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Review of trace elements and their deportment in gold processing.

Part 1: Mineralogy, aqueous solution chemistry and toxicity.

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## **ABSTRACT**

A literature review on the department of trace elements in gold processing by cyanidation is presented. The review compiles the current knowledge in this area and highlights the gaps in the current knowledge and understanding. This review, together with further research based on gaps in the current knowledge of the thermodynamics and kinetics of these systems, will support the development of computer models to predict the chemical speciation and department of these elements through the various stages of the gold cyanidation process. The review covers lead, cadmium, mercury, arsenic, antimony, bismuth, selenium, and tellurium. Presented in this paper is the first part of this review which is a collation of the relevant information on trace element mineralogy, aqueous solution chemistry and toxicity.

Although there is much information available about the aqueous solution chemistry of the trace elements, their chemistry in cyanide leach solutions remains largely unexplored. Chemical speciation modelling can assist in understanding the chemistry of the trace elements in gold cyanidation solutions, however, many significant differences exist between the predicted speciation of these trace elements for different types of modelling software. This is due to differences in the thermodynamic data used, the paucity of data that exists under appropriate non-ideal conditions, and the methods used by the software packages to estimate thermodynamic parameters under these conditions.

The trace elements reviewed, particularly the species that exist in aqueous solutions, generally have significant toxicities to humans, and more so to plants and animals. Cadmium, mercury and arsenic are classified as human carcinogens whereas selenium is an essential trace element for human health, but is toxic in excess. This review

highlights that further understanding of their chemistry during cyanidation is required to better understand the health and environmental risks associated with the presence of these elements in gold ores.

## 1. INTRODUCTION

The deportment of trace elements during mineral processing is an area of increasing concern to the mining industry because metal extraction processes tend to concentrate trace elements to levels that may present hazards to both human health and the environment. The primary focus of this review is the role of the minor trace elements in gold processing by cyanidation; in particular lead, cadmium, mercury, arsenic, antimony, bismuth, selenium and tellurium; including their mineralogy, aqueous solution chemistry, and toxicology. Copper has been omitted from the review as it is not considered to be a trace element in gold ores, but rather a significant impurity that has been extensively studied and is the subject of a recent review (Lu et al., 2002). A separate paper will focus on their chemical behaviour during the cyanidation process for gold recovery (including carbon adsorption and elution), tailings disposal and also capture related information from the treatment of industrial wastes and wastewaters, including fixation and encapsulation processes that may be applicable in gold processing.

Traditionally, these trace elements have been investigated in minerals processing as impurities in commodities such as base metals and concentrates. However, more recently this research has been aimed at increasing employee safety and meeting environmental regulations. In Australia, the trace elements antimony, arsenic, beryllium, cadmium, chromium (III&VI), cobalt, copper, lead, manganese, mercury, nickel, selenium and zinc are listed by the Australian National Pollutant Inventory (NPI) as monitoring targets that need to be measured and reported annually for all mine and mineral processing facility outputs. The NPI is a public database listed on the internet that displays information about diffuse sources and emissions of 90

different substances to air, land and water reported by industrial facilities. The most recent reports can be viewed on their website (<http://www.npi.gov.au>). The latest relevant Australian emissions data for the trace elements of interest to this review are listed in Table 1. Bismuth and tellurium are excluded as they are not required to be reported under current legislation. Several other countries also collate similar data which is available publicly on the Internet (e.g. USA – Toxics Release Inventory; Canada – National Pollution Release Inventory).

The Australian data, which includes emissions from all aspects of the mining and mineral processing operations including the burning of fossil fuels on site, indicates that the main trace metal emissions to the environment from metal processing operations are lead, arsenic, antimony and cadmium. In general, emissions to air dominate the total emissions, although for certain trace elements (e.g., selenium) water emissions can also be significant. The main emissions from gold mining operations are arsenic which is largely fugitive (dust containing arsenic minerals), and mercury (~0.7 tonnes/year), which is mainly stack emissions from ore roasting and carbon regeneration.

Lead toxicity is now well established, and cadmium is widely classified as a human carcinogen, but little is known of their deportment in the gold processing solutions. Similarly mercury toxicity from its use in gold amalgamation is well known, but mercury as a trace element of concern in ore roasting, pressure oxidative leaching and gold cyanidation is a more recent issue (Newmont Mining Corporation, 2009).

Arsenic, another known carcinogen, has been widely studied in gold processing (Reddy et al., 1988) particularly the precipitation and disposal of solubilised arsenical wastes, and several commercial processes now exist for the fixation and encapsulation

of arsenical wastes from the roasting, pressure leaching or bacterial leaching of gold ores and concentrates (Connor, 1990; Reddy and Ramachandran, 2005; Dolomatrix International, 2011). Research into the long term stability of these treated wastes continues, as do investigations into the behaviour and deportment of arsenic aimed at further reducing health and environmental risks, especially in tailings discharges. Much less is known about antimony and bismuth due to their generally lower concentrations in gold ores, and while bismuth has a lower toxicity, antimony can be compared to arsenic in its toxic effects on humans.

Selenium is an essential nutrient in trace amounts but it is very toxic at higher concentrations (Cai, 2000); it has been ranked as the third most toxic trace element after mercury and lead (Peters et al., 1997). Tellurium is thought to be less toxic but must be handled with care. Little information is currently available regarding the deportment of selenium or tellurium in mineral processing plants. Hence, the health and environmental risks of antimony and selenium, and to a lesser extent bismuth and tellurium, require that more is known of their chemical behaviour during gold processing.

## 2 MINERALOGY AND AQUEOUS SOLUTION CHEMISTRY

### 2.1 Lead, cadmium and mercury

Lead, cadmium and mercury are the key heavy metals covered in this review.

Although the solution chemistry of lead differs significantly from cadmium and mercury, these metals are often grouped together in environmental studies on account of their toxicities.

Lead is in Group IVB of the Periodic Table. It is a relatively abundant element in the earth's crust at an estimated average abundance of 10 to 14 parts per million by mass. Its principal valence states are 0, +II and +IV. Its principal sulfide mineral is galena (PbS) from which most lead is extracted. Secondary oxidised minerals include cerussite (PbCO<sub>3</sub>) and anglesite (PbSO<sub>4</sub>) which commonly occur in the near-surface weathered or oxidised zone of a lead orebody. Lead forms lead(II) oxide (PbO), lead(IV) oxide (PbO<sub>2</sub>) and the mixed valence state oxide Pb<sub>3</sub>O<sub>4</sub> (called red lead). Native lead is rare.

