

Thermally Speciated Mercury in Mineral Exploration

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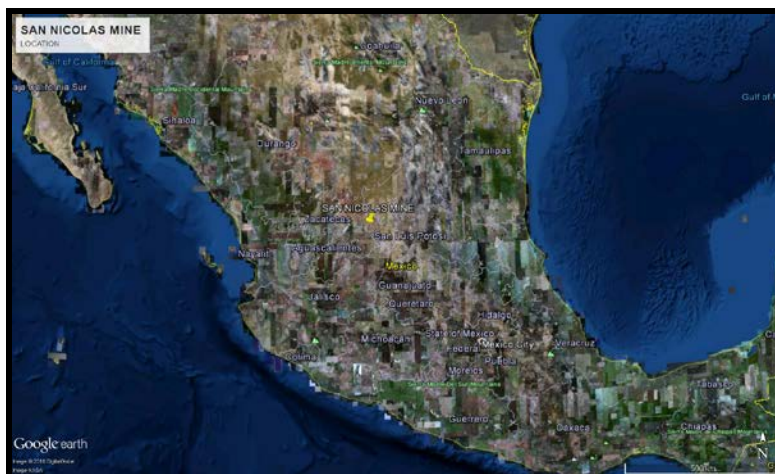
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San Nicolas Mine, Zacatecas, Mexico

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 (Biester, 1999). These methods focus on data derived from the thermal desorption of soil above 150C. However, detectable mercury is released below 150C, 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.



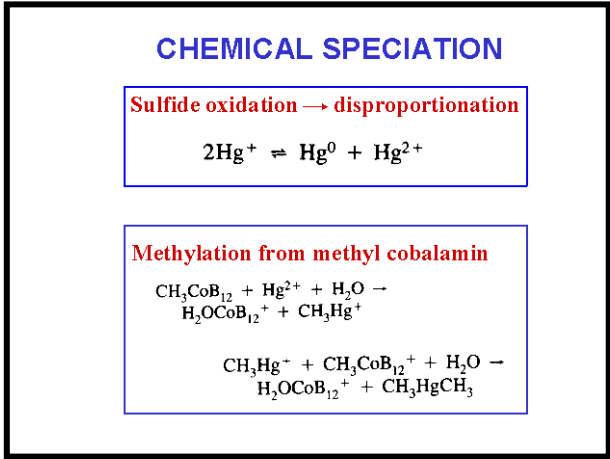
Introduction

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 metals that is associated with this contemporaneous and late hydrothermal activity. As the solutions cool and the associated metals are deposited, a spatial relationship is created where

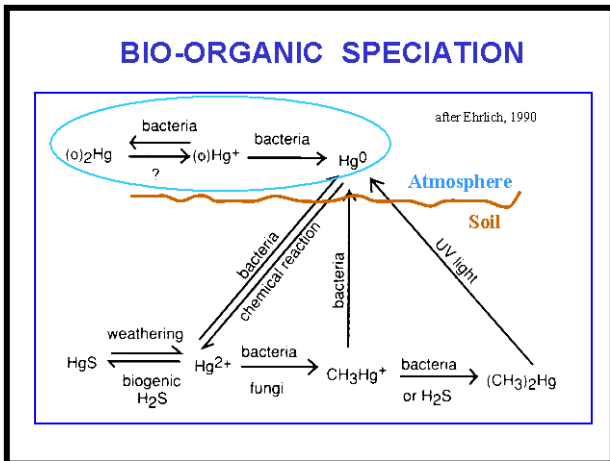
mercury and the other metals can be used as geochemical pathfinders in the search for these ores and geothermal occurrences.

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.



