

**Report for the Experiment EC-404, 11-19/2/2009**  
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**Title: Validating the Liquid Bismuth Collector Model: Speciation and solubility of Bismuth in hydrothermal fluids**

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**Aims:**

Many gold deposits show elevated amounts of bismuth. The nature of this association remains poorly understood, and the aqueous geochemistry of Bi in hydrothermal solutions poorly constrained. Recently, a “liquid bismuth collector model” (LBCM) was proposed in which molten bismuth scavenges gold from solution [2]. This represents a major paradigm shift in our understanding of the formation of hydrothermal Au deposits. The Au-Bi association was previously interpreted in terms of similar Au and Bi geochemistry leading to similar depositional processes [1], but the LBCM suggests that Au may be concentrated in deposits by Bi melts even from Au-undersaturated solutions. This has profound implications for the exploration for new gold deposits, as Bi geochemistry becomes a primary control on the location and grade of Au ores. Recently, we have used equilibrium thermodynamics to show that the Bi-melts are indeed expected to effectively scavenge Au even from strongly undersaturated fluids [3].

Understanding Bi geochemistry is critical in establishing the relevance of the LBCM and its consequences for exploration and mineral processing. A recent review [1] suggests that Bi(III) hydroxy- and chloro-complexes dominate Bi transport in hydrothermal systems, but only one experimental study extends to hydrothermal conditions (mainly solubility; to 300°C [4]). EC-404 aimed to provide the first data on aqueous Bi geochemistry at  $T > 300^{\circ}\text{C}$ , under sub- and super-critical conditions, and to characterise the nature and geometry of the main aqueous species responsible for Bi transport under hydrothermal conditions.

**Results:**

- We collected solubility, XANES and EXAFS spectra for Bi in  $\text{H}_2\text{O}$ -NaCl-HCl- $\text{H}_2\text{S}$  solution at  $P=600$  bar at  $T$  to  $600^{\circ}\text{C}$ .
- Precipitation of metallic bismuth in the beam was (to our surprise) a significant problem at temperatures below the melting point of metallic bismuth. However, since the precipitate formed on the wall of the glassy carbon cell, we were able to obtain clean solution spectra using adequate collimation. Above  $\sim 250^{\circ}\text{C}$  these problems were greatly reduced, probably because the melted Bi did not accumulate under the beam.
- We succeeded in collecting good EXAFS spectra for  $\text{Bi}(\text{OH})_3(\text{aq})$ , which is predicted to be the predominant Bi complex under wide ranges of hydrothermal conditions. The geometry of this complex appears to change little with  $P$  and  $T$ . This data complements similar datasets for Group 15 metalloids,  $\text{As}(\text{OH})_3(\text{aq})$  and  $\text{Sb}(\text{OH})_3(\text{aq})$ , collected at the same beamline [5,6].
- We obtained solubility data for  $\text{Bi}_2\text{O}_3(\text{s})$  that are consistent with our autoclave experiments, and extend the  $T$  range from  $250^{\circ}\text{C}$  to  $500^{\circ}\text{C}$ .

- We confirmed that Bi-cluster species that have been identified in some solids do indeed exist in aqueous solution, and that these species disappear at elevated temperature. This is important in explaining discrepancies for thermodynamic properties of Bi species at low temperatures, since many studies did not consider these polynuclear species.
- We also measured EXAFS spectra for the Bi chloro-complexes that are dominant in acidic brines up to magmatic hydrothermal conditions, and obtained preliminary data in S-rich systems that suggest that Bi bisulfide complexes probably do not play a large role in Bi transport.

This experiment is an integral part of Blake Tooth PhD thesis. Blake is preparing two manuscripts based on the results on this experiment (Bi-O-H system; Bi-O-Cl-S system), combined with autoclave solubility studies and UV-Vis-NIR spectroscopy. Blake aims to submit his PhD (by publication) in March 2010.

### **Publications (\* indicates publications resulting from this experiment)**

- [1] Skirrow, R.G et al., *Economic Geology*, Vol. 97, 2002, pp. 1167-1202
- [2] Douglas, N, .et al., 2000, *Geological Society of Australia, AGC abstract volume*, 59, 135
- [3] Tooth, B.A., Brugger, J., Ciobanu, C. and Liu, W. (2008): Modeling of gold scavenging by bismuth melts coexisting with hydrothermal fluids. *Geology*, 36, 815-818.
- [4] Kolonin G. R. et al. *Geokhimiya*, 11, 1621-1631, (1982) (journal published in Russian)
- [5] Testemale, D., Hazemann, J.L., Pokrovski, G.S., Joly, Y., Roux, J., Argoud, R. and Geaymond, O., 2004. Structural and electronic evolution of the As(OH)(3) molecule in high temperature aqueous solutions: An x-ray absorption investigation. *Journal Of Chemical Physics*, 121(18): 8973-8982.
- [6] Pokrovski, G.S., Roux, J., Hazemann, J.L., Borisova, A.Y., Gonchar, A.A. and Lemesko, M.P., 2008. In situ X-ray absorption spectroscopy measurement of vapour-brine fractionation of antimony at hydrothermal conditions. *Mineralogical Magazine*, 72(2): 667-681.
- \*[7] Tooth, B. A., Brugger, J. and Ciobanu, C.L. (2009) Experimental observation of gold scavenging by bismuth melts coexisting with hydrothermal fluids. GEOFLUID 2009 Conference, April 15-18 2009, Adelaide, South Australia. *J. Geochemical Exploration*, 101, p. 104. doi:10.1016/j.gexplo.2008.11.063.