Supplementary Material for:

Arsenic condensation and reaction mechanisms in Flash Smelting off-gas line conditions

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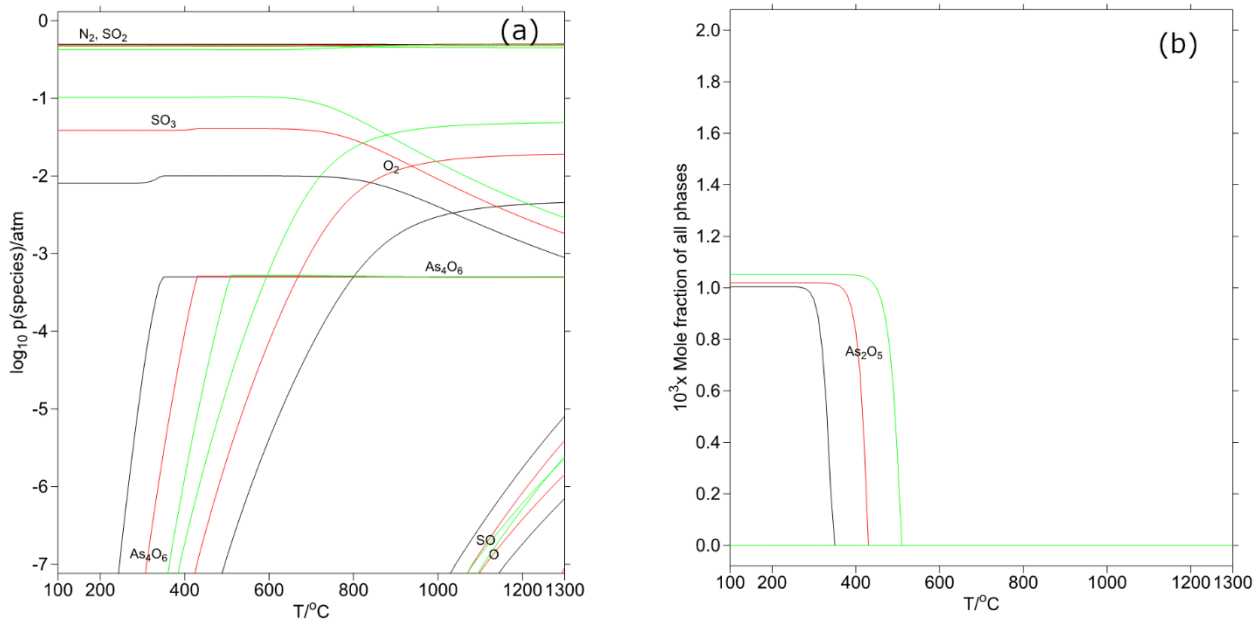


Figure S-1. The calculated equilibrium gas speciation (a) and amount of condensed phase (b) in the As-O-S-N_2 system in temperature range of 1300 to 100 °C with 0.5, 2 and 5 vol% O_2, and 50 vol% SO_2; the molar ratio of gas to As_2O_3 in the initial mixture was 1000 and amount of gas 10 mol. The thermodynamic data were retrieved from MTOX database [1] and the calculations were carried out in the MTDATA environment[2] (0.5 vol% O_2 —, 2.0 vol% O_2 — and 5 vol% O_2 —).

Table S-I. The compositions of the arsenic dust samples at different oxygen partial pressure and temperature.

No.	Temperature	Atmosphere	Phases	Phase composition(wt%)			
			Arsenic compounds	O	S	As	Ag
Standard			As	0.0	0.0	100	0.0
			As_2O_3	24.3	0.0	75.7	0.0
			As_2O_5	34.8	0.0	65.2	0.0
			AsS	0.0	29.9	70.1	0.0
			As_2S_3	0.0	39.1	60.9	0.0
50% SO_2 -49.5% N_2-0.5% O_2							
As-1	38~107 °C	50% SO_2 -49.5% N_2-0.5% O_2	Arsenic oxide	24.8 ± 1.2	0.1 ± 0.2	73.3 ± 0.8	1.8 ± 0.1
			Arsenic	0.2 ± 0.3	0.2 ± 0.2	96.1 ± 1.5	3.4 ± 0.1
As-2	107~133 °C	50% SO_2 -49.5% N_2-0.5% O_2	Arsenic oxide	24.7 ± 0.9	0.2 ± 0.2	73.4 ± 0.9	1.7 ± 0.1
			Arsenic	0.3 ± 0.2	0.1 ± 0.0	96.1 ± 1.0	3.4 ± 0.1
			Arsenic sulphide	0.3 ± 0.1	14.3 ± 1.8	82.7 ± 0.9	2.7 ± 0.1
			Arsenic sulphide	0.3 ± 0.1	18.7 ± 5.3	77.6 ± 5.0	2.5 ± 0.3
As-3	133~158 °C	50% SO_2 -49.5% N_2-0.5% O_2	Arsenic oxide	24.1 ± 0.9	0.0 ± 0.9	74.0 ± 1.5	1.8 ± 0.1
			Arsenic	0.5 ± 0.2	0.1 ± 0.1	96.0 ± 1.9	3.4 ± 0.1
			Arsenic sulphide	0.0 ± 0.9	12.1 ± 0.3	85.0 ± 2.7	2.9 ± 0.2
As-4	158~187 °C	50% SO_2 -49.5% N_2-0.5% O_2	Arsenic oxide	24.5 ± 0.2	0.0 ± 0.0	73.8 ± 0.2	1.8 ± 0.1
			Arsenic	0.4 ± 0.3	0.4 ± 0.1	95.8 ± 1.3	3.4 ± 0.1
			Arsenic sulphide	0.6 ± 0.4	12.0 ± 0.3	84.7 ± 3.8	2.7 ± 0.4
As-5	187~222 °C	50% SO_2 -49.5% N_2-0.5% O_2	Arsenic oxide	23.3 ± 0.7	0.0 ± 0.0	74.8 ± 0.1	1.8 ± 0.0
			Arsenic	0.6 ± 0.0	0.9 ± 0.4	95.1 ± 1.1	3.3 ± 0.1
			Arsenic sulphide	0.0 ± 0.0	11.2 ± 2.3	85.9 ± 4.2	2.9 ± 0.3
As-6	222~239 °C	50% SO_2 -49.5% N_2-0.5% O_2	Arsenic oxide	24.3 ± 0.8	0.0 ± 0.0	73.9 ± 1.0	1.8 ± 0.0
			Arsenic	0.2 ± 0.4	0.4 ± 0.3	95.9 ± 0.6	3.5 ± 0.5
			Arsenic sulphide	0.1 ± 0.2	15.0 ± 5.3	82.2 ± 6.7	2.8 ± 0.4
As-7	239~286 °C	50% SO_2 -49.5% N_2-0.5% O_2	Arsenic	0.3 ± 0.0	0.0 ± 0.0	96.3 ± 0.8	3.4 ± 0.1
50% SO_2 -48% N_2-2 % O_2							
As-8	31~38 °C	50% SO_2 -49.5% N_2-2 % O_2	Arsenic oxide	23.8 ± 1.5	0.0 ± 0.0	74.3 ± 2.5	1.8 ± 0.1
			Arsenic sulphide	0.1 ± 0.2	27.2 ± 5.2	70.7 ± 5.0	1.9 ± 0.5
As-9	38~60 °C	50% SO_2 -49.5% N_2-2 % O_2	Arsenic oxide	24.4 ± 0.7	0.1 ± 0.0	73.8 ± 1.6	1.8 ± 0.1
			Arsenic	0.0 ± 0.0	0.3 ± 0.0	96.3 ± 4.3	3.4 ± 0.3