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



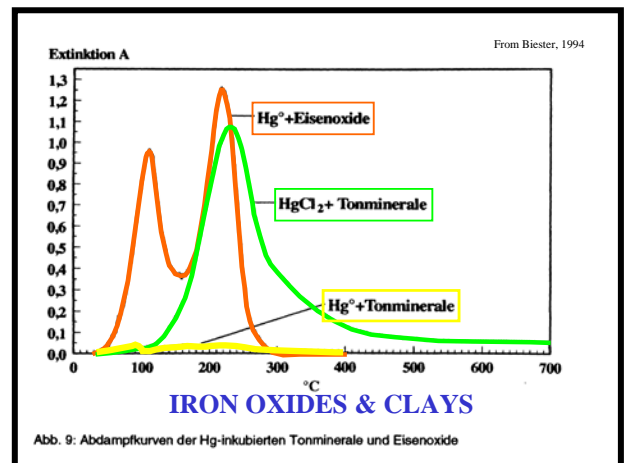
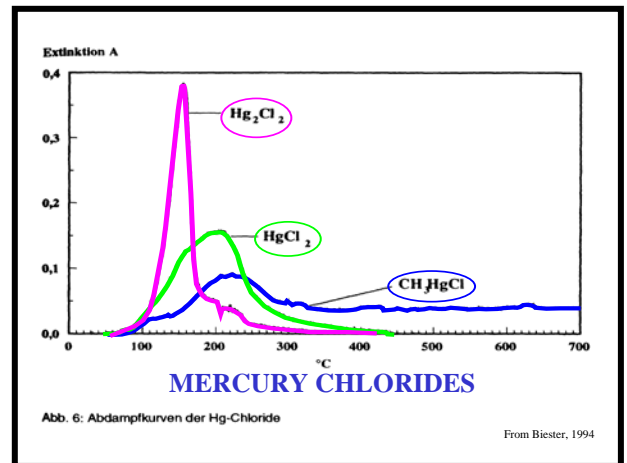
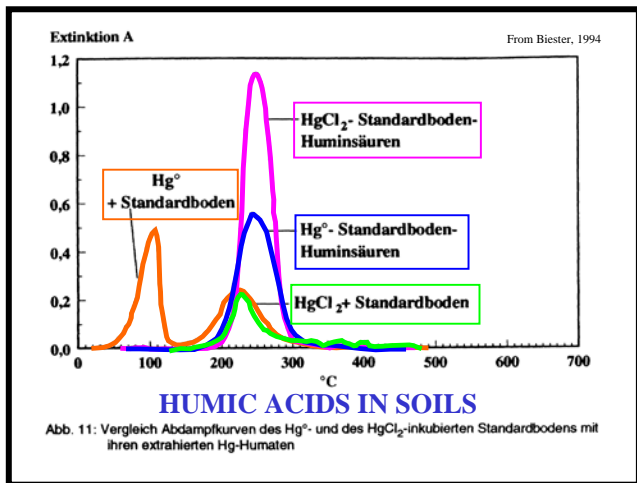
finding precious metal, base metal, and PGM deposits, as well as very deeply buried geothermal occurrences.

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 sublimes 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 (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.



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 have invested over 15 years on R&D of this low temperature desorption method and have had ever increasing success as we improve our knowledge and understanding about extremely volatile mercury species. Here is just one of many examples of our work:

San Nicolas Mine, Zacatecas, Mexico



Figs 1 & 2. San Nicolas mine location.

Teck-Cominco discovered the San Nicolás in the 1996 with Western Copper Holdings Ltd. It is a volcanic hosted, massive sulfide deposit containing ore-grade copper and zinc with associated gold and silver. Reserve estimates in 2002 were 99.5 million metric tonnes grading 1.4% copper and 1.6% zinc (with 0.4 g/T gold and 23.7 g/T silver), making it one of the largest massive sulfide deposits in Mexico (IMDEX 2002 Report). Prior to discovery of the San Nicolas and nearby El Salvador deposits, the region was not recognized as having the potential to host world class copper-zinc ore bodies (Johnson et al., 2000).

Geologic Setting

The paleotectonic regime in which the San Nicolás deposit formed is a transition from a back-arc basin to an arc, and possibly a fore-arc setting (Danielson, 2000). The deposit is hosted in marine volcanic and sedimentary rocks, locally known as the Chilitos Formation, of Upper Jurassic to Lower Cretaceous age, (Johnson et al., 2000). Mineralization is predominately found along a time-line that occurs between the formation of rhyolitic lava domes and the deposition of overlying mafic extrusives. These rocks include:

- mafic, intermediate, and rhyolite flows and shallow intrusions,
- felsic tuffs,
- volcanoclastic sediments,
- mudstone,
- chert, and
- limestone.

