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Editor's Note

This is the first of E2Geochemisty's Newsletters and it's been a long time in preparation. It is our sincere hope that the information will be of use to you and others, and we encourage you to freely distribute it with appropriate reference to this newsletter. We also invite you to submit material for future newsletters or comments about the articles contained herein. Address communications directly to me at: ronschmiermund@msn.com

Thallium – A Potential Environmental and Occupational "Driver" for Mining?

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Introduction/Abstract

Since its discovery in 1860, thallium seems to have been relegated to the back-water of the periodic table, never achieving the status of precious metals or the industrial demand of many base metals. In fact it has taken the advent of high-tech communications to give it recognition and importance beyond that of rat poison and a popular murder weapon in fiction and in fact. Those traditional uses, however, are based on the same property of thallium that makes it worthy of our close attention now – its extreme toxicity. NRIAGU (1998) provides the most recent overview of thallium's history, chemistry, analytics and toxicology but does not address the metal's relationship to mining.

Only one mine currently produces thallium as the principal commodity but byproduct thallium from roasting, smelting and refining of other ores has been recovered for years. Today it is recognized as an associated element is some of the most sought-after commodities and deposit types.

Currently, only a limited number of environmental regulations include thallium but they are notable for their very low limits for acceptable concentrations. Unfortunately, while the recognition of thallium grows along with the list of strict regulations, the repertoire of techniques to manage and remediate thallium-contaminated media does not.

In the decade since this author first encountered a major mining operation where thallium was clearly an ongoing, albeit unrecognized, issue, the element has been appearing seemingly everywhere. This sudden change in perception seems to be related to ever-increasing availability of high quality, highly sensitive and affordable analytical techniques for waters, specifically ICP-MS. It is now possible to routinely measure thallium in water, rock, soils, vegetation and animal tissue reliably and at concentrations that are environmentally significant. The global database is expanding rapidly.

Now that we are looking for thallium, and can measure it meaningfully, it is clear that it is an issue that we must acknowledge and become highly proactive about. Thallium, with its great potential toxicity and demanding regulatory limits to match, its typically undocumented backgrounds and baselines in mining districts, combined with limited treatment options, can become the limiting variable (i.e., the "driver") in meeting environmental and social obligations for new mining ventures.

Thallium Occurrence and Mineral Deposit Associations

The earliest comprehensive report of thallium concentrations in rocks of the earth's crust was made by SHAW (1952) and included details of the then state-of-the-art analytical techniques, an enhancement of DC-arc emission spectroscopy with glass photographic plates. Two emission lines were found suitable for low and high concentrations, respectively. This method allowed thallium to be reported with an average sensitivity of 50 ppb and ±20% accuracy in most silicate rocks. Average igneous rocks ranged from 15 ppb to 3.6 ppm, sedimentary rocks from 180 ppb to 2 ppm, and individual K-rich phylosilicates and K-feldspar up to 95 ppm. Deep-sea sediments ranged from 0.16 to 1.5 ppm with Mn nodules being anomalous at 30 to 100 ppm. These older values agree quite well with RUDNICK and GAO (2003) who report thallium in the upper continental crust ranging from 0.524 to 1.55 ppm and LI and SCHOONMAKER (2003) who report 0.7 to 4.8 ppm in deep water sediments and 34 ppm in mid-ocean ridge sediments. Again Mn nodules were anomalous with 150 ppm. These latter compilations still contain some analyses that are 30+ years old and did not have the advantage of the most recent analytical technology. Nevertheless, this sampling of data should provide context for thallium concentrations associated with mineral deposits.

In comparison, measured thallium concentrations in water are relatively sparse in the literature and reveal the need for much greater analytical sensitivity. GAILLARDET et al. (2003) lists only two thallium concentrations in river waters (0.0400 and 0.0076 ppt) and summarizes the range as 1 to 10 ng/L (ppb). One of the two values (FREI et al., 2000a) was confirmed to have been obtained by ICP-MS techniques. The list of analyses provided by Chou and Moffett (1998) would suggest the range proposed by Gaillardet et al. (op. cit) was too low and too narrow and should be extended to several hundred ppb.

With respect to mineral deposits, thallium is rather broadly represented and an accompaniment to many hydrothermal systems. The following survey of deposits is intended to be a source of data for more detailed pursuits, and to provide a framework for judging thallium concentrations. It is not complete to be sure, but availability of thallium data in the ore deposit literature must still be considered relatively sparse.