Cadmium and mercury are in Group IIB of the Periodic Table. The principal valence state of both elements is +II, though mercury also forms mercury metal (0) and a number of mercurous(I) compounds (e.g. calomel, Hg<sub>2</sub>Cl<sub>2</sub>). Cadmium(I) compounds are rare. Cadmium is a rare element in the earth's crust at an estimated average abundance of 0.11 to 0.15 parts per million by mass, which is much higher than mercury with an estimated average crustal abundance of only 0.05 to 0.08 parts per million by mass. Since mercury does not blend geochemically with those elements that constitute the majority of the crustal mass, mercury ores can be extraordinarily concentrated considering the element's low abundance in ordinary rock. The richest mercury ores contain up to 2.5 % mercury by mass, and even the leanest concentrated deposits are at least 0.1 % mercury.

Greenockite (CdS) is the only important cadmium mineral. It is nearly always associated with sphalerite (ZnS) and is produced mainly as a by-product from zinc ore processing. Mercury is found most commonly as the brick-red mineral cinnabar (HgS). Some of the other mercury minerals associated with gold or silver are



tiemannite (HgSe), corderoite (Hg<sub>3</sub>S<sub>2</sub>Cl<sub>2</sub>), coloradoite (HgTe), and gold or silver mercury amalgams (Zarató, 1985). Native mercury metal is rare.

In cyanidation solutions these minerals may dissolve to form a number of stable complexes. The overall formation constants ( $\text{Log } \beta_n$ ) for the formation of several complexes with these metals are presented in Table 2. Lead may form the very weak cyano complexes  $\text{Pb}(\text{CN})^+$  and  $\text{Pb}(\text{CN})_2^0$  in aqueous solution, but only below pH 8 (Perera, 2001). Cadmium forms relatively weak cyano complexes,  $\text{Cd}(\text{CN})_2^0$ ,  $\text{Cd}(\text{CN})_3^-$  and  $\text{Cd}(\text{CN})_4^{2-}$ , but the mercury complexes,  $\text{Hg}(\text{CN})_3^-$  and  $\text{Hg}(\text{CN})_4^{2-}$  are considerably stronger. Cadmium cyano complexes therefore report as weak acid dissociable (WAD) cyanide, whereas mercury complexes are included in the total cyanide analysis. Depending on the conditions, all the metals can form a number of hydroxo and chloro complexes. Unlike most metals, lead forms an insoluble chloride ( $\text{PbCl}_2$ ) and, being amphoteric, the hydroxide is soluble at high pH forming a number of hydroxo complexes including  $\text{Pb}(\text{OH})_3^-$  and  $\text{Pb}(\text{OH})_4^{2-}$  (plumbite). In solutions containing carbonate or sulfate ions, carbonato or sulfato complexes with lead may also form, depending on the concentrations of the complexing ions in solution (Powell et al., 2009).

#### *Chemical Speciation Modelling*

Thermodynamic properties have been determined for many of these species, mostly for “ideal” solutions (i.e. 25 °C and 1 atmosphere pressure, in very dilute solution) and thus thermodynamic equilibrium modelling can provide information as to the equilibrium speciation for particular solution conditions (i.e. pH,  $E_H$ , salinity, temperature). Several commercial thermodynamic equilibrium modelling packages are available, such as OLI (<http://www.olisystems.com>), JESS (May and Murray,

2000; Murray and May, 2008; <http://jess.murdoch.edu.au>), STABCAL ([http://www.mtech.edu/CAMP/documents/camp\\_brochure.pdf](http://www.mtech.edu/CAMP/documents/camp_brochure.pdf)) and HSC (<http://www.outotec.com>), that can provide information on the speciation and deportment of minor elements during gold processing. However, variations exist in the extent of the databases, the quality of the thermodynamic constants chosen, and the treatment of solution non-ideality in the calculations (Popov and Wanner, 2005).

In modelling the deportment of these elements during gold processing, consideration also needs to be given to the rate of reactions as they move towards the equilibrium condition (i.e. chemical kinetics). In cases where the reactions are very slow, often “pseudo-equilibrium” conditions better describe the speciation and deportment of the species in the short term.

The thermodynamic equilibrium models for the speciation of these trace elements in cyanidation solutions were determined using the JESS and OLI software packages which had the most extensive data on the trace elements of interest. The aim was to compare not only the thermodynamic models produced, but also to investigate the information on the trace elements contained within the respective databases. Figure 1 shows the thermodynamic equilibrium distributions calculated using JESS for lead, mercury and cadmium species in a typical gold processing solution of low ionic strength that is free of sulfides. The speciation differs slightly from that calculated using OLI (Figure 2) and can be explained by the slightly different values of the formation constants for the main species used in the determination. These values, as well as the preferred formation constants discussed in this review, are listed in Table 2.

Both JESS and OLI predict that lead is mainly in the solid state up to pH 11 or 12 as the basic lead carbonate, hydrocerussite ( $\text{PbCO}_3 \cdot 2\text{Pb(OH)}_2$ ). Hydrocerussite is now generally believed to be the stable solid phase in alkaline solutions rather than lead hydroxide (Todd and Parry, 1964). The most recent and accurate determination of the  $\Delta G_f^\circ$  for hydrocerussite has been reported by Mercy et al. (1998) who used electrochemical cell measurements. This value is in good agreement with earlier determinations of -1699 kJ/mol by Garrels (1957), who adjusted the earlier data of -1711 kJ/mol of Randall and Spencer (1928), and  $-1705 \pm 11$  kJ/mol by Taylor and Lopata (1984) using solubility measurements. The value by Mercy et al. (1998) is recommended as the preferred value, as it is less reliant on the speciation model chosen to interpret the data.

The lead redissolves above pH 11 to predominantly form the hydrogen dioxylead ion,  $\text{HPbO}_2^-$  (OLI) or a number of different lead hydroxide complexes, ( $\text{Pb(OH)}_2^0$  followed by  $\text{Pb(OH)}_3^-$  and  $\text{PbO(OH)}^-$  with minor  $\text{Pb(OH)}_4^{2-}$ ) as the pH increases (JESS). It should be noted that the ions  $\text{HPbO}_2^-$ ,  $\text{PbO(OH)}^-$ , and  $\text{Pb(OH)}_3^-$  are all thermodynamically equivalent in aqueous solutions, differing only in the way the ions are described or the extent of hydration. One issue with thermodynamic databases is to describe these thermodynamically identical ions in a consistent manner (Filella and May, 2003).

