrite.

References

Rytuba (1986), Saupe (1990), and Mason and others (1994).

GEOLOGIC FACTORS THAT INFLUENCE POTENTIAL ENVIRONMENTAL EFFECTS

Deposit size

The deposits are typically large and contain more than 10 million metric tonnes. The deposits are clustered in stratigraphic units deposited within the same submarine basin. Most deposits have been mined by underground methods but one deposit is mined by open pit methods; the visual impact related to mining these deposits is relatively limited except for large associated tailings (calcine) piles.

Host rocks

Most deposits are hosted in quartzite and mafic to intermediate composition pyroclastic and intrusive rocks. Organic rich shale and siltstone are locally important host rocks, especially where shale is in contact with pyroclastic rocks.

Surrounding geologic terrane

Surrounding terranes typically do not contain carbonate rocks or other acid buffering alteration assemblages.

Wall-rock alteration

Pyroclastic and intrusive rocks are argillically and carbonate altered. Ultramafic xenoliths within sills and dikes are altered to carbonate-bearing mineral assemblages. Strontium isotopes indicate that intrusive and volcanic rocks have interacted extensively with sea water. Quartzite displays secondary overgrowths of quartz although silicification is not pervasive. Pyrite comprises from about 2 to 6 volume percent of pyroclastic rocks. Carbonate vein assemblages are present primarily in gash fractures.

Nature of ore

Most orebodies are massive replacement bodies that are stratiform in quartzite and form more irregular replacement orebodies in pyroclastic and intrusive rocks. Orebodies in mafic dikes and sills consist of tabular to irregular replacement masses localized at the terminations of dikes or along the upper parts of sills. Very high grade ore composed of cinnabar commonly is present at contacts between black shale and pyroclastic and intrusive rocks. Where black shale clasts are absent, native mercury is the dominant ore mineral in pyroclastic-hosted orebodies. In quartzite-hosted orebodies, ore is present near the top of the units. Discrete veins and breccia bodies are present, but most veins fill gash fractures developed during low grade regional metamorphism.

Deposit trace element geochemistry

In addition to mercury, the trace element geochemistry of the ore is very simple. Of the common ore-related elements, only iron is present in anomalous amounts; abundances of metals typically associated with mercury, 1 to 13 ppm arsenic and 0.2 to 1.6 ppm antimony, are low. In quartzite-hosted orebodies, light rare earth element abundances are elevated as a consequence of the primary trace element content of heavy minerals in quartzite. In volcanic-hosted deposits localized within caldera structures, base-metal concentrations, including as much as 50 ppm lead and as much as 80 ppm copper, are somewhat anomalous. Zinc abundances, which are typically less than 50 ppm in sediment-hosted orebodies, are as high as 4,600 ppm in volcanic-hosted deposits.

Ore and gangue mineralogy and zonation

Primary ore minerals are cinnabar and native mercury; native mercury is more common in orebodies hosted by pyroclastic rocks. Veins of barite and native mercury are peripheral to the ore zone. Volcanic and intrusive rocks are altered to a carbonate assemblage. Stratiform pyrite beds are above quartzite-hosted ore.

Mineral characteristics

Cinnabar is generally fine grained, about 0.2 to 6 mm, in replacement orebodies but is typically coarser grained, as much as 2 cm, in gash fractures. Mercury globules as much as several millimeters wide are present in host rocks; during mining operations, these may become concentrated in globules as much as several centimeters wide. Pyrite ranges from 1 to 10 mm in maximum dimension.

Secondary mineralogy

In near-surface parts of deposits, pyrite is exposed to weathering, which results in limonite and iron oxide formation. Cinnabar and native mercury are not affected by weathering process because of their low solubilities under ambient conditions and reducing conditions associated with the black shale.

Topography, physiography

Where cut by volcanic craters, orebodies are associated with resistant ledges of quartzite. Where quartzite ledges are interrupted by craters, the area of the craters is topographically more subdued.

Hydrology

Increase in hydrologic head during wet periods results in ground water fluid flow along regional structures that control the location of craters and dikes.