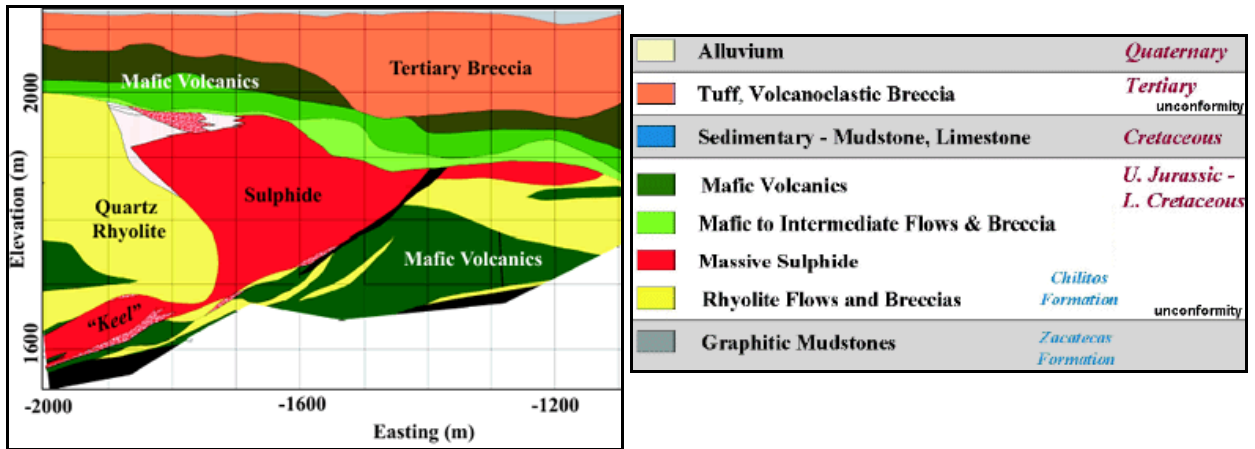
This package of rocks was subsequently accreted to North America, possibly in the mid-Cretaceous. Northeast-directed thrusting in the Late Cretaceous to Early Tertiary resulted in the juxtaposition of the Chilitos formation against carbonates and siliciclastic sedimentary rocks. Throughout the region, the rock assemblages are intruded by Late Cretaceous to Early Tertiary granitic plutons, and are unconformably overlain by Tertiary aged felsic volcanic flows and tuffs, (Johnson et al., 2000). North-, northwest-, and west-striking faults cut the assemblage. The age and displacement of these faults are unknown, although they could be synvolcanic extensional or postvolcanic strike-slip faults (Johnson et al., 2000). A section of rocks, which includes the Chilitos Formation, has also been uplifted to form a horst, within which the San Nicolás deposit is found. Tertiary volcanic rocks have intruded along the northwest-striking faults, and along north-striking faults at the west of the horst.

The deposit itself is bounded to the southwest by the northeast flank of a rhyolite dome, and by a southwest dipping fault to the northeast. The deposit is copper-rich towards the bottom with a high-grade polymetallic cap at the top. Also, the sulfide is granular and fragmented in the lower zone and laminated in the upper zone, typical of VMS deposits. Silicification and barite are present along the fault that bounds the deposit to the northeast. Extensive hydrothermal alteration of the host rocks is also observed.

Genesis

Massive sulfide deposits are often formed close to plate margins (Lydon, 1988). Mineral-rich hydrothermal fluids, either originating from a magmatic source or circulating in the sediments and being driven by the heat from a magmatic source, react with sea water and deposit sulfide minerals. These deposit types are usually quite small and the duration of mineral deposition short-lived. Several deposits can be found in the same area often in association with submarine volcanic flows and sediments (Lydon, 1988).

San Nicolás, although probably formed by a similar process, is larger than usual and was possibly formed in a tectonic environment not commonly associated with massive sulfide deposits. This makes San Nicolás an unusual massive sulfide deposit, and provides a new and exciting type of exploration target for this region. Consequently, the regional potential for discovering other deposits is high because exploration programs in this area have not previously focused on this type of deposit.



