Appendix: Supplementary Materials for

The transport of bismuth in HCl-bearing aqueous vapour and low-density aqueous supercritical fluids: Implications for natural systems

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Included files: Figs. S1-S3 and Tables S1-S5.

Fig. S1. The Raman spectrum of BiOCl(s) after an experiment at 400 °C.

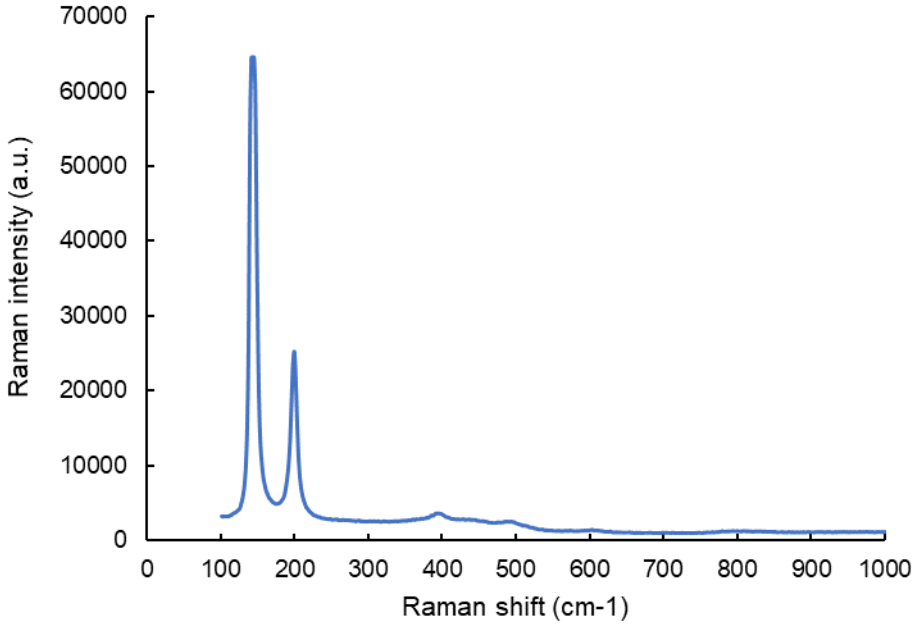

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Fig. S2. An X-ray diffractogram of BiOCl(s) after an experiment at 400 °C.

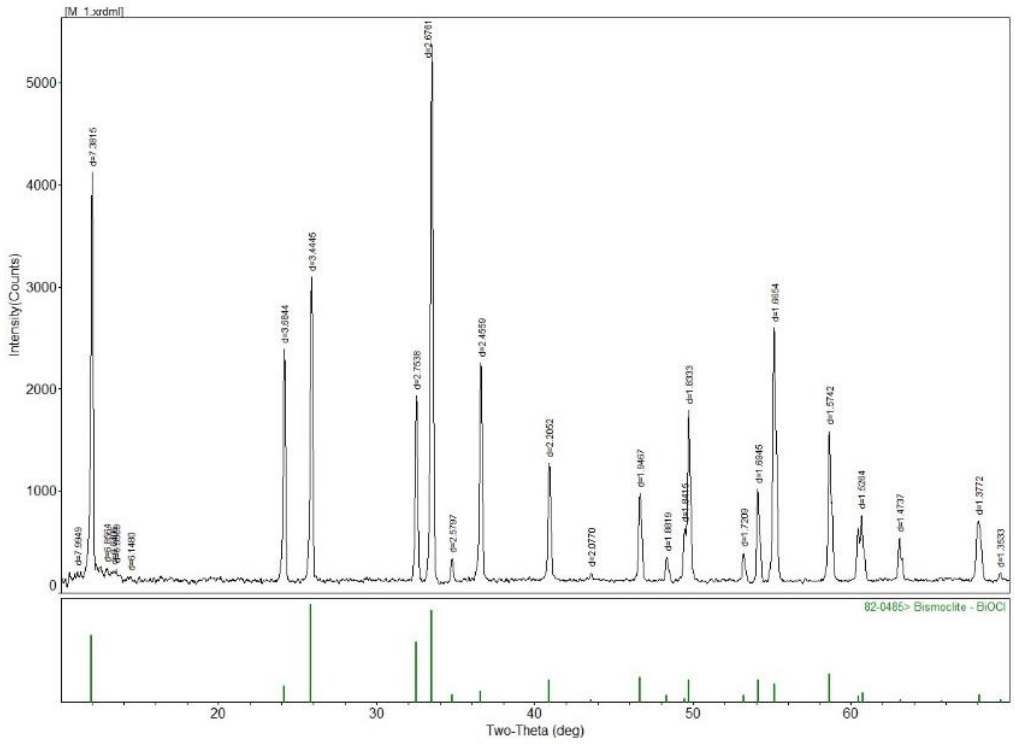

Fig. S3. The results of DSC-TG (Differential Scanning Calorimeter and Thermal Gravitational) analyses of the reactant, BiOCl(s), after an experiment at 400 °C. The blue and green lines represent the typical measured residual mass fraction (left Y-axis, %) and heat flow (right Y-axis, mW) as a function of temperature (°C), respectively. The abrupt decrease in the mass fraction and corresponding change in the heat flow at 600 ºC record the decomposition of BiOCl.