A critical review of lead hydroxo complex stability constants has recently been compiled by Powell et al. (2009). Formation constants calculated from these data are included in Table 2 as recommended values. The  $\text{Pb(OH)}_4^{2-}$  complex was excluded from this review, and also Table 2, as its formation was considered as still uncertain.

The cadmium and mercury speciations are similar for both models even though for mercury there are significant differences between the formation constants used in the calculations. The tetracyanide complexes predominate at high pH over the tricyanide complexes, and the lower complexes, having lower formation constants, tend to form only to a limited extent (as in the dicyanides) or not at all (the mono-cyanide complexes).

Another factor to be considered in speciation modelling is the salinity of the process water. In certain parts of Western Australia, the process water used in gold cyanidation is hypersaline having total dissolved solids concentrations ranging from about two times up to seven times seawater (that is, from ~60 to ~210 g/L). The salinity, which consists mainly of sodium, chloride, magnesium, and sulfate (in order of decreasing molar concentration), causes a range of ionic strength effects including changes in the dissociation constant for hydrogen cyanide (Verhoeven et al., 1990) and changes in the stability constants for a range of cyano-complexes (Rees and Van Deventer, 1999). For copper, the more highly complexed species are favoured at higher ionic strengths (Lukey et al., 1999), and the same dependence may apply to cadmium and mercury cyano complexes, although to our knowledge this has not been confirmed.

## 2.2 Arsenic, antimony and bismuth

These elements are all in Group VB of the periodic table, and as such have similar chemical properties. Arsenic and antimony are metalloids, although they are generally grouped with metals for environmental purposes. Bismuth is a metal and is similar to lead in its properties (Smith, 1973). All are chalcophiles preferring to bond with sulfur rather than oxygen, and they generally occur in nature as sulfides.

Their principal valence states are 0, -III, +III and +V, but for bismuth only 0 and +III are formed under normal conditions. The Bismuth(-III) hydride ( $\text{BiH}_3$ ) will only form under extremely reducing conditions ( $E^\circ = -0.97 \text{ V}$ ) and is thus very unstable. Bi(V) is highly oxidising, being able to oxidise water to oxygen ( $E^\circ = +2.1 \text{ V}$ ) (Smith, 1973).

Arsenic is a relatively abundant element (1.8 parts per million) and is widely distributed in the earth's crust in more than 300 minerals. The most common commercial source of arsenic is arsenic trioxide, a by-product from the processing of base and precious metals ores (Smith, 1973). Antimony is less abundant than arsenic, although over a hundred minerals of antimony are found in nature. Estimates of the abundance of antimony in the Earth's crust range from 0.2 to 0.5 parts per million.

The most common arsenic sulfide minerals are the red-orange realgar ( $\text{As}_4\text{S}_4$ ) and its weathering product, yellow orpiment ( $\text{As}_2\text{S}_3$ ). Arsenic is also found in association with metals as arsenides, for example in the common mineral arsenopyrite ( $\text{FeAsS}$ ) and base metal arsenides such as enargite ( $\text{Cu}_3\text{AsS}_4$ ), cobaltite ( $\text{CoAsS}$ ) and gersdorffite ( $\text{NiAsS}$ ). In arsenical ores formed at high temperature like arsenopyrite, gold may be incorporated into the lattice either in solid solution or on the growing crystal faces. Often sub-microscopic gold may account for the majority of the gold present, rendering the ore refractory and can be difficult to treat. Oxidised minerals include claudetite or arsenolite ( $\text{As}_2\text{O}_3$ ), pharmacolite ( $\text{CaHAsO}_4 \cdot 2\text{H}_2\text{O}$ ), mimetite ( $\text{Pb}_5(\text{AsO}_4)_3\text{Cl}$ ) and erythrite ( $\text{Co}_3(\text{AsO}_4)_2 \cdot 8\text{H}_2\text{O}$ ) (Smith, 1973).

Stibnite ( $\text{Sb}_2\text{S}_3$ ) is the predominant mineral of antimony (USGS, 2010a), and the main antimony mineral associated with gold. Other minor minerals with gold associations are tetrahedrite ( $\text{Cu}_{12}\text{Sb}_4\text{S}_{13}$ ), berthierite ( $\text{FeSb}_2\text{S}_4$ ), gudmundite ( $\text{FeSbS}$ ) and

aurostibite ( $\text{AuSb}_2$ ) (Davies and Paterson, 1986; Millard, 2005). The most common oxide minerals are the dimorphous minerals valentinite and senarmontite ( $\text{Sb}_2\text{O}_3$ ) and the oxyhydroxide stibiconite ( $\text{Sb}_3\text{O}_6(\text{OH})$ ). All are derived from the oxidation of stibnite. In natural waters, soluble antimony is present exclusively as  $\text{Sb}(\text{OH})_6^-$  under oxic conditions, and as  $\text{Sb}(\text{OH})_3^0$  in anoxic waters (Filella and May, 2003).

Bismuth is the heaviest of the 'heavy metals'. At an estimated 8 parts per billion by mass in the Earth's crust it is much rarer than its counterparts but about twice as abundant as gold. Its most common mineral is bismuthinite,  $\text{Bi}_2\text{S}_3$  (USGS, 2010b) and is generally found with or without its oxidation products bismite ( $\text{Bi}_2\text{O}_3$ ) and bismutite,  $\text{Bi}_2(\text{CO}_3)\text{O}_2$ . Generally, these occur in minute quantities within ores of other metals, such as gold, silver, lead, zinc, and tungsten (Smith, 1973). Other bismuth minerals found in association with gold-bismuth deposits in China include native bismuth (Bi), montanite ( $\text{Bi}_2\text{TeO}_6 \cdot 2\text{H}_2\text{O}$ ), pavonite ( $\text{AgBi}_3\text{S}_5$ ), hedleyite (possibly  $\text{Bi}_7\text{Te}_3$ ) and others (Yunsheng et al., 2005).