			Arsenic sulphide	1.9 ± 0.2	26.2 ± 3.4	70.0 ± 5.2	1.9 ± 0.2
As-10	60~87 °C	50% SO_2 -49.5% N_2-2 % O_2	Arsenic oxide	23.7 ± 2.3	0.4 ± 0.8	74.0 ± 2.2	1.8 ± 0.1
			Arsenic	0.6 ± 0.3	0.5 ± 0.1	95.6 ± 3.8	3.3 ± 0.3
			Arsenic sulphide	11.8 ± 0.4	14.1 ± 0.9	68.1 ± 0.8	1.0 ± 0.0
As-11	87~107 °C	50% SO_2 -49.5% N_2-2 % O_2	Arsenic oxide	23.6 ± 0.7	0.0 ± 0.4	74.5 ± 0.6	1.8 ± 0.1
			Arsenic	0.3 ± 0.4	0.2 ± 0.2	96.2 ± 4.0	3.4 ± 0.2
			Arsenic sulphide	0.4 ± 0.4	28.8 ± 3.9	68.9 ± 4.4	1.9 ± 0.5
As-12	107~133 °C	50% SO_2 -49.5% N_2-2 % O_2	Arsenic oxide	23.1 ± 0.8	0.0 ± 0.0	75.1 ± 0.6	1.8 ± 0.1
			Arsenic	0.7 ± 0.1	0.1 ± 0.1	95.9 ± 1.9	3.3 ± 0.1
As-13	133~158 °C	50% SO_2 -49.5% N_2-2 % O_2	Arsenic oxide	24.2 ± 0.7	0.1 ± 0.1	73.9 ± 0.8	1.8 ± 0.1
			Arsenic	0.8 ± 0.3	0.2 ± 0.1	95.6 ± 1.4	3.4 ± 0.1
			Arsenic sulphide	1.5 ± 0.2	28.5 ± 3.3	67.9 ± 4.9	2.1 ± 0.3
As-14	158~187 °C	50% SO_2 -49.5% N_2-2 % O_2	Arsenic oxide	24.4 ± 1.7	0.3 ± 0.2	73.6 ± 3.5	1.7 ± 0.2
			Arsenic	0.4 ± 0.1	0.4 ± 0.3	95.9 ± 2.9	3.3 ± 0.2
			Arsenic sulphide	0.0 ± 0.0	7.4 ± 0.1	89.9 ± 4.9	2.7 ± 0.4
As-15	187~222 °C	50% SO_2 -49.5% N_2-2 % O_2	Arsenic sulphide	1.9 ± 1.3	37.7 ± 3.2	58.3 ± 3.8	1.7 ± 0.2
50% SO_2 - 45% N_2-5 % O_2							
As-16	38~ 60 °C	50% SO_2 - 49.5% N_2-5 % O_2	Arsenic oxide	23.8 ± 1.7	0.0 ± 0.0	73.5 ± 3.5	1.8 ± 0.2
			Arsenic	0.1 ± 0.3	0.6 ± 0.3	95.9 ± 1.7	3.4 ± 0.1
			Arsenic sulphide	0.0 ± 0.0	4.7 ± 0.0	92.1 ± 2.8	3.1 ± 0.2
As-17	60~87 °C	50% SO_2 - 49.5% N_2-5 % O_2	Arsenic oxide	24.7 ± 1.6	0.1 ± 0.0	72.8 ±1.4	1.7 ± 0.1
			Arsenic	0.4 ± 0.1	0.8 ± 0.4	95.5 ± 3.8	3.2 ± 0.3
As-18	87~107 °C	50% SO_2 - 49.5% N_2-5 % O_2	Arsenic oxide	25.1 ± 1.0	0.1 ± 0.0	72.2 ± 1.0	1.8 ± 0.1
			Arsenic	0.1 ± 0.3	0.7 ± 0.1	95.6 ± 1.4	3.5 ± 0.1
As-19	107~133 °C	50% SO_2 - 49.5% N_2-5 % O_2	Arsenic oxide	24.1 ± 1.0	0.1 ± 0.0	73.3 ± 1.2	1.8 ± 0.1
			Arsenic	0.6 ± 0.1	0.3 ± 0.1	95.7 ± 2.5	3.4 ± 0.2
As-20	133~158 °C	50% SO_2 - 49.5% N_2-5 % O_2	Arsenic oxide	24.0 ± 1.3	0.1 ± 0.0	73.5 ± 1.4	1.8 ± 0.1
			Arsenic	0.7 ± 0.1	0.6 ± 0.2	95.3 ± 0.9	3.4 ± 0.1
			Arsenic sulphide	0.0 ± 0.1	7.7 ± 0.4	89.1 ± 1.7	3.2 ± 0.1
As-21	158~187 °C	50% SO_2 - 49.5% N_2-5 % O_2	Arsenic oxide	22.6 ± 1.1	0.3 ± 0.1	74.5 ± 0.1	1.9 ± 0.1
			Arsenic	0.8 ± 0.1	0.3 ± 0.1	95.6 ± 1.5	3.4 ± 0.1
			Arsenic sulphide	0.2 ± 0.4	6.7 ± 0.2	89.9 ± 1.4	3.2 ± 0.2
As-22	187~222 °C	50% SO_2 - 49.5% N_2-5 % O_2	Arsenic oxide	23.7 ± 0.1	0.0 ± 0.0	73.7 ± 0.3	1.8 ± 0.1
			Arsenic	0.5 ± 0.1	0.6 ± 0.2	95.5 ± 3.5	3.4 ± 0.2

Table S-II. The average compositions of metal, oxide and sulphide phases in the deposits measured with EDS (non-normalised after matrix correction).

Compounds	Average phase composition (wt%)		
	O	S	As
Arsenic			
0.5 % vol O_2	0.4 ± 0.2	0.3 ± 0.3	95.9 ± 0.4
2.0% vol O_2	0.5 ± 0.3	0.3 ± 0.1	95.9 ± 0.3
5.0 % vol O_2	0.4 ± 0.2	0.0 ± 0.0	95.6 ± 0.2
Arsenic oxide			
0.5 % vol O_2	24.3 ± 0.5	0.1 ± 0.1	73.9 ± 0.5
2.0 % vol O_2	23.9 ± 0.5	0.1 ± 0.2	74.2 ± 0.5
5.0 % vol O_2	24.0 ± 0.8	0.8 ± 0.1	73.3 ± 0.7
Arsenic sulphide			
0.5 % vol O_2	0.4 ± 0.5	13.9 ± 2.8	83.0 ± 3.0
2.0 % vol O_2	1.0 ± 0.9	26.0 ± 10.0	70.9 ± 10.3
5.0 % vol O_2	0.1 ± 0.1	6.3 ± 1.5	90.4 ± 1.6

Table S-III. The average compositions of metal, oxide and sulphide phases in the deposits measured with EPMA (non-normalised after matrix correction).