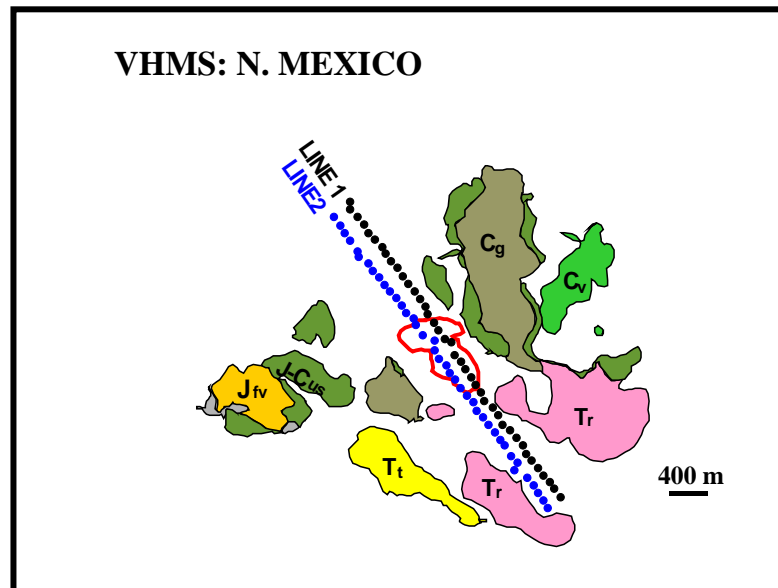
Figs 3& 4. San Nicolas mine detailed cross-section and stratigraphy.

Deposit scale geology

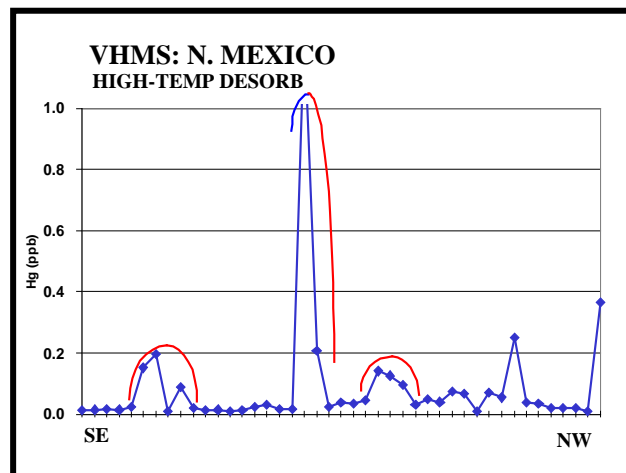
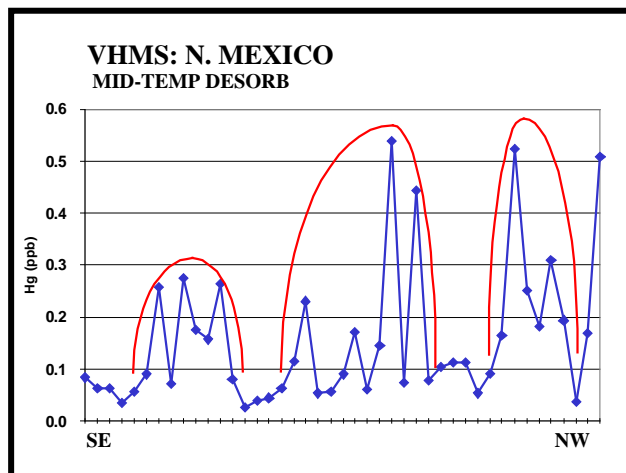
The deposit is hosted in a series of interwoven mafic and felsic volcanic rocks of the Upper Jurassic to Lower Cretaceous Chilitos Formation. These volcanic rocks lie unconformably over graphitic mudstones of the Zacatecas Formation. The deposit is almost entirely bounded to the east by a southwest-dipping fault, which could have been a feeder structure. Mineralization continues to follow the fault at depth in an unconstrained part of the deposit referred to as the "keel".

To the west, the deposit is flanked by a thick package of rhyolites. These rocks contain a steeply dipping north-south fault. The top of the massive sulfide lies 150-220 m below the surface and is covered by up to 100 m of unmineralized mafic volcanic flows, fragmental rocks, and volcanoclastic and argillaceous sedimentary rocks of presumed similar age to the underlying volcanic sequence and massive sulfides (Upper Jurassic-Lower Cretaceous). These rocks are in turn covered by 50-150 m of Tertiary volcanoclastic breccias, which locally contain saline ground waters (SEG News, 2002). Outcrops of the breccia have been mapped to the northwest, but an overlying thin veneer of Quaternary alluvium is present in the vicinity of the deposit. Hydrothermal alteration is prevalent throughout the deposit and surrounding geology.