Mining and milling methods

Individual deposits are generally large and most mines are underground operations involving open-stope mining of high grade, stratiform orebodies. Waste rock, only a small fraction of which is brought to the surface, is used to back fill underground workings. High grade ore zones have sharp contacts with low grade ore. High grade orebodies exposed in the near-surface have been mined by open pit methods.

Ore has been processed in large retorts in the past, but most recent operations use several types of furnaces. Condensing systems that cool vapor from the furnaces in order to separate liquid mercury from other stack gases are complex multiple-pipe condensers. The furnaces include Herreshoff and rotary furnaces. Rotary furnaces consist of a rotating, inclined iron cylinder into which ore is continuously fed and from which calcine is removed. Mercury vapor and other gases are drawn from the cylinder into a condenser. The Herreshoff furnace consists of a series of circular hearths into which ore is continuously fed and mechanically advanced to successive higher temperature hearths. Calcine is removed from the base and gases are fed through a dust collector and then a condensing system. Calcium carbonate may be used to aid mechanical coagulation of finely condensed mercury particles from soot on a steam table.

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

Data that characterize drainages have not been published. The presence of associated acid mine drainage has not yet been reported.

Metal mobility from solid mine wastes

Sulfide minerals in ore are oxidized during roasting so that calcines have a distinctive red color related to iron oxide minerals in the calcine. In this highly oxidizing environment, iron is readily leachable. Mercury in calcine is present as native mercury as well as a variety of mercury oxychloride and sulfate minerals that are readily solubilized.

Soil, sediment signatures prior to mining

Mercury abundances in soil range from one to several thousand ppm and may reach several thousand ppm directly over exposed orebodies. Other trace metal abundances are not anomalous in soil, except those of zirconium, which range from 200 to greater than 1,000 ppm, and nickel, which range from 50 to 150 ppm. Base-metal concentrations in soil, including <100 ppm lead and <50 ppm copper and zinc, are low. Sediment signatures prior to mining have not been published.

Potential environmental concerns associated with mineral processing

Mine tailings, commonly termed calcine, consist of the rock aggregate generated after the mercury ore has been processed by roasting in a retort or furnace to remove mercury. Mercury recovery during ore retorting ranges from 90 to 95 percent, which results in calcine that may contain 5 to 10 percent of the mercury originally present in the ore. During the roasting process, pyrite is oxidized to iron oxide minerals giving the calcine dumps their characteristic red color.

Mercury abundances in calcine ranges from ten to several thousand ppm depending on the efficiency of the retorts and furnaces used. Calcine adjacent to the condensing pipes where mercury was recovered and bottled into flasks may have very high mercury content because mercury was commonly spilled in this area and was absorbed by iron oxide coatings on calcine fragments. Calcine in these areas may contain as much as several thousand ppm mercury.

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 may be oxidized and along with mercury oxychloride and sulfate minerals can be methylated in aqueous environments. The fine grained nature of calcine also increases water turbidity.

Smelter signatures

Large retorts and more efficient rotary and Herschoff type furnaces have been used to process ore from these deposits. Prior to the 1970s, significant amounts of elemental mercury as vapor, ionic mercury complexed as a chloride or sulfate, and mercury adhering to particulates were vented to the atmosphere. Elevated ambient air concentrations of mercury result in increased wet and dry deposition of mercury and leaf uptake by plants downwind from smelter sites. These processes result in elevated mercury concentrations in soil, water, and, through wash off and litter fall, to the forest floor. SO₂ released to the atmosphere during ore roasting may increase acid and sulfate concentrations in water, which in turn enhance mercury methylation.

Climate effects on environmental signatures

In wet climates conducive to plant growth, mercury degassing from soil is minimized by plant leaf mercury uptake. However, oxidation and dissolution of pyrite increase the potential for acid mine drainage generation in wet climates. Formation of sulfate minerals and derivation of organic carbon from plants enhance mercury methylation by sulfate reducing bacteria in wet climates. In dry climates, soil gas emission of elemental mercury may be important especially during high temperature seasons; this process may increase the area affected by elevated mercury if adjacent plant communities uptake mercury in their leaves through both wet and dry deposition of mercury.