Sample#	Wt%				
(phase)	O	S	As	Ag	Total
3(1)	25.9 ±0.3	0.01 ±0.01	74.2 ±0.5	0.00	100.2 ±0.6
3(2)	0.19 ±0.1	15.3 ±1.1	84.2 ±1.2	0.00	99.6 ±0.3
3(3)	0.17 ±0.02	0.14 ±0.03	99.1 ±0.5	0.00	99.4 ±0.5
7(1)	1.3 ±0.3	0.07 ±0.03	98.6 ±0.3	0.00	100.0 ±0.2
13(1)	25.5 ±0.7	0.0 ±0.0	74.2 ±0.9	0.00	99.7 ±0.8
13(2)	0.2 ±0.04	0.22 ±0.1	98.6 ±0.6	0.00	99.0 ±0.6
13(3)	0.7 ±0.2	37.5 ±0.1	61.4 ±0.7	0.01	99.7 ±0.6
15(1)	0.3 ±0.06	41.1 ±1.0	55.8 ±0.4	0.00	97.2 ±1.2
20(1)	25.1 ±0.4	0.0 ±0.0	74.9 ±0.3	0.00	100.0 ±0.2
20(2)	0.2 ±0.04	0.4 ±0.4	98.4 ±1.0	0.01	99.0 ±0.6
22(1)	0.2 ±0.02	0.5 ±0.1	96.6 ±1.0	0.00	97.4 ±0.7
22(2)	25.7 ±0.6	0.0 ±0.0	72.8 ±0.2	0.00	98.5 ±0.5

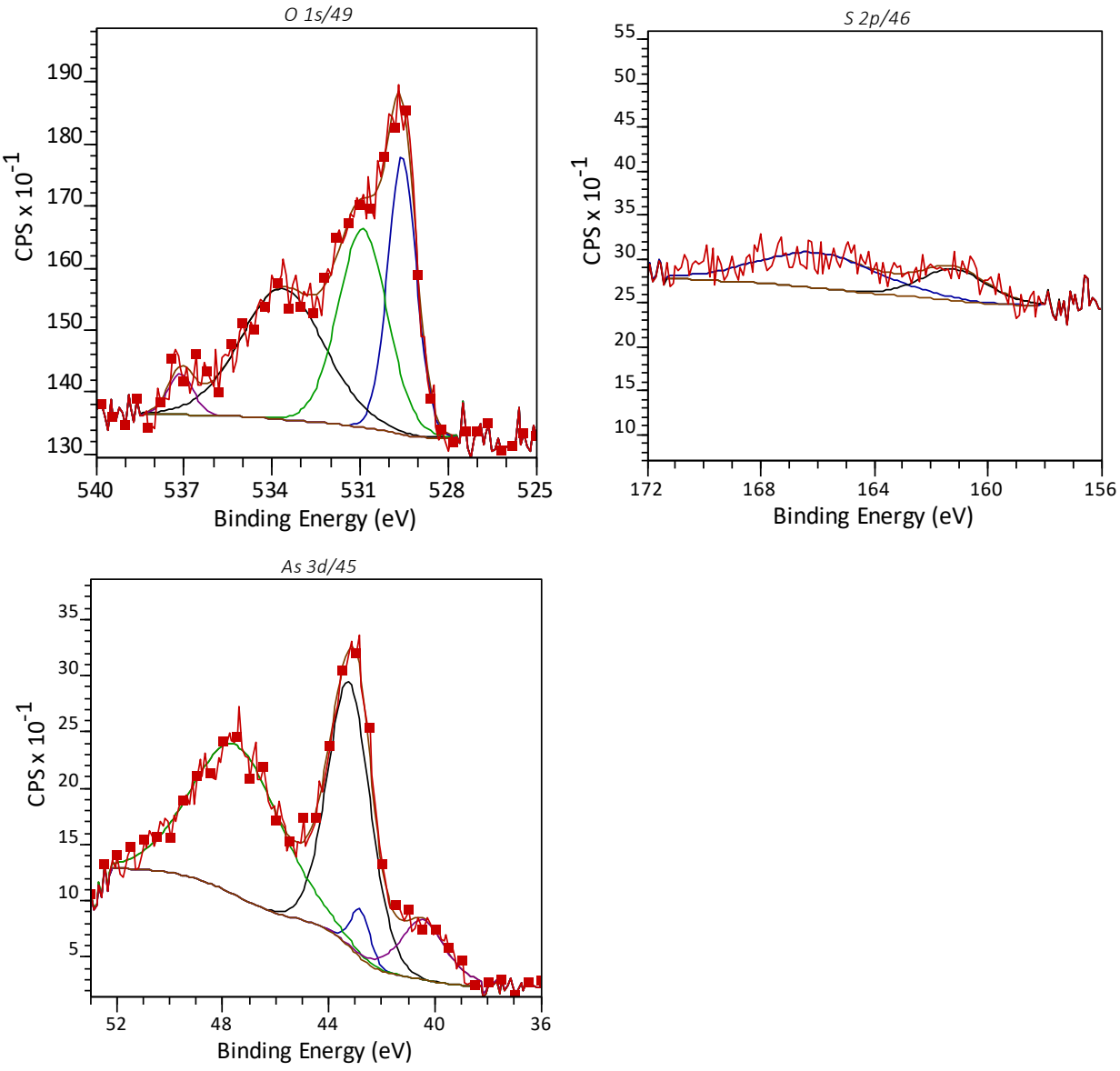
Table S-IV.

The XPS As 3d spectra recorded after 10 min electron radiation exposure, the analysed components, and their fitting data.

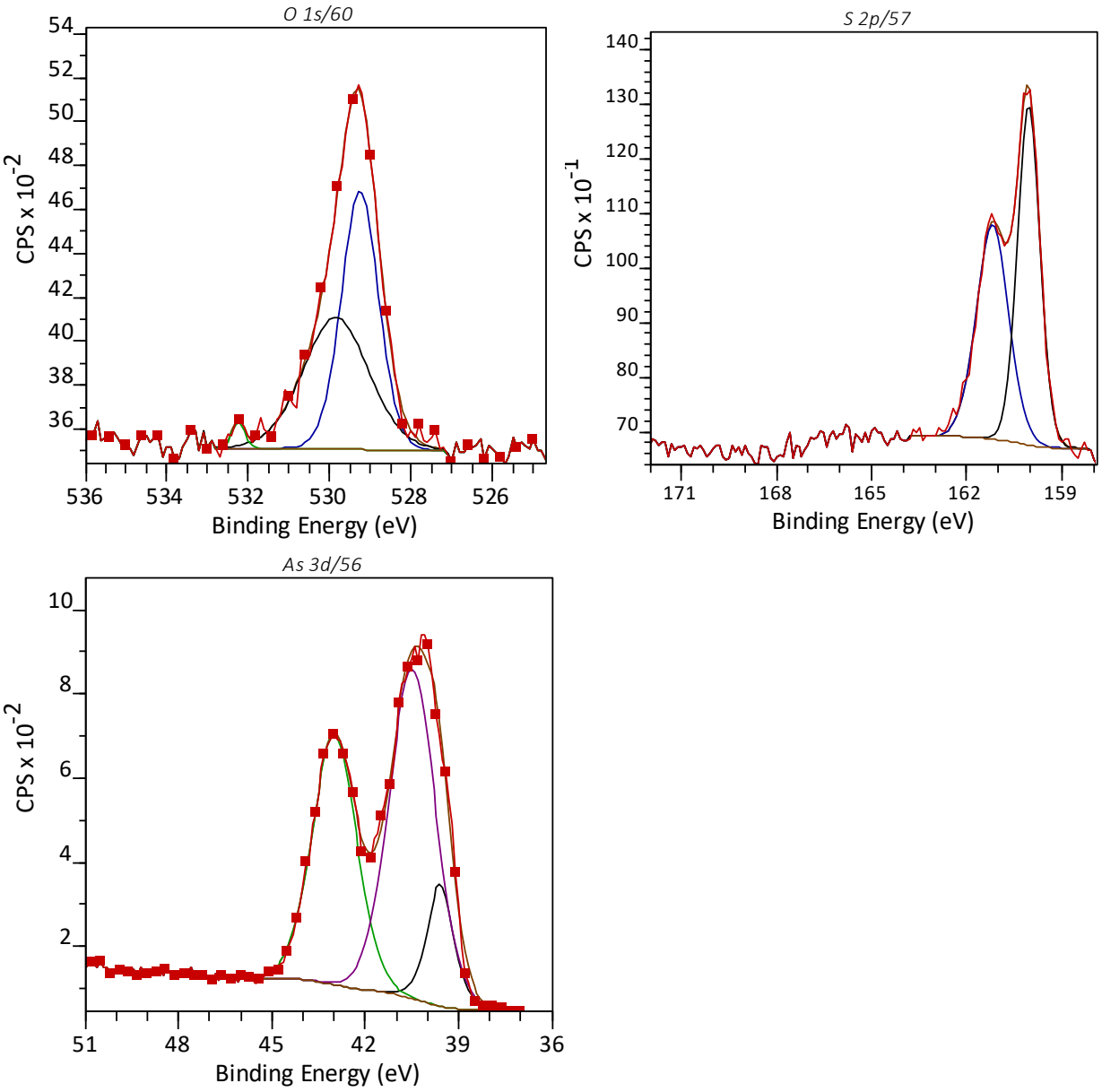
			BE/eV					
Sample #	Atmosphere	Temperature/°C	As°	As(S-II, III)	As(O-III)	As(O-V)	FWHM/eV	Residual STD
3	0.5 vol% O_2	133-158	40.45				1.99	0.97
				42.80			0.86	
					43.22		1.90	
						47.48	3.91	
4		158-187	39.58				0.98	1.85
				40.48			1.74	
					42.98		1.68	
5		187-222		42.40			1.30	1.02
					44.11		2.67	
6		222-239		42.39			1.41	0.96
					43.87		2.48	
7		239-352		42.07			0.56	0.91
				42.72			1.33	
					45.08		2.17	
ABC	2 vol% O_2	87-107		41.00			2.85	1.74
				42.50			0.82	
					43.10		1.31	
DEF		107-133		41.85			1.17	2.07
				42.65			0.78	
					45.42		2.03	
13		133-158	39.71				1.22	1.60
				42.79			1.59	
14		158-187		42.88			1.34	1.66
				41.65			0.45	
					45.26		1.56	
						46.84	1.94	
18	5 vol% O_2	87-107	39.86				1.47	3.22
				42.61			0.87	
					43.19		1.75	
20		133-158	39.81				1.31	1.79
				42.69			1.41	
					44.00		1.50	
22		187-222		42.28			1.23	1.17
					43.13		1.76	
						45.71	1.88	

