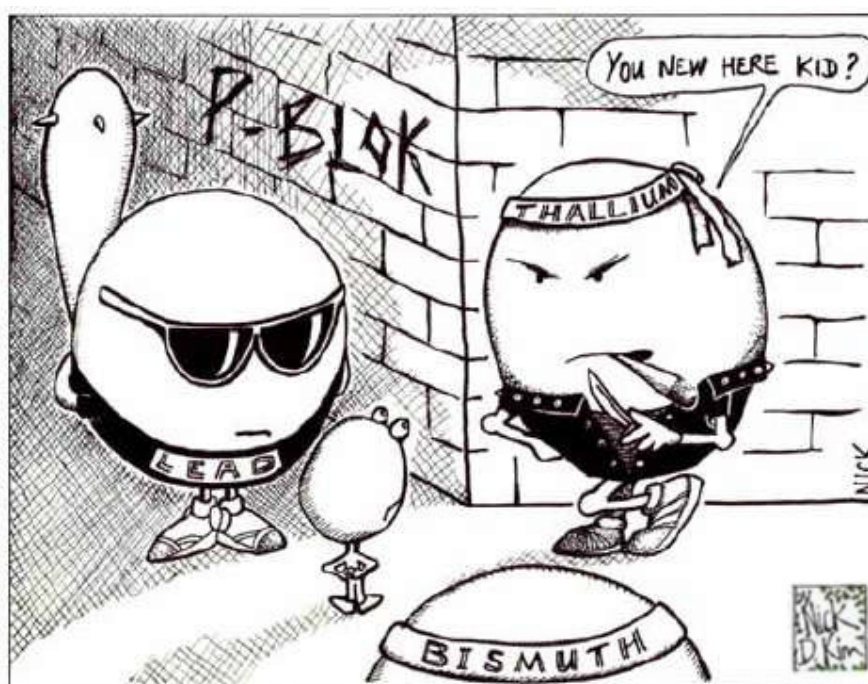


The Hydrothermal Chemistry of Bismuth and The Liquid Bismuth Collector Model

A Thesis Submitted for the Degree of Doctor of Philosophy of
the University of Adelaide January 2013



Unwittingly, and against his mother's advice, Vince the first-row Transition Metal had been lured far away from home, and now found himself surrounded by heavier elements of the P-Block.

Cartoon by Nick D. Kim (www.lab-initio.com),

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Abstract

Bismuth is an element used in a limited range of industrial, medical, cosmetic and other specialty applications. Because of a relatively low economic value, bismuth is rarely targeted directly in mining applications, since adequate supplies are obtained as a by-product of lead and copper production. With no compelling reason to investigate the variables that relate to the prospectivity of bismuth, there is relatively little known about the hydrothermal chemistry of Bi that may be applicable in geological environments such as those relative to ore deposit formation. However, understanding the hydrothermal geochemistry of Bi is important for understanding the Au-Bi association observed in many Au deposits, and its significance in terms of mineral exploration and mining, since Bi causes difficulties in Au metallurgy. Recently, a direct involvement of liquid bismuth in gold-partitioning reactions with aqueous fluids has been proposed as a mechanism responsible for the Au-Bi association. The aims of this thesis centre on three areas to advance the understanding of hydrothermal bismuth chemistry as it applies to the formation of gold deposits in particular, and those containing Bi more generally.

Currently available thermodynamic data for Bi and Au compounds (metals, alloys, and minerals) and aqueous chemistry were compiled into a self-consistent thermodynamic database. Existing data for the system H-O-S-Bi-Cl-Na was fitted within the framework provided by the HCh software package, with the most novel development being the coupling of a non-random two liquids model for the Au-Bi melt with an aqueous phase described in terms of the Helgeson-Kirkham-Flowers (HKF) and Ryzhenko-Bryzgalin models. This provided a framework for exploring the interaction of gold-containing hydrothermal fluids and molten bismuth, providing estimates for the efficiency of the gold partitioning into liquid bismuth that is the central feature of the liquid bismuth collector model. The modelling predicted the ability of Bi-melt to scavenge Au from heavily undersaturated fluids, as well as Au:Bi ratios comparable to field observations.

Experiments were conducted to simulate a hydrothermal ore forming environment and in particular test the ability of fluid-rock interaction to cause the precipitation of Bi-melt, and the ability of these melts to scavenge gold from solution. The flow-through experiments produced droplets of native bismuth via interaction with pyrrhotite. The textures are consistent with precipitation as a melt, and the droplets contained gold-rich inclusions in proportions consistent with Au-Bi melt phase relationships.

An investigation of bismuth mineral solubility (bismuth oxide), using a combined spectroscopic (XANES/EXAFS) and solubility approach, provided thermodynamic data for the $\text{Bi}(\text{OH})_{3(\text{aq})}$ species up to 609°C and 800 bar. For other group 15 metalloids (As, Sb) analogous complexes

(As(OH)_{3(aq)}, Sb(OH)_{3(aq)}) are the most important aqueous species under hydrothermal conditions and so this species was the first goal for a study into hydrothermal Bi chemistry. These experiments allowed the derivation of thermodynamic properties for the revised HKF equation of state for metal complexes and aqueous electrolytes – a commonly used framework for thermodynamic modelling of ore deposit formation. XANES spectroscopy confirms that the Bi(OH)_{3(aq)} complex carries a stereochemically active lone electron pair, and EXAFS data suggest that the geometry of the complex changes little over the temperature range 380-609 °C at 800 bar, with three oxygen neighbours at ~2.08 Å.

The wealth of fundamental data collected in this study provides a much improved understanding of reactive transport of Bi and Au in hydrothermal systems, and allows a quantitative assessment of the role of Bi-melts in scavenging Au in gold deposits.

Declaration

This work contains no material which has been accepted for the award of any other degree or diploma in any university or other tertiary institution and, to the best of my knowledge and belief contains no material previously published or written by another person, except where due reference has been made in the text.

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Date: 9/07/2013

Blake Alfred Tooth

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There are always many people to thank when completing a piece a work such as a PhD. I would like to thank everyone who has helped and supported me for their patience. In particular my long suffering wife, Sophie and supervisors Joel, Cristi, Gleb, Pascal and John.

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I would be remiss if I did not also thank the support and technical staff at the School of Chemical Engineering - Geoff, Jason and Mike who were always able to find solutions for technical problems that could range from the mundane to the extreme. Likewise I would also like to thank the staff at Adelaide Microscopy, in particular Len Green who suffered Cristi and I with great fortitude and patience during tense times on the FIB.

Finally a thank you to those I met on the way and helped me by sharing their research, opinions, ideas and encouragement. John Mavrogenes and Andy Tomkins are two individuals in particular who I would like to thank as they were both very open and willing to talk about their pioneering work on the 'liquid bismuth collector model'.

Preface

This thesis is submitted as a collection of three published journal articles according to the *PhD Rules and Specifications for Thesis of the University of Adelaide*. The journals in which the papers were published or submitted are related, but have different emphasis in the fields of Geology (1 article: *Geology*) and Geochemistry (2 articles: *Geochimica et Cosmochimica Acta*). This is also reflected in the project work which relates to the collection of fundamental chemical data, use of that data in modelling an applied problem in geochemistry, and experiments to test aspects of how that model may work in practice. The relevant statistics in the table below are all from *Journal Citations Reports* (JCR), Thomson, 2010.

Journal Title	5 Year Impact Factor†	2010 Total Citations*	Cited Half-life‡	Article Influence Score§
Geology	4.773	23,735	10	2.316
Geochimica et Cosmochimica Acta	4.517	37,678	>10	1.829

†The 5-year journal Impact Factor is the average number of times articles from the journal published in the past five years have been cited in the JCR year.

*The total number of citations to the journal in the JCR year.

‡The median age of the articles that were cited in the JCR year.

§The *Article Influence* determines the average influence of a journal's articles over the first five years after publication. The mean *Article Influence Score* is 1.00. A score greater than 1.00 indicates that each article in the journal has above-average influence. A score less than 1.00 indicates that each article in the journal has below-average influence.

The main body of the Thesis is based on the following three papers:

1. Tooth, B. Brugger, J., Pokrovski, G., Etschmann, B., Testemale, D., Bismuth in hydrothermal fluids: A combined EXAFS and solubility study, 2012, *Geochimica et Cosmochimica Acta*, v.101, p. 156-172.

2. Tooth, B., Brugger, J., Ciobanu, C., and Liu, W., 2008, Modeling of gold scavenging by bismuth melts coexisting with hydrothermal fluids: *Geology*, v. 36, p. 815-818.

3. Tooth, B., Ciobanu, C.L., O'Neill, B., Green, L., and Brügger, J., 2011, Melt formation and gold scavenging from hydrothermal fluids: an experimental study: *Geochimica et Cosmochimica Acta*, v. 75, p. 5423-5443.

Additional material includes:

- A Brief, general introduction to Bismuth, and its significance.
- A literature survey of bismuth chemistry including as summary of currently available thermodynamic data.
- A conclusion summarising the significance of the studies presented in this thesis and suggestions for future research.

Chapter 1

Introduction

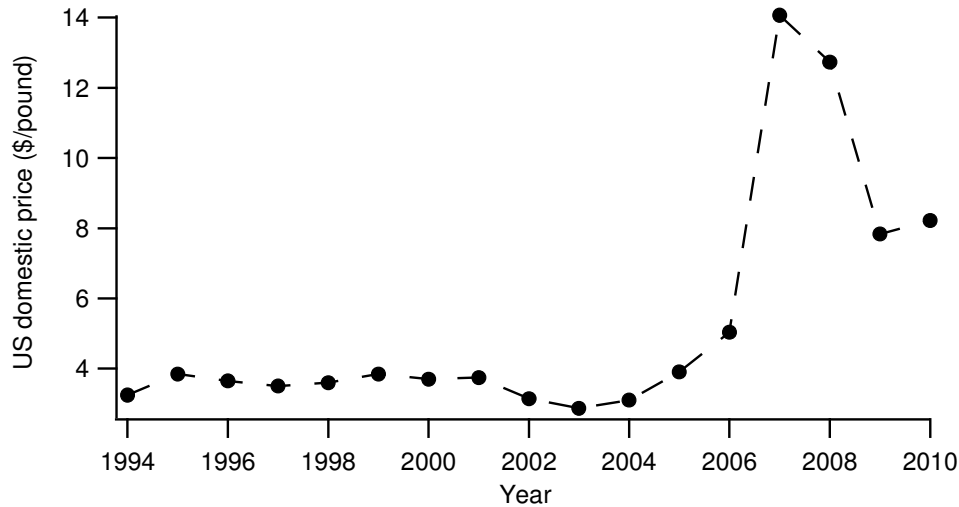
Chapter 1 Introduction

1. Uses of Bismuth and Economic Aspects

The chemistry of Bismuth has been described as ‘the least well established of the heavier stable elements’ (Briand and Burford, 1999). The only naturally occurring isotope of bismuth (^{209}Bi) has since been shown to undergo α -decay with a half-life of 1.9×10^{19} years (de Marcillac et al., 2003). Bismuth is a group 15 (pnictogens; including As and Sb) element often considered a metalloid or semi-metal, as it is close to the p-block transition from non-metals to metals. Bismuth has a relatively low crustal abundance (8ppb), it is the 69th element in order of abundance, and is less common than silver, indium, cadmium and only twice as common as gold (Carlin, 2009). However, bismuth forms many common minerals such as bismuthinite (Bi_2S_3), bismite (Bi_2O_3), bismuthite ($(\text{BiO})_2\text{CO}_3$) and bismoclite (BiOCl) along with numerous sulfosalts and tellurides. Bismuth is primarily obtained as a by-product of the smelting of other ores, in particular lead, from which 95% of Bi production is obtained, and copper (Naumov, 2007). Bismuth is typically viewed as a nuisance in the production of other metals, often reducing recovery from high value ores such as gold (Chryssoulis and McMullen, 2005; Ciobanu et al., 2009).