Arsenic, antimony and bismuth do not form stable complexes with cyanide. Arsenic sulfide minerals decompose in solution to form arsenite ( $\text{AsO}_3^{3-}$ ) and arsenate ( $\text{AsO}_4^{3-}$ ) and the partially oxidised thioarsenites ( $\text{AsS}_3^{3-}$ ) and thioarsenates ( $\text{AsS}_4^{3-}$ ). Antimony sulfide minerals tend to form the equivalent oxyanions and thioanions to arsenic. Bismuth is more metallic in nature and does not form oxyanions in aqueous solution. It is only sparingly soluble above pH 4 (concentrations of bismuth in solution of 0.01 to 0.1 millimolar), and in weakly acid or alkaline solutions precipitates as  $\text{Bi}(\text{OH})_3$  or  $\text{BiOOH}$ . Bismuth forms a number of mono- and polynuclear hydroxo complexes at high pH, namely  $[\text{Bi}(\text{OH})_2]^+$ ,  $[\text{Bi}(\text{OH})_3^0]$ ,

$[\text{Bi}(\text{OH})_4^-]$  and  $[\text{Bi}_6\text{O}_4(\text{OH})_4]^{6+}$  with minor  $[\text{Bi}_3(\text{OH})_4]^{5+}$  (Kragten and Decnop-Weever, 1993; Godfrey et al., 1998).

### *Chemical Speciation Modelling*

Figure 1 shows the thermodynamic equilibrium distributions calculated using JESS for arsenic, antimony and bismuth species in a typical gold processing solution of low ionic strength. The speciation calculated using OLI (Figure 2) is similar for bismuth, however, there are a number of significant differences for arsenic and antimony.

The speciation for arsenic and antimony are very dependent on the oxidative capacity of the system. As this is generally high in well oxygenated solutions such as modelled here ( $E_H$  varied from 850 down to 450 mV over the pH range for an oxygen partial pressure of 0.2), the equilibrium species will contain mainly the most highly oxidised forms of the trace elements. The oxidation of As(III) to As(V) is generally slow (except in the presence of strong oxidising agents) and so both oxidation states can often co-exist in solution, with the arsenite(III) species being more soluble than the arsenate(V) species (Magalhães, 2002). However the thermodynamic equilibrium species predicted by these models are all in the As(V) oxidation state.

In aqueous oxygenated solutions containing calcium and arsenate ions, a range of solid species may precipitate, depending on the pH and Ca:As ratios. Many species have been reported, but from recent carefully executed solubility experiments, the most prominent species formed in alkaline solutions appear to be johnbaumite ( $\text{Ca}_5(\text{OH})(\text{AsO}_4)_3$ ) and calcium arsenate ( $\text{Ca}_3(\text{AsO}_4)_2 \cdot x\text{H}_2\text{O}$ ) at Ca:As ratios below 2.0, with  $\text{Ca}_4(\text{OH})_2(\text{AsO}_4)_2 \cdot x\text{H}_2\text{O}$  forming at higher Ca:As ratios (Bothe and Brown, 1999; Zhu et al., 2006). The most recent equilibrium data ( $\text{p}K_{sp}$ ) of Zhu et al. at 25°C

differ slightly from the earlier data of Bothe and Brown (23°C), mainly due to differences in their speciation modelling. The latter data are recommended (Table 3).

The modelling using JESS predicts that all the arsenic will be present as the solid species  $\text{Ca}_{10}(\text{OH})_2(\text{AsO}_4)_6$  (Mahapatra et al., 1987), which is thermodynamically equivalent to johnbaumite ( $\text{Ca}_5(\text{OH})(\text{AsO}_4)_3$ ). The JESS database contains two calcium arsenate species, johnbaumite and  $\text{Ca}_3(\text{AsO}_4)_2$ . The OLI model indicates the arsenic will be soluble and present only as the hydrogen arsenate ion ( $\text{HAsO}_4^{2-}$ ). The only solid calcium species in the OLI database is  $\text{Ca}_3(\text{AsO}_4)_2$ .

The available thermodynamic data for antimony have been recently critically reviewed and evaluated (Filella and May, 2003) and represent the best information available at present on antimony equilibria in aqueous solutions. The most relevant and recommended stability constants are shown in Table 3. The current modelling using JESS predicts that all antimony will be soluble as the antimony(V) complex  $\text{Sb}(\text{OH})_6^-$ . The OLI database does not have data for Sb(V) species and hence only Sb(III) species are modelled. Predominantly the Sb(III) species are the soluble hydroxide ( $\text{Sb}(\text{OH})_3^0$ ) and the insoluble solid trioxide ( $\text{Sb}_2\text{O}_3$ ) up to pH 11, after which both species hydrolyse further to the  $\text{Sb}(\text{OH})_4^-$  ion.

The models predict bismuth is present mainly as the insoluble oxyhydroxide,  $\text{BiOOH}$  (JESS) or the thermodynamically equivalent hydroxide,  $\text{Bi}(\text{OH})_3$  (OLI) respectively over the entire pH range, with minor amounts (less than 1% in JESS and about 10% in OLI) of the soluble species  $\text{Bi}(\text{OH})_3(\text{aq})$  and  $\text{Bi}(\text{OH})_4^-$ , the latter increasing at pHs above 12. For both models, the bismuth solubility is less than expected from the measurements of Kratgen and Decnop-Weever (1993), who measured bismuth



solubility and equilibrium constants for the bismuth hydroxo complexes in one molar nitrate and perchlorate media.

### 2.3 Selenium and tellurium

Selenium and tellurium are in Group VIB of the Periodic Table, the same group as sulfur, and have similar chemical properties. They are classified chemically as non-metals with principal valence states of 0, -II, +IV and +VI. Selenium and tellurium are extremely rare elements having estimated crustal abundances of 50 and 1 - 5 parts per billion respectively. The principal sources of selenium and tellurium are anode sludges produced during the electrolytic refining or smelting of base metals such as copper and lead.