Figures S-2.

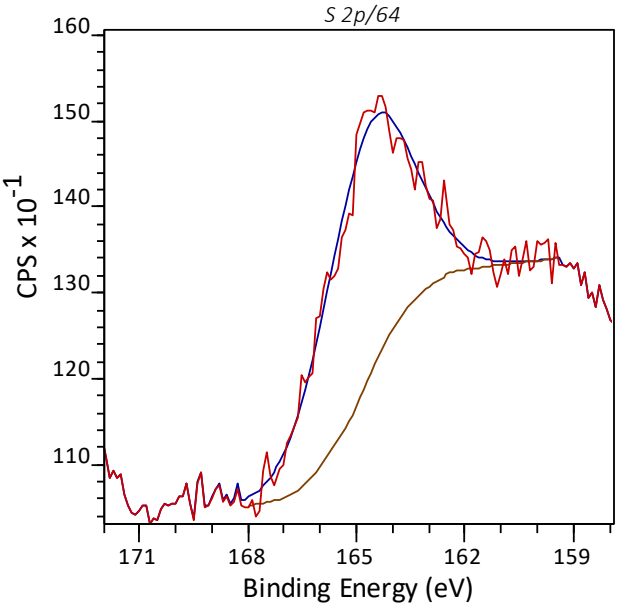
The obtained XPS spectra and their fitted components for the samples at different temperatures and in different atmospheres; the S 2p spectra have been reproduced without individual points for clarity.



(a) Sample #3 – 0.5 % O_2-50 % SO_2; t = 133-158 °C.



(b) Sample #4 – 0.5 % O_2-50 % SO_2; t = 158-187 °C.