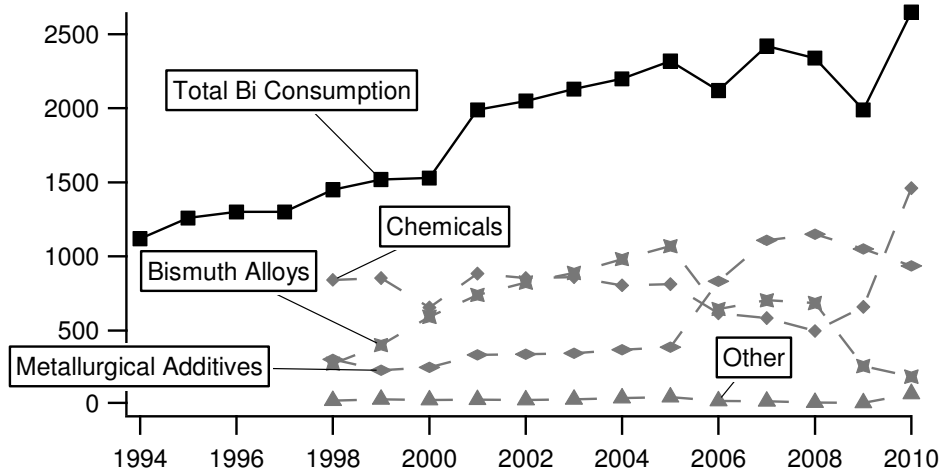
Bismuth is used in a diverse range of industrial applications, but the lack of a large dynamic end use results in low demand and a relatively low economic value (George, 2003). An illustrative fact is the existence of a single mine with bismuth as the primary product worldwide, the Tasna Mine in Bolivia; this mine has been on standby for an extended period, awaiting a significant increase in the Bi price as indicated in USGS minerals yearbook summaries for the last fifteen years (Brown, 1994; Carlin, 2009). Charts of the domestic US price for Bi and the world price for Bi are presented in figure 1. The low, but slowly growing demand, and a supply dictated by the production of lead (rather than demand for Bi) has led to long periods of relative price stability, however this also leaves Bi prices open to price shocks, as demand and supply are not directly linked. An episode in 1970-1974 saw the price increase dramatically (by 400%) to historic highs of ~\$20 per pound, as Bi use in metallurgical additives increased but the supply base was slow to respond (Naumov, 2007). Most recently, a spike in US domestic price data in 2007 as indicated in figure 1 was caused by trade restrictions and tariffs imposed by China the world’s largest producer of bismuth (Carlin, 2009).

Figure 1 US domestic price of bismuth in dollars per pound



Bismuth is used as a non-toxic substitute for lead in brass plumbing fixtures, fire assaying, ceramic glazes, crystal ware, fishing weights, shot for waterfowl hunting, lubricating greases, pigments and solders. All of these areas have been highlighted as growth areas for Bi. The primary reason for this assumption was both the passage of the United States Safe Drinking Water Act in 1996, and new standards passed by the US EPA in 2000 regarding the amount of lead used in common products. As similar legislation has since been passed in several other countries, there is a need to replace lead in many applications (Carlin, 2009). However, viable substitutes for Bi in applications (e.g. plastic pipes for Bi-alloys in plumbing fixtures, Sn and W for Bi some alloys) has kept growth in consumption low. Figure 2 shows the total domestic consumption of Bi in the United States for the period 1994-2010; major areas of consumption are indicated on the same chart for the period 1998-2010.

Figure 2 US domestic consumption of bismuth in metric tons



Bi has long been used in pharmaceutical applications and cosmetics. Bismuth is an important ingredient in stomach remedies (e.g. Pepto-Bismol). It is used in a new range of anti-microbial drugs with soothing properties particularly effective for treating stomach ulcers caused by *helicobacter pylori* infections (Sadler et al., 1999). Bismuth is also used in MRI contrast agents and for a range of other medical applications (Briand and Burford, 1999). Bismuth oxychloride (BiOCl; bismoclite) is also very commonly used in cosmetics for its pearlescent lustre (Naumov, 2007).

Growing specialty applications for bismuth include as a catalyst in organic synthesis. Bismuth compounds are actively being pursued in materials science for applications such as thermo-electrics (Bi_2Te_3) (Naumov, 2007).

2. The Au-Bi Association

The frequent Au-Bi-(Te) association which occurs in deposits of ‘reduced’ character, but in a wide range of settings, provides a compelling reason to understand the hydrothermal chemistry of bismuth. This association has been noted in diverse deposit types including high metamorphic grade deposits, but also across the hydrothermal spectrum in deposits such as skarns, intrusion related gold (IRG), orogenic gold and volcanic massive sulphide (VMS) settings. The growing number of deposits showing direct Au-Bi correlations has sparked a need for data relating to hydrothermal Bi chemistry. Currently there is insufficient data to discriminate between co-precipitation or a direct genetic role for Bi in gold deposition such as in ‘melt collector models’ that have been advanced for low melting point chalcophile elements (LMCE: (Ciobanu et al., 2006; Douglas et al., 2000; Frost et al., 2002; Tomkins et al., 2007)), a category that includes Bi.

Bismuth alloys that melt at low temperatures, many at temperatures less than that of the pure element (271 °C), are frequently used in industrial applications. It is not inconceivable that these molten alloys containing Bi, 'polymetallic melts', will also be present in a range of conditions where ore deposits are formed. As outlined by Douglas et al. (2000), in scenarios where liquid bismuth coexists with a gold-bearing hydrothermal fluid the gold will be preferentially partitioned into the liquid bismuth. The partitioning is an equilibrium-driven process, the solubility of gold in liquid bismuth being much higher than for any hydrothermal fluid under conditions where both are stable. The 'liquid bismuth collector model' is an important conceptual link between fluids and poly-metallic melts as these phases are generally considered in isolation for ore forming models. The coupling of these phases in models may have significant implications for the local distribution of Au, and may be another physico-chemical 'trap' for localising metals transported by hydrothermal fluids during ore deposit formation that can potentially be applied to a wider range of polymetallic melt forming elements.

The Au-Bi association outlined above was the main point of interest driving this study. If bismuth exerts a significant chemical control over gold distribution in an economic hydrothermal deposit, it offers a new compelling reason to understand the hydrothermal chemistry of bismuth. The delicate nature of the textures which are the best evidence for melt formation is a further reason to have a greater understanding of the chemistry of bismuth, because in many cases the textures resulting from a melt collector process may have been completely obscured by subsequent changes. A timely illustration of the significance of the association is the opening of the NICO Au-Co-Bi-Cu mine, it will increase world bismuth production by 30% when it comes online in 2014 (www.fortuneminerals.com) and is estimated to be ~15% of world bismuth reserves.

3. Aims

The aims of this thesis are directed towards two broad areas;

1) Gathering of data relating to bismuth speciation from room temperature to hydrothermal conditions (up to 600 °C, 800 bar):

- Batch reactor solubility experiments at both high and low temperature
- XAS (X-ray absorption) experiments including XANES (x-ray absorption near edge spectroscopy) for derivation of dissolution kinetics, oxidation state, and complex geometry; and EXAFS (extended X-ray absorption fine structure) to determine bond lengths and coordination numbers. Concentrations can also be calculated from edge heights, so that solubility and kinetic data can be determined in conjunction with structural and chemical data.

2) Investigation of gold/ bismuth extraction reactions at conditions approaching ore deposit formation.

- Collating available data into an equilibrium thermodynamic model for gold scavenging reactions of bismuth melt using the hydrochemistry (HCh) program from Geoscience Australia.
- Experimental work aiming to re-create the conditions present in natural systems where melt scavenging of gold, dissolution and re-precipitation of minerals is important.

Successful results for the second aim provide a proof of principle of the melt model, help to identify the critical chemical and physical controls on the occurrence and efficiency of the melt collector model. This is coupled with qualitative results that explore applications, providing results consistent with that observed in natural deposits and giving the first indications of the complex mechanisms that may be studied successfully on laboratory timescales.

4. Thesis Organisation

This thesis is submitted as a combination of published papers and written chapters formatted for submission as publications according to the *PhD Rules and Specifications for Thesis of the University of Adelaide*. The journals in which the papers were published or submitted are

related, but have different emphases in the fields of Geology and Geochemistry. This is also reflected in the project work which relates to collection of fundamental chemical data, the use of that data in modelling an applied problem in geology, and experiments to test aspects of how that model may work in practice, more detail on the specific publications and journals is provided in the preface.

This thesis is divided into 3 main chapters detailing the work, a literature review and conclusions. Each chapter consists of a publication and related material. Several updates to what is presented in the papers, particularly relating to preferred thermodynamic models is presented in the literature review.

Chapter 3 presents a multi-technique study of bismuth oxide solubility in hydrothermal fluids aimed at investigating the neutral bismuth hydroxide complex ($\text{Bi}(\text{OH})_{3\text{aq}}$), similar species have been shown to be the most important for the closely related group 15 elements arsenic and antimony. Thermodynamic parameters for the revised HKF equation of state are derived for this species, as well as a structural investigation of the complex in solution by EXAFS and XANES.

Chapter 4 presents the collation of thermodynamic data from a wide range of fields and the construction of a thermodynamic model, able to accommodate coexisting aqueous fluids and polymetallic melts. This was done using the HCh software of Geoscience Australia, the aqueous fluid being modelled using the revised HKF framework and the melt using the non-random two liquids model. This chapter is presented in 2 parts with an original research paper, and the electronic annex of this paper detailing the thermodynamic model.

Chapter 5 presents the results of novel experiments aimed at reproducing some of the conditions of a natural system. The experimental work is highly original using leaching and precipitation reactions in a circulating hydrothermal system. The results are qualitative, but show that precipitation/partitioning reactions related to the Au-Bi association are observable on a laboratory timescale with important features from natural settings reproduced experimentally.

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Chapter 2

Review of Bismuth Chemistry

Chapter 2 Review of Bismuth Chemistry

Some repetition of material in the introductory sections of each individual paper is unavoidable for a complete literature review of bismuth chemistry. A larger amount of background data are presented here, however, reflecting the research during the development of the thermodynamic models used in Chapters 3 and 4 for modelling calculations.

As noted by (Crerar et al., 1985) complexes with intermediate or hard ligands, such as OH^- and Cl^- , will become more stable at elevated temperature. This prediction is borne out by the observed increase in hydroxyl complex stability (i.e. hydrolysis) with temperature (Baes and Mesmer, 1981; Seward and Barnes, 1997) and the increased stability of chloro-complexes with temperature (Seward, 1981). As temperature increases the dielectric constant of water also decreases markedly, this favours ion association and neutral or weakly charged complexes with low ligand numbers (Crerar et al., 1985). For example, the predominance of neutral and low charge chloro and hydroxy complexes of another group 15 element, antimony, is illustrative. Antimony has been shown to occur predominantly as $\text{Sb}(\text{OH})_{3(\text{aq})}$, $\text{Sb}(\text{OH})_2\text{Cl}_{(\text{aq})}$, $\text{Sb}(\text{OH})_3\text{Cl}^-$ at high temperature (Pokrovski et al., 2006). It is likely similar species will be significant for bismuth as well. Currently available data at low temperatures indicate that Bi has a high affinity for OH^- (Baes and Mesmer, 1976) and somewhat lesser affinity for Cl^- (Rai et al., 2010; Savenko et al., 1998; Suganuma et al., 1987). In hydrothermal solutions that are most relevant for ore-forming environments (Kolonin and Laptev, 1982; Wood et al., 1987) the importance of Bi-hydroxy complexes appears to greatly outweigh that of chloride complexes.

This introductory review covers bismuth chemistry in a range of aqueous solutions, primarily concentrating on those of variable pH and chloride concentration. Most data are available for acidic ($\text{pH} \leq 1$) solutions of high chloride concentration (1-5 molal total chloride); a substantial amount of data are available in solutions of varying pH, usually using perchlorate as the background electrolyte. The majority of the solution chemistry discussed here is $\leq 25^\circ\text{C}$ and at atmospheric pressure, but as these data are the primary inputs for thermodynamic extrapolations to higher temperature and pressure, this is reviewed in some detail.

The implications for some available HKF extrapolations of Bi^{3+} properties are also considered in this introductory section on the basis of the most recent data relating to the solvation of this ion. The review that follows also extends to hydrothermal settings summarising the available studies and extrapolated values currently available. A possible role for Bi-sulfide complexes in hydrothermal systems is briefly considered, as well as some arguments for and against the role of such species in Bi transport in hydrothermal environments.