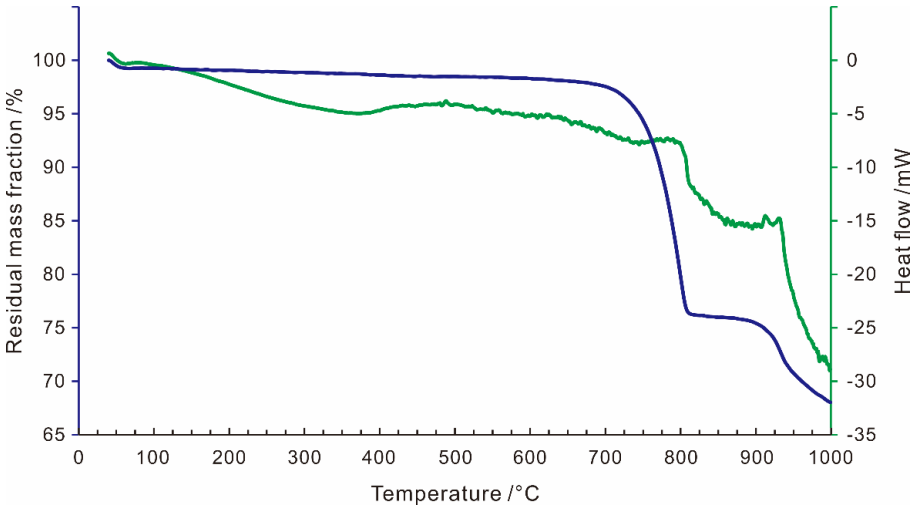

Table S1. The compositions of the experimental solutions of the kinetic experiments at 250 °C, which are illustrated in Figure 2.

Time, days	Density, g/cm^3	H_2O, g	HCl, mol	*n*(Bi), mol	*P*(H2O), bar	*X*(HCl)	Bi, ppm	*X*(Bi)	*φ*(H2O)	*φ*(HCl)	log *f*(H_2O)	log *f*(HCl)	log *P*(Bi)
0.5	0.0153	0.740	0.000172	5.95E-08	33	0.00417	16.78	1.44E-06	0.892	0.970	1.47	-0.88	-4.32
1	0.0153	0.762	0.000177	1.37E-07	33	0.00417	37.56	3.22E-06	0.892	0.970	1.47	-0.88	-3.97
1.5	0.0153	0.741	0.000172	1.61E-07	33	0.00417	45.38	3.90E-06	0.892	0.970	1.47	-0.88	-3.89
2	0.0153	0.753	0.000175	2.84E-07	33	0.00417	78.79	6.76E-06	0.892	0.970	1.47	-0.88	-3.65
3	0.0153	0.750	0.000174	2.43E-07	33	0.00417	67.80	5.82E-06	0.892	0.970	1.47	-0.88	-3.72
4	0.0153	0.760	0.000176	5.18E-07	33	0.00417	142.40	1.22E-05	0.892	0.970	1.47	-0.88	-3.39
5	0.0153	0.743	0.000172	3.45E-07	33	0.00417	96.95	8.32E-06	0.892	0.970	1.47	-0.88	-3.56
6	0.0153	0.737	0.000171	5.76E-07	33	0.00417	163.32	1.40E-05	0.892	0.970	1.47	-0.88	-3.33
7	0.0153	0.752	0.000174	3.67E-07	33	0.00417	101.98	8.75E-06	0.892	0.970	1.47	-0.88	-3.54
8	0.0153	0.749	0.000174	4.90E-07	33	0.00417	136.73	1.17E-05	0.892	0.970	1.47	-0.88	-3.41
9	0.0153	0.749	0.000174	5.17E-07	33	0.00417	144.40	1.24E-05	0.892	0.970	1.47	-0.88	-3.39
10	0.0153	0.743	0.000173	9.99E-07	33	0.00416	280.99	2.41E-05	0.892	0.970	1.47	-0.88	-3.10
12	0.0153	0.750	0.000174	1.44E-06	33	0.00416	401.02	3.44E-05	0.892	0.970	1.47	-0.88	-2.94
14	0.0153	0.743	0.000172	7.50E-07	33	0.00416	211.11	1.81E-05	0.892	0.970	1.47	-0.88	-3.22
15	0.0153	0.742	0.000172	6.28E-07	33	0.00417	176.88	1.52E-05	0.892	0.970	1.47	-0.88	-3.30

Table S2. Compositions of the quenched experimental solutions.