GAS'm Survey



The San Nicolas VHMS deposit lies under a thin veneer of alluvium overlying approximately 270 – 350 m of volcanic and volcanoclastic rocks. 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 higher temperature and three anomalous zones appear. The robust anomalies from the high temperature desorption were only vaguely captured by the mid-range desorption profile, so a third, low-temperature run was done. At this temperature a coherent zone spanning 1200 m in length appears and which is highly correlated with the mid- and high-temperature desorption profiles.

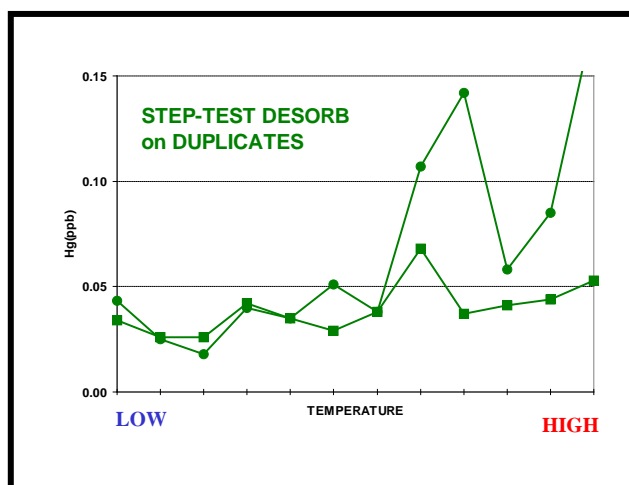


Figs 6 & 7. Mid-thermal and high-thermal desorption GAS’ m profiles on Line 1.

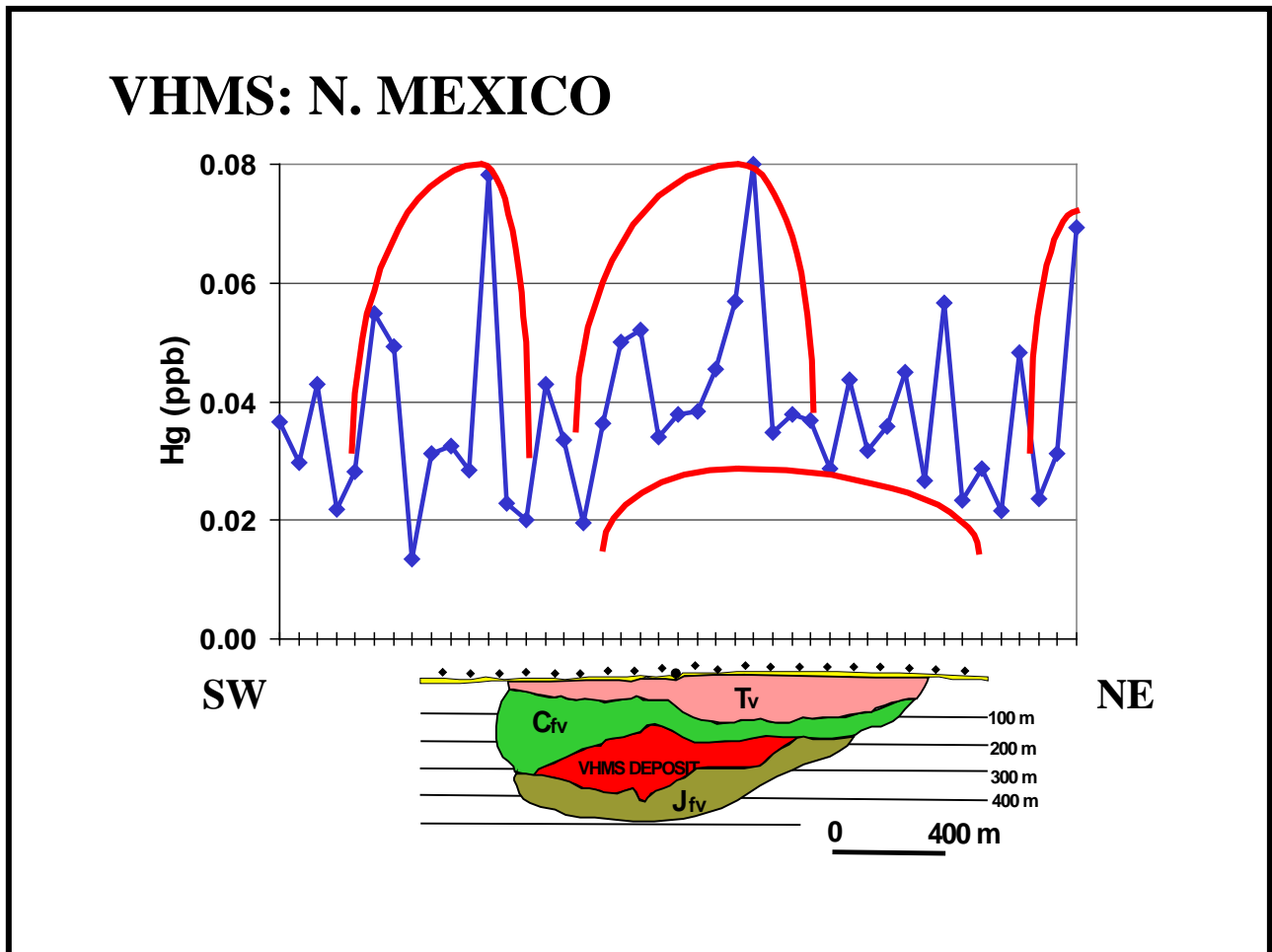
This VHMS example illustrates how the signature desorption profile can be used to determine the most effective desorption temperatures for exploration in various terrain, geologic, and economic settings. Furthermore, the differences in the release of mercury as a function of temperature should indicate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