1. Properties of the element

In contrast to the elements of the d-block, such as the transition metals, the heavier p-block metals favour low oxidation states. In particular the heavier members all favour oxidation states 2 less than the group oxidation number. For example, as the heaviest member of group 15 (V), bismuth favours Bi^{3+} . The same trend is observed for lead and tin, and all of these elements are easily reduced in their group oxidation states when compared to lighter elements in the same group. Bismuth shares the status of the least abundant p-block element with thallium (Shriver and Atkins, 1999).

Bismuth has the electronic configuration $[\text{Xe}]4f^{14}5d^{10}6s^26p^3$ and of the two major oxidation states of bismuth (III and V), Bi(III) is the most common and stable oxidation state. Bismuth and the closest comparable group 15 elements arsenic and antimony show an increasing stability of the M(V) oxidation state as one moves from Bi up the group. An important property of Bi, related to the increasing stability of lower oxidation states for heavier elements, is the influence of relativistic effects on Bi chemistry; the inert pair ($6s^2$) and its effects on stereochemistry of Bi-complexes is a related phenomenon relevant to aqueous Bi chemistry.

The oxidation states II and IV are also known (Cotton et al., 1999). There is also a single report of a Bi(I) complex in solution, obtained by dissolving metallic Bi in concentrated HCl (6.9 M Bi^{3+} , 26.1M total Cl), however this solution was reported unstable to both heating (to 100 °C) and dilution (Ulvenlund and Bengtsson, 1994; Ulvenlund and Bengtsson, 1995). Bi(V) is powerful oxidant in aqueous solution ($\text{Bi}^{5+}_{(\text{aq})} + 2\text{e}^- = \text{Bi}^{3+}_{(\text{aq})}$; $E^\ominus = +2$ V; Shriver and Atkins, 1999), although two complexes with sterically bulky benzenoid and non-benzenoid arene ligands have been reported stable in aqueous media (Sadler, 1999). Therefore the vast bulk of

aqueous bismuth chemistry is dominated by Bi(III), particularly in those environments of geological relevance.

2. Aqueous Bi(III) Chemistry

According to Pearson's hard-soft acid-base theory (Pearson, 1963), Bi(III) is a border-line metal ion. This has led to speculation that soft ligands such as sulphur (S_2^- , HS^-) will be important in aqueous bismuth chemistry (e.g. (Skirrow and Walshe, 2002), but these assertions remain to be validated by experimental data; simple extrapolations are also complicated by relativistic/inert pair effects, as further elaborated in section 2.5. Bi(III) has also been shown to strongly bind to a range of organic ligands containing oxygen and nitrogen electron donors. Relatively strong, but labile bonds between Bi(III) and the thiolate sulphur of the tripeptide glutathione have also been demonstrated (Sadler et al., 1999). There is a relatively well established chemistry of Bi(III) with a wide range of organic ligands which usually stems from applications for Bi in pharmaceutical preparations ((Briand and Burford, 1999; Sadler et al., 1999). However, it has been noted that there is a lack of data for families of related Bi-compounds to demonstrate fundamental chemical and structural trends that can be used as a basis for solution studies (Briand and Burford, 1999).

2.1 Revised HKF parameters for the Bi^{3+} ion

Although unlikely to be an important species in solutions of relevance for geochemistry the data now available for Bi^{3+} allows updated extrapolations of thermodynamic properties. These extrapolations are likely to be useful when manipulating available thermodynamic data for bismuth which is usually described in terms of the non-hydrolysed cation (Bi^{3+} ; e.g. (Kolonin and Laptev, 1982; Ruaya, 1988), section 2.7).

Using data for 8-coordinated aquo ions, in conjunction with a revised ionic radius for Bi^{3+} , an updated estimate of the partial molar entropy of aqueous Bi^{3+} can be calculated by the method of (Sassani and Shock, 1992). This new estimate can be used as part of the revised HKF equation of state framework. The partial molar entropy is estimated using equation 1 (Sassani and Shock, 1992):

$$\bar{S}_j^0 = M_{Z_j, C.N.} \left(\frac{Z_j^2}{r_{e,j}} \right) + B_{Z_j, C.N.} \quad (1)$$

Where M and B are fitting variables derived from correlations, Z_i is the ionic charge of ion i , and $r_{e,j}$ is the effective ionic radius of the ion i . In the original estimate provided by (Sassani and Shock, 1992) the coordination number was assumed to be six as structural investigations of Bi^{3+} in solution had not been conducted at the time of publication. A change of the coordination number from 6 to 8 means that values of $M = -126.67$ and $B = 241.3$ from Table 2 of (Sassani and Shock, 1992) are more suitable than those chosen in the original estimation procedure. The ionic radius of Bi^{3+} ($r_{x,j}$) used by Sassani and Shock (1992) in calculating the effective ionic radius ($r_{e,j}$) parameter was taken from the compilation of (Shannon, 1976). A larger ionic radius for Bi (1.07 Å; C.N. = 8) than that originally used (1.03 Å; C.N. = 6) has been observed in aqueous solution (Naslund et al., 2000). The new value of $r_{x,j}$ can be used to recalculate the $r_{e,j}$ parameter using equation 2 (Sassani and Shock, 1992) for cations at 25 °C;

$$r_{e,j} = r_{x,j} + 0.94(Z_j) \quad (2)$$

From these calculations the value of \bar{S}_j^0 is estimated to be $-51.8 \text{ cal mol}^{-1} \text{ K}^{-1}$, rather than $-45.0 \text{ cal mol}^{-1} \text{ K}^{-1}$ (Table 5 in (Shock, 1994)). This is closer to an earlier estimate of this property, $-50.0 \text{ cal mol}^{-1} \text{ K}^{-1}$ from (Shock and Helgeson, 1988). The close agreement of the \bar{S}_j^0 estimate presented here and that from Shock and Helgeson (1988) is likely due to the inclusion of rare earth elements in the earlier regressions of correlations of HKF parameters for trivalent ions, the rare earths were excluded in subsequently revised regression schemes. The revised HKF parameter estimates are presented in Table 1 for Bi^{3+} based on the recalculated effective ionic radius and partial molar entropy calculations, as well as using the $\log K_2$ value of the reaction $\text{Bi}^{3+} + 3\text{H}_2\text{O} = \text{Bi}(\text{OH})_{3(\text{aq})} + 3\text{H}^+$ (Rai et al., 2010), in conjunction with $\Delta_f G^\circ_{\text{Bi}(\text{OH})_{3(\text{aq})}}$ derived from the $\log K_1$ value from the same authors to calculate $\Delta_f G^\circ_{\text{Bi}^{3+}}$. The recalculated parameters are then carried through the necessary calculations using equations for estimation of HKF parameters from (Sverjensky et al., 1997).

Table 1. The standard molal thermodynamic properties at 25 °C and 1 bar and HKF equation of state parameters for $[\text{Bi}(\text{H}_2\text{O})_8]^{3+}$ estimated in this study.

Reference	$\Delta_f G^\circ_{298}$ cal mol ⁻¹	$\Delta_f H^\circ_{298}$ cal mol ⁻¹	S°_{298} cal mol ⁻¹ K ⁻¹	a_1 10 cal mol ⁻¹ bar ⁻¹	a_2 10 ⁻² cal K mol ⁻¹	a_3 cal K mol ⁻¹ bar ⁻¹	a_4 10 ⁻⁴ cal mol ⁻¹	c_1 mol K	c_2 10 ⁻⁴ cal K mol ⁻¹	ω 10 ⁻⁵ cal mol ⁻¹	$r_{e,j}$ Å
This Study	21263	15744	-51.8	-3.7579	-16.9618	12.8917	-2.0778	-17.1781	-10.7523	2.2251	3.89
Shock, 1997	22880	19360	-45	-1.0957	-10.4536	9.8506	-2.3467	27.5027	-2.8715	2.2651	
Sassani and Shock, 1992,1994			-45								
Helgeson and Shock, 1988			-50							2.3369	3.78

$\Delta_f G^\circ_{298}$ for Bi^{3+} calculated using the logK from Rai et al (2010) for the reaction $\text{Bi}(\text{OH})_{3(\text{aq})} + 3\text{H}^+ = \text{Bi}^{3+} + 3\text{H}_2\text{O}$, and $\Delta_f G^\circ_{298}$ of $\text{Bi}(\text{OH})_{3(\text{aq})}$ derived from solubility experiments in Chapter 3.

a_1 : eqn 33 in Sverjensky (1997)

a_2 : eqn 34 in Sverjensky (1997)

a_3 : eqn 35 in Sverjensky (1997)

a_4 : eqn 36 in Sverjensky (1997)

c_2 : eqn 37 in Sverjensky (1997)

c_1 : eqn 30 in Sverjensky (1997)

S: eqn 11 in Sassani and Shock (1992)

$r_{e,j}$: eqn 7 in Sassani and Shock (1992) and $r_{x,j} = 1.07$ Å from Naslund et al (2000)

C°_p : eqn 91 in Shock and Helgeson (1988), using the δ (-298.8) and δ' (-0.26) parameters for heavy rare earth cations and Al^{3+}

Ω : eqns 45, 46 and 47 in Shock and Helgeson (1988)

Table 2. Formation constants for Bi-OH complexes at room temperature from the literature.

Reaction	log β	error	Medium	Reference
$\text{Bi}^{3+} + \text{H}_2\text{O} = \text{Bi}(\text{OH})^{2+} + \text{H}^+$	-2.394*	0.5	HClO ₄ , variable I	(Brachmann et al., 1994)
	-1.634*		0.1M NH ₄ ClO ₄	(Bidleman, 1971)
	-1.594*			Korenman and Vorontsova (1968)
	-1.994*		1M (H,Na)ClO ₄	Hataye et al. (1982)
	-1.09		compiled value	Baes and Mesmer (1976)
	-1.536-			
	1.325		0.1-1M NaClO ₄	Antonovich et al. (1975)
	-1.4		1M NaClO ₄	Kragten et al. (1993)
	-1.58	0.02	3M NaClO ₄	Olin (1957)
	-1.547		1M NaClO ₄	Dragalescu et al. (1972)
-1.2		calculated	Barnum (1983)	
$\text{Bi}^{3+} + 2\text{H}_2\text{O} = \text{Bi}(\text{OH})_2^+ + 2\text{H}^+$	-5.088*	0.6	HClO ₄ , variable I	Brachmann et al. (1994)
	-3.588*		0.1-1M NaClO ₄	Antonovich et al (1975)
	-12.188*			Korenman and Vorontsova (1968)
	-4.488*	0.3	HClO ₄ , variable I	Kolonin and Laptev (1982)
	-5.088*		1M (H,Na)ClO ₄	(Hataye et al., 1982)
	-4.37		1M NaClO ₄	Dragalescu et al. (1972)
	-4.1	0.1	1M HClO ₄ /NaClO ₄	Kragten et al. (1993)
	-4		compiled value	Baes and Mesmer (1976)
	-3.6		calculated	Barnum (1983)
	-3.56		I=0.1-1M	Antonovich et al. (1975)
$\text{Bi}^{3+} + 3\text{H}_2\text{O} = \text{Bi}(\text{OH})_{3(\text{aq})} + 3\text{H}^+$	-8.793*	0.01		Korenman and Vorontsova (1968)
	-8.083*		1M (H,Na)ClO ₄	(Hataye et al., 1982)
	-11.927*		compiled value	Baes and Mesmer
	-6.033*		0.1-1M NaClO ₄	Antonovich et al. (1975)
	-10.043*	0.1	0.1 NH ₄ ClO ₄	Bidleman (1971)
	-9.043*		I = 0	Kolonin and Laptev (1982)
	-8.95	0.5	I = 0	Rai et al. (2010)
	-9.9	0.1		Kragten et al. (1993)
	-6.05			Antonovich 1975
	$\text{Bi}^{3+} + 4\text{OH}^- = \text{Bi}(\text{OH})_4^-$	-23.077*	0.15	variable I
-21.8		0.1		compiled value
-19.9			calculated	Barnum (1983)

An overview of literature values for Bi-OH formation constants, the preferred set of values used in the speciation diagram depicted in Figure 1 is emboldened and highlighted. All formation constants have been re-calculated as β values using a logK_w of -13.9942 from the HCh database, which is in turn based on data from Marshall and Frank (1981).