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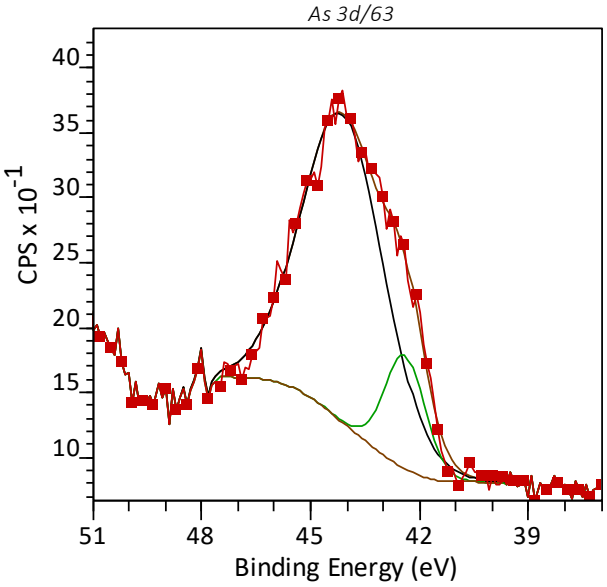
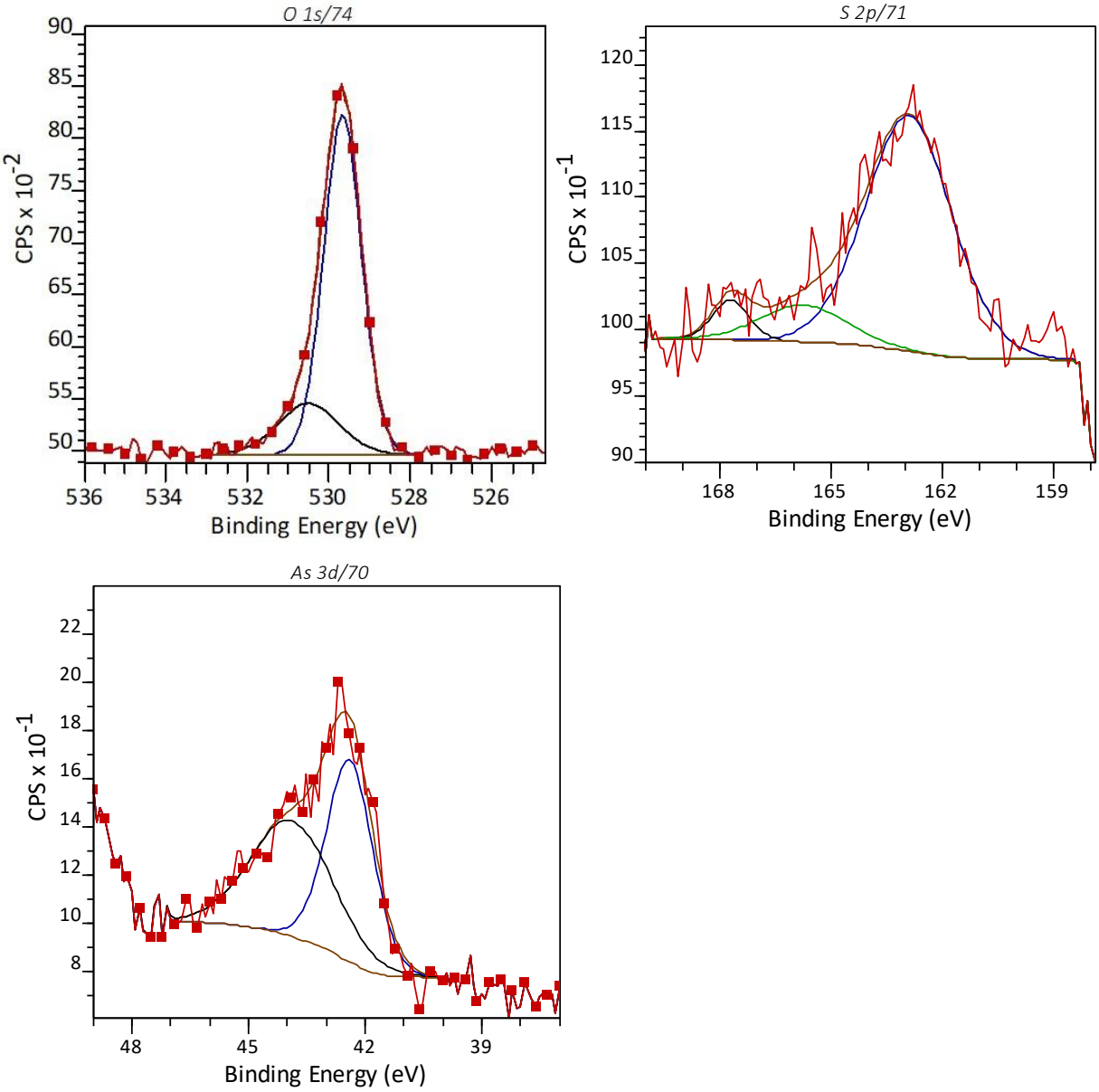
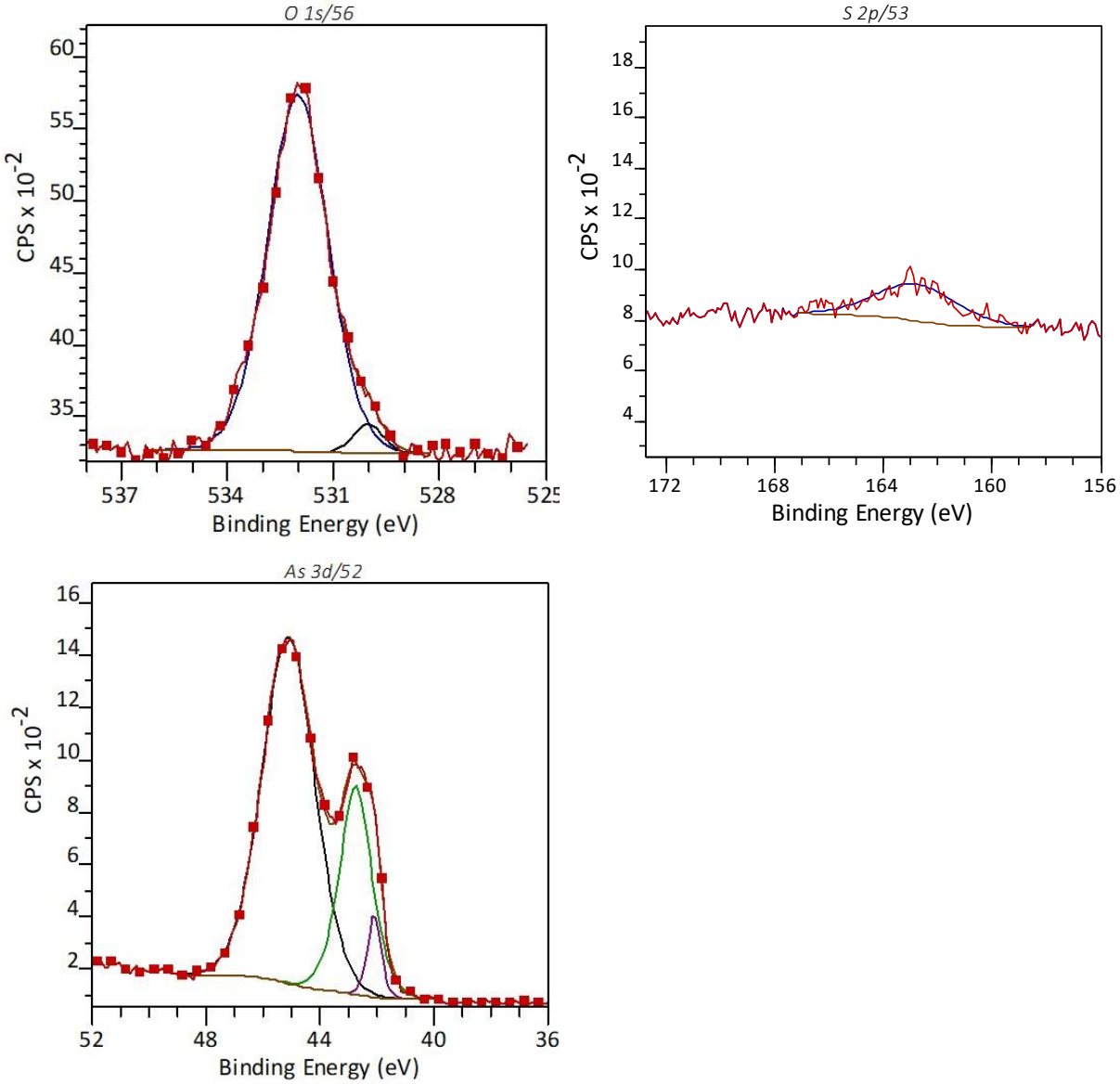


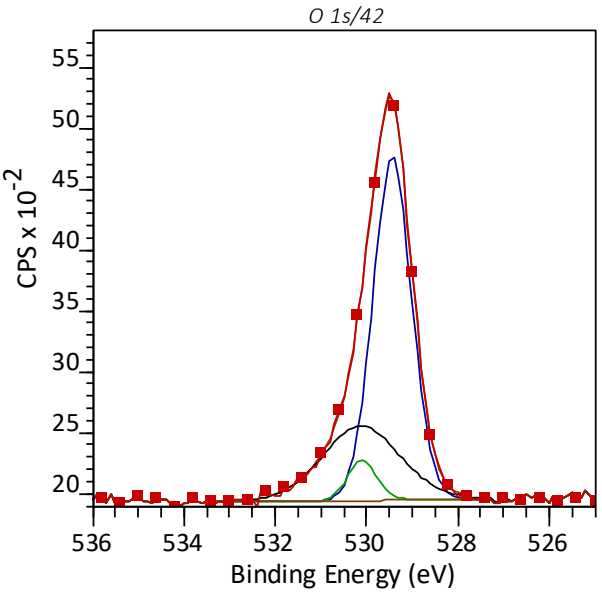
(c) Sample #5 – 0.5 % O_2-50 % SO_2; t = 187-222 °C.

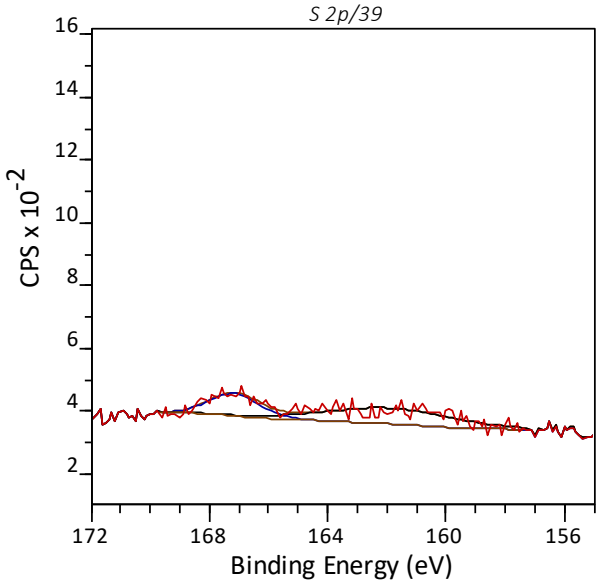


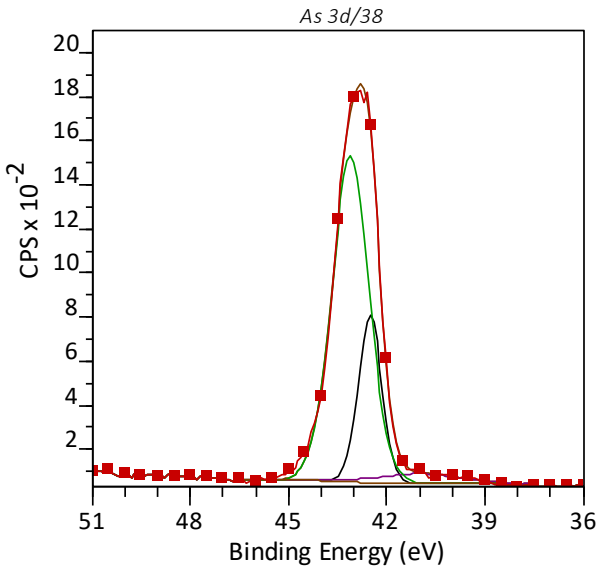
(d) Sample #6 – 0.5 % O_2-50 % SO_2; t = 222- 239 °C.