T, °C	Density, g/cm^3	H_2O, g	*n*(HCl), mol	*n*(Bi), mol	*P*(H_2O), bar	*X*(HCl)	Bi, ppm	*X*(Bi)	φ(H_2O)	φ(HCl)	log *f*(H_2O)	log *f*(HCl)	log *P*(Bi)	Hydration number [a]
250	0.0021	0.110	1.80E-04	7.84E-07	5	2.86E-02	1485	1.24E-04	0.9835	0.9953	0.69	-0.85	-3.21	0.81
250	0.0021	0.105	1.72E-04	6.53E-07	5	2.86E-02	1297	1.09E-04	0.9835	0.9953	0.69	-0.85	-3.27	0.81
250	0.0035	0.178	1.76E-04	5.05E-07	8.2	1.74E-02	592	5.01E-05	0.973	0.9924	0.90	-0.85	-3.39	0.99
250	0.0036	0.176	1.73E-04	9.2E-07	8.5	1.74E-02	1092	9.25E-05	0.9719	0.9921	0.92	-0.83	-3.10	1.01
250	0.0047	0.234	1.67E-04	1.03E-06	11	1.27E-02	916	7.80E-05	0.9637	0.9898	1.03	-0.86	-3.07	1.12
250	0.0059	0.289	1.69E-04	1.39E-06	13	1.04E-02	1009	8.60E-05	0.9572	0.9879	1.09	-0.87	-2.95	1.19
250	0.0059	0.286	1.67E-04	9.47E-07	13.5	1.04E-02	693	5.91E-05	0.9555	0.9875	1.11	-0.86	-3.10	1.21
250	0.0078	0.379	1.68E-04	1.33E-06	17.5	7.93E-03	731	6.25E-05	0.9425	0.9838	1.22	-0.86	-2.96	1.32
250	0.0090	0.436	1.67E-04	1.16E-06	20	6.85E-03	556	4.76E-05	0.9343	0.9816	1.27	-0.87	-3.02	1.39
250	0.0105	0.505	1.63E-04	1.47E-06	23	5.78E-03	610	5.23E-05	0.9246	0.9789	1.33	-0.89	-2.92	1.47
250	0.0144	0.707	1.64E-04	2.53E-06	30.5	4.16E-03	747	6.41E-05	0.9002	0.9722	1.44	-0.91	-2.71	1.65
250	0.0148	0.726	1.68E-04	2.52E-06	31.1	4.16E-03	725	6.22E-05	0.8983	0.9717	1.45	-0.90	-2.71	1.66
250	0.0153	0.749	1.71E-04	2.23E-06	33	4.08E-03	622	5.34E-05	0.8921	0.97	1.47	-0.88	-2.75	1.71
250	0.0185	0.895	1.67E-04	3.06E-06	37.4	3.35E-03	715	6.14E-05	0.8779	0.9662	1.52	-0.92	-2.64	1.81
250	0.0185	0.885	1.65E-04	4E-06	37.4	3.35E-03	944	8.11E-05	0.8779	0.9662	1.52	-0.92	-2.52	1.81
250	0.0142	0.728	4.42E-05	8.06E-08	30	1.09E-03	23.1	1.99E-06	0.9019	0.9727	1.43	-1.50	-4.22	1.63
250	0.0142	0.718	9.07E-05	1.19E-07	30	2.27E-03	34.6	2.97E-06	0.9019	0.9727	1.43	-1.18	-4.05	1.63
250	0.0142	0.728	1.35E-04	9.73E-07	30	3.32E-03	279	2.40E-05	0.9019	0.9727	1.43	-1.01	-3.14	1.63
250	0.0142	0.727	1.72E-04	6.08E-07	30	4.23E-03	175	1.50E-05	0.9019	0.9727	1.43	-0.91	-3.35	1.63
250	0.0142	0.724	2.20E-04	5.39E-07	30	5.44E-03	156	1.33E-05	0.9019	0.9727	1.43	-0.80	-3.40	1.63
250	0.0142	0.728	2.79E-04	1.19E-06	30	6.86E-03	342	2.93E-05	0.9019	0.9727	1.43	-0.70	-3.06	1.63
250	0.0142	0.726	3.37E-04	9.63E-06	30	8.28E-03	2771	2.37E-04	0.9019	0.9727	1.43	-0.62	-2.15	1.63
250	0.0142	0.730	3.64E-04	1.03E-05	30	8.90E-03	2950	2.52E-04	0.9019	0.9727	1.43	-0.59	-2.12	1.63