3. The Hydrolysis of Bismuth

The aqueous chemistry of bismuth is dominated by cationic hydrolysis products at $\text{pH} > 1$, at low concentrations of Bi these are mononuclear, but at Bi concentrations $\geq 1 \times 10^{-5}$ M, polynuclear species containing 6 or 9 Bi atoms are increasingly important. For dilute solutions ($[\text{Bi}] \leq 1 \times 10^{-5}$ M), mononuclear complexes predominate over a wide range of pH values (Figure 1).

3.1 Bismuth Aquo-Ion

Extensive hydrolysis has been such a hallmark of bismuth chemistry that it was not until 1995 that a solid analogue of the Bi(III) aquo ion was isolated as a triflate salt, $[\text{Bi}(\text{H}_2\text{O})_9](\text{SO}_3\text{CF}_3)_3$, in which Bi(III) is coordinated to nine water molecules in a structure analogous to that of lanthanide compounds of the type $[\text{Ln}(\text{H}_2\text{O})_9](\text{SO}_3\text{CF}_3)_3$ (Frank et al., 1995).

EXAFS studies of Bi(III) in solution ($[\text{H}^+] = 1.9870\text{-}2.700$ M, $[\text{Bi}^{3+}] = 0.662\text{-}0.800$ M, $[\text{ClO}_4^-] = 3.856\text{-}5.100$ M), have indicated that at 25 °C Bi(III) is present in solution as an eight-coordinated aquo-ion $[\text{Bi}(\text{H}_2\text{O})_8]^{3+}$ (Naslund et al., 2000). This is in contrast to La^{3+} ($\text{La}(\text{H}_2\text{O})_9^+$; (Kuta and Clark, 2010) with which Bi is iso-structural in the solid state. However, trivalent rare earths appear to have aquo-ions that decrease from 9 to 8 coordinated water molecules as one moves across the period. A movement across the Lanthanoid period from La to Yb is from lighter to heavier elements, but ionic radius actually decreases due to the lanthanide contraction (Shriver and Atkins, 1999). This is relevant for Bi as elements towards the end of this period exhibit 9 coordinated aquo-salts in the solid state, and 8 coordinated aquo-ions in solution; a consideration of the ionic radii of Bi would place it amongst those elements near the 9-8 transition when considered on a the basis of a charge/radius ratio. Note that ab-initio molecular dynamic calculations suggest 9-fold coordination (Durdagi et al., 2005) and ab-initio geometry, frequency and energy calculations are consistent with either 8- or 9-fold coordination (Pye et al., 2007). The difference between the experimental and theoretical hydration numbers may be due to the influence of second hydration shells on charge stabilisation as has been observed for the lanthanides (Kuta and Clark, 2010). For the very salty solutions in which the experimental solutions in question are conducted ($\sim 3\text{-}4$ M of electrolyte) the

disruption of surrounding solution structure would be expected to have a significant effect on the observed coordination.

3.2 Mononuclear Species

A selection of values of the formation constants for Bi-OH mononuclear species is presented in Table 2. It can be seen that for mononuclear complexes bismuth follows a stepwise addition of OH⁻ such that Bi(OH)_x^(3-x) (where x ≤ 4) complexes are formed sequentially as pH rises.

The most cited source of data for bismuth hydrolysis reactions is Baes and Mesmer (1976), however, in their summary they expressed uncertainty for the logK value for Bi(OH)₂⁺. This appears to have resulted in the exclusion of Bi(OH)₂⁺ from calculations of speciation diagrams presented by these authors (Baes and Mesmer, 1976); page 382). The result is a relative over-estimation of the stability of polynuclear species at low Bi concentrations; (Baes and Mesmer, 1976) depict Bi-6 and Bi-9 species predominating at pH values ~3-7 at a Bi concentration of 1×10⁻⁵ m; a situation not observed by experimenters (e.g. (Bidleman, 1971), Chapter 3 of this thesis). With the inclusion of Bi(OH)₂⁺ in the speciation calculation (Figure 2), mononuclear species predominate at all pH values at this concentration, and polynuclear species are not observed in significant amounts until a concentration of 1×10⁻⁴ m Bi is approached. These observations are consistent with the experiments of (Olin, 1957, 1959) and (Dragalescu et al., 1972a, b). The uncertainty for the logβ₂ value of Bi(OH)₂⁺ appears to have been lessened with the appearance of new experimentally determined values since Baes and Mesmer (1976) published their authoritative work. The original estimate presented by these authors (logβ₂ = -4.0) has been confirmed by solubility/precipitation (Kragten et al., 1993), and spectrophotometric (Antonovich et al., 1975; Brachmann et al., 1994, 2004) methods. A calculated logβ₂^o value is also presented based on a correlation algorithm developed by (Barnum, 1983).

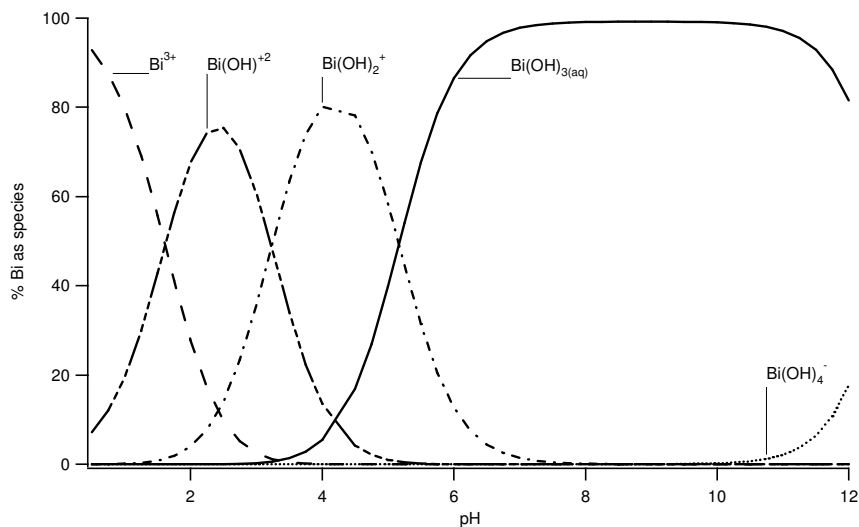


Figure 1. Speciation diagram using preferred formation constants from Table 2. The diagram is drawn at $I = 1$ molal, with 10^{-6} molal bismuth. At this Bi concentration the concentration of polynuclear species is insignificant, becoming visible at $\sim 10^{-5}$ molal Bi, and accounting for 80% of Bi concentration at pH 4 and $\sim 1 \times 10^{-4}$ molal Bi. Note this diagram differs significantly from that presented by Baes and Mesmer (1976), the exclusion of the Bi(OH)_2^+ species gives rise to the predominance of polynuclear species at lower Bi concentrations ($\sim 10^{-5}$ molal Bi) in the pH range 1-5. Further studies released since the publication of Baes and Mesmer (1976) (see Table 2) further support this value.

3.3 Polynuclear Species

The hydrolysis of Bi(III) has been studied extensively, and the consensus has been reached that a polynuclear hexameric cluster predominates at higher pH values > 1 , when $[\text{Bi}] > 10^{-4}$ m (Baes and Mesmer, 1976; Cotton et al., 1999). In neutral perchlorate solutions the main species was previously proposed to be $\text{Bi}_6\text{O}_6^{6+}$ or its hydrated form $\text{Bi}_6(\text{OH})_{12}^{6+}$ and at higher pH $\text{Bi}_6\text{O}_6(\text{OH})_3^{3+}$ by various authors (Baes and Mesmer 1976). The predominant hexameric species was shown to have an octahedral arrangement of bismuth atoms (e.g. (Maroni and Spiro, 1965)) and subsequent studies offered a revised formula of $\text{Bi}_6\text{O}_4(\text{OH})_4^{6+}$ with oxygen or hydroxyl groups capping each face (Sundvall, 1974; Sundvall, 1980; Sundvall, 1983).

At $\text{pH} > 5$ it was suggested that this complex undergoes further hydrolysis to form a series of Bi-9 polynuclear products with the general formula $[\text{Bi}_9(\text{OH})_n]^{27-n+}$, where $n = 20-22$ (Dragalescu et al., 1972b; Olin, 1959). As with the Bi-6 species, the isolation of a salt with $\text{Bi}_9\text{O}_8(\text{OH})_6^{5+}$ units from acidic perchlorate solutions confirmed the main conclusions of early solution studies (Thurston et al., 2005). The $\text{Bi}_9\text{O}_8(\text{OH})_6^{5+}$ perchlorate salt is obtained from acidic solutions partially neutralised

with NaOH (to a value pH 6.5), the addition of tris(hydroxymethyl) ethane was found necessary to form crystals fit for single crystal diffraction analysis. The isolation of the Bi-9 species from solutions of such a pH ($[\text{Bi}] = 0.07 \text{ m}$) accords well with that expected from using the currently available properties for Bi-polynuclear species (e.g. (Smith, 1989)) as indicated in Figure 2 a Bi-9 species with a charge of +5 is expected at these conditions.

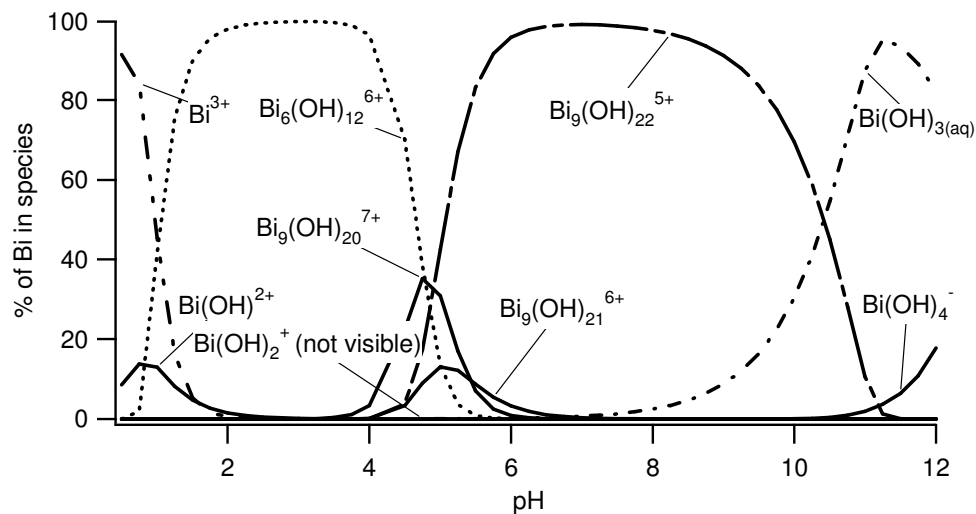


Figure 2. Bismuth speciation in a solution of 0.06 m Bi showing Bi speciation with the inclusion of polynuclear species in a modelled $\text{HClO}_4/\text{NaClO}_4$ solution.

Table 3. Formation constants for polynuclear Bi-OH complexes at room temperature from the literature.