Selenium often occurs together with sulfide minerals as selenides and is found in sulfide ores such as pyrite, partially replacing the sulfur in the ore matrix. Typical selenide minerals include klockmannite (CuSe), stellite (ZnSe), berzelianite (CuSe), clausthalite (PbSe), penroseite (NiSe) and tiemannite (HgSe). Although these minerals are not abundant, they can occur together with copper, zinc and nickel ores. Recently, other selenide minerals such as aguilarite ( $\text{Ag}_4\text{SeS}$ ), naumannite ( $\text{Ag}_2\text{Se}$ ), Sb-pearceite ( $(\text{Ag,Cu})_{16.9}(\text{Fe,Zn})_{0.24}(\text{Sb,As})_{1.98}(\text{S,Se})_{11}$ ) and polybasite ( $(\text{Ag,Cu})_{16.9}(\text{Sb,As})_{1.98}(\text{S,Se})_{11}$ ) have been identified in the Waihi district of the Hauraki goldfield in New Zealand (Staley, 2005).

Tellurium is sometimes found in its native (elemental) form and as the tellurides of gold, and often with associated silver. Typical gold and silver minerals are calaverite,  $\text{AuTe}_2$ , krennerite,  $\text{AuTe}_2$ , petzite,  $\text{Ag}_3\text{AuTe}_2$ , sylvanite,  $(\text{Ag,Au})\text{Te}_2$ , hessite,  $\text{Ag}_2\text{Te}$ , and coloradoite,  $\text{HgTe}$  (Bagnall, 1973; Ahmad et al., 1987). Gold-telluride associations also occur with antimony in montbrayite ( $[\text{AuSb}]_2\text{Te}_3$ ) and copper in

kostovite [CuAuTe<sub>4</sub>] while non-gold associated minerals include coloradoite (HgTe) and altaite (PbTe) (Ellis, 2005).

Selenium forms the stable selenocyanate anion (SeCN<sup>-</sup>) in the presence of cyanide (Flynn and Haslem, 1995) while cyanotellurate (TeCN<sup>-</sup>) is known but is much less stable (Klaeboe et al., 1977). In cyanide solutions, both selenite and selenate ions should be reduced to selenocyanate by cyanide ions, the latter being oxidised to cyanate (Table 4). Although thermodynamically favourable, the rates of these reactions are unknown. In acidic solutions, selenocyanate will decompose to selenium(0) and hydrocyanic acid (Boughton and Keller, 1966).

Selenocyanate is analogous to the sulfur species thiocyanate (SCN<sup>-</sup>) and can form complexes with metal ions such as gold, zinc, cadmium, mercury and iron (Norbury, 1975). As expected for a “soft” base such as selenocyanate, the formation constants for its complexes of mercury are much larger than for cadmium (Table 5, OECD, 2005).

Analogous to sulfides, selenides and tellurides may be oxidised to form oxyanions in cyanide solutions (e.g. selenite, SeO<sub>3</sub><sup>2-</sup> or selenate, SeO<sub>4</sub><sup>2-</sup> and tellurite, TeO<sub>3</sub><sup>2-</sup> or tellurate, TeO<sub>4</sub><sup>2-</sup>) with the +IV species predominating except at high redox potentials and/or high pH. The selenides (-II) and tellurides (-II) are immobile in anoxic environments but are rapidly oxidised in air to elemental selenium and tellurium (Haygarth, 1994).

The selenate and tellurate ions are strong oxidising agents in acidic solutions with standard reduction potentials values greater than 1.0 volt, but are much less oxidising

in alkaline solutions (see Table 4) where the values fall to around zero volts (OECD, 2005; Greenwood and Earnshaw, 1997).

### *Chemical Speciation Modelling*

Figure 1 shows the thermodynamic equilibrium distributions calculated using JESS for selenium and tellurium species in a typical gold processing solution of low ionic strength. Again, there are a number of differences between the JESS and OLI models (Figure 2).

For selenium modelling, both JESS and OLI predict virtually all the selenium to be present as the soluble selenate(VI) ion,  $\text{SeO}_4^{2-}$ . Because of the very low  $\text{pK}_a$  (1.75 or 1.91, see Table 4) of hydrogen selenate, it will only exist in minor amounts except at very low pH. JESS also includes minor amounts of the aqueous complexes  $\text{CaSeO}_4^0$  and  $\text{MgSeO}_4^0$  while OLI predicts minor hydrogen selenate,  $\text{HSeO}_4^-$ . Neither model predicts selenite(IV) ion to be present under the oxidising conditions in the cyanide leach, nor the existence of selenocyanate in oxic cyanide solutions, although it appears to be thermodynamically stable at lower  $E_H$  (Table 4).

For tellurium, JESS predicts all is present as soluble Te(VI) species, predominantly the hydrogentellurate ion,  $\text{HTeO}_4^-$  at lower pH and the deprotonated tellurate ion,  $\text{TeO}_4^{2-}$  at higher pH. OLI modelling, however, predicts tellurium(VI) is predominantly soluble below about pH 8.5, as orthotelluric acid ( $\text{H}_6\text{TeO}_6$ ), pentahydrogen ( $\text{H}_5\text{TeO}_6^-$ ), and the hydrogentellurite(IV) ion,  $\text{HTeO}_3^-$ , with the latter two having similar distributions with pH. Orthotelluric acid, and orthotellurate ions, are a six-coordinate form of the tellurate, structurally different from the four-coordinate form, called metatellurate. Unlike selenate ion, in solution, the ortho-form

predominates (Greenwood and Earnshaw, 1997) and, unless specifically differentiated as the four-coordinate metatellurate the formula  $\text{TeO}_4^{2-}$  refers to the six-coordinate species.

Above pH 8.5, OLI predicts the insoluble tellurite salts calcium tellurite(IV) monohydrate ( $\text{CaTeO}_3 \cdot \text{H}_2\text{O}$ ) and magnesium tellurite(IV) are the major tellurium species formed. The JESS database for Tellurium does not contain these species.

## 2.4 Conclusions

Although there is much information available about the aqueous solution chemistry of the trace elements, much more remains to be learned. In particular, the chemistry of the trace elements as applied to cyanide leach solutions remains largely unexplored.

Chemical speciation modelling can assist in understanding the chemistry of the trace elements in gold cyanidation solutions, however, many significant differences exist between the predicted speciation of these trace elements for different types of modelling software (Popov and Wanner, 2005). A comparison between the predicted speciation models using JESS and OLI software has been used to examine these differences, which exist due to differences in the thermodynamic data used, the paucity of data that exists under appropriate non-ideal conditions, and the methods used in the software packages to estimate thermodynamic parameters under such conditions.

