

## 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:**

**Speciation and solubility of tellurium in hydrothermal fluids**

**Experiment number:**

CH - 3135

**Beamline:**

30-BM-B

**Date of experiment:**

from: 23 June 10 to: 29 June 10

**Date of report:**

30 Aug 10

**Shifts:**

18

**Local contact(s):**

Denis Testemale

*Received at ESRF:*

**First paper published:** Brugger, J., Etschmann, B., Grundler, P., Liu, W., Testemale, D. and Pring, A. 2012. XAS evidence for the stability of polytellurides in hydrothermal fluids up to 599 °C, 800 bar. *American Mineralogist*, 97, 1519-1522.

Second paper submitted 31 May 2012: Grundler, P., Brugger, J., Etschmann, B., Helm, L., Liu, W., Spry, Paul G., Tian, Y., Testemale, D. and Pring, A. Speciation of aqueous tellurium(IV) in hydrothermal solutions and vapors and the role of oxidized tellurium species in gold metallogenesis. *Geochimica et cosmochimica acta*.

**Report: Aim**

The aim of this experiment was to identify unambiguously and characterize structurally the Te species present in the H<sub>2</sub>O-Cl-f<sub>O2</sub> space. This is necessary as, in order to be able to model the processes occurring in hydrothermal systems (T 150-600 °C; P ambient to 5 kbar), a thorough knowledge of the nature and thermodynamics of the aqueous species of Te under various P-T conditions is required.

**Experimental**

Data were collected at the Te K-edge (31.814 keV) at the BM-30B (FAME) beam line, using the high T-P cell developed by the CNRS. The energy was calibrated with metallic Te, such that the maximum of the first derivative was at 31.814 keV. At this energy the harmonic rejection mirrors could not be used. The harmonic content of the beam was estimated to be ~ 5%, by measuring I<sub>0</sub> and I<sub>1</sub> for Ag foils with different thicknesses.

Sample	Conditions	Sample	Conditions
Te metal	pellet 20 C, 1 bar	Te(OH) <sub>6</sub>	pellet 20 C, 1 bar
TeO <sub>2</sub>	pellet 20 C, 1 bar	Na <sub>2</sub> Te	Sol 1 20 C, 1 bar
Na <sub>2</sub> TeO <sub>3</sub>	Sol 2 20 C, 1 bar	Na <sub>2</sub> Te <sub>x</sub>	Sol 3 20 C, 1 bar
TeO <sub>2</sub> in sulphate buffer, pH ~ 1.56	Sol 4 30-530 C, 800 bar		
TeO <sub>2</sub> in phosphate buffer, pH ~ 6.72	Sol 5 30-530 C, 800 bar	TeO <sub>2</sub> in phosphate buffer, pH ~ 2.01	Sol 6 100-530 C, 800 bar
TeO <sub>2</sub> in 5 m NaCl + 0.1 m HCl	Sol 7 30-430 C, 800 bar	Calaverite (AuTe <sub>2</sub> ) in aq. 1% hydrazine	Sol 8 330 C, 800 bar
TeO <sub>2</sub> in 5 m NaCl + 1 m HCl	Sol 9 30-275 C, 800 bar	TeO <sub>2</sub> in 5 m NaCl + 1 m HCl	Sol 10 330 C, 800 bar
TeO <sub>2</sub> in 12 m LiCl + 1 m HCl	Sol 11 30-275 C, 800 bar	Solution of Te(OH) <sub>6</sub>	Sol 12 30-430 C, 800 bar
Solution of Na <sub>2</sub> Te <sub>x</sub> (~24 mmol)	Sol 13 100-630 C, 800 bar	(NH <sub>4</sub> ) <sub>2</sub> TeS <sub>3</sub> in H <sub>2</sub> O	Sol 14 20 C, 1 bar
Solution of Na <sub>2</sub> Te <sub>x</sub> (~ 50 mmol)	Sol 15 100-330 C, 800 bar	Na <sub>2</sub> Te in 4 m NaCl + borate buffer	Sol 16 525 C, 800-500 bar

**General observations**

Between 250-500 °C, the synchrotron beam reduced all oxidised Te species.

**Sol4,5,6:** Solubility decreases with increasing temperature, as the pKa of the buffer increases and the solubility is controlled by the pH.

**Sol 7:** Te appears to be bonded to 4 O atoms at room temperature; and coordinated to 2 O atoms at 430 °C. (100 and 220 °C spectra are similar to room temperature spectrum in E-space; peak height decreases with temperature in R-space.)

**Sol 9:** Precipitation of Te occurred at and above 275 °C. From 30 to 220 °C, Te appears to be bonded to a total of four atoms; changing from ~3 O + 1 Cl atoms at room temperature, ~2 O + 2 Cl atoms at 150 °C and ~1 O + 3 Cl atoms at 220 °C. This is reflected in the E-space spectra which change very little with temperature (ie no major change in geometry), and in the R-space spectra where the O peak decreases and the Cl peak increases with temperature.

**Sol 11:** Te is bonded to Cl – the coordination number changing from 4.5 Cl atoms at room temperature to 3.7 Cl atoms at 220 °C. Precipitation occurred at and above 275 °C.