- Epigenetic Systems

  Modern hot springs - SILBERMAN and BERGER (1985) report Tl ranging from 3.3 to 2290 ppm in various deposits associated with the Broadlands, Waiotapu (NZ) and Steamboat Springs, NV hot springs. HEDENQUIST and HENLEY (1985), KRUPP and SEWARD (1987) and WEISSBERG (1969) support this range and further illustrate the variability

High-sulfidation, quartz-alunite systems – Literature on these deposits relative to thallium is surprisingly limited but the author is aware of deposits of this type with whole rock concentrations up to 70 ppm. GRAY and COOLBAUGH (1994) observed Tl to be enriched in the argillic zones flanking vuggy quartz veins in 10-to 15-meter thick selvages.

Low sulfidation, quartz-adularia systems - SILBERMAN and BERGER (1985) describe Tl and associated trace metal anomalies as being deep and highly variable. BERGER and SILBERMAN (1985) show profiles of Tl, As, Sb and Hg various locations in the Hasbrouck Mt (NV) deposit where Tl is commonly between 50 and 200 ppm over 500 vertical feet in the central epiclastic deposits. JOHN et al. (2003) reports modest Tl enrichment (1.2 to 10.2 ppm) in the Mule Canyon, NV ore zone but concentrations similar to crustal averages in associated rocks. WARREN et al. (2007) documented Tl concentrations in volcanic host rocks surrounding the El Peñón (northern Chile) low-sulfidation veins (1 to 6.5 ppm Tl) relative to average compositions of local unaltered volcanics (< 1 ppm Tl). GEMMELL (2007) provides over 100 analyses of altered volcanic and sedimentary rocks associated with the Gosowong (Indonesia) low-sulfidation system and reveals a very consistent Tl concentration (0.0X to <3 ppm Tl) and a correlation with K_2O but not S.

Carlin-type systems –

WALLACE (1989) notes a direct association of Tl with Au and reports values up 13 ppm. KUEHN and ROSE (1992) found 160 and 22 ppm Tl in gold-enriched, high As, Sb and Hg zones in the Carlin mine and BETTLES (2002) tabulates 3.2, 24.8 and 5.9 ppm Tl as averages for gold bearing zones (> 1 ppm) at the Screamer, Meikle and Rodeo mines, respectively. EMSBO et al. (2003) provides a more extensive list of analyses from the Meikle deposit where Tl ranges from 1 to 45 ppm in altered igneous rock and varies directly with Au, As, Sb and Hg. Emsbo (op cit.) also examined pyrite concentrates from Meikle and found 830 to 1200 ppm Tl in main ore-stage pyrites and 6.8 to 610 in the late ore-stage pyrites. However, the strong positive correlation between Tl and As, Sb and Hg is distinctly absent in the pyrite concentrates. CLINE (2001) also observed Tl enrichment (up to 631 ppm) in sulfides at the Getchell mine without parallel enrichment in As, Sb and Hg. In addition, Emsbo reports analyses of 58 whole rock samples of “representative and variably mineralized rocks of the northern Carlin trend” ranged from <0.2 to 357 ppm Tl.

Volcanogenic massive sulfide systems (VHMS) -

LARGE et al. (2001b) discuss Tl and Sb halos surrounding a continuum of Australian deposits in the Mount Reed volcanics ranging from purely VHMS (Roseberry, Hellyer and Thanlanga) to high-sulfidation types (Mt. Lyell). Thallium is enriched variously in the hanging wall, foot wall and laterally in the ore horizon for hundreds of meters. Concentrations at Rosebury reach 60 ppm in the hanging wall and host horizon (SMITH and HUSTON, 1992). Additional detail on distributions is provided in LARGE et al. (2001a).

Sediment-hosted massive sulfide systems -

LARGE et al. (2000) describes the very

extensive (Pb+Zn+Tl) anomaly extending hundreds of meters above the HYC deposit and over 20 km along the favorable horizon. Within in this envelope Tl is everywhere > 4 ppm but concentrations between 200 and 1000 ppm Tl occur up to 100 meters above, and 50 meters below, the ore horizon. SLACK et al. (2004) has compiled compositional data for altered wall rock to the Red Dog deposits and reports pervasive enrichment with maximum values of 60 to 110 ppm Tl. Pyrite in the wall rock is highly enriched up to 12,200 ppm Tl.

Porphyry copper systems –
CHAFFEE (1976) notes a depletion of thallium (0.8 background to 0.3 ppm) centered on the potassic core and possible enrichment in the distal propylitic zones.

Chinese thallium-only deposits –
Xiangquan, the world's first thallium-only deposit is reported by ZHOU et al. (2005) and may represent a partially re-mobilized submarine hot spring enrichment of calcareous sediments. Ore zones range from 532 to 16000 ppm Tl while the hosting pyrite can contain up to 35000 ppm Tl.