300	0.0039	0.188	1.85E-04	7.64E-07	10	1.74E-02	848	7.19E-05	0.9749	0.9937	0.99	-0.76	-3.14	0.67
300	0.0059	0.283	1.83E-04	5.84E-07	15	1.15E-02	431	3.67E-05	0.9625	0.9906	1.16	-0.77	-3.26	0.79
300	0.0080	0.390	1.94E-04	4.46E-07	20	8.90E-03	239	2.04E-05	0.9501	0.9875	1.28	-0.75	-3.39	0.92
300	0.0105	0.512	1.90E-04	5.29E-07	26	6.63E-03	216	1.85E-05	0.9352	0.9839	1.39	-0.77	-3.32	1.07
300	0.0123	0.594	1.92E-04	3.4E-07	30	5.78E-03	120	1.03E-05	0.9254	0.9815	1.44	-0.77	-3.51	1.17
300	0.0151	0.737	1.85E-04	5.78E-07	36	4.51E-03	164	1.41E-05	0.9107	0.9779	1.52	-0.80	-3.30	1.31
300	0.0195	0.938	1.89E-04	3.38E-07	45	3.61E-03	75.2	6.46E-06	0.8888	0.9727	1.60	-0.80	-3.54	1.51
300	0.0221	1.063	1.85E-04	6.14E-07	50	3.12E-03	121	1.04E-05	0.8766	0.9698	1.64	-0.82	-3.29	1.61
300	0.0307	1.509	1.91E-04	5.97E-07	65	2.27E-03	82.7	7.11E-06	0.8403	0.9615	1.74	-0.85	-3.33	1.93
300	0.0339	1.628	1.86E-04	9.62E-07	70	2.06E-03	123	1.06E-05	0.8283	0.9588	1.76	-0.86	-3.13	2.04
300	0.0374	1.839	1.91E-04	2.47E-06	75	1.87E-03	281	2.42E-05	0.8162	0.9562	1.79	-0.87	-2.74	2.16
300	0.0374	1.840	1.91E-04	6.61E-07	75	1.87E-03	75.1	6.46E-06	0.8162	0.9562	1.79	-0.87	-3.31	2.16
300	0.0412	1.994	1.93E-04	2.43E-06	80	1.74E-03	255	2.19E-05	0.8041	0.9535	1.81	-0.88	-2.76	2.28
300	0.0412	1.977	1.91E-04	1.21E-06	80	1.74E-03	128	1.10E-05	0.8041	0.9535	1.81	-0.88	-3.06	2.28
300	0.0276	1.420	4.70E-05	2.56E-08	60	5.96E-04	3.76	3.24E-07	0.8524	0.9643	1.71	-1.46	-4.71	1.83
300	0.0276	1.402	9.87E-05	1.98E-07	60	1.27E-03	29.6	2.55E-06	0.8524	0.9643	1.71	-1.13	-3.82	1.83
300	0.0276	1.420	2.04E-04	5.93E-07	60	2.58E-03	87.3	7.51E-06	0.8524	0.9643	1.71	-0.83	-3.35	1.83
300	0.0276	1.418	2.95E-04	2.26E-06	60	3.73E-03	332	2.85E-05	0.8524	0.9643	1.71	-0.67	-2.77	1.83
300	0.0276	1.413	3.46E-04	3.26E-06	60	4.40E-03	483	4.14E-05	0.8524	0.9643	1.71	-0.59	-2.60	1.83
300	0.0276	1.421	3.91E-04	3.92E-06	60	4.94E-03	577	4.95E-05	0.8524	0.9643	1.71	-0.54	-2.53	1.83
300	0.0276	1.425	4.87E-04	6.87E-06	60	6.12E-03	1007	8.63E-05	0.8524	0.9643	1.71	-0.45	-2.29	1.83
350	0.0057	0.282	1.77E-04	1.07E-06	16	1.12E-02	792	6.75E-05	0.9692	0.9933	1.19	-0.75	-2.97	0.60
350	0.0095	0.460	1.76E-04	6.63E-07	26	6.86E-03	301	2.58E-05	0.9501	0.9893	1.39	-0.75	-3.17	0.67