Reproducibility tests on duplicate soil samples show better results from low-temperature than from high temperature desorption. Low temperature mercury is very weakly bound to the soil substrate and is likely a vapor. High temperature mercury seems to evolve from discrete mineral particles that are unevenly distributed. It might be that reactive mercury vapor from high temperature desorption variably interacts with the substrate and other mineral phases which causes increasingly poor reproducibility. Nevertheless, the lack of reproducibility does not overwhelm high temperature desorption data from identifying zones of high mercury flux in the soil column. In fact, the lack of reproducibility in zones of high mercury flux seems to be a hallmark of the pattern and the geochemical processes that are occurring in those areas.

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Figs 8. Low-thermal desorption GAS'm profiles on Line 1. The SW anomaly may be a response to the deep, high grade copper "keel" shown in cross-section in Fig 3.

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.



Figs 5 & 6. San Nicolas mine development in 2011 and 2014.

References

- Barton, M.D., Staude, J-M. G., Zurcher, L., and Megaw, P.K.M., Porphyry Copper and Other Intrusion-Related Mineralization on Mexico, in Pierce, F.W, and Bolm, J.G. (Editors), Porphyry Copper Deposits of the American Cordillera, Arizona Geological Survey Digest 20, Tucson, AZ, 1995.p. 487-524.
- Biester, H., Gosar, M., and Muller,G., 1999., Mercury speciation in tailings of the Idrija mercury mine. *Journal Geochemical Exploration* 65, 195-204.
- Chavez Martinez, L, Ubaldo Alarcon L, F. and Parga P, J de J, 1999, Mining exploration potential of VMS and carbonate-hosted polymetallic deposits in central Mexico, In: Jambor, J.J. (ed), VMS and Carbonate-Hosted Polymetallic Deposits of Central Mexico, B.C. and Yukon Chamber of Mines Cordilleran Roundup, p. 1-13.
- de Cserna, Z., 1976, Geology of the Fresnillo area, Zacatecas, Mexico, *Geol. Soc. America Bull.*, v. 87, p. 1191-1199.
- Johnson, J., Montante, A., Kearvell, G., Janzen, J. and Scammell, R., 1999, Geology and exploration of the San Nicolas polymetallic (Zn-Cu-Au-Ag) volcanogenic massive sulfide deposit, In: Jambor, J.J. (ed), VMS and Carbonate-Hosted Polymetallic Deposits of Central Mexico, B.C. and Yukon Chamber of Mines Cordilleran Roundup, p. 45-54.
- Klusman, R.W., Soil Gas and Related Methods for Natural Resources Exploration. John Wiley & Sons, New York. pp.483
- Kromer, E., Griedrich, G., and Wallner, P. (1981) Mercury and mercury compounds in surface air, soil gas, and rocks. *Journal Geochemical Exploration* 15, 51-62.
- Maciolek and Jones (ca. 1988, unpublished research)
- Phillips, N. MSc Thesis, "Geophysical Inversion in an Integrated Exploration Program: Examples from the San Nicolas Deposit", Univ. British Columbia, Canada, 2002.