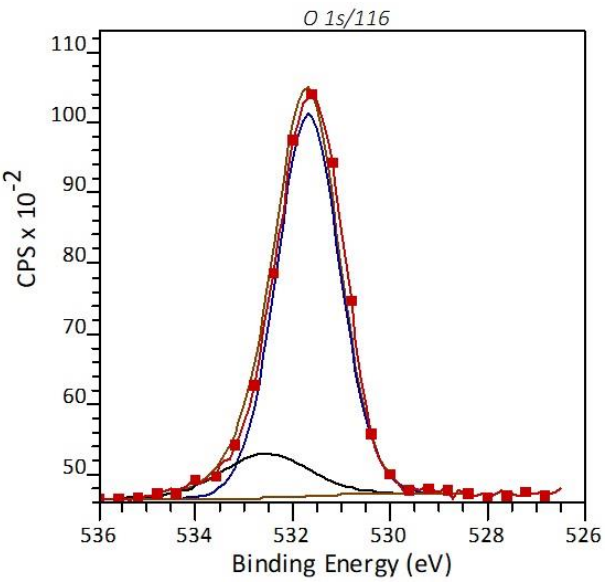
(e) Sample #7 – 0.5 % O_2-50 % SO_2; t = 239-286 °C.

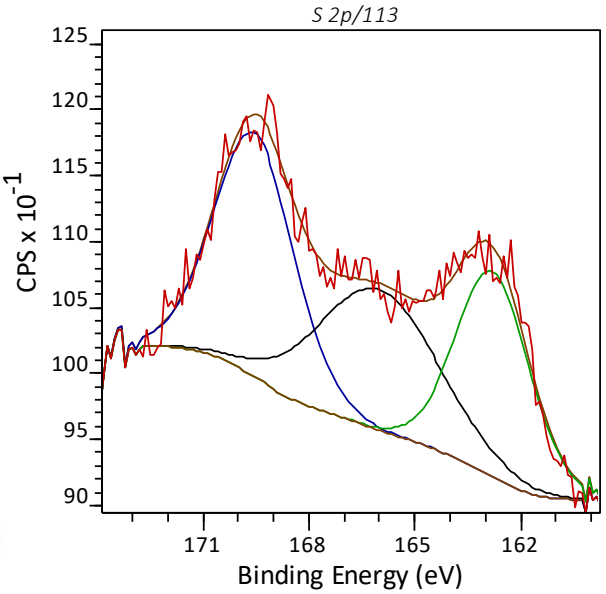


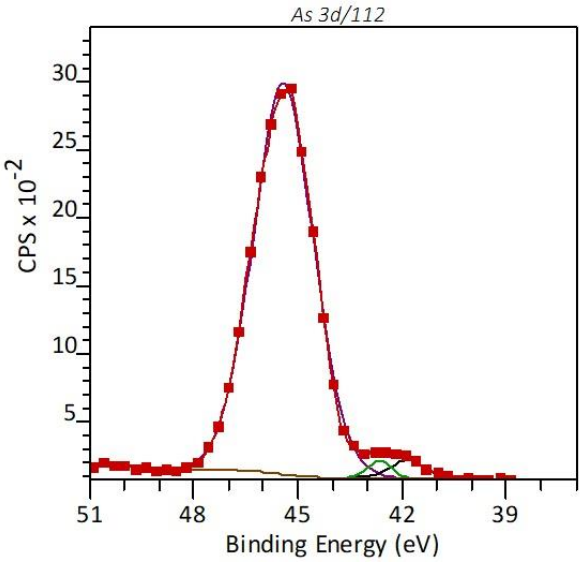




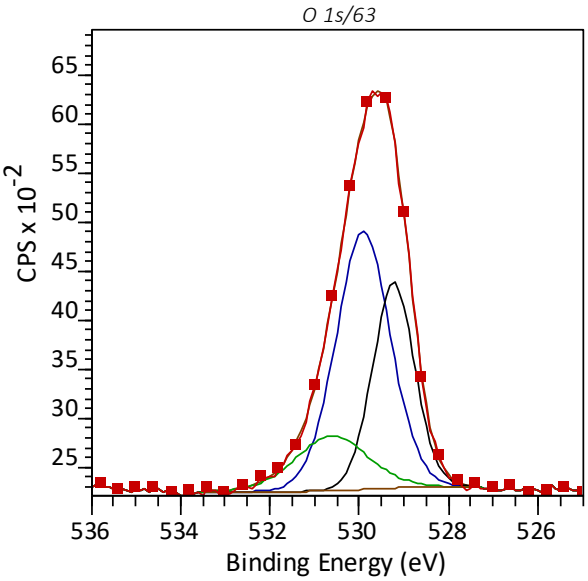
(f) Sample ABC – 2.0 % O_2-50 % SO_2; t = 87-107 °C.