Geochemical Behavior

The behavior of thallium in the environment has received considerable attention but numerous unresolved issues remain. Thallium is a "soft" cation with a large number (six) of outer shell electrons. The thallous (Tl(I)) form with its large ionic radium (1.4 A) is generally thought to dominate thallium chemistry with the thallic (Tl(III)) form being far less common. As a large monovalent cation, Tl^+ resembles K^+, Rb^+ and Ag^+ in its geochemical behavior.

At least 30 minerals containing structural thallium are known, the majority of which are sulfides (mostly sulphosalts), antimonides and selenides with Tl(I). Arsenic is present in over half of the known minerals. Tl(III) is known in one oxide and one sulfate mineral. Nriagu (1998) provides names and formulas. Despite the number of thallium minerals, they are all rare and thallium may be far more commonly associated with pyrite and other iron sulfides as an impurity. As such, Tl can be concentrated by geochemical H_2S "traps" and concentrate in organic-rich sediments. Exposure of such sulfide minerals and their hosting sediments are likely to result in oxidizing and acidic environments like those generating ARD with associated release of thallium. In addition to its presence in sulfides and sulphosalts, Tl^+ substitutes for K^+ in silicates and tends to be sorbed by clays. DUTRIZAC et al. (2005) discussed thallium incorporation into jarosites during precipitation.

KAPLAN and MATTIGOD (1998), LIN and NRIAGU, (1998) and VINK (1998) discuss thallium's behavior in terms of classic thermodynamics and XIONG (2007) expands the thermodynamic database for thallium-bearing solids through estimation techniques and calculates speciation to 300°C. These authors and other conclude that the aqueous geochemistry of thallium is expected to be completely dominated by Tl(I), with Tl(III) only expected to be stable near or above the upper stability limit of water. However LIN and NIARGU (1999) found 68 ± 6% of thallium in Lake Erie to be present as Tl(III) in direct contrast to the thermodynamic predictions. Subsequent discussion CHEAM (2000) and LIN and NRIAGU (2000) raise numerous issues such as complexation, sorption, colloid stabilization and analytical artifacts. TWISS et al. (2003) reports sorption of thallium on dead and living organic matter and FREI et al. (2000b) discusses complexation in waters with low acid-neutralizing potential.

It seems likely that Tl(I) indeed dominates thallium behavior in dilute systems, but that increasing TDS may induce significant complexation and partitioning. It should also be kept in mind that the typically very low concentrations of thallium are many orders of magnitude lower than potential complexing ions so that even "dilute" waters may alter the distribution and form of thallium.

Toxicity

By all accounts, thallium should be regarded as having the potential to be highly toxic, depending on the chemical form. Nriagu (1998) discusses the early use of thallium as a rodenticide and for treatment of (various diseases. He also includes chapters addressing thallium's human, reproductive and developmental toxicity, it's similarity to K^+ in cellular function and it's influence on the human optic system. Repetto et al. (1998) compare accute end chronic thallium toxicity. The onset of even acute thallium poisoning is insidious and may only develop over months into a wide array non-specific maladies that can be difficult to attribute to thallium. Even when not fatal, recovery from thallium exposure is lengthy and may not be complete. Sub-acute and chronic thallium intoxication is associated with accumulation of the metal in tissue over time but sudden release of that stored thallium can trigger acute responses. Symptoms of chronic poisoning are equally non-specific and even harder to diagnose. Excitation and insomnia may be the earliest symptoms but hair loss may be the first symptom to be connected to thallium but may also be absent. Gastroenteritis, polyneuritis and polyneuropathy (inflammation and simultaneous malfunction of distal nerves, respectively) and alopecia (hair loss) are most commonly observed but, again, the causes of these symptoms are extremely varied. Following termination of thallium exposure, significant abnormalities persisted after 8 years in some groups studied. Repetto et al. (op. cit.) conclude that "Thallotoxicosis is a serious illness with high morbidity and mortality, the outcome of which is hard to estimate."

Peter and Viraraghavan (2005) provide an update to the knowledge of thallium toxicity and state that "Thallium is more toxic to humans than mercury, cadmium, lead, copper or zinc and has been responsible for many accidental, occupational, deliberate, and therapeutic poisonings ". They report that thallium poisoning may occur via ingestion and dermal contact as well as inhalation. Documented cases of occupational poisoning are rare but the causal connection to industrial activities is strong. In particular, agricultural soils have been contaminated by thallium in the vicinity of coal-burning power plants, cement kilns and smelters resulting in human uptake via the crops produced on those soils. The southwestern Guizhou Province of China, where "natural" thallium concentrations in soils are significantly elevated, is plagued by persistent and serious thallium poisoning XIAO et al. (2004). However, the influence of the 250-year long, and likely largely artisanal, mining history is not discussed.

