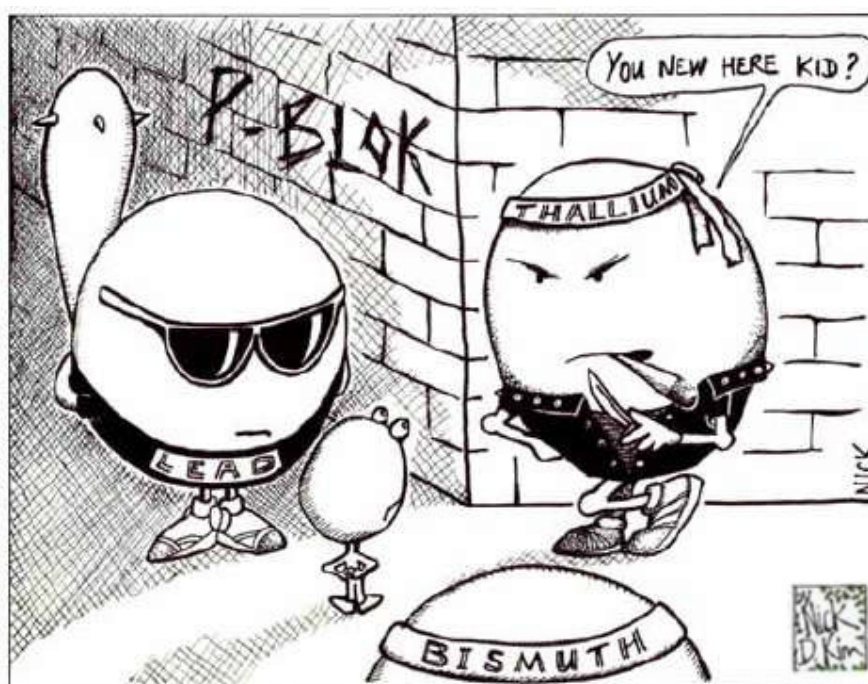


# The Hydrothermal Chemistry of Bismuth and The Liquid Bismuth Collector Model

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](http://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)<sub>3(aq)</sub>, Sb(OH)<sub>3(aq)</sub>) 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)<sub>3(aq)</sub> 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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Signed:

Date: 9/07/2013

Blake Alfred Tooth



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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.