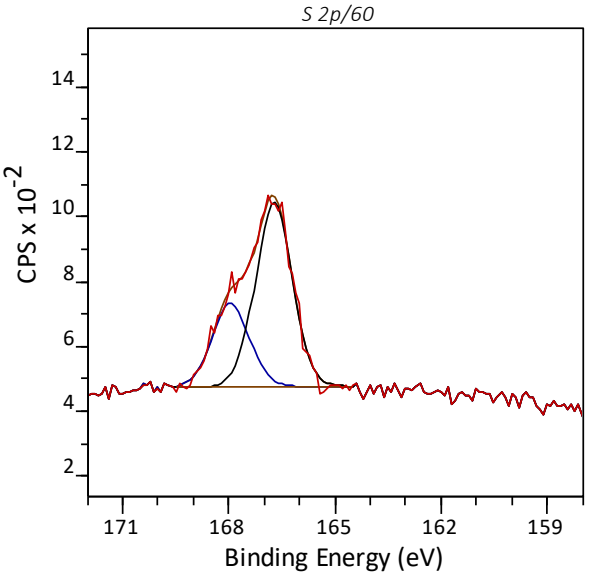


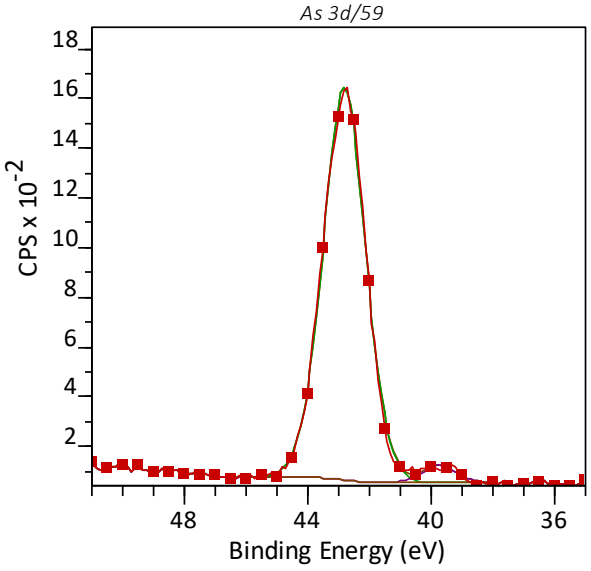




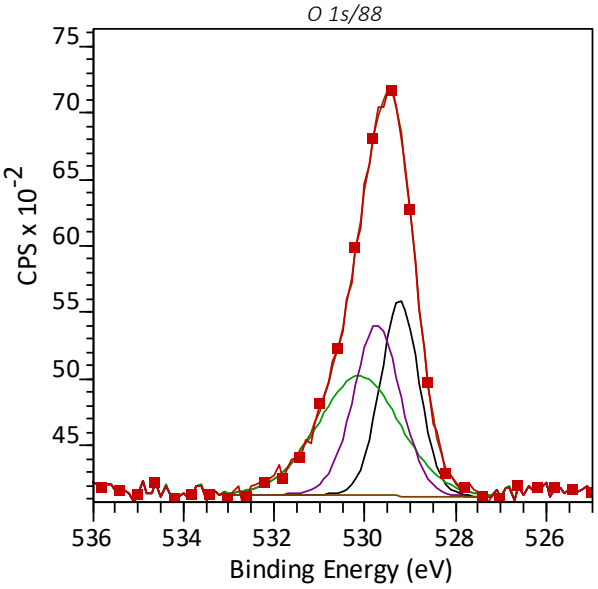
(g) Sample DEF – 2.0 % O_2-50 % SO_2; t = 107-133 °C.

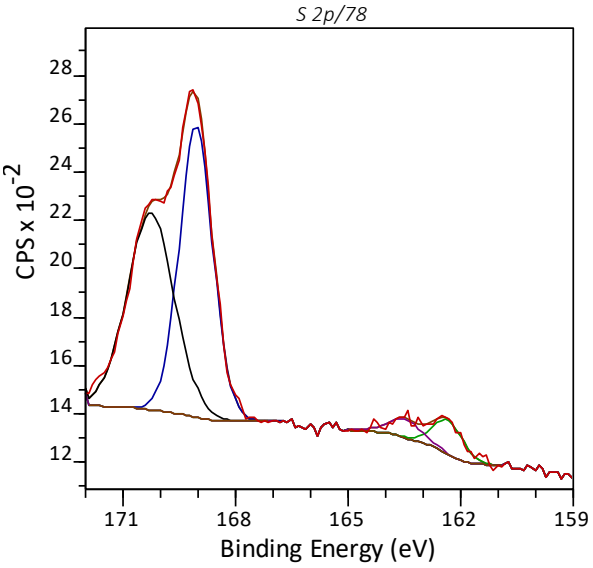


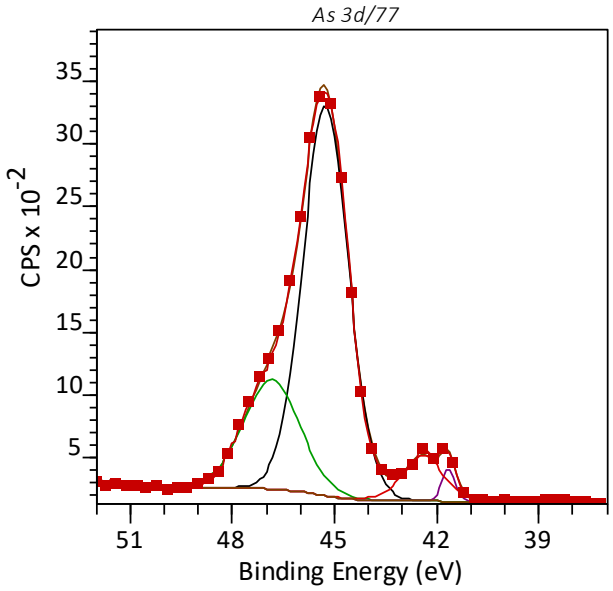




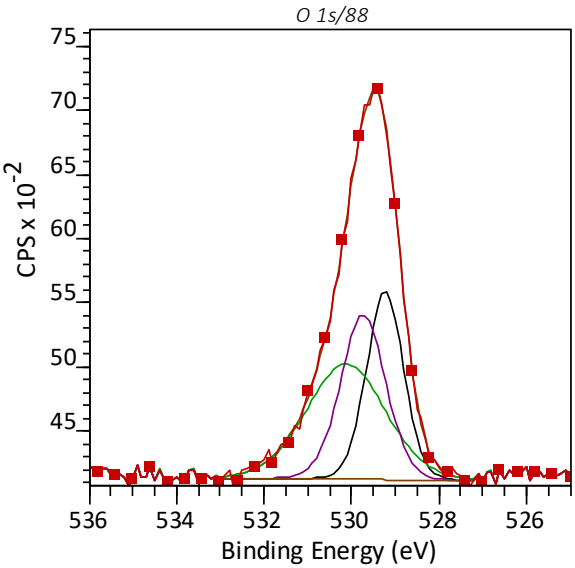
(h) Sample #13 – 2.0 % O_2-50 % SO_2; t = 133-158 °C.

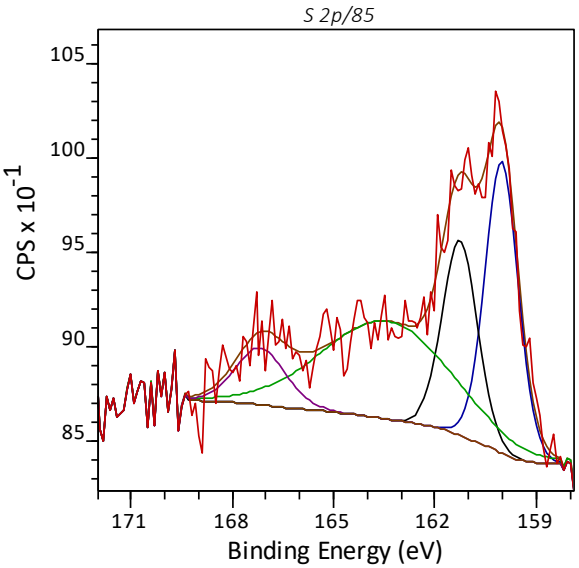


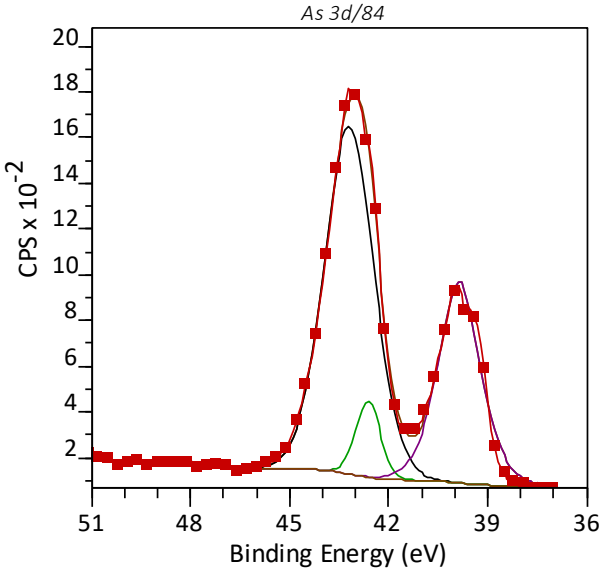




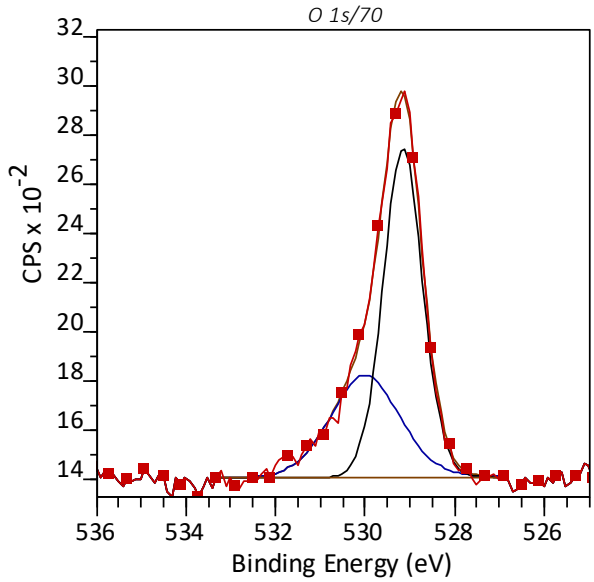
(i) Sample #14 – 2.0 % O_2-50 % SO_2; t = 158 -187 °C.

