

Thermally Speciated Mercury in Mineral Exploration



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Abstract

The high fugacity of elemental mercury and its various mobile compounds and complexes, make it well suited for soil gas surveys in search of blind and deeply buried mineralization.

Mercury is easily oxidized and reduced by the influences of both inorganic and organic processes. These create suites of mercury species that are part of the total mercury flux. By comparing the various mercury species that are detected in soils overlying deep zones of metal enrichment, vectoring strategies that relate near-surface to deep ore can be explored.

Novel fingerprint methods using stepped thermal desorption reveal differences between naturally occurring and anthropogenic sources of mercury (Beister et al, 1999). These methods focus on data derived from the thermal desorption of soil above 100°C. However, detectable mercury is released below 100°C, and this mercury seems to be related to emanations from deeply buried mineralization. These low reduction enthalpies suggest that extremely volatile mercury compounds, possibly organo-Hg complexes, are responsible for the anomalies that indicate the deepest ore.

Introduction

Many base and precious metal ores are associated with mineralizing events that include the hydrothermal circulation of saline solutions in and around metallic deposits. Mercury is one of a suite of toxic metals that is associated with this contemporaneous and late hydrothermal activity. As the solutions cool and the toxic metals are deposited, a spatial relationship is created where mercury and the other toxics can be used as geochemical pathfinders in the search for these ores and geothermal occurrences.

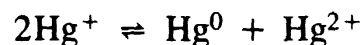
The evolution of mercury vapor from deeply buried ground water/mineral interaction results in a vertically migrating flux that probably occurs as a mixture of various mercury species. Depending on the changing conditions of the oxidation-reduction potential of the rock/soil column,

one or several species of mercury may be responsible for its vertical and lateral dispersion at any given time. For instance, mercury can exist as a relatively mobile chloride, as a less mobile sulfate, or as a refractory sulfide. The mobilities of these various mercury species are also affected by the composition of the rock / soil column. For example, the bonds between mercuric chloride and clay are stronger than the bonds between native mercury and iron oxide, but weaker than the bonds between native mercury and humic acid.

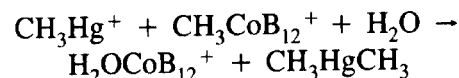
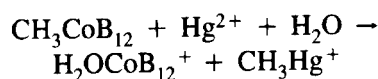
Controlled thermal desorption of soils and sediment is not a new concept in mineral exploration. McNerny and Buseck (1977) used it as they improved methods related to their Jerome Mercury Detector. Kromer et al. (1981) did several studies over two lead-zinc vein deposits where they determined mercury speciation by differential thermal analysis (DTA). They were able to demonstrate that various mercury species evolve from an oxidizing vein deposit, but were unable to show that speciation analysis improves the likelihood of finding deep (>12 m) mineralization. Maciolek and Jones (1988) also used DTA to reveal concentric mercury halos lying over precious metal deposits. Their work drew significantly from Russian literature (circa 1980), where mercury desorption and sublimation curves are discussed for various deposits through temperatures ranging from 200°C to 600°C.

CHEMICAL SPECIATION

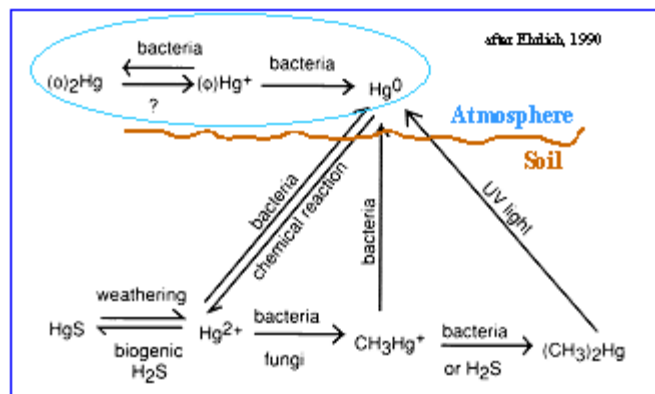
Sulfide oxidation → disproportionation



Methylation from methyl cobalamin



BIO-ORGANIC SPECIATION



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The current work looks at mercury evolved from thermally desorbed soils and analyzed by cold vapor atomic fluorescence spectrometry (CVAFS). This offers an immense improvement in analytical capability and permits the detection of all natural background concentrations. The typical reporting range for the method is 10 ppb to 0.010 ppb Hg. Consequently, the very smallest of mercury concentrations can be detected, making it possible to see very weakly bound mercury on the surfaces of soil particles without disturbing other mineral species in the substrate. This achieves a response that is similar to buried integrative collectors that require 8-10 weeks to load. In addition, other mercury species can be detected by systematically increasing the desorption temperature. The result is a mercury response to deeply buried mineralization that permits several vectoring strategies as the relationships of near-surface to deep ore are explored. Overall, this new mercury method achieves new levels of reliability in finding precious metal, base metal, and PGM deposits, as well as very deeply buried geothermal occurrences.