### 3 TOXICITY AND ENVIRONMENTAL GUIDELINES

#### 3.1 Sources and toxicities

Most of the trace elements are toxic to plants and animals because they do not have a natural physiological role, and their toxicity can be ascribed to their interference in certain critical biochemical processes (May and Bulman, 1983). Therefore, the sources and toxicities of the trace elements to humans are important from an environmental health and safety perspective. In addition, the toxicity of the trace elements to aquatic and terrestrial flora and fauna is now a key issue for the gold processing industry. The ingestion of wastewater from tailings storage facilities by birds and animals has been documented by Donata et al. (2007). However, information on the toxicity of metal cyanides to birds and to plant life surrounding the tailings impoundment, including species that may be used for revegetation following mine closure, or even for phytoremediation (the use of plants in bioremediation) is minimal.

#### Lead, cadmium and mercury

Lead, cadmium and mercury are generally considered to be the most toxic of the heavy metals in the environment (Landis and Yu, 2003). Until recently, lead in gasoline was the primary source of environmental lead, followed by lead emissions from smelting operations and household paints. Lead is accordingly ubiquitous in the environment. Cadmium outputs are mainly from metal refining, the burning of fossil fuels and its presence in phosphate fertilisers and cigarettes. Mercury comes from natural sources (volcanic activity) as well as smelting operations and its use in industry and agriculture.

The systemic toxic effects of lead in humans have been well-documented up to 1990 by the USEPA (1990), who extensively reviewed and evaluated data reported in the literature. Due to their solubility in acids and therefore stomach fluids, the lead salts of carbonate, monoxide, and sulfate are considered to be more toxic than metallic lead or other lead compounds. One of the main health concerns is the retardation of brain development in children. Lead is a probable carcinogen (Silbergeld et al., 2000).

Cadmium is absorbed more efficiently by the lungs than by the gastrointestinal tract, and is excreted primarily in the urine. Inhalation of cadmium is associated with lung cancer while gastrointestinal intake affects the liver and kidneys (May and Bulman, 1983). Cadmium is classified as a human carcinogen by World Health Organization's International Agency for Research on Cancer and the United States National Toxicology Program (Waalkes, 2003).

Mercury and most of its compounds are extremely toxic, particularly its organic compounds, such as methyl mercury and dimethyl mercury. Fish and shellfish have a natural tendency to concentrate mercury (May and Bulman, 1983). The World Health Organization treats mercury as an occupational hazard, and has established specific occupational exposure limits.

Methylmercury is a neurological poison affecting primarily brain tissue and at high doses can cause severe damage to the developing brain. Today a chief concern is with the more subtle effects arising from prenatal exposure such as delayed development and cognitive changes in children. Mercury is a possible human carcinogen (Clarkson, 1997).

Lead, cadmium and mercury are all toxic to plants and animals, and when in solution are especially toxic to aquatic flora and fauna. In plants, they inhibit germination and

photosynthesis, and in higher plants accumulate in leaves where they become available to grazing animals (Yu, 2001). Little is known of the ability of plants to assimilate the cyanide complexes of these metals.

#### Arsenic, antimony and bismuth

Arsenic is ubiquitous in the environment and its anthropogenic sources include paints, insecticides, herbicides and rodenticides, and until recently was also used as a wood preservative. Antimony and bismuth are less common although antimony is used in many products as a flame retardant, and bismuth is being increasingly used as a substitute for lead. The main sources of emissions are from mining and smelting operations where they are generally present as impurities.

In the European Union (EU), elemental arsenic and its compounds are classified as "toxic" and "dangerous for the environment". The EU and the International Agency for Research on Cancer (IARC) both recognize arsenic and arsenic compounds as carcinogens. Human exposure to arsenic is mainly through water consumption. In general, arsenic(III) compounds are more toxic than arsenic(V) compounds, and those that are water soluble are more toxic than those that are not. One of the most toxic inorganic arsenic compounds is arsine gas,  $\text{AsH}_3$  (Graeme and Pollack, 1998).

In plants and animals, arsenic is toxic at relatively low (ppb) levels (e.g. Gebel, 1997; Smedley and Kinniburgh, 2002) and can inhibit nitrification and the growth of microorganisms.

Antimony and many of its compounds are toxic with antimony(III) being more toxic than antimony(V) compounds (Gurnani et al., 1994; Gebel, 1997). The main route of exposure is by inhalation of the dust. Deposits of inhaled antimonials may be retained

in the lungs for years. The toxicity of stibine ( $\text{SbH}_3$ ) is analogous to that of arsine ( $\text{AsH}_3$ ). Antimony(III) is a possible carcinogen (De Wolff, 1995).

Bismuth is considered one of the less toxic of the heavy metals, and its salts are used in cosmetics and medicines. However, serious and sometimes fatal poisoning may occur from over-use. Bismuth is not considered to be a human carcinogen (Slikkerveer and De Wolff, 1989; Lambert, 1991).

### Selenium and tellurium

Selenium is an essential trace element for human health, and has been shown to reduce occurrences of a range of conditions including cancers when taken as a supplement in selenium-deficient regions (Ni et al., 1994; Brown, 2000). It is, however, toxic if taken in excess. Elemental selenium and metallic selenides have relatively low toxicities because of their low bioavailability. By contrast, selenates and selenites are very toxic, having a mode of action similar to that of arsenic trioxide (Tinggi, 2003). Hydrogen selenide gas is an extremely toxic and corrosive gas.

Selenium compounds are not considered to be carcinogens.

Soluble tellurium and its compounds are highly toxic to most microorganisms (Turner et al., 2001). They are also considered to be toxic to humans and need to be handled with care, although acute poisoning is rare. They are not considered to be carcinogenic (Taylor, 1996).

### 3.2 Environmental guidelines

The World Health Organisation (WHO, 2001) has developed guidelines for the maximum quantities of chemicals that should be present in drinking water to protect human health, and Australia has developed similar guidelines for the Australian



environment (NHMRC, 2004). In addition, the Australian and New Zealand Environmental and Conservation Council (ANZECC, 2000) have developed guidelines using a risk based approach for the maximum quantities of elements/chemicals that should be present in both freshwater and marine aquatic ecosystems for the protection of the aquatic flora and fauna. The WHO and Australian drinking water guidelines, together with the ANZECC guidelines for the protection of freshwater aquatic ecosystems, are listed in Table 6. These guidelines are constantly being updated as new knowledge comes to hand. Aquatic organisms are much more sensitive to changes to toxic elements than humans, and therefore the guidelines are generally much lower than the drinking water guidelines.