Reaction	Log β	Error	logK	Medium	Reference
Bi-6 Species					
$6\text{Bi}^{3+} + 12\text{H}_2\text{O} = \text{Bi}_6(\text{OH})_{12}^{6+} + 12\text{H}^+$	0.33	0.005		3M HClO ₄ /NaClO ₄	Olin (1957)
$6\text{Bi}^{3+} + 12\text{H}_2\text{O} = \text{Bi}_6(\text{OH})_{12}^{6+} + 12\text{H}^+$	0.26	0.02		1M HClO ₄ /NaClO ₄	(Dragalescu et al., 1972a)
$6\text{Bi}^{3+} + 6\text{H}_2\text{O} = \text{Bi}_6\text{O}_6^{6+} + 12\text{H}^+$	-0.53			1M HClO ₄ /NaClO ₄	Tobias (1960)
$\text{Bi}_6\text{O}_6^{6+} + 3\text{H}_2\text{O} = \text{Bi}_6\text{O}_6(\text{OH})_3^{3+}$				1M HClO ₄ /NaClO ₄	Tobias (1960)
$6\text{Bi}^{3+} + 12\text{H}_2\text{O} = \text{Bi}_6(\text{OH})_{12}^{6+} + 12\text{H}^+$	-5.22			Compiled value	(Smith, 1989)
Bi-9 Species					
$9\text{Bi}^{3+} + 20\text{OH}^- = \text{Bi}_9(\text{OH})_{20}^{7+}$	266.92			Compiled value	(Martell and Smith, 1989)
$1.5\text{Bi}_6\text{OH}_{12}^{6+} + 2\text{H}_2\text{O} = \text{Bi}_9(\text{OH})_{20}^{7+} + 2\text{H}^+$	-3.9	0.2		0.1 M HClO ₄ /NaClO ₄	Olin (1959)
$1.5\text{Bi}_6\text{OH}_{12}^{6+} + 2\text{H}_2\text{O} = \text{Bi}_9(\text{OH})_{20}^{7+} + 2\text{H}^+$	-3.5	0.1		0.1 M HClO ₄ /NaClO ₄	(Dragalescu et al., 1972b)
$9\text{Bi}^{3+} + 21\text{OH}^- = \text{Bi}_9(\text{OH})_{21}^{6+}$	276.76			Compiled Value	(Martell and Smith, 1989)
$\text{Bi}_9(\text{OH})_{20}^{7+} + \text{H}_2\text{O} = \text{Bi}_9(\text{OH})_{21}^{6+} + \text{H}^+$	-3.2	0.2		0.1 M HClO ₄ /NaClO ₄	Olin (1959)
$\text{Bi}_9(\text{OH})_{20}^{7+} + \text{H}_2\text{O} = \text{Bi}_9(\text{OH})_{21}^{6+} + \text{H}^+$	-3.2	0.4		0.1 M HClO ₄ /NaClO ₄	(Dragalescu et al., 1972b)
$\text{Bi}_9(\text{OH})_{21}^{6+} + \text{H}_2\text{O} = \text{Bi}_9(\text{OH})_{22}^{5+} + \text{H}^+$	-2.6	0.2		0.1 M HClO ₄ /NaClO ₄	Olin (1959)
$\text{Bi}_9(\text{OH})_{21}^{6+} + \text{H}_2\text{O} = \text{Bi}_9(\text{OH})_{22}^{5+} + \text{H}^+$	-2.8	0.1		0.1 M HClO ₄ /NaClO ₄	(Dragalescu et al., 1972b)

4. Bismuth in chloride-containing solutions

Bi-chloro complexes are likely to be important in hydrothermal fluids as in many natural geochemical systems chloride is the most abundant ligand available for metal complexation (Seward and Barnes, 1997). Amongst the most common settings for observations of high bismuth grades are ore deposits where hypersaline ($\geq 5-10$ wt% NaCl) fluids are frequently observed such as gold skarns (Meinert, 2000). A review of Bi-Cl complexation in solution is presented here as additional material for the speciation model presented in Chapter 4.

The most comprehensive data available for aqueous Bi complexes is also for chloro complexes, of particular note are a large number of studies published in countries of the former Soviet Bloc; the number of these studies is likely to be related to the adoption of lead-bismuth eutectic cooled nuclear reactors in the former soviet states. Lead-bismuth eutectic reactors have recently become a topic of significant new research interest for the next generation of nuclear reactors (Gorse-Pomonti and Russier, 2007; Terlain et al., 2007).

4.1 Acidic chloride solutions

The hydrolysis reactions of Bi(III) compete with complex-forming reactions between Bi(III) and common inorganic ligands of hydrothermal systems. For this reason most studies of aqueous Bi(III) chemistry have been conducted at very low pH (≤ 1) when compared to that present in many natural systems. There are many studies of Bi-Cl species at ~ 25 °C in acidic chloride solutions. Studies of bismuth-chloro complexes include spectrophotometric (Newman and Hume, 1957), potentiometric (Mironov et al., 1963; Senanayake and Muir, 1988), Raman (Oertel and Plane, 1967; Spivakov et al., 1979; Zolotov et al., 1979) and solubility studies (Ahrland and Grenthe, 1957, 1961; Haight et al., 1964; Johansson, 1969; Vasil'ev et al., 1973) . All of these studies are limited to ~ 25 °C in temperature and atmospheric pressure. A comprehensive list of $\log\beta$ values derived from various studies is presented in Table 4, along with the $\log\beta^\circ$ values derived by Rai and Vas'ilev that are convenient meta-analyses of many of the references also presented in the table.

4.2 Disagreements concerning BiCl_5^{2-} and BiCl_6^{3-} in the speciation scheme

A notable problem concerning Bi speciation in acidic chloride solutions is the lack of agreement concerning the final members of the Bi-Cl speciation scheme. It is currently not obvious whether the complete $\text{BiCl}_n^{(3-n)+/-}$ (where $n=1-6$) series of complexes exists, or whether the final member is BiCl_5^{2-} . Senanayake and Muir compared measured Eh values in Bi solutions (10^{-4} M Bi in CaCl_2 , MgCl_2 , NaCl/HCl solutions containing up to 10 M Cl Γ) with that calculated from the logK values presented in the compilation of (Sillen and Martell, 1971), and found that the data are best reproduced by a model that assumes BiCl_5^{2-} as the final species, rather than BiCl_6^{3-} .

Table 4: Formation Constants for Bi-Cl complexes based on original tables in Rai et al (2010) and Vas'ilev and Ikohnnikov (1972).

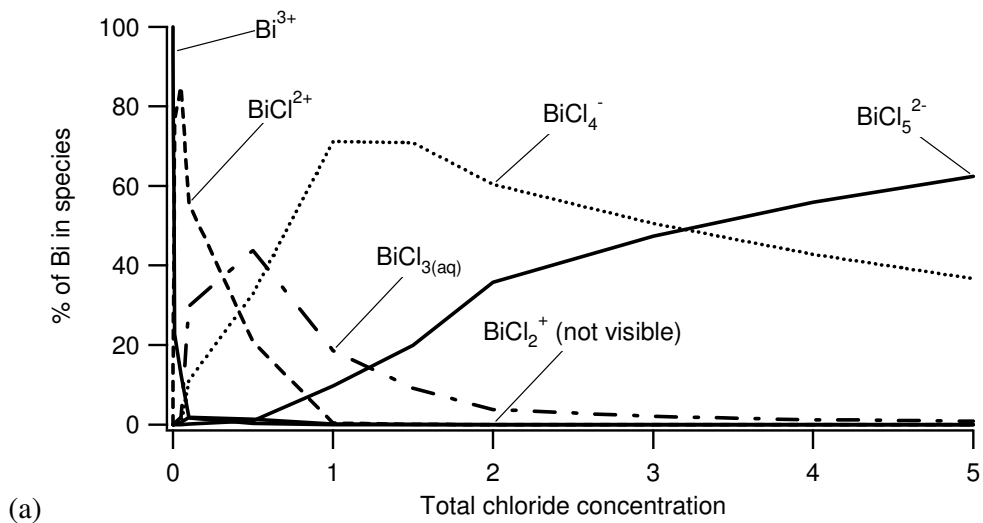
Reference	Technique	I (M)	I (m)	Medium	β_1	\pm	β_2	\pm	β_3	\pm	β_4	\pm	β_5	\pm	β_6	\pm
Rai et al. (2010)	SIT model	0	0	lit. review & extr to infinite dilution	3.61	0.18	5.56	0.24	6.98	0.37	8.04	0.2	7.36	0.37	-	
Vas'ilev and Ikohnnikov (1972)	SIT model	0	0	lit. review & extr to infinite dilution	3.56	0.35	5.51	0.35	7.34	0.59	7.91	0.74	7.87	0.75	7.7	
Vas'ilev et al. (1973)	Solubility (BiOCl)	2-4		exp. & extr to infinite dilution from HClO ₄ , NaClO ₄ , HCl media	3.5	0.02	5.5	0.02	7.3	0.03	8.3	0.04	9.20	0.05	-	
Fedorov et al. (1974)		0.5	0.51	HClO ₄	2.82		4.44		5.45		6.23		6.11		6.68	
Fedorov et al. (1974)		1	1.05	HClO ₄	2.71		4.04		5.18		6.41		5.95			
Newman and Hume (1957)	UV-Vis Solvent	1		HClO ₄ , NaClO ₄ , HCl	2.4		3.5		-		-		-		-	
Suganuma et al. (1987)	extraction	1	1.05	HClO ₄	2.36		3.61		4.95							
Desideri and Pantani (1959)	Electrochemical Cation	1	1.05	(Na, H)ClO ₄	2.18		3.74		4.87		6.9		6.65			
Loman (1966)	Exchange Solubility	1.9			2.3		3.9		5.3							
Ahrland and Grenthe (1957)	(BiOCl)	2	2.21	NaClO ₄	2.4		3.7		5.4		6.1		6.72		6.56	
Ahrland and Grenthe (1961)	erratum to 1957 paper Solubility	2	2.21	NaClO ₄			3.8									
Haight (1964)	9	2	2.21	NaClO ₄			4.16				6.56				6.833	
Bond (1970)		2	2.21	NaClO ₄	2.16		3.82		5.6		6.9					

Table 4: Continuation from previous page.

Reference	Technique	I (M)	I (m)	Medium	β_1	\pm	β_2	\pm	β_3	\pm	β_4	\pm	β_5	\pm	β_6	\pm
Desideri and Pantani (1959)	Electrochemical	2	2.21	(Na, H)ClO ₄	2.08		4.22		5.71		7.18		6.75			
Desideri and Pantani (1959)	Electrochemical	2.5	2.84	(Na, H)ClO ₄	2		4.04		5.3		7.47		8.04			
Mironov et al. (1963)	Electrochemical	3	3.32	LiClO ₄	2.2	0.1	3.5	0.1	5.8	0.1	6.75	0.15	7.3	0.2	7.36	0.1
Fedorov et al (1974)		3	3.47	HClO ₄	2.53		4.66		6.32		7.93		8.18		6	
Desideri and Pantani (1959)	Electrochemical	3	3.5	(Na, H)ClO ₄	2.09		3.9		5.4		6.87		7.68			
	Solubility															
Johansson (1969)	(BiOCl)	4	4.95	NaClO ₄ , NaCl, HCl	3		4.3		6.7		6.9		8.6		8.4	
Desideri and Pantani (1959)	Electrochemical	4	4.95	(Na, H)ClO ₄	1.96		4.54		6.11		6.91		8.49		7.54	
Newman and Hume (1957)	UV-Vis	5		HClO ₄ , NaClO ₄ , HCl			-		5.8		6.2		6.7		-	
Kakare (1970)		5	6.58	NaClO ₄	2.35		4.4		5.45		6.65		7.29		7.06	
Desideri and Pantani (1959)	Electrochemical	6	8.45	(Na, H)ClO ₄	1.91		4.58		5.9		7.69		9.29		7.7	
Mironov et al. (1963)																
45 °C	Electrochemical	3	3.32	LiClO ₄	2.2	0.2	3.75	0.2	6.1	0.1	7	0.15	7.3	0.2	7.36	0.1
Mironov et al. (1963)																
65 °C	Electrochemical	3	3.32	LiClO ₄	2.2	0.2	3.9	0.1	6.3	0.1	7.15	0.15	7.6	0.2	7.36	0.1

Raman studies are useful to consider as they provide a different view on the range of possible species; these studies focus on the variation of structural characteristics of the solution species, rather than fitting formation constants. (Oertel and Plane, 1967) present a Raman study using varying ratios of Bi:Cl in acidic solutions ($[\text{Bi}] = 0.21\text{--}0.58\text{ M}$; $[\text{Cl}] = 1.5\text{--}1.87$; $[\text{H}^+] = 8.8\text{--}4.6\text{ M}$) and several organic solvents. They compare the solution spectra with solids and conclude that the complete series of $\text{BiCl}_n^{(3-n)}$ ($n=4\text{--}6$) is present for the higher order species. The smooth trend in observed species leads the authors to conclude that the coordination geometry does not abruptly change from tetrahedral to octahedral. The conclusion that the BiCl_4^- is distorted in some way from the coordination of solvent or the action of the $6s^2$ electron pair was found to be the former by (Spivakov et al., 1979) in a Raman study by comparison with organic solvent extracts and solids. Spivakov present the tetrachloride species as being hydrated (i.e. $\text{BiCl}_4^- \cdot 2\text{H}_2\text{O}$) but BiCl_5^{2-} and BiCl_6^{3-} as non hydrated; these authors suggest that the reason for the lack of hydration of BiCl_5^{2-} is the stereochemically active $6s^2$ lone pair, however this activity is generally not evident for Bi complexes with a coordination number greater than four (Carmalt and Norman, 1998).