Chronic thallium toxicosis in a human population is probably best confirmed by analysis of urine and hair samples (Xiao et al., 2007). Analysis of nail, feces, saliva and blood may also allow detection. CONERLY and BLAIN (2008) review data on human thallium toxicity.

Analytical Methods

Although a variety of sensitive analytical methods have existed for some time, measuring thallium at environmentally-significant concentrations has been less than practical on a day-to-day commercial basis prior to the common availability of ICP-MS. Chou and Moffatt (1998) review a wide range of analytical techniques for thallium measurement. Carden (1998) surveys the typical detection limits reported for various analytical techniques. The most common (commercial) analytical, tools applied during recent decades (e.g., atomic absorption and ICP-AES spectroscopy) suffer from insensitivity (1 to 100 ppb detection limits in water) and interference resulting in undependable data on thallium in many older environmental baselines. As a result thallium was typically ignored in environmental surveys and routine monitoring, at least in part because of the known analytical limitations.

Shand et al. (1998) report detection limits in raw water at 0.1 to 0.5 µg/L (ppb) by ICP-MS but by adding a pre-concentration step, detection limits of 0.3 to 2.6 ng/L (ppt) were achieved. Carden (1998) reports a mean thallium detection limit for ICP-MS as 0.04 µg/L. Medek et al. (2001) reports on ICP-MS determination of thallium in soils. A further advantage of ICP-MS is that two isotopes of thallium (^{203}Tl and ^{205}Tl (aprox 30% and 70%, respectively) may be determined to confirm the analysis.

Regulatory Status

Thallium has yet to be included in many regulatory lists, probably for some of the same reasons cited above associated with analytical difficulties. Table 1 lists selected regulatory databases that include, or conspicuously exclude, thallium and compares the limits to other better known contaminants. Thallium regulatory limits are generally similar to or less than those for mercury and significantly less than other environmentally sensitive contaminants. It is reasonable to assume that organizations that do not currently recognize thallium will eventually do so, and the fact that other credible organizations acknowledge the toxicity of thallium requires that mining companies proactively adopt a standard.

Conclusion

Thallium is an under-recognized and under-appreciated contaminant with special significance to, and potentially dire consequences for, the mining industry. A consideration of the ore deposit type(s) present at a given operation should provide some insight into the likelihood that thallium may be present in sufficient quantities to potentially be an environmental problem. However, the databases on thallium abundances and occurrences remain limited and routine inclusion of thallium in environmental baselines and monitoring programs is recommended until it’s concentrations can be ascertained.

The extreme toxicity of thallium, and/or its extremely low regulatory limits (where available) warrant inclusion of the element in monitoring programs. The low relevant concentrations make sample handling and analytical considerations very important. Laboratories should be selected carefully and blind QA/QC measures employed to make the efforts worthwhile and dependable. Dual thallium isotope analysis can add great credibility to its measurement.

Old environmental data on thallium should be checked to determine if detections limits were sufficiently low to be useful in the light of regulations. Just as important, high concentrations previously reported and possibly ignored due to lack of applicable regulations should be investigated. If anomalous concentrations do appear and measurements were made by ICP-AES or AA methods, the values may be completely erroneous. However, it is incumbent upon the operator to confirm or refute the values to prevent future liability.

Occupational exposure to thallium in the mining industry is probably even less well-recognized than environmental contamination. In particular, exposure to dust during blasting, loading, hauling and crushing could be a significant source of worker poisoning and great liability.

With respect to whether thallium may be a future regulatory limitation for mining, this author believes that the potential is very real. Extreme environmental regulatory limits combined with enormous water treatment difficulties (think reverse osmosis or similar active treatment) can place thallium at the head of the list of environmental concerns and long-term liabilities for a modern mining operation. Absence of existing regulatory standards is a foolish excuse for ignoring thallium today, because future regulations are likely in most jurisdictions. In addition, recent examples of devastating public health problems and corporate liabilities due to occupational exposure to asbestos should illustrate the need to accurately assess similar threats from thallium.