The toxicity of the trace elements are generally listed as the total elemental concentration in the water, but as the importance of the elemental speciation is becoming more recognised, more data is becoming available on the toxic effects of different chemical species. For example, the toxicity effects of arsenic(III) and arsenic(V) are now listed separately in the ANZECC (2000) guidelines.

In cyanidation waste waters, some of the elements may exist as cyanide complexes and hence also contribute to the toxic effect of cyanide on fauna (Donato et al., 2007).

The toxicity of metal cyano complexes to aquatic life and information pertaining to aquatic plant uptake of these metal-cyanide species is largely unknown, with only a few studies addressing plant uptake and metabolism of ferro- and ferricyanide being found (Ebbs, 2004; Samiotakis and Ebbs, 2004 and references therein).

## 6 CONCLUSIONS

A literature review on the mineralogy, aqueous solution chemistry and toxicity of the trace elements lead, cadmium, mercury, arsenic, antimony, bismuth, selenium, and

tellurium in gold processing by cyanidation is presented. The review compiles the current knowledge in this area and highlights the gaps in the current knowledge and understanding.

### 6.1 Lead, cadmium and mercury

The principal sulfide minerals are galena (PbS), greenockite (CdS) and cinnabar (HgS). Lead(II) has a very low solubility under gold cyanidation conditions forming the relatively insoluble hydroxide, whereas cadmium minerals dissolve to form a range of relatively weak cyano-complexes that are readily dissociated, and report as WAD cyanide. The mercury cyano-complexes are much stronger and persistent in tailings solutions and the environment.

Lead, cadmium and mercury are heavy metals and are all very toxic to humans, with cadmium and mercury being classified as human carcinogens. They are also toxic to plants and animals, especially the aqueous species.

### 6.2 Arsenic, antimony and bismuth

Arsenic and antimony are metalloids. The most common arsenic sulfide minerals are realgar (As<sub>4</sub>S<sub>4</sub>), orpiment (As<sub>2</sub>S<sub>3</sub>), and arsenopyrite (FeAsS). The antimony mineral associated with gold is stibnite (Sb<sub>2</sub>S<sub>3</sub>), and bismuth is generally found as bismuthinite (Bi<sub>2</sub>S<sub>3</sub>).

In alkaline waters, both arsenic and antimony can be present in solution at very high concentrations as oxy- or hydroxy-anions. Bismuth is insoluble except under acidic conditions and in alkaline solutions precipitates as bismuthyl salts or bismuth hydroxide (Bi(OH)<sub>3</sub>) or oxyhydroxide (BiOOH).

Their compounds are classified as "toxic" and "dangerous for the environment". In general, arsenic and antimony (III) compounds are more toxic than the arsenic and antimony (V) compounds respectively. While arsenic is recognised as a carcinogen, antimony(III) is not. Bismuth, a metal, is less toxic and is not a carcinogen.

### 6.3 Selenium and tellurium

Selenium occurs with sulfide minerals as selenides while tellurium is found as tellurides of gold and silver. Selenide minerals have been reported to form selenocyanate ( $\text{SeCN}^-$ ) during cyanidation, which may predominate over the oxyanions selenite and selenate under certain conditions, but was not predicted in current models produced using OLI and JESS. Tellurocyanate is unstable with tellurite being the most stable oxyanions except under oxidising conditions at high pH where tellurate may form.

Selenium is an essential trace element for human health but is toxic in excess. Selenates and selenites are very toxic, with a mode of action similar to their arsenic analogues. Soluble tellurium and its compounds are highly toxic to most micro-organisms and also toxic to humans. Neither is considered to be carcinogenic.

The application of two currently available software packages (JESS and OLI) for thermodynamic modelling of these trace elements in cyanidation solutions has been investigated. The results have shown significant differences between the models, and have highlighted the need for further development of these software packages, as well as further input to their databases to produce more accurate models of the systems under study.

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**Table 1: Estimated NPI Reported Emissions (2007-08) from metal ore mining and basic non-ferrous metal manufacturing in Australia (tonnes/year).**

<b>Metal ore mining</b>	<b>Pb</b>	<b>Cd</b>	<b>Hg</b>	<b>As</b>	<b>Sb</b>	<b>Se</b>
Air	220	5.9	1.4	55	2.5	2.9
Water	13	1.4	<0.1	3.1	1.5	1.0
<b>Total</b>	<b>240</b>	<b>7.4</b>	<b>1.4</b>	<b>60</b>	<b>5</b>	<b>4</b>
<b>Basic non-ferrous metal manufacture</b>	<b>Pb</b>	<b>Cd</b>	<b>Hg</b>	<b>As</b>	<b>Sb</b>	<b>Se</b>
Air	340	15	8.7	72	21	0.8
Water	2.9	0.6	<0.1	1	0.6	0.5
<b>Total</b>	<b>340</b>	<b>16</b>	<b>8.8</b>	<b>74</b>	<b>22</b>	<b>1.4</b>

**Table 2: WHO (2001) and NHMRC (2004) drinking water guidelines and ANZECC (2000) Guidelines for protection of freshwater aquatic species ( $\mu\text{g/L}$ )**

<b>Guideline<sup>1</sup></b>	<b>Pb</b>	<b>Cd</b>	<b>Hg</b>	<b>As</b>	<b>Sb</b>	<b>Se</b>
WHO	10	3	6	10	20	10
NHMRC	10	2	1	7	3	10
ANZECC (99%)	1	0.06	0.06 <sup>2</sup>	1.8 <sup>3</sup>	-	5 <sup>4</sup>

<sup>1</sup> There are currently no guidelines for bismuth or tellurium.