Geoenvironmental geophysics

Pyrite oxidation and dissolution, which can result from weathering Almaden type mercury deposits, may produce conductive acid water that can be detected using electromagnetic, direct current resistivity, and probably induced polarization methods. Ground penetrating radar can detect acid ground water at depths of less than a few meters. Information concerning the change of fluid properties, such as resistivity, with varying concentrations of mercury ions or compounds is not available. Similarly, remote sensing reflectance variations of vegetated areas in which mercury uptake has been variable has not been documented; however, these subjects should be investigated.

REFERENCES CITED

- Compeau, G.C., and Bartha, R., 1985, Sulfate reducing bacteria: principal methylators of mercury in anoxic estuarine sediment: *Applied Environmental Microbiology*, v. 50, p. 498-502.
- Hernandez, A., 1985, Estructura y genesis de los yacimientos de mercurio de la zona de Almaden: Unpub. resumen de tesis doctoral, University Salamanca, 64 p.
- Hurley, J.P., Krabbenhoft, D.P., Babiarz, C.L., and Andren, A.W., 1994, Cycling of mercury across the sediment-water interface in seepage lakes, *in* Baker, A., ed., *Environmental chemistry of lakes and reservoirs*: American Chemical Society Series No. 237, p. 425-449.
- Lindberg, S.E., Jackson, D.R., Huckabee, J.W., Janzen, S.A., Levin, M.J., and Lund, J.R., 1979, Atmospheric emission and plant uptake of mercury from agricultural soils near the Almaden mercury mine: *Journal of Environmental Quality*, v. 8, p. 572-578.
- Lindberg, S.E., Kim, K., Meyers, T.P., and Owens, J.G., 1995, Micrometeorological gradient approach for quantifying air/surface exchange of mercury vapor: tests over contaminated soils: *Environmental Science and Technology*, v. 29, no. 1, p. 126-135.
- Lindberg, S.E., Meyers, T.P., Taylor, G.E., Turner, R.R., and Schroeder, W.H., 1992, Atmosphere-surface exchange of mercury in a forest: results of modeling and gradient approaches: *Journal of Geophysical Research*, v. 97, no. D2, p. 2519-2528.
- Mason, R.P., Fitzgerald, W.F., and Morel, F.M.M., 1994, The biogeochemical cycling of elemental mercury: Anthropogenic influences: *Geochimica et Cosmochimica Acta*, v. 58, no. 15, p. 3191-3198.
- Nriagu, J.O., and Pacyna, J.M., 1988, Quantitative assessment of worldwide contamination of air, water and soils by trace metals: *Nature*, v. 333, p. 134-139.
- Rytuba, J.J., 1986, Descriptive model of Almaden Hg, *in* Cox, D.P., and Singer, D.A., eds., *Mineral deposit models*: U.S. Geological Survey Bulletin 1693, p. 180.

- Rytuba, J.J., Rye, R.O., Hernandez, A.M., Deen, J.A., and Arribas, A., Sr., 1988, Genesis of Almaden-type mercury deposits: Almaden, Spain, 28th International Geologic Congress Abstracts with Program, p. 2-741.
- Saupe, Francis, 1990, Geology of the Almaden mercury deposit, Province of Ciudad Real, Spain: *Economic Geology*, v. 85, p. 482-510.
- Summers, A. O., 1986, Organization, expression, and evolution of genes for mercury resistance: *Annual Reviews of Microbiology*, v. 40, p. 607-634.
- Varekamp, J.C., and Buseck, P.R., 1986, Global mercury flux from volcanic and geothermal sources: *Applied Geochemistry*, v. 1, p. 65-73.
- Verta, M., Mannio, J., Iivonen, P., Hirvi, J.P., Jarvinen, O., and Piepponen, S., 1990, Trace metals in Finnish headwater lakes-effects of acidification and airborne load, *in* Kauppi and others, eds., *Acidification of Finland*, p. 883-908.