In the reviews of (Vasil'ev and Ikonnikov, 1972) and (Rai et al., 2010) the data for BiCl_6^{3-} was not of sufficient quality to include it in their fitting of ionic interaction parameters, spread between the various sources was large. Both of these authors also conducted solubility studies on BiPO_4 (Rai et al., 2010) and BiOCl (Vasil'ev et al., 1973) respectively, and in each case did not require a BiCl_6^{3-} species to satisfactorily fit their data. This is in contrast to (Johansson, 1969) who required a BiCl_6^{3-} species to satisfactorily fit his solubility data for BiOCl . A BiCl_6^{3-} species was also included by (Ahrland and Grenthe, 1957) in a more limited BiOCl solubility study. In a solubility study of a substituted ammonium salt, $[\text{NCH}_3]\text{Bi}_2\text{Cl}_9$, (Haight et al., 1964) doubted the existence of the BiCl_5^{2-} species, presenting an interpretation of his data that involved the equilibrium between BiCl_6^{3-} and BiCl_4^- as the highest order species; this is a view that has not been confirmed in any other studies. The dataset presented by (Mironov et al., 1963) based on potentiometric measurements (at 25, 45 and 65 °C) includes the BiCl_6^{3-} species and the $\log\beta$ values (with no correction for ionic strength) he proposed have been those most frequently used for high temperature extrapolations and thermodynamic modelling (Kolonin and Laptev, 1982; Ruaya, 1988; Skirrow and Walshe, 2002).



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(b)

Figure 3. (a) Speciation of 10^{-6} molal Bi in a $\text{Cl}^-/\text{ClO}_4^-$ solution at $I=5$ using the SIT model parameters and $\log K_s$ presented by Rai et al (2010) (b) The same plot using the values presented by (Vasil'ev and Ikonnikov, 1972)

4.3 The Brønsted-Guggenheim-Scatchard Specific Ion Interaction (SIT) model for activity coefficients

The Bronsted-Guggenheim-Scatchard (SIT) model is a semi-empirical specific ion interaction model of calculating activity coefficients of aqueous electrolytes and is of

particular interest in bismuth geochemistry because it allows extrapolations to high ionic strength (~3-4 molal). These concentrations approach the brines commonly associated with a large portion of the hydrothermal deposits that contain significant bismuth. SIT theory utilises an analogous approach to Pitzer ion-interaction models (Pitzer, 1991), using a different Debye-Hückel term for describing long range electrostatic forces; and a specific ion-interaction term that is a function of the molality of the electrolyte to model short range interactions, which are increasingly important at high ionic strengths (Grenthe and Plyasunov, 1997). As the determination of Pitzer parameters from logK data is an ill-conditioned problem, the SIT model, or correlations between SIT and Pitzer parameters are advocated by the Nuclear Energy Agency for determination of medium effects on thermodynamic data (Grenthe and Plyasunov, 1997). Bismuth is of particular interest in geochemical modelling of nuclear waste repositories, therefore, two extensive reviews have used closely related variants of the SIT model for Bi-Cl solutions (Rai et al., 2010; Vasil'ev and Ikonnikov, 1972). The inclusion of SIT keywords and datablocks in the Phreeqc software package is a recent development in Version 2.17.0 that makes modelling of high salinity solutions using the SIT model a more accessible possibility for many geochemistry researchers and so the model is discussed here (February 25, 2010; http://wwwbrr.cr.usgs.gov/projects/GWC_coupled/phreeqc/RELEASE.5570.TXT).

The main difference between the SIT and Pitzer approaches is that fewer ion interaction parameters are used in SIT model. Hence, the SIT approach lends itself to studying complex formation in systems where limited data at varying ionic strengths are available and the many Pitzer parameters with their strong interrelations and correlations are difficult to fit (Grenthe and Plyasunov, 1997). In particular the different contributions of Debye-Hückel terms and the ionic strength dependence of the β^0 and β^1 terms in the Pitzer model make 'reduced' (i.e. only selected variables fitted) Pitzer models less accurate than the SIT model in systems where limited data are available. This is typical of datasets of conditional formation constants, determined in solutions of different ionic strengths. The SIT model performs particularly well where the measured formation constants used for fitting are at ionic strength values greater than 0.5 mol.kg⁻¹ (Grenthe and Plyasunov, 1997).

The main equation that make up the SIT model are outlined below. Equation 1 shows the particular form of the Debye Huckel term used in the SIT model.

$$D = \frac{A\sqrt{I_m}}{1 + 1.5\sqrt{I_m}} \quad (3)$$

Where A is the limiting Debye-Hückel law slope of the activity coefficient. The value of $1.5\text{kg}^{1/2}.\text{mol}^{-1/2}$ in the denominator of Equation 3 is an empirical value of the product a_jB in the Debye_Hückel term where a_j is an effective ion diameter and B is a constant determined by the temperature and the physical properties of pure water. I_m is the ionic strength.

Equation 4 relates the activity coefficient of a solute to the Debye Huckel term, charge, ionic interaction parameters and concentration:

$$\log_{10} \gamma_i = -Z_i^2 D + \sum_k \varepsilon(i,k) m_k \quad (4)$$

$\varepsilon(i,k)$ is a species interaction coefficient which describes the specific short range interactions between aqueous species i and k. The summation extends over all species k, with molality m_k present in solution where Z is the charge of species k and D is the Debye-Hückel term from Equation 3.

In the simplest approximation of the SIT model the coefficients are considered to be concentration independent, there is evidence against this, but the variation is only pronounced at low ionic strengths where the contribution of the parameters is quite small. At high ionic strengths $\varepsilon(i,k)$ is nearly constant.

The relation between activity coefficient and LogK value is illustrated by Equation 5.

$$\log_{10} K^\circ = \log_{10} K - Z_i^2 D + \sum_k \varepsilon(i,k) m_k \quad (5)$$

Rearranging Equation 5 and evaluating the sigma epsilon term we arrive at Equation 6. Equation 6 is used to derive SIT parameters empirically from linear plots of $(\log_{10} K - Z_i^2 D)$ vs ionic strength where $\log_{10} K^\circ$ is evaluated from the vertical intercept and SIT parameters can be determined from the slope by evaluating $\Delta\varepsilon$.

$$\log_{10} K^\circ - \Delta\varepsilon I_m = (\log_{10} K - Z_i^2 D) \quad (6)$$

The studies of Vas'ilev and Ikhunikov (1972) and Rai et al. (2010) utilise the specific ion interaction theory (SIT) to calculate activity coefficients and ion interaction parameters using variations of Equation 6 and data from literature surveys of $\log K$ determinations at various ionic strengths. Vas'ilev and Ikonikov (1972) include several early or obscure (for a non-Russian speaker) Russian works that are not included in the later work by Rai et al (2010). A representative spread of $\log \beta$ determinations at a range of ionic strengths is presented in Table 4 based on the reviews in these two studies. Both studies agree within stated errors, but small differences in the $\log \beta$ values for the $n = 4-6$ complexes lead to significant differences in speciation at higher chloride concentrations. Figure 3 shows the speciation calculated for 5 molal $\text{Na}^+ - \text{H}^+ - \text{ClO}_4^- - \text{Cl}^-$ solutions with $[\text{H}^+]$ of 1 molal and $[\text{Cl}^-]$ ranging from 0-5 molal. The $\epsilon_{i,k}$ SIT parameters of Rai et al. (2010) are used in modelling each set of $\log K^\circ$ values for consistency. It is important to note that the slightly different formulation of the SIT model used by Vas'ilev and Ikhunikov (1972), with respect to that of Rai et al. (2010) and the phreeqc software package, means that the specific ion interaction parameters they fit cannot be used in phreeqc without modification to the activity coefficient model invoked with the SIT keyword.

4.4 Bismuth hydrolysis in chloride solutions of varying pH

Studies of Bi-Cl-(OH) species in chloride-bearing solutions of variable pH are actually very few, although these species are likely to be of particular interest to geochemists further study of multi-component solutions is greatly hindered by the lack of a thorough understanding of the Bi-Cl species that are the end-member species in such solutions.

Mixed chloro-hydroxy species are hypothesised to be important at intermediate pH values in brines of chloride concentrations ≥ 0.05 m (Kolonin and Laptev, 1982; Savenko et al., 1998).

Some formation constants have been reported by (Kolonin and Laptev, 1982) and a number of hydroxy-chloro species with different stoichiometries were also identified by Savenko et. al. (1998). Savenko et. al. (1998) measured Bi concentrations in BiOCl solubility experiments from over and under-saturated conditions in 0.05 m NaCl and 35% sweater solutions. These authors estimated predominance regions for mixed complexes with 2 or 3 hydroxyl ligands that included $\text{Bi}(\text{OH})_2\text{Cl}_{(\text{aq})}$,

$\text{Bi}(\text{OH})_2\text{Cl}_2^-$ and $\text{Bi}(\text{OH})_3\text{Cl}^-$, and $\text{Bi}(\text{OH})_3\text{Cl}_2^{2-}$. These authors give the predominance regions for these species as $\text{pH} < 7.5$ for the 2-hydroxyl species and > 8.0 species for the 3-hydroxyl species. A further study by (Suganuma et al., 1987) used an extraction technique in an aqueous 1 M HCl/NaCl and carbon tetrachloride/1% dithizone system to study mixed hydroxyl-chloro bismuth complexes over a range of pH and chloride values. Bismuth concentrations were estimated using a radiochemical technique allowing these authors to work at low concentrations (1×10^{-11} M). They present a set of mixed hydroxyl-chloride complexes including $\text{BiCl}_5(\text{OH})^{3-}$, $\text{BiCl}_4(\text{OH})^{2-}$, and $\text{BiCl}_3(\text{OH})_2^{3-}$ with $\log\beta$ values of 10.9, 17.5 and 30.2 respectively. The speciation scheme presented by these authors uses a $\text{BiCl}_5(\text{H}_2\text{O})^{2-}$ complex as a predominant species in acidic chloride solutions that is subsequently de-protonated, with substitution of (OH) ligands for Cl^- ligands as pH increases.

5. Bismuth in sulfur-bearing solutions

Bismuth sulfide (Bi_2S_3 ; Bismuthinite) has a very low solubility ($K_{\text{sp}} 1 \times 10^{-97}$), however, it has been suggested that in reduced sulfidic solutions at higher temperatures ($> 150^\circ\text{C}$) that sulfide complexes play an important role in metal transport (Skirrow and Walshe, 2002; Törmänen and Koski, 2005). Similar solubility trends for Au and Bi sulfide-complexes are proposed by (Skirrow and Walshe, 2002) as the source of the commonly observed association of Bi and Au. (Skirrow and Walshe, 2002) also note that no thermodynamic data have been previously reported for sulfide-complexes or mixed sulfide-hydroxy complexes of Bi(III).

Despite the lack of experimental data there are still strong grounds for investigating possible bismuth sulfide-complexes. Consideration of hard-soft behaviour of ligands and As, Sb and Bi, which are all pnictides (group 15 elements), suggest that these Bi complexes should be relatively stable. In particular the similar electronegativity and ionic potential of Sb and Bi suggest that similar complexes should be formed. $\log K$ values of hypothetical sulfide and sulfide-hydroxy complexes of bismuth have been estimated by (Skirrow and Walshe, 2002) using a correlation method with the known $\log K$ s of sulfide and sulfide-hydroxyl complexes of As and Sb. The results indicate that sulfide-complexes of Bi may be important in reduced, sulfur-rich fluids. These authors mention a personal communication that supports their prediction of sulfide-

complexing of Bi based on solubility experiment data using a synthetic fluid inclusion method at 600-750 °C and 0.9-2.5 kbars using hematite-magnetite, cobalt-cobalt oxide, and pyrite-pyrrhotite-magnetite buffers (Douglas, 2000). However, the usefulness of these experiments is limited because they survey a small set of physical and chemical parameters. Despite indications of their potential importance, the bismuth sulfide complexes and associated data so far proposed in the literature are ultimately of questionable value because of the lack of independent evidence for the existence of the proposed complexes (Rickard and Luther, 2006).