<sup>2</sup> Hg (inorganic)

<sup>3</sup> Total As (As(III) = 1 and As(V) = 0.8)

<sup>4</sup> Total Se

**Table 3. Formation Constants,  $\text{Log}(\beta_n/M^{-1})$ , for Pb, Cd and Hg Complexes for aqueous solutions at zero ionic strength and 25°C (from Morel, 1983 and others as indicated).**

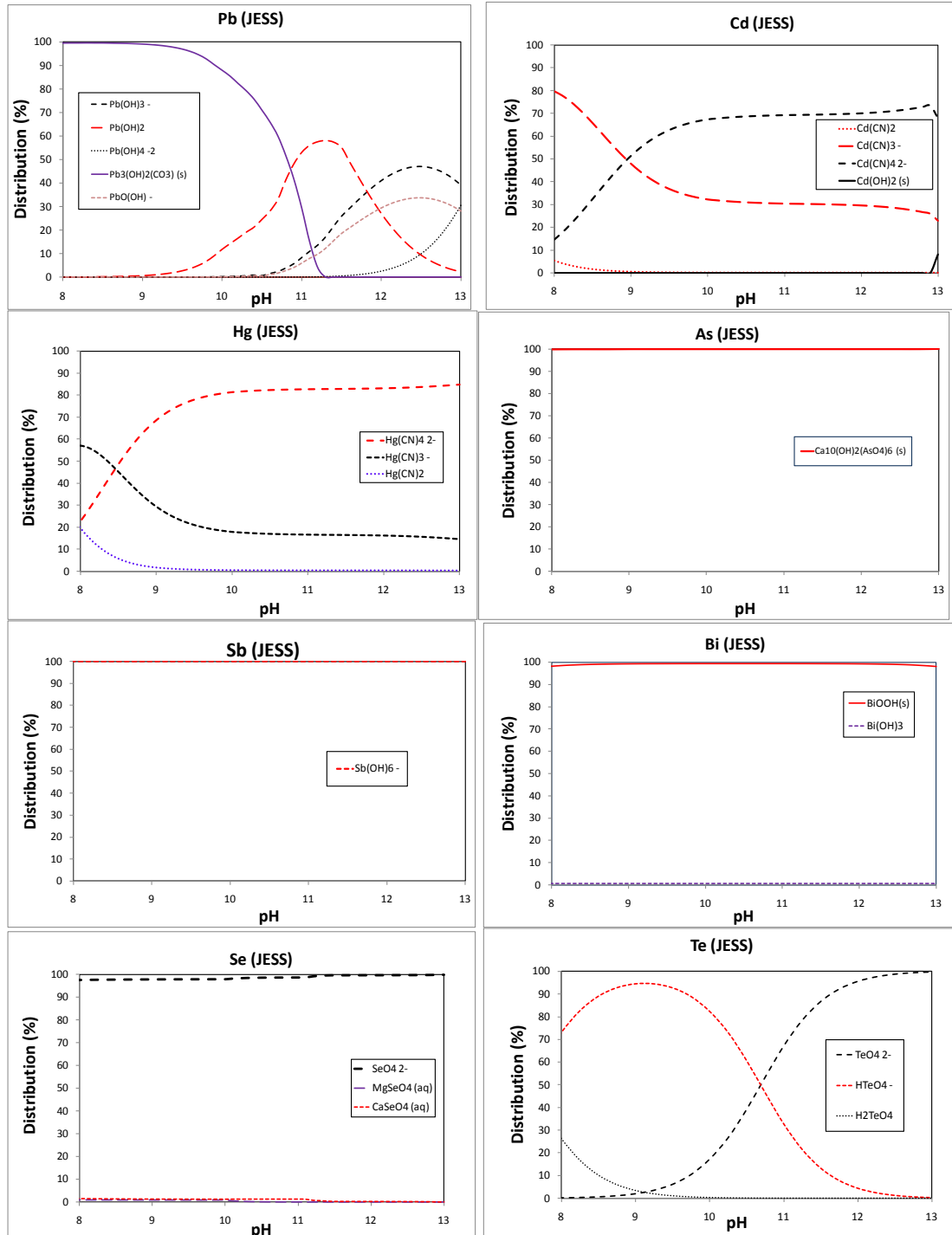
<b>L</b>	<b>n</b>	<b>For <math>\text{Pb}(\text{L})_n^{2-2n}</math></b>	<b>For <math>\text{Cd}(\text{L})_n^{2-2n}</math></b>	<b>For <math>\text{Hg}(\text{L})_n^{2-2n}</math></b>
<b>CN</b> (Beck, 1987)	1	2.7 <sup>3</sup>	5.5	17.0
	2	4.3 <sup>3</sup>	10.6	32.8
	3		15.3	36.3
	4		18.9	39.0
<b>SeCN<sup>-</sup></b> (OECD, 2005)	1		2.24	-
	2		3.34	22.3
	3		3.81	26.8
	4		4.60	29.3
<b>OH</b>	1	6.35 <sup>1</sup>	3.9	10.6 <sup>1</sup>
	2	11.1 <sup>1</sup>	7.6	22.0 <sup>1</sup>
	3	14.0 <sup>1</sup>	-	20.9
<b>Cl</b>	1	1.5 <sup>1</sup>	2.0	7.3 <sup>1</sup>
	2	2.1 <sup>1</sup>	2.6	14.0 <sup>1</sup>
	3	2.0 <sup>1</sup>	2.4	14.9 <sup>1</sup>
	4	-	1.7	15.5 <sup>1</sup>
<b>L</b>	<b>n</b>	<b>For <math>\text{Pb}(\text{L})_n^{2-2n}</math></b>	<b>For <math>\text{Cd}(\text{L})_n^{2-2n}</math></b>	<b>For <math>\text{Hg}(\text{L})_n^{2-2n}</math></b>
<b>SO<sub>4</sub></b>	1	2.7 <sup>1</sup>	2.3	2.5
	2	-	3.2	3.6
	3	-	2.7	-
<b>CO<sub>3</sub></b>	1	6.5 <sup>1</sup>	4.7 <sup>2</sup>	-
	2	10.1 <sup>1</sup>	6.5 <sup>2</sup>	-

<sup>1</sup>Powell et al., 2005, 2009

<sup>2</sup>Rai et al., 1991

<sup>3</sup>Perera, 2001

**Figure 1: Distribution of individual trace elements from JESS thermodynamic package ( $10^{-4}$  M of the target element, 7.7 mM NaCN, 14 mM NaCl, 2.88 mM  $\text{MgSO}_4$ , and 1.12 mM  $\text{CaCO}_3$  with pH adjusted with HCl or NaOH) in air-saturated solutions.**





**Figure 2: Distribution of individual trace elements from OLI thermodynamic package ( $10^{-4}$  M of the target element, 7.7 mM NaCN, 14 mM NaCl, 2.88 mM  $\text{MgSO}_4$ , and 1.12 mM  $\text{CaCO}_3$  with pH adjusted with HCl or NaOH) in air-saturated solutions.**

