

Experiment Report Form

The double page inside this form is to be filled in by all users or groups of users who have had access to beam time for measurements at the ESRF.

Once completed, the report should be submitted electronically to the User Office using the **Electronic Report Submission Application:**

<http://193.49.43.2:8080/smis/servlet/UserUtils?start>

Reports supporting requests for additional beam time

Reports can now be submitted independently of new proposals – it is necessary simply to indicate the number of the report(s) supporting a new proposal on the proposal form.

The Review Committees reserve the right to reject new proposals from groups who have not reported on the use of beam time allocated previously.

Reports on experiments relating to long term projects

Proposers awarded beam time for a long term project are required to submit an interim report at the end of each year, irrespective of the number of shifts of beam time they have used.

Published papers

All users must give proper credit to ESRF staff members and proper mention to ESRF facilities which were essential for the results described in any ensuing publication. Further, they are obliged to send to the Joint ESRF/ ILL library the complete reference and the abstract of all papers appearing in print, and resulting from the use of the ESRF.

Should you wish to make more general comments on the experiment, please note them on the User Evaluation Form, and send both the Report and the Evaluation Form to the User Office.

Deadlines for submission of Experimental Reports

- 1st March for experiments carried out up until June of the previous year;
- 1st September for experiments carried out up until January of the same year.

Instructions for preparing your Report

- fill in a separate form for each project or series of measurements.
- type your report, in English.
- include the reference number of the proposal to which the report refers.
- make sure that the text, tables and figures fit into the space available.
- if your work is published or is in press, you may prefer to paste in the abstract, and add full reference details. If the abstract is in a language other than English, please include an English translation.


Experiment title:

Minor Ore Fluid Components Matter: The role of bromide in the transport and deposition of gold.

Experiment number:

CH - 3352

Beamline: 30-BM-B	Date of experiment: from: 22 June 2011 to: 28 June 2011	Date of report: 26 Feb 12
Shifts: 18	Local contact(s): Denis Testemale + Vincent Ranieri	<i>Received at ESRF:</i>

Names and affiliations of applicants (* indicates experimentalists):

Joel Brugger*, Adelaide University

Weihua Liu*, CSIRO

Barbara Etschmann*, Adelaide University

Denis Testemale, CNRS/ESRF

Kirsten Rempel*, Potsdam+Curtin

Aim: The aim of this experiment was to explore the role of minor ore fluid components (Br in this case) in the geological transport and deposition of metals (Au(I) in this case). Speciation calculations using available thermodynamic properties suggest a very strong stability of the mixed bromo-hydroxo Au(I) complex, Au(I)Br(OH)^- at neutral pH, even with a Cl:Br ratio of 1000. Though sulfur is the predominant ligand in Au(I) complexing under many geological conditions, such halide complexes could play a critical role for example in magmatic hydrothermal deposits.

Experimental: Data were collected at the Au L_3 -edge (11.919 keV) at the BM-30B (FAME) beam line, using the high T-P cell developed by the CNRS. The energy was calibrated with metallic Au, such that the maximum of the first derivative was at 11.919 keV.

Sample	Conditions	Sample	Conditions
Au	Metal foil 20 C, 1 bar	AuBr ₄ (standard) solution	20 C, 1 bar
Au(III) + 0.258m HCl Br/Cl = 0	Stock2 (100 % Cl) 35 C, 1 bar	Au(III) + 0.14 m Br, (Br+Cl) ~ 0.5 m Br/Cl = 0.4	RT3 35 C, 1 bar
Au(III) + 0.021 m Br, (Br+Cl) ~ 0.5 m, Br/Cl = 0.08	RT1 35 C, 1 bar	Au(III) + 0.25 m Br, (Br+Cl) ~ 0.5 m Br/Cl = 1	RT4 35 C, 1 bar
Au(III) + 0.045 m Br, (Br+Cl) ~ 0.5 m Br/Cl = 0.2	RT2 35 C, 1 bar	Au(III) + 0.19 m Br, (Br+Cl) ~ 0.5 m Br/Cl = 0.6	RT5 35 C, 1 bar
Au + 2m NaHS	Sol 1 200-440 C, 700 bar	Au + 0.25m HBr + 0.25 m NaBr	Sol 8 35-420 C, 700 bar
Au + NaAuBr ₄ + 1m NaBr + 0.015 m HBr	Sol 2 35-170 C, 700 bar	Au + 0.25m HCl + 0.15m NaCl + 0.1 m NaBr	Sol 9 100-330 C, 700 bar
Au+NH ₃ + HNO ₃ , pH 5	Sol 3 35-436 C, 700 bar	4mm HAuCl ₄ + 0.28m HCl + 0.15m NaCl + 0.1m NaBr	Sol 10 35-222 C, 700 bar
Au+NH ₃ + HNO ₃ , pH 9	Sol 4 114-329 C, 700 bar	Au + 4mm HAuCl ₄ + 0.28m HCl + 0.25m NaCl	Sol 11 35-168 C, 700 bar
Au + 0.2m NaHS + 2m NaBr	Sol 5 222-436 C, 700 bar	4mm HAuCl ₄ + 0.25m HCl + 0.08m NaCl+0.17m NaBr	Sol 12 35-222 C, 700 bar
Au + As + 0.5m HCl + 0.5 m NaBr	Sol 6 114-329 C, 700 bar	Au + 1m NH ₃ + 0.2m NaHS	Sol 13 220-440 C, 700 bar
Au + As + 0.25 m HBr + 0.25 m NaBr	Sol 7 114-222 C, 700 bar	4mm HAuCl ₄ + 0.25m HCl +0.25m NaBr	Sol 14 35-114 C, 700 bar
		Au + H ₂ O ₂ + Na ₂ CO ₃	Sol 16 35-436 C, 700 bar

General observations

Sols RT+Stock: These spectra demonstrate that Au(III) complexes quite strongly with Br. With a of Br:Cl=1, the AuBr₄⁻ species predominates. We collected a systematic series of spectra at varying Cl:Br ratio, enabling comparison with recent UV-Vis data used to derive thermodynamic properties for Au(III)-chloride-bromide complexes.