350	0.0130	0.682	1.82E-04	6.72E-07	35	4.77E-03	206	1.77E-05	0.9331	0.9858	1.51	-0.78	-3.21	0.76
350	0.0175	0.840	1.74E-04	3.37E-07	46	3.73E-03	83.8	7.20E-06	0.9125	0.9816	1.62	-0.77	-3.48	0.91
350	0.0192	0.984	1.81E-04	5.29E-07	50	3.30E-03	112	9.65E-06	0.905	0.9801	1.66	-0.79	-3.32	0.97
350	0.0192	0.984	1.81E-04	4.4E-07	50	3.30E-03	93.4	8.02E-06	0.905	0.9801	1.66	-0.79	-3.40	0.97
350	0.0237	1.216	1.75E-04	5.52E-07	60	2.58E-03	94.9	8.16E-06	0.8865	0.9764	1.73	-0.82	-3.31	1.14
350	0.0260	1.248	1.72E-04	4.6E-07	65	2.48E-03	77.1	6.63E-06	0.8773	0.9746	1.76	-0.80	-3.37	1.22
350	0.0321	1.558	1.74E-04	3.71E-07	77.5	2.01E-03	49.7	4.28E-06	0.8544	0.9703	1.82	-0.82	-3.48	1.45
350	0.0388	1.900	1.71E-04	5.13E-07	90.2	1.62E-03	56.4	4.85E-06	0.8312	0.966	1.87	-0.85	-3.36	1.70
350	0.0435	2.099	1.68E-04	4.38E-07	98.3	1.44E-03	43.6	3.75E-06	0.8166	0.9634	1.90	-0.87	-3.43	1.88
350	0.0544	2.677	1.75E-04	8.48E-07	115	1.17E-03	66.2	5.70E-06	0.7864	0.9582	1.96	-0.89	-3.18	2.27
350	0.0620	2.975	1.73E-04	1.19E-06	125	1.05E-03	83.3	7.18E-06	0.7684	0.9552	1.98	-0.90	-3.05	2.53
350	0.0707	3.471	1.69E-04	9.89E-07	135	8.77E-04	59.6	5.13E-06	0.7503	0.9524	2.01	-0.95	-3.16	2.83
350	0.0810	3.985	1.66E-04	1.23E-06	145	7.49E-04	64.4	5.54E-06	0.7321	0.9496	2.03	-0.99	-3.09	3.16
350	0.0992	4.804	1.66E-04	2.16E-06	158.2	6.21E-04	94.0	8.09E-06	0.7078	0.9461	2.05	-1.03	-2.89	3.65
350	0.1006	5.171	1.78E-04	2.64E-06	159	6.21E-04	107	9.18E-06	0.7063	0.9459	2.05	-1.03	-2.84	3.68
350	0.1024	5.262	1.79E-04	2.86E-06	160	6.11E-04	113	9.77E-06	0.7045	0.9457	2.05	-1.03	-2.81	3.72
350	0.1024	4.905	1.66E-04	2.38E-06	160	6.11E-04	102	8.75E-06	0.7045	0.9457	2.05	-1.03	-2.85	3.72
350	0.1105	5.653	1.82E-04	2.89E-06	164	5.80E-04	107	9.22E-06	0.697	0.9446	2.06	-1.05	-2.82	3.89
350	0.0544	2.797	9.02E-05	1.56E-07	115	5.81E-04	11.7	1.01E-06	0.7864	0.9582	1.96	-1.19	-3.94	2.30
350	0.0544	2.793	1.89E-04	6.79E-07	115	1.22E-03	50.8	4.37E-06	0.7864	0.9582	1.96	-0.87	-3.30	2.30
350	0.0544	2.782	3.11E-04	2E-06	115	2.01E-03	150	1.29E-05	0.7864	0.9582	1.96	-0.66	-2.83	2.30
350	0.0544	2.760	4.12E-05	2.91E-08	115	2.69E-04	2.20	1.90E-07	0.7864	0.9582	1.96	-1.53	-4.66	2.30
350	0.0544	2.797	9.02E-05	7.71E-08	115	5.81E-04	5.76	4.97E-07	0.7864	0.9582	1.96	-1.19	-4.24	2.30
350	0.0544	2.793	1.34E-04	4.95E-07	115	8.61E-04	37.0	3.19E-06	0.7864	0.9582	1.96	-1.02	-3.44	2.30
350	0.0544	2.797	2.30E-04	1.03E-06	115	1.48E-03	77.2	6.65E-06	0.7864	0.9582	1.96	-0.79	-3.12	2.30