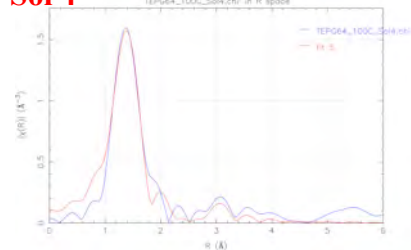
**Sol 12:** The oxidation state of Te changed from Te(VI) to Te(IV) between 220 and 380 °C. Coordination changes from ~4.5 O atoms (30 to 220 °C) to ~1.5 (380-430 °C).

**Sol 13:** Existence of poly-tellurides; spectra change with temperature. Coordination of Te appears to change from 2 Te (220 °C) to ~1 Te (630 °C).

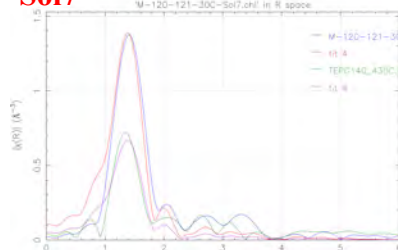
**Preliminary Fits:** [ $k^2$  weighting, Hanning window,  $2 \leq k \leq 10$  (Sol 13:  $2 \leq k \leq 8$ )]

Solution	T (°C)	ligand	n	R	$\sigma^2$	$E_0$	$\chi^2_{red}$
Sol4	100 °C	O	4.3(5)	1.90(1)	0.004(2)	9(1)	10
		Te	1	3.23(5)	0.005(6)		
Sol7	30 °C	O	4.0(7)	1.91(1)	0.004(3)	9(2)	60
	430 °C	O	1.9(4)	1.90(1)*	0.004(3)		
Sol9	30 °C, 1 bar	O	2.4(3)	1.906(5)**	0.0021(9)**	10(7)	59
		Cl	1 (fix)	2.50(1)	0.011(2)		
	30 °C	O	2.6(2)	1.906(5)	0.0021(9)		
		Cl	1 (fix)	2.50(1)	0.011(2)		
	150 °C	O	1.9(2)	1.906(5)	0.0021(9)		
		Cl	2.2(4)	2.50(1)	0.011(2)		
	220 °C	O	1.3(2)	1.906(5)	0.0021(9)		
		Cl	2.8(6)	2.50(1)	0.011(2)		
Sol11	30 °C	Cl	4.5(5)	2.509(8)***	0.009(1)	10.9(8)	68
	110 °C	Cl	4.2(5)	2.509(8)	0.009(1)		
	220 °C	Cl	3.7(5)	2.509(8)	0.012(2)		
Sol12	30 °C	O	4.7(4)	1.914(5)	0.0023(7)	7.1(7)	105
	110 °C	O	4.7(3)	1.914(5)	0.0023(7)		
	220 °C	O	4.5(4)	1.914(5)	0.0023(7)		
	380 °C	O	1.6(2)	1.881(5)*	0.0023(7)		
	430 °C	O	1.4(3)	1.881(5)*	0.0023(7)		
Sol13 (a)	630 °C	Te	1.2(4)	2.65(3)	0.011(6)	9(1)	6
Sol13 (b)	220 °C	O	0.13(5)	1.83(4)	0.003 (fix)	7(1)	21
		Te	0.5 (fix)	2.42(8)	0.018(8)		
		Te	1.8(9)	2.77(4)	0.02(1)		

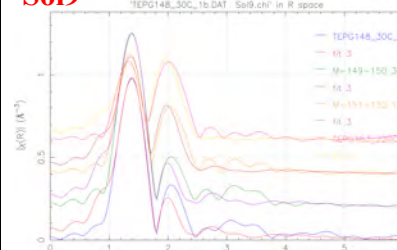
**Sol 4**



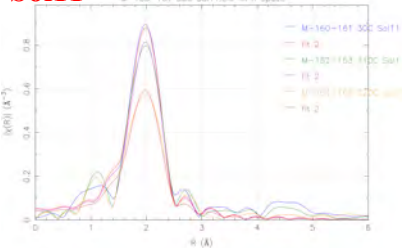
**Sol7**



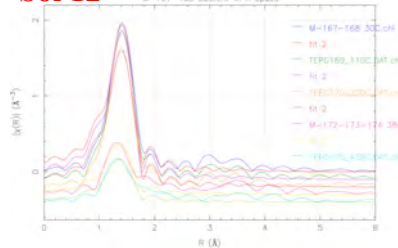
**Sol9**



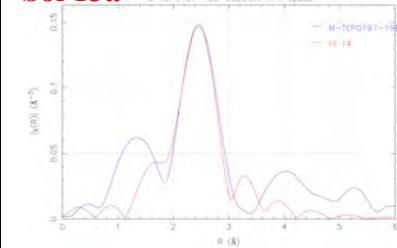
**Sol11**



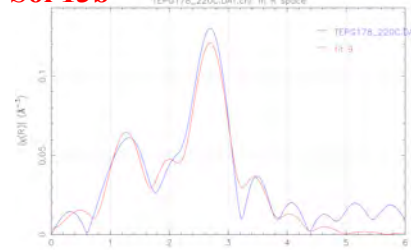
**Sol 12**



**Sol 13a**



**Sol 13b**



\*distance was  $r \cdot \alpha$  ( $\alpha$ =expansion coefficient, error on  $\alpha$  not included in error here)

\*\* used same bond length and Debye-Waller for O and Cl at all temperatures. Not much difference/improvement if allow bond lengths to expand.

\*\*\* used same bond length for Cl at all temperatures.