TABLE 1 Selected regulatory standards

Source	Tl (mg/L)	Hg (mg/L)	Cd (mg/L)	Pb (mg/L)	Sb (mg/L)	As (mg/L)
(1)	0.002	0.002	0.005	0.015 (a)	0.006	0.01
(2)	none	0.001	0.005	0.01	0.006	0.01
(3)	none	0.006 (b)	0.003	0.01	0.02	0.01
(4)	0.013	0.002	0.005	0.05	0.146	0.05
(5)	0.002	0.002	0.005	0.0075	0.006	0.05
(6) (c)	0.00024	0.0005	0.005	0.015	0.0056	0.01
(d)	0.002	0.002	0.005	0.015	0.006	0.01
(e)	0.0003	n/a	0.0001	0.0001	0.0004	n/a
(7)	none	0.01	0.1	0.1 - 0.2	none	0.1

(1) U.S. Environmental Protection Agency, primary drinking water Maximum Contaminant Level (MCL), http://www.epa.gov/safewater/ contaminants/index.html#inorganic
(2) Guidelines for Canadian Drinking Water Quality, Maximum Acceptable Concentrations (MAC) http://www.hc-sc.gc.ca/ewh-semt/pubs/ water-eau/sum_guide-res_recom/chemical-chimiques-eng.php#tbl4

(3) World Health Organization, Guidelines for drinking-water quality http://www.who.int/water_sanitation_health/dwq/gdwq0506_ann4.pdf
(4) Nevada Standards for Toxic Materials Applicable to Designated Waters, Municipal or Domestic Supply, NAC 445A.144 in http://www.leg.state.nv.us/nac/nac-445a.html
(5) Illinois Groundwater Quality Standards for Class I, Potable Groundwater Resource, http://www.ilga.gov/commission/jcar/admincode/035/035006200D04100R.html
(6) Montana Numeric Water Quality Standards (DEQ-7), http://www.deq.mt.gov/wqinfo/standards/CompiledDEQ-7.pdf
(7) World Bank Effluent Discharge Guidelines, http://www-wds.worldbank.org/ external/default/WDSContentServer/WDSP/IB/2008/03/28/ 000334955_20080328071714/Rendered/PDF/261240NWP0REPL1sment0and0Protection.pdf

(a) = action level
(b) = inorganic mercury
(c) = surface water
(d) = groundwater
(e) = trigger (action) level

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Potential Method for On-Site APP Measurement

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A need for “real-time” measurement of acid-producing potential (APP) is often encountered at some point in mine development. Typically a waste characterization program will identify several categories of rock that should be segregated based on APP either to minimize ARD generation or to provide for construction material. Excellent three-dimensional waste rock sampling arrays are available via blast holes, but the challenge is to measure the APP rocks in a reliable and rapid way prior to excavation and transport. Visual estimation of pyrite content is commonly used but is notoriously undependable, especially if many estimators are involved or if other criteria such as dominant mineralogy are considered in the classification. Instrument analysis of pyrite content based on induction furnaces (e.g., Leco sulfur analyzers) involve relatively high costs and a reasonable laboratory facility, operator training and maintenance – frequently at a time when revenue is not yet being generated. Simple wet chemical techniques have been applied to the problem. These include net-acid producing potential (NANP) in which hydrogen peroxide is employed to oxidize “all” sulfides resulting in a pH drop that is a net function of APP and acid-neutralizing potential (ANP).

Burton et al. (2008) describe another technique potentially applicable for non-instrumental real-time waste rock testing. The method determines chromium-reducible sulfur (CRS) and is based on the Cr(II)-induced reduction of all sulfur with a valence of less than + 6 (i.e., not sulfate) to H_2S gas which is then quantitated by a simple titration. The method is described as simple, inexpensive and relatively quick (48 hours) with the advantage of allowing for many simultaneous analyses with minimal operator training. It is further described as a simplification of previous purge-and-trap method that required significant volumes of compressed nitrogen. The method was used to estimate reduced inorganic sulfur (RIS) in acid sulfate soils.

Although the method is not reported as having been used to characterize typical sulfidic waste rock, it seems reasonable that it should be applicable. Sample preparation includes pulverization, which is facilitated by using blast-hole cuttings. An aliquot of sample is placed in a simple screw-cap centrifuge tube equipped with a tube and valve allowing purging of the headspace with nitrogen and introduction of the acidic chromium reagent. Evolved H_2S is allowed to react by diffusion with a separate vial inside the centrifuge tube containing an alkaline Zn solution over a period of 48 hours. The precipitated ZnS is then dissolved and the resultant solution titrated to a colorimetric endpoint.

By establishing a relationship between conventional APP measurements for a given deposit and the CRS measurements obtained by the above method, it should be possible to rapidly obtain credible estimates of APP. A small on-site facility should be capable of processing all the samples produced by a blast hole drilling program in a given day and returning data in 48 hours.

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