350	0.0544	2.790	2.77E-04	1.79E-06	115	1.78E-03	134	1.15E-05	0.7864	0.9582	1.96	-0.71	-2.88	2.30
350	0.0544	2.806	3.13E-04	2.57E-06	115	2.01E-03	192	1.65E-05	0.7864	0.9582	1.96	-0.66	-2.72	2.30
400	0.0133	0.644	2.81E-04	4.61E-06	39	7.80E-03	1498	1.28E-04	0.9421	0.99	1.57	-0.52	-2.30	0.61
400	0.0173	0.495	1.70E-04	2.83E-06	50	6.14E-03	1196	1.02E-04	0.9262	0.9875	1.67	-0.52	-2.29	0.65
400	0.0211	1.015	2.76E-04	1.88E-06	60	4.87E-03	386	3.32E-05	0.9118	0.9852	1.74	-0.54	-2.70	0.70
400	0.0250	1.224	2.83E-04	1.47E-06	70	4.14E-03	252	2.16E-05	0.8975	0.983	1.80	-0.55	-2.82	0.76
400	0.0295	0.846	1.69E-04	1.03E-06	81	3.59E-03	255	2.19E-05	0.8819	0.9807	1.85	-0.54	-2.75	0.85
400	0.0334	1.639	2.85E-04	1.07E-06	90	3.12E-03	137	1.18E-05	0.8693	0.9789	1.89	-0.56	-2.98	0.94
400	0.0425	1.217	1.71E-04	1.31E-06	110	2.53E-03	225	1.94E-05	0.8415	0.9751	1.97	-0.57	-2.67	1.19
400	0.0474	1.357	1.71E-04	8.12E-07	120	2.27E-03	125	1.08E-05	0.8278	0.9734	2.00	-0.58	-2.89	1.35
400	0.0541	1.551	1.71E-04	1.23E-06	133	1.98E-03	166	1.43E-05	0.8101	0.9712	2.03	-0.59	-2.72	1.59
400	0.0662	1.897	1.70E-04	1.03E-06	154	1.61E-03	113	9.73E-06	0.7818	0.9679	2.08	-0.62	-2.82	2.09
400	0.0753	2.157	1.73E-04	1.03E-06	168	1.44E-03	100	8.60E-06	0.7631	0.9659	2.11	-0.63	-2.84	2.51
400	0.0817	2.340	1.70E-04	2.85E-06	177	1.31E-03	254	2.19E-05	0.7511	0.9647	2.12	-0.65	-2.41	2.83
400	0.1052	3.013	1.69E-04	1.48E-06	205	1.01E-03	103	8.84E-06	0.7142	0.9612	2.17	-0.70	-2.74	4.17
400	0.1177	3.371	1.70E-04	3.77E-06	217	9.08E-04	234	2.01E-05	0.6984	0.96	2.18	-0.72	-2.36	4.92
400	0.1272	3.643	1.74E-04	2.76E-06	225	8.60E-04	158	1.36E-05	0.6879	0.9591	2.19	-0.73	-2.51	5.48
400	0.1393	3.991	1.70E-04	5.28E-06	234	7.67E-04	277	2.38E-05	0.6761	0.9583	2.20	-0.76	-2.25	6.16
400	0.1571	4.499	1.71E-04	3.86E-06	245	6.84E-04	179	1.55E-05	0.6616	0.9573	2.21	-0.79	-2.42	7.04
400	0.1772	5.074	1.69E-04	6.23E-06	255	6.00E-04	256	2.21E-05	0.6484	0.9565	2.22	-0.83	-2.25	7.88
400	0.1892	5.419	1.74E-04	6.27E-06	260	5.80E-04	242	2.08E-05	0.6418	0.9561	2.22	-0.84	-2.27	8.30
400	0.2378	6.812	1.72E-04	8.84E-06	275	4.54E-04	271	2.34E-05	0.6218	0.955	2.23	-0.92	-2.19	9.55
400	0.2378	6.812	1.71E-04	1.5E-05	275	4.53E-04	461	3.97E-05	0.6218	0.955	2.23	-0.92	-1.96	9.55
400	0.3345	9.579	1.70E-04	1.82E-05	295	3.19E-04	398	3.43E-05	0.5954	0.9539	2.24	-1.05	-2.00	11.13
400	0.3393	9.717	1.72E-04	1.21E-05	296	3.19E-04	261	2.25E-05	0.5941	0.9538	2.25	-1.05	-2.18	11.20