(Crerar et al., 1985) discuss the possible influence of relativistic effects on the behaviour of metals observed in their experimental work (Wood et al., 1987). The velocity of the inner s and p electrons of the heavier metals such as Pt, Au, Pb, Bi and Hg approach the speed of the light. The s and p electrons of these elements are therefore drawn closer to the nucleus of the atom and are more difficult to remove than in lighter elements. The contraction of the s and p orbitals consequently increases shielding of the d and f orbitals. Crerar et al. (1985) claim that quantum-mechanical calculations show that the heavier metals should display a greater tendency toward covalent bonding because of this shielding effect, which has a pronounced impact on the properties of all elements heavier than Xe. Crerar et al. conclude that relativistic effects probably explain an apparent preference of bismuth for chloride ligands compared with a preference of antimony for bisulfide ligands. This apparent trend is in spite of the similar charge to ionic strength ratio and electronegativity of trivalent Bi and Sb. It is unclear how to translate such observations into thermodynamic properties, however, the relativistic effects described here underscore the difficulty of using simple extrapolations in models of Bi transport in sulfur-bearing hydrothermal systems.

6. Hydrothermal Chemistry of Bismuth

Kolonin and Laptev (1982), Ruaya (1988), and Shock (1997) present the only available formation constants for Bi complexes at hydrothermal conditions. Experimental studies of mineral solubilities are presented by Kolonin and Laptev (Bi_2O_3 ; solutions), Wood et al. (Py-Po-Mt buffered; CO_2 -NaCl-sulfide assemblage) and Kruszewski and Wood (2009) (Bi – Bi_2O_3 solubility in water vapour). These studies are discussed further in Chapter 3. We present here the logK data for hydrothermal Bi complexes currently available and note some updates for the thermodynamic model presented in Chapter 4.

The preferred data source for modelling hydrothermal reactions with Bismuth has been the 1982 paper by Kolonin and Laptev (e.g. Skirrow and Walshe, 2002), both Kolonin and Laptev (1982) and Ruaya (1988) rely on the 25 °C data from Mironov et al. (1963) for Bi-Cl_n formation constants. A possible reason for this is that these constants appear in the landmark publications of formation constants by Martell and Smith (1974-1989). As shown in Section 2.4.1 these constants were obtained in 4 M perchlorate solutions and are quoted without any ionic strength correction. Thus extrapolations that rely on this dataset as starting point at 25 °C should be updated with a more comprehensive dataset such as that presented by Rai et al. (2010) or Vas'ilev and Ikhunikov (1972).

Available properties for Bi-OH complexes are summarised in table 5 and for chloride complexes in table 6. The figures indicated in bold are those preferred for thermodynamic modelling studies and should be considered to supersede those presented in chapter 4. Properties for mixed chloro-hydroxy complexes are also presented in table 7, there are no comparable datasets for reference at 25 °C (that of Sugunama uses a different set of mixed Bi-Cl-OH species).

Table 5. Hydrolysis Constants for the reaction $\text{Bi}^{3+} + n\text{OH}^- = \text{Bi}(\text{OH})_n^{(3-n)+}$ at 200 and 300 °C. The data are a combination of extrapolations (Shock) and experimental values (this study, Kolonin and Laptev 1982).

$\log\beta_n(T)$	Kolonin and Laptev (1982)	Shock (1997)	This Study
$\log\beta_1(200)$		0.52 (0.30*)	
$\log\beta_1(300)$		0.51 (1.44*)	
$\log\beta_2(200)$	23.4	11.54 (12.37*; BiO^+)	
$\log\beta_2(300)$	24.3	12.21 (14.19*; BiO^+)	
$\log\beta_3(200)$	31.37	-1.84† (HBiO_2)	32.95
$\log\beta_3(300)$	33.15	-0.22† (HBiO_2)	36.58
$\log\beta_4(200)$	-	11.26 (12.09*; BiO_2^-)	-
$\log\beta_4(300)$	-	13.12 (15.10*; BiO_2^-)	-

*Values derived using recalculated properties for Bi^{3+} in preceding section.

†No difference to calculated value when using recalculated value of Bi^{3+} .

Notes: Figures in bold are the recommended values for thermodynamic modelling, the values for $\text{Bi}(\text{OH})^{2+}$ are in addition to that presented in Tooth et al. (2008) (Chapter 4), and the values for $\log\beta_3$ supersede the values presented in Chapter 4, the derivation of $\log\beta_3$ and thermodynamic properties for $\text{Bi}(\text{OH})_{3(\text{aq})}$ is the subject of Chapter 3.

No data are available for the $\log\beta_4$ species at $T > 25$ °C.

Table 6. Formation constants for the reaction $\text{Bi}^{3+} + n\text{Cl}^- = \text{Bi}(\text{Cl})_n^{(3-n)+}$ at 200 and 300 °C. The data of Ruaya are extrapolated and that of Kolonin and Laptev (1982) are based on experimental measurements of $\text{Bi}_2\text{O}_{3(\text{s})}$ in NaCl solutions.

$\log\beta_n(T)$	Kolonin and Laptev (1982)	Ruaya (1988)
$\log\beta_1(200)$	3.7	4.10
$\log\beta_1(300)$	5.7	6.01
$\log\beta_2(200)$	4.9	6.24
$\log\beta_2(300)$	7.2	9.72
$\log\beta_3(200)$	6.9	9.63
$\log\beta_3(300)$	9.3	14.78
$\log\beta_4(200)$	7.8	10.37
$\log\beta_4(300)$	10.5	15.43

Figures in bold are the recommended values for thermodynamic modelling, they are the same as those that feature in Tooth et al. (2008) (Chapter 4).

Table 7. Formation constants for mixed chloro/hydroxy complexes from Kolonin and Laptev (1982).

Temperature °C	$\log\beta \text{Bi}(\text{OH})\text{Cl}_{2(\text{aq})}$	$\log\beta \text{Bi}(\text{OH})_2\text{Cl}_{(\text{aq})}$
25	16.0	25.0
200	16.0	25.2
300	18.2	26.2

7. Aqueous Bismuth Chemistry: Summary

The knowledge of aqueous bismuth chemistry currently has large areas of uncertainty, this is particularly marked at temperatures above 25 °C and in the characterisation of sulfide-complexes. Although considerable consensus exists for the formation constants of mono-nuclear hydroxy species and the identity of the most dominant polynuclear hydroxy-complex.

Reported formation constants for the other polynuclear species are derived from a limited number of different ionic strengths, so a test of activity coefficient accuracy or derivation for a model such as the SIT has not been conducted. The persistence of these species with increasing temperature has never been investigated.

Chloro-complexes are well characterised at room temperature, despite some conflicting studies, a stepwise series of complexes up to BiCl_5^{2-} is well established, the existence of the BiCl_6^{3-} complex and the magnitude of formation constants for these final two species in the series has not been conclusively resolved. Several studies have recognised the importance of mixed chloro-hydroxy-complexes, but the reported stoichiometries of such complexes vary. In highly saline brines with typical values for natural pH, these complexes are likely to be extremely important.

Finally, Bi sulfide-complexes are only hypothesised and extrapolated, with no published experimental studies. The likelihood of a degree of sulfide complexation material to geochemists modelling hydrothermal environments is by no means certain. Throughout the studies conducted during this work, comparisons with As and Sb have been important in planning how to study a likely Bi speciation scheme. Given the few studies of Bi in hydrothermal fluids, and the likely importance of the neutral Bi-hydroxide complex, based on the predominance of this complex for As and Sb, the experimental work conducted in this thesis concentrates on Bi in pure water over a range of temperature and pressure. Chloride-bearing solutions, are seen as this ligand predominates in most ore-forming settings and is particularly relevant for the hydrothermal brines encountered in many Bi-bearing deposits - the typical example being gold skarns (Meinert, 2000).

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Chapter 3

Bismuth Speciation in Hydrothermal Fluids: An X-Ray Absorption Spectroscopy and Solubility Study

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Chapter 4

Modeling of Gold Scavenging by Bismuth Melts Coexisting with Hydrothermal Fluids.

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Chapter 5

Bi-melt Formation and Gold Scavenging from Hydrothermal Fluids: An Experimental Study

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Chapter 6

Conclusions and Future Work

Conclusions and Future Work

Although specialisation and focus are the hallmarks of many PhD projects, the approach taken here has been to tackle the central subject of the ‘liquid bismuth collector model’ from several perspectives. The main contributions of this thesis to current knowledge include new fundamental data about the geochemistry of Bi in hydrothermal systems, the experimental demonstration of the efficiency of the ‘liquid bismuth collector model’, and qualitative investigation of reactions for Bi in hydrothermal systems. These contributions have involved conducting solubility experiments, innovative leaching and precipitation experiments, and thermodynamic modelling.

1. Thermodynamic and Structural Properties

The simple case of bismuth oxide dissolving in water over a wide range of temperature and pressure is the logical starting point for a sound understanding of Bi in more complex fluids, such as hydrothermal brines. Solubility experiments conducted with a range of methods were the base for this part of the research presented in Chapter 3. By using a mixture of well established (e.g. batch reactors) and new techniques (e.g. high temperature and pressure EXAFS) data was collected on thermodynamic and structural properties of Bi over a wider range of temperatures and pressures than was previously available.

This work also yielded a set of HKF parameters for $\text{Bi}(\text{OH})_{3(\text{aq})}$ for reactive transport modelling. Given the importance of analogous aqueous hydroxide species in hydrothermal environments for the closely related metalloids As and Sb, the improved thermodynamic properties will likely be important for modelling of ore deposits that contain Bi. These properties are also significant because they complete a set of thermodynamic and structural properties for the group that may also be useful to other researchers seeking to understand periodic trends.

2. Melts in Hydrothermal Systems

Additional contributions of this thesis relate to the integration of hydrothermal fluids and metallic melts in numerical models, and novel experiments to replicate important features of complex natural systems.

2.1 Numerical Modelling

Numerical models such as that presented in Chapter 4 show potential for use as a predictive or interpretative tool, especially in parageneses where the role of melts may have been obscured by subsequent reworking. This type of numerical model is also

likely to be a useful framework for the design and testing of future experiments. The numerical modelling approach employed in this research coupled a thermodynamic model of a non-aqueous liquid (non-random two liquids; NRTL) with an aqueous hydrothermal fluid (HKF model) using the HCh software published by Geoscience Australia.

The developed model illustrates the sound theoretical foundations of the ‘liquid-bismuth collector model’ as proposed by (Douglas et al., 2000) by combining data from disparate sources and replicating natural observations. The numerical model was shown to reproduce Au and Bi deposition and elemental ratios present in natural systems. The observed Au-Bi association of the Escanaba Trough (Toermanen and Koski, 2005) was used as a specific example. Significantly as new data comes to light it can be included in the same framework, new data for hydrothermal speciation of Bi in particular will increase the future usefulness of this model to geochemists.

2.2 Experiments

Research into coexisting hydrothermal fluids and melts has been further augmented by hydrothermal experiments to investigate the interaction of Bi rich melts, hydrothermal fluids, and exploring how these relate to mineral reactions in circulating hydrothermal systems. The design of the experiments aims to reproduce the natural paradigm of source-transport-deposition; a thermosiphon driven flow through reactor was adapted to simplify the technical aspects of implementation.

Significant results from the experiments include:

- Replication of natural features consistent with melt formation:
 - Au and Bi are intimately associated and form blebs and droplet, with internal textures consistent with solidification from a melt;
 - Au is intimately associated with Bi in proportions consistent with melt formation at the temperature and pressure of the experiment.
- Au was always localised at the same sites as Bi in the experiments.
- Bi (and Au) precipitation is observed in redox reaction zones of pyrrhotite and magnetite, and onto graphite-containing substrates.
- Demonstration that Bi-melts can scavenge Au from hydrothermal fluids on timescales practical for conducting laboratory experiments.