Speciation

Mercury compounds derive from inorganic processes, organic, and bio-organic processes. Disproportionation is an inorganic equilibrium between elemental mercury and two of its “reactive” states. The Hg^+ and Hg^{2+} ions are available for reactions with metabolic by-products (like cobalamin) that shift the disproportionation equilibrium to increasing amounts of elemental mercury, Hg^{2+} , and the formation of dimethylmercury. Bacteria and fungi intervene to create several more organomercury compounds. These various mercury species can be detected by step-wise thermal desorption. As a mercury containing mineral is heated, it sublimates to give mercury vapor. If the temperature is plotted versus the amount of mercury given off at that temperature, a signature profile is constructed for that compound. Biester et al (1999) has done much of this work showing characteristic profiles for HgCl_2 , Hg_2Cl_2 , CH_3HgCl , HgSO_4 , HgO , and various forms of HgS . He also shows signature profiles for mercury and mercury compounds that result from bonding to various substrates, like iron oxide, clay, a standard soil, and humic acid. Curiously, many of the mercury-compound and mercury-substrate profiles display multiple peaks, suggesting that bonds of different strengths are being broken as mercury is driven from the compound or the substrate.

Substrate Effects

The sublimation of elemental mercury is affected by the substrate to which the mercury mineral is bound. Biester demonstrates this with sublimation curves using iron oxide, clay and humic soils. Generally, higher desorption temperatures are required to release mercury minerals from the substrate.

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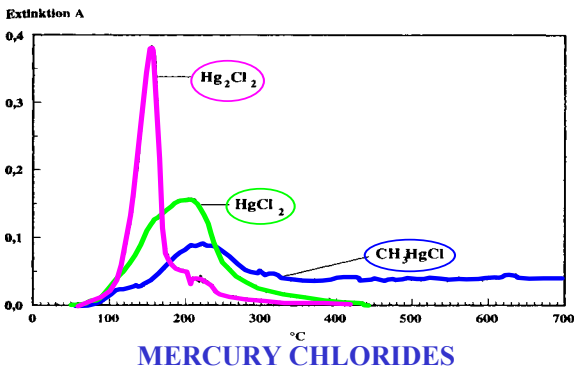
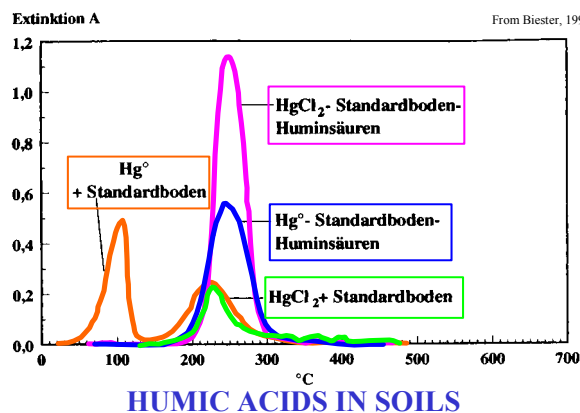


Abb. 6: Abdampfkurven der Hg-Chloride

From Biester, 1994

Abb. 11: Vergleich Abdampfkurven des Hg°- und des HgCl₂-inkubierten Standardbodens mit ihren extrahierten Hg-Humaten

From Biester, 1994

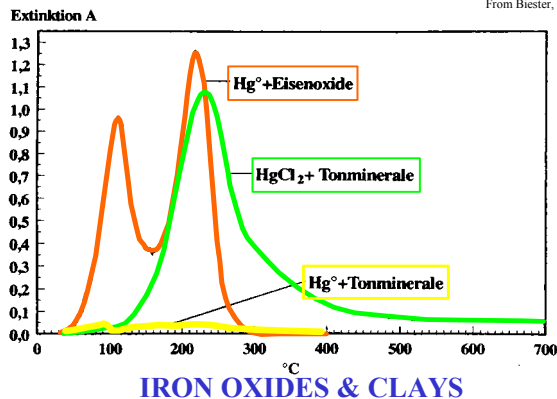


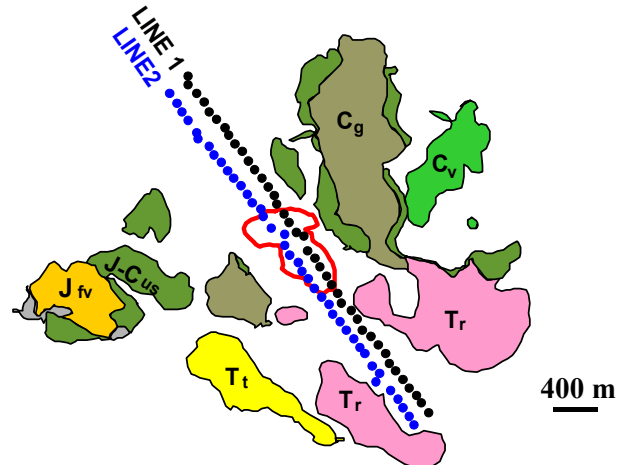
Abb. 9: Abdampfkurven der Hg-inkubierten Tonminerale und Eisenoxide