400	0.0173	0.841	1.57E-04	1.29E-06	50	3.35E-03	320	2.75E-05	0.9262	0.9875	1.67	-0.78	-2.86	0.65
400	0.0173	0.849	2.37E-04	1.1E-06	50	5.01E-03	272	2.33E-05	0.9262	0.9875	1.67	-0.61	-2.93	0.65
400	0.0173	0.841	3.11E-04	2.21E-06	50	6.63E-03	549	4.70E-05	0.9262	0.9875	1.67	-0.48	-2.63	0.65
400	0.0173	0.840	3.73E-04	2.12E-06	50	7.93E-03	529	4.52E-05	0.9262	0.9875	1.67	-0.41	-2.65	0.65
400	0.0173	0.832	4.87E-04	7.89E-06	50	1.04E-02	1980	1.69E-04	0.9262	0.9875	1.67	-0.29	-2.07	0.65
400	0.0173	0.832	5.95E-04	3E-05	50	1.27E-02	7539	6.41E-04	0.9262	0.9875	1.67	-0.20	-1.49	0.65
400	0.0839	2.404	9.12E-05	6.86E-07	180	6.83E-04	59.6	5.14E-06	0.7471	0.9643	2.13	-0.93	-3.03	3.01
400	0.0839	2.404	1.35E-04	9.56E-07	180	1.01E-03	83.1	7.16E-06	0.7471	0.9643	2.13	-0.76	-2.89	3.01
400	0.0839	2.404	1.97E-04	2.02E-06	180	1.47E-03	175	1.51E-05	0.7471	0.9643	2.13	-0.59	-2.57	3.01
400	0.0839	2.404	2.38E-04	3.06E-06	180	1.78E-03	266	2.29E-05	0.7471	0.9643	2.13	-0.51	-2.39	3.01
400	0.0839	2.404	2.65E-04	4.32E-06	180	1.98E-03	375	3.23E-05	0.7471	0.9643	2.13	-0.46	-2.24	3.01
400	0.0839	2.404	2.96E-04	4.91E-06	180	2.21E-03	427	3.67E-05	0.7471	0.9643	2.13	-0.42	-2.18	3.01
400	0.0839	2.404	3.59E-04	6.35E-06	180	2.69E-03	552	4.75E-05	0.7471	0.9643	2.13	-0.33	-2.07	3.01
400	0.0133	0.6429	8.12E-05	2.47E-07	39	2.27E-03	80	6.91E-06	0.9421	0.99	1.57	-1.06	-3.57	0.61
400	0.0173	0.852	8.45E-05	2.07E-07	50	1.78E-03	51	4.37E-06	0.9262	0.9875	1.67	-1.06	-3.66	0.65
400	0.0242	1.2048	8.77E-05	2.4E-07	68	1.31E-03	42	3.58E-06	0.9003	0.9835	1.79	-1.06	-3.61	0.75
400	0.0295	1.4478	8.79E-05	2.22E-07	81	1.09E-03	32	2.76E-06	0.8819	0.9807	1.85	-1.06	-3.65	0.85
400	0.0449	2.2047	9.39E-05	1.76E-07	115	7.67E-04	17	1.44E-06	0.8346	0.9742	1.98	-1.07	-3.78	1.27
400	0.0474	2.3008	9.57E-05	1.26E-07	120	7.49E-04	11	9.85E-07	0.8278	0.9734	2.00	-1.06	-3.93	1.35
400	0.0525	2.5803	9.81E-05	1.34E-07	130	6.84E-04	11	9.36E-07	0.8141	0.9717	2.02	-1.06	-3.91	1.53
400	0.0694	1.9871	6.22E-05	1.05E-07	159	5.64E-04	11	9.49E-07	0.7751	0.9671	2.09	-1.06	-3.82	2.23
400	0.0662	3.2221	1.04E-04	3.11E-07	154	5.80E-04	20	1.74E-06	0.7818	0.9679	2.08	-1.06	-3.57	2.09
400	0.1052	3.013	7.32E-05	2.74E-07	205	4.38E-04	19	1.64E-06	0.7142	0.9612	2.17	-1.06	-3.47	4.17
400	0.1393	3.9909	8.38E-05	1.31E-06	234	3.78E-04	68	5.89E-06	0.6616	0.9573	2.19	-1.07	-2.86	5.49

400	0.1571	4.4986	9.13E-05	1.64E-06	245	3.66E-04	76	6.58E-06	0.6616	0.9573	2.21	-1.07	-2.79	7.04
400	0.1571	4.4986	9.13E-05	8.16E-07	245	3.66E-04	38	3.27E-06	0.6444	0.9563	2.20	-1.07	-3.10	6.09
400	0.1842	5.2753	1.07E-04	2.48E-06	258	3.66E-04	98	8.46E-06	0.6444	0.9563	2.22	-1.04	-2.66	8.13
400	0.3194	9.147	1.57E-04	8.32E-06	292	3.10E-04	190	1.64E-05	0.5993	0.954	2.24	-1.06	-2.32	10.90

Note: [a] The hydration number is calculated using Equation (17).