These experiments are qualitative because the complexity of the chemical system under study, lack of in-situ observation of melt growth and chemical evolution, and complex reaction path sets some limitations to the quantitative interpretation of the results. However, the chosen experimental design also leads to some fascinating insights into the complexity of reactive transports in hydrothermal systems. In particular, the experiments illustrate the role of non-equilibrium processes and micro-

environments as well as the coupling with dissolution-reprecipitation reactions for metals that form polymetallic melts at low temperatures (i.e. ~ 241 to 300 °C). The experiments unambiguously show the interaction of molten Au and Bi in a hydrothermal system, with Au localised at sites where liquid bismuth is present; this genetic link is the significant feature of the liquid bismuth collector model in ore deposition. The experiments also indicate that melt transport and precipitation may be related to other common mineral reactions present in hydrothermal systems such as redox reactions between common Fe minerals, that create local conditions suitable for Bi melt formation.

3. Future Work – Thermodynamic and Structural Properties

The importance of Bi and the liquid bismuth collector model to the potential formation of gold deposits points to the obvious need to explore Bi species commonly inferred to be present in hydrothermal fluids during ore deposit formation.

Further Work on $\text{Bi(OH)}_{3(\text{aq})}$ that would refine the HKF parameters determined in Chapter 3 include:

- A vapour partitioning study in the simple $\text{Bi}_2\text{O}_{3(\text{s})}$ - H_2O system such as that conducted by (Pokrovski et al., 2008) or solubility measurements over a wider range of pressure such as those conducted by (Zotov et al., 2003) could be used to estimate the Gibbs free energy of hydration for $\text{Bi(OH)}_{3(\text{aq})}$, and volumetric properties. This data would facilitate the use of the updated correlations for determination of the HKF a1 to a4 parameters (Plyasunov and Shock, 2001).
- A solubility study in a fluid mixture such as $\text{H}_2\text{O-N}_2$ would allow variation of the solution dielectric permittivity, the data obtained from such experiments would allow a determination of the Born parameter (ω) using the algorithm employed by Zotov et al (2003) for Sb.

The prominent role of reduced sulfur-bearing fluids in gold deposit formation, from transport to deposition, indicates that the role of Bi sulfide complexes is something that needs to be explored. A common transport agent and a similar sensitivity to physical and chemical conditions, such as sulfur degassing or boiling may also be possible reasons for the close association of Bi and Au observed in several ore deposits. Sulfur species also delineate the limits for applicability of the liquid bismuth collector model as the formation of bismuthinite (melting temperature ~ 763 °C) rather than liquid Bi (melting temperature ~271 °C) requires temperatures several hundred degrees higher for melting to occur .

A role for simple organic ligands should also be explored, many deposits where Au and Bi are shown to be correlated also show significant reactions with carbonaceous sediments, shales and similar rocks with reduced carbon components. The recent example of the Escanaba Trough used as the model for Chapters 4 and 5 also contains significant organic carbon, and the experiments in Chapters 5 are all conducted with an acetate buffer which may itself contribute to Bi transport in these experiments.

Au-Bi-(Te) associations are considered one of the distinguishing features of gold skarns, and the frequent occurrence of saline hydrothermal solutions and brines (often with >20% NaCl contents by weight) indicate that hydrothermal studies of Bi-Cl complexes are also likely to be a fruitful area of study. Extensive groundwork has already been laid down by previous researchers for Bi-Cl complexes in acidic solutions at low temperatures (~25 °C) as summarised in Chapter 2. The direct relevance of Bi-Cl complexes to natural systems means that further work in elucidating thermodynamic properties for these complexes at higher temperatures should be a priority for future research. Work using simple solubility experiments at temperatures from 25 °C to several hundred degrees Celsius would be extremely useful in consolidating current knowledge at low temperatures and extending this to conditions useful for geologists and geochemists. Bismuth solids such as bismuth sulfide (bismuthinite; Bi_2S_3) and to a more limited extent bismuth oxychloride (bismoclite; BiOCl) can be successfully studied in a relatively wide salinity-pressure-temperature series to achieve this aim.

4. Future Work on Melts in Hydrothermal Systems

The work covering Bi melts in hydrothermal systems presented in this thesis probes several interesting areas. However, unlike the study of chapter of thermodynamic and structural properties in Chapter 3, the problems investigated lack a well established methodology for study, the chemical systems are more complicated and new questions arise with each experiment.

4.1 Numerical Model of Partitioning between Au and Bi

Simple batch experiments could be used to test the numerical model outlined in Chapter 4. Without the complicating factors of fluid flow, temperature gradients and dissolution/re-precipitation reactions, solubility experiments of Au-Bi mixtures could be done relatively simply, and require only control of pH and redox parameters such as $f\text{O}_{2(g)}$. Rocking Autoclaves as used for solubility experiments in Chapter 3, or higher temperature equipment such as those manufactured by Core-Test and employed by (Pokrovski et al., 2008) could be used to directly sample fluids and collect data over a wide range of temperature and pressure. The activity of Au and Bi could be accurately determined from the recovered alloys in the manner Gammons and

Williams-Jones (1995) used for a solubility study on Au-Ag alloys, however the simple silica tube techniques employed by these authors are likely to be unsuitable for working with molten samples.

4.2 Experimental study of Bi.

Several shortcomings in the employed methodology for the experiments conducted in Chapter 5 could be addressed in future work.

In particular, the closed nature of the apparatus used in Chapter 5 made sampling fluid at temperature and pressure difficult. The difficulty of fluid sampling led to a heavy reliance on the interpretation of solid phases present after cooling to estimate conditions at temperature. The closed loop thermosiphon system can be adapted for sampling, but the limited volume of liquid able to be withdrawn without affecting fluid circulation is a factor that will require some work to resolve. For example, in experiments where a reduction in recovered fluid volume was observed, a breakdown of the relationship between temperature at the 'hot' and 'cold' points of the reactor was also always observed. Excess fluid volume in the cell is also not a suitable solution as tubing outside the direct fluid circulation path is essentially a 'dead volume' with little mixing occurring. The inefficiency of mixing is indicated by the lack of temperature change measured by thermocouples placed at points of the reactor loop that contained fluid, but protruded from the main circuit.

The other major drawback of the closed loop design was that the reactor does not lend itself to incremental experiments as each experiment takes considerable time to prepare and the internal surfaces and cavities of the reactor are difficult to inspect and clean. To survey such a chemical system effectively an array of batch reactors would be useful, but then the chemical gradients that result from the fluid flow of the thermosiphon reactor cannot be replicated. Significant effects for reaction progression in iron sulphides have been shown previously (Fang Xia, personal communication) when comparing the same reaction studied in a similar flow-through reactor and a batch design.

An open loop reactor design with a once-through fluid flow would be useful, especially if mass balance calculations could be accurately determined for fluid both entering and leaving the system. Such a system would require trials of various combinations of mineral leaching at temperature and solution preparation at ambient laboratory conditions to have input concentrations of Au and Bi that are reproducible and predictable. Soluble Bi and Au compounds that would allow simple solution preparation at ambient laboratory conditions are difficult to find, and some kind of leach procedure at high temperature, followed by the mineral/chemical trap may be necessary. Complications arising from precipitation on cooling, and the redox stability of various aqueous Au species also need to be considered for the sampling

methodology. Nevertheless, volume constraints for sampling and input can be effectively eliminated with a 'once-through' design as large amounts of fluid can be pumped through a small reaction vessel and temperature and chemical gradients can be effectively controlled.

4.3 Applications to other Systems

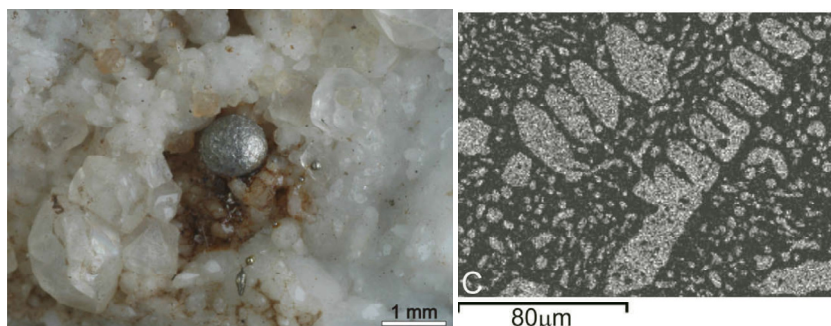
The extension of similar experiments to other metals is likely to be a fruitful area of study. Au-Bi alloys are not the only metals that have melting points that are within the common scope of hydrothermal systems and extension to a range of low melting elements, and a range of precipitation conditions are topics worthy of exploration. The coupling of melt formation to precipitation and partitioning processes can enrich deposits and move metals on a local scale, but may be active over a range larger than has previously been considered, for example on a scale that may be hundreds of metres rather than centimetres or less.

In conclusion, the work of Dekov et al. (2009) is offered as an example of how the the general principles of coupling of hydrothermal transport and melt precipitation may apply in other polymetallic systems:

“We assume interaction of seawater fluids carrying metals leached from basaltic rocks with hydrocarbons from sedimentary units as a prerequisite for the formation of the organometallic complexes. The zeolites lining the basaltic vesicles might have destabilized the migrating organo-Sn and Pb compounds causing their breakdown and precipitation of Sn–Pb alloy.”(Dekov et al., 2009)

As can be seen in the pictures below the droplet and bleb-like shapes of the precipitated metals (Sn and Pb) and the intimate association of Sn and Pb in eutectic-like textures are features similar to those observed at both the Escanaba Trough and the experiments detailed in Chapter 5. Although Dekov et al. only discuss metal precipitation in terms of nanoparticle formation, the Sn:Pb ratio quoted by these authors of 88:12 would make melt formation feasible at the proposed precipitation temperature of <210 °C. This temperature would be in a range bounded by the melting temperatures of pure tin at 232 °C and the eutectic of 183 °C (Sn:Pb ratio of 62:38).

Figure 1. Images from Dekov et al. (2009). Left: Photograph of the internal part of an amygdale showing an aggregate of white to transparent crystals hosting silver-white metallic spherules. Right: Internal microtexture of an Sn–Pb spherule using Pb M α X-ray mapping.



This outlines a similar process to that replicated in the flow through reactor, and the Escanaba Trough where the main features are as follows:

- Low melting point metals are leached from source minerals by a hydrothermal fluid.
- The low melting point metals are transported as dissolved metal complexes.
- The low melting point metals are precipitated ('the trap') by a chemical reaction (e.g. with pre-existing minerals) or changes in physical conditions (e.g. pressure or temperature) – the efficiency of the trap is determined by the metal and the specific complex.
- Other metals are accumulated in the melt which can occur by several processes:
 - partitioned after later transport by a hydrothermal fluid;
 - partitioned immediately as they are present in the same fluid;
 - or precipitated by another mechanism, the timing of which is unrelated to melt formation, and then subsequently incorporated into the melt.

Table 1. A summary of important features for melt transport, precipitation and partitioning reactions and how these apply to the different physical and chemical systems investigated in Chapter 5 and the paper of Dekov et al. (2009).

Important Features	Hydrothermal System	
	<i>Flow Through Reactor</i>	<i>Dekov (Seafloor)</i>
Primary Melt Components	Bi-Au	Sn-Pb
Temperature of Melt Formation	241-300 °C	<210 °C
Melt leached from	Bi ₂ S ₃ , Au-Cl solution precipitate	Basalt
Proposed Metal Complexes (primary melt component)	Bi Cl _x	'Organic' – M _n (C _x H _y O _z) _n
'The Trap'	Py-Po, reduced carbon	Zeolites
Precipitation Reaction	Reduction by reaction with iron sulphides	De-stabilisation by sequestration of organic ligands
Partitioning	Partitioning of dissolved or colloidal Au into Bi melt	Co-precipitation of components as melt

Although in the cases where melt mechanisms are likely to be of most interest (i.e. ore deposits), distinguishing features are likely to be destroyed or obscured by subsequent reworking, a knowledge of the conditions for which melt models can work for groups of metals may lead to advances in mineral prospecting or could be adapted to new processing techniques. The coupling of polymetallic melts with transport and precipitation processes should prove to be a fruitful area of further study.

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