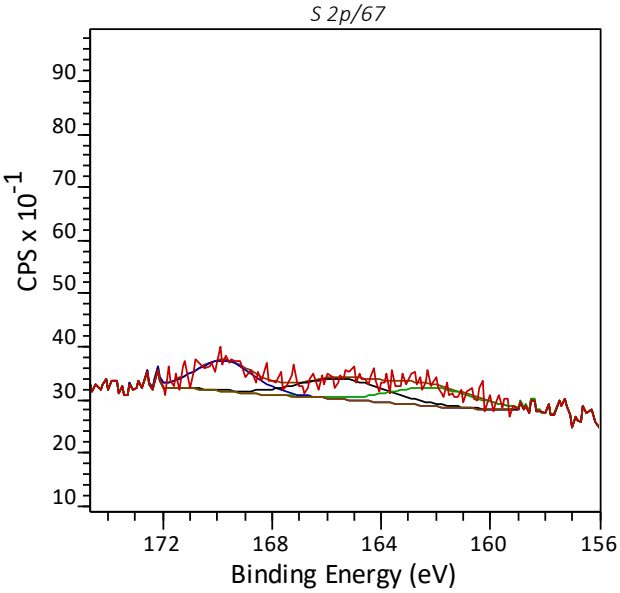


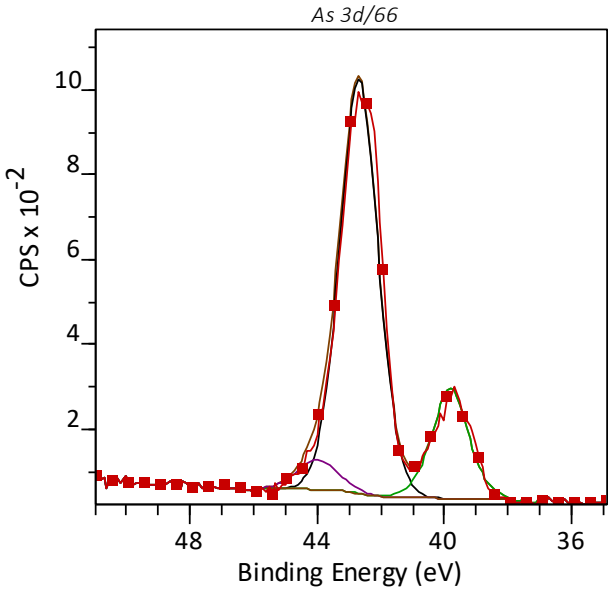




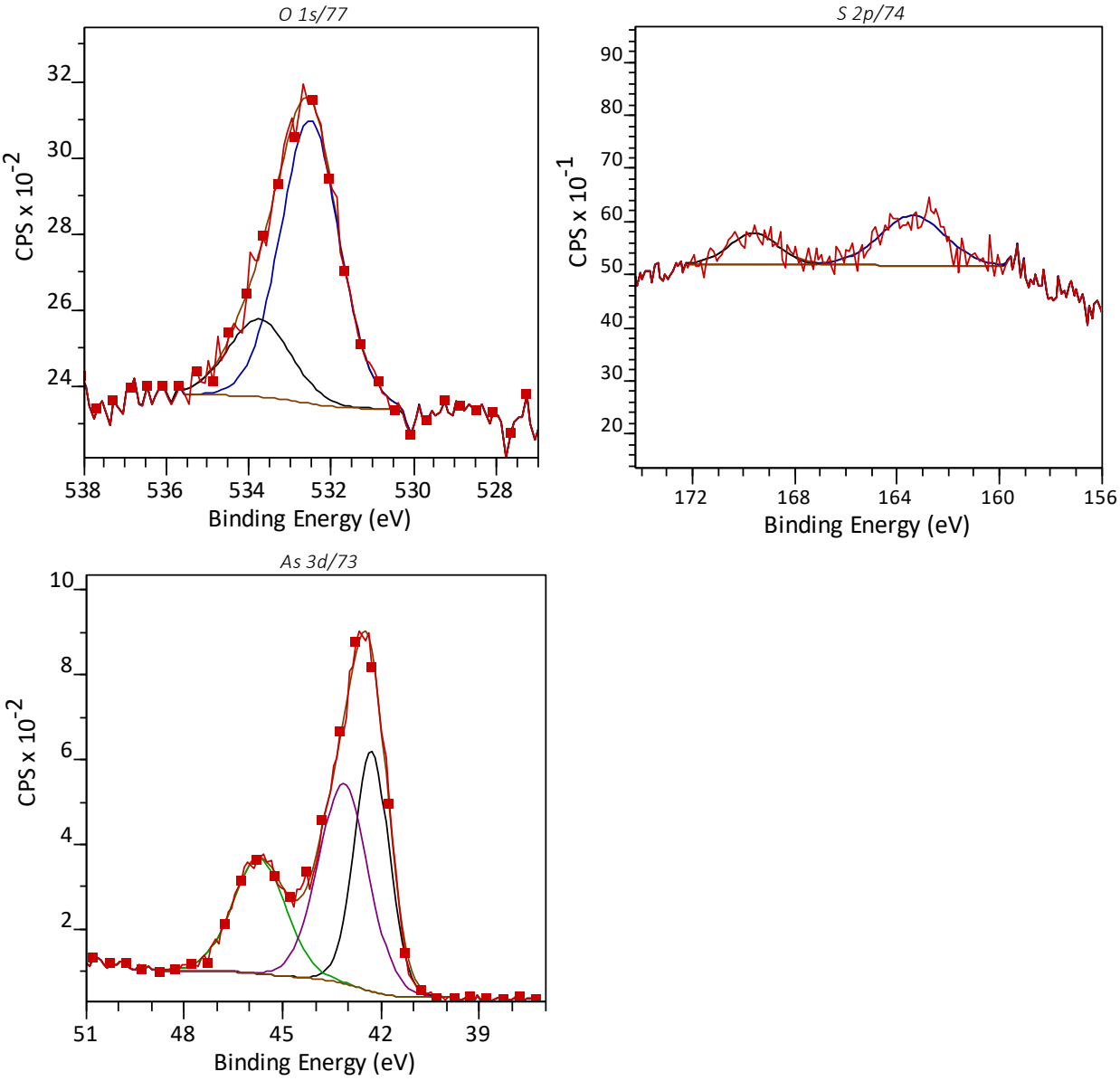
(j) Sample #18 – 5.0 % O_2-50 % SO_2; t = 87-107 °C.







(k) Sample #20 – 5.0 % O_2-50 % SO_2; t = 133-158 °C.



(l) Sample #22 – 5.0 % O_2-50 % SO_2; t = 187-222 °C.

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1. Gisby J., Taskinen P., Pihlasalo J., Li Z., Tyrer M., Pearce J., Avarmaa K., Björklund P., Davies H., Korpi M., Martin S., Pesonen L., Robinson J.: *Metall. Mater. Trans. B,* 2017, vol. 48B (1), 91-98.

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