Sol 1: XANES, k and R-space similar for all temperatures. This is consistent with the result of Pokrovski et al. (2009), that AuS_2^- is the dominant Au-species in near-neutral ($4.5 \leq \text{pH} \leq 8.9$) over a wide range of TPx. The spectra are similar to the Au-S spectra in basic solutions from Pokrovski et al. (2009), and can be fitted with AuS_2^- .

Sol2: $[\text{AuBr}_4^-]$ at 35 °C; loses pre-edge upon heating and spectra become increasingly metallic (3rd spectrum at 170 °C closely resembles metallic Au), precipitates evident in solution.

Sol3,4,16: Very little Au in solution at all temperatures, spectra resemble metallic-like Au.

Sol 5: *Competition between Br and S.* Spectra at all temperatures (222-436 °C) look similar. These experimental spectra are all identical to Sol1 and not at all like Sol8 (114 °C); **this implies that the bonding is AuS_2^- , with no Br!!**

Sol 6: *Competition between Br and Cl.* High background due to As, very little Au in solution. Spectra (114 °C) almost identical to Sol8 (114 °C, AuBr_2^-) and quite different to Sol11 (114 °C, AuCl_2^-). At higher temperatures there are particles in solution and the pre-edge decreased, implying Au is precipitating. **This implies that at 114 °C Au(I) preferentially binds with Br rather than Cl.**

Sol 7: High background due to As; very little Au in solution. Spectra looked similar for all temperatures; spectra identical to Sol8 (114 °C).

Sol 8: $[\text{AuBr}_4^-]$ at 35 °C; spectra resemble metallic-Au at 420 °C (with precipitates in solution). At intermediate temperatures (114-222 °C), spectra are very similar and most closely resemble that of the AuCl_2^- standard (Reith, pers comm) – but the white line is lower. This lower white line is due to Br being the ligand, rather than Cl (see RT spectra, the more Br, the lower the white line even though total halide concentration was constant); Sol8 can be fitted as AuBr_2^- .

Sol 9: *Competition between Br and Cl.* Spectra resemble Sol11 (114 °C, AuCl_2^-) at all temperatures. Interestingly, **in this solution Au seems to be predominantly bonded to Cl**; apparently the Br:Cl ratio is important (Br:Cl=1:1, preferentially bonded to Br, Sol6.)

Sol 10: *Competition between Br and Cl.* $[\text{AuBr}_4^-]$ at 35 °C; first 114 °C spectrum is ~halfway between Sol8 (114 °C, AuBr_2^-) and Sol11 (114 °C, AuCl_2^-), the fourth spectrum (114 °C) is more similar to Sol8 (114 °C), but still has some Cl component. At 168 °C spectra are almost identical to Sol8 (114 °C). *It is interesting that Sol9 and Sol10 seem so different, why is this?*

Sol 11: $[\text{AuCl}_4^-]$ at 35 °C (spectrum is a bit different to $[\text{AuBr}_4^-]$). White line decreases on heating, becoming AuCl_2^- .

Sol 12: *Competition between Br and Cl.* Interestingly the spectrum at 35 °C closely resembles $[\text{AuBr}_4^-]$ (standard solution rather than Sol8 ...); with heating the white line decreases, at 222 °C the spectrum is more similar to Sol8 (114 °C, AuBr_2^-) than to Sol11 (114 °C, AuCl_2^-).

Sol 13: Spectra identical for all measured temperatures, and are identical to Sol1 (AuS_2^-).

Sol 14: *Competition between Br and Cl.* At 114 °C the spectrum is more similar to Sol8 (114 °C, AuBr_2^-) than to Sol11 (114 °C, AuCl_2^-).

Preliminary Fits: [Hanning window]

Solution	T (°C)	ligand	n	R	σ^2	E_0	χ^2_{red}	k weight	Data range (\AA^{-1})
Stock2	35 °C	Cl	4 (fix)	2.271(4)	0.0023(3)	6.6(5)	300	1,2,3	2 - 15.85
RT4	35 °C	Cl	0					1,2,3	2 - 15.85
		Br	4.3(3)	2.417(3)	0.0026(3)	6.6(5)	300	1,2,3	2 - 15.85
Sol1	300 °C	S	2 (fix)	2.29(1)	0.0023(7)	4(1)	176	2	2 - 10
		S (ms)		4.58(1)					
Sol8	114 °C	Br	2 (fix)	2.398(6)	0.0007(2)	8(1)	758	1,2,3	2 - 11.9
		Br (ms)		4.796(6)	0.008(4)				
Sol11	35 °C	Cl	3.4(3)	2.264(6)	0.0007(9)	6.6(9)	60	2	2 - 10
		Cl (ms)		4.529					
	114 °C	Cl		2.26(2)	0.0004(47)	6.6(9)	60	2	3 - 9
		Cl (ms)		4.52(2)					