Table S3. Parameters for the equation $y = a + b*X^c$ used to provide preliminary fits to the experimental data at high water fugacity illustrated in Figure 3.

T °C	a	b	c	# pts [a]	Adj. R^2 [b]	dy/dx Maximum [c]
250	-1.59	1.53E-01	3.99	15	0.91	3
300	-1.89	4.11E-07	24.38	10	0.74	10
350	-1.84	1.91E-08	24.57	16	0.97	12
400	-1.86	6.19E-08	21.19	18	0.91	17

Note:

[a] # pts = number of points

[b] Adj. R^2 = adjusted R-square

[c] dy/dx Maximum = the maximum value of the derivative, representing the slope of the tangent.

Table S4. Values of Standard enthalpy ($\Delta_h H_m^\circ$, kJ/mol) and entropy ($\Delta_h S_m^\circ$, J/mol·K) of the stepwise formation of the hydrated bismuth species, $BiCl_3(H_2O)_n$, at each $m*$ values.

$BiCl_3(H_2O)_n$	$\Delta_h H_1^\circ$	$\Delta_h H_2^\circ$	$\Delta_h H_3^\circ$	$\Delta_h H_4^\circ$	$\Delta_h H_5^\circ$	$\Delta_h H_6^\circ$	ΔH_{m*}°
m*=2	-87.796						-25.892
m*=3	-93.841	-50.158					-19.745
m*=4	-90.278	-56.187	-26.826				-21.393
m*=5	-90.576	-70.058	-30.146	-28.070			-19.164
m*=6	-87.117	-74.455	-35.030	-31.934	-21.495		-17.557
m*=7	-78.178	-61.774	-37.427	-33.331	-31.857	-21.287	-19.687

$BiCl_3(H_2O)_n$	$\Delta_h S_1^\circ$	$\Delta_h S_2^\circ$	$\Delta_h S_3^\circ$	$\Delta_h S_4^\circ$	$\Delta_h S_5^\circ$	$\Delta\Delta_h S_6^\circ$	ΔS_{m*}°
m*=2	-176.243						-87.734
m*=3	-214.831	-92.646					-78.640
m*=4	-230.274	-85.004	-83.520				-81.129
m*=5	-254.400	-91.121	-90.951	-78.263			-77.814
m*=6	-252.173	-96.600	-96.506	-89.275	-75.479		-75.458
m*=7	-216.376	-96.600	-96.600	-96.563	-92.100	-80.149	-78.686

Note: The uncertainties in these values are ~10%, estimated from the deviation of the data from the fits. If $m* = x$, $\Delta H_{m>x}^\circ = \Delta H_x^\circ$ and $\Delta S_{m>x}^\circ = \Delta S_x^\circ$. For further detail please refer to the section of 4.2. Derivation of thermodynamic data.

Table S5. Sources of data used in the thermodynamic calculations.

Species and solid phases	Formation	References	Species and solid phases	Formation	References
	$BiCl_3H_2O(g)$	This study		$H_2(g)$	Holland and Powell, 1998
	$BiCl_3H_2O_2(g)$	This study		$O_2(g)$	Holland and Powell, 1998
	$BiCl_3H_2O_3(g)$	This study		HCl(g)	Robie and Hemingway, 1995
	$BiCl_3H_2O_4(g)$	This study		$H_2O(g)$	Holland and Powell, 1998
	$BiCl_3H_2O_5(g)$	This study		$H_2S(g)$	Robie and Hemingway, 1995
	$BiCl_3H_2O_6(g)$	This study		MoO_2	Robie and Hemingway, 1995
	$BiCl_3H_2O_7(g)$	This study		MoO_3	Robie and Hemingway, 1995
	$BiCl_3H_2O_8(g)$	This study	Hematite	Fe_2O_3	Holland and Powell, 2011
	$BiCl_3H_2O_9(g)$	This study	Magnetite	Fe_3O_4	Holland and Powell, 2011
	$BiCl_3H_2O_{10}(g)$	This study	Fayanite	$FeSiO_4$	Holland and Powell, 2011
	$BiCl_3H_2O_{11}(g)$	This study	Quartz	SiO_2	Holland and Powell, 2011
	$BiCl_3H_2O_{12}(g)$	This study		BiOCl	Schmidt and Oppermann, 2000
	$BiCl_3(g)$	Barin, 2008	Bismuth	Bi	Barin, 2008
	Bi(g)	Barin, 2008	Bismuthinite	Bi_2S_3	Barin, 2008
	$Bi_2(g)$	Barin, 2008		Bi_2O_3	Barin, 2008
	BiCl(g)	Barin, 2008			