GAS'm™

The introductory work by Biester and other investigators provides a basis for the use of operationally defined thermal desorption in mineral exploration. Assuming that appropriate sample collection and preparation procedures give each sample in a survey a relatively constant composition (clay-rich), then the application of a specific desorption temperature should evolve proportional amounts of mercury from sample to sample depending on the equilibrium condition of that sample in the mercury flux.

MEG Labs has invested over 7 years into the development of this low temperature desorption method and has had increasing success as we improve our knowledge and understanding about extremely volatile mercury species. Here is just one of many examples of our work:

Volcanogenic Hydrothermal Massive Sulfide



Example from Sonora, Mexico

This unidentified VHMS deposit lies under a thin veneer of alluvium overlying approximately 300 m of Tertiary volcanic and volcanoclastic rocks. The closest approach of the deposit to the surface is 150 m. Soil samples were taken on 100 meter centers. The samples were first desorbed at a mid-range temperature, but the resulting profile was not particularly diagnostic. The samples were then desorbed at a high temperature and three anomalous zones appear. The robust anomalies from the high temperature desorption were

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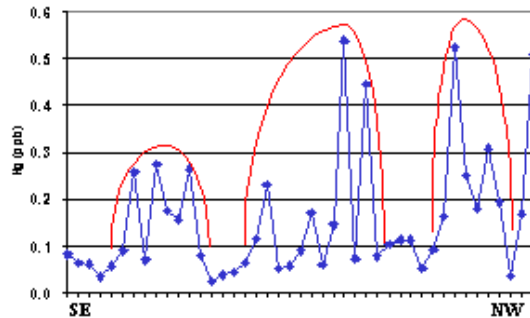
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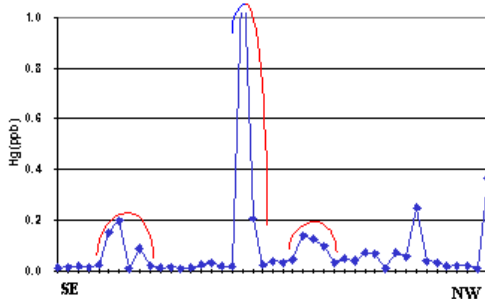


only vaguely captured by the mid-range desorption profile, so a third, low-temperature run was done. At this temperature a coherent zone 1200 m in length appears that is highly correlated with the mid- and high-temperature desorption profiles.

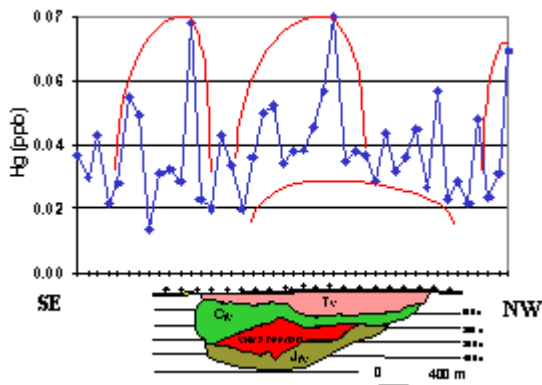
MID-TEMP DESORB



HIGH-TEMP DESORB



LOW-TEMP DESORB



This VHMS example illustrates how the signature desorption profile can be used to determine the most effective desorption temperatures for exploration in various terrain, geologic, and economic settings. Furthermore, the differences in the release of mercury as a function of temperature should indicate certain geometries of the deposit, including the influences of local structure.

Conclusions

Mercury soil gas is a reliable way to locate deep mineral occurrences using surface soil samples. Soils are desorbed with incremental thermal treatments. Weakly bound mercury is released at low temperatures while more refractory mercury species are decomposed at higher temperatures. Thermal desorption is directly proportional to the energy required to break the bonds that hold elemental mercury in mineral compounds and to the soil substrate. The

relationships between low-thermal and high thermal anomalies indicate the geochemical processes that created the operationally defined mercury speciation.

Mercury soil gas is an excellent tool for mapping structures, which are usually indicated by high-thermal desorption data. The more subtle patterns from low-thermal desorption data usually indicate deep mineralization, particularly if the geometry and footprint of those patterns suggest a body of significant tonnage.

References

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