Appendix

To assess the accuracy of our measurements we compared the NaCl wt.% equivalent values determined by microthermometry with the Cl concentration values acquired by LA-ICP-MS. We assumed that Ca, Mg and Fe build $CaCl_2$, $MgCl_2$ and $FeCl_2$ complexes respectively, and each K cation couples with a single Cl anion and all of the remaining Cl should build NaCl complexes. Theoretically, and provided that no Cl is present in the vapour phase, no Cl should be left over when the calculated $NaCl_{LAICPMS}$ is subtracted from the salinities obtained by micro-thermometry (NaCl wt.% equivalent). The following calculation was carried out: (mCl-mK-2mMg-2mCa-2mFe) x 58.44 = $NaCl_{LAICPMS}$ where m stands for the concentrations in moles measured in fluid inclusions, 58.44 is the molar mass of NaCl and $NaCl_{LAICPMS}$ is the NaCl content of the fluid inclusion in wt.% based on LA-ICP-MS measurements, which use Na as the internal standard. Fluid inclusions in the LD sample (Table A.2) have an average $NaCl_{LAICPMS}$ of 24 ± 1.6, which is within error of value of 22.3 ± 0.2 NaCl wt.% equivalent obtained by microthermometry. It can be concluded that (a) there are no significant other cations in these fluids than shown in Table A.2, and (b) the LA-ICP-MS agree with $NaCl_{equivalent}$ salinities to better than 10%. The slightly higher $NaCl_{total}$ values obtained by LS-ICP-MS may indicate that more Na^+ is required than given as the internal standard to fully couple with Cl^-. Alternatively, it is feasible that Cl^- couples with other species that we have not considered in our calculations. It is likely that Cl builds complexes with Cu and Pb, but such complexes would not affect the budget significantly due to their relatively low concentrations. However, due to the fact that the fluid inclusions are hosted in sphalerite the Zn composition in the fluid inclusions is at that stage not resolvable. In the case of the CM inclusions, a wider range of $NaCl_{LAICPMS}$ values were obtained ranging

from 10.0–29.6 wt.% and most of the calculated $NaCl_{LAICPMS}$ values are between 15 and 19 wt.%. The average is 17.1 ± 2.9 wt.% $NaCl_{LAICPMS}$, whereas the values from micro-thermometry measurements are 15.8 ± 0.4 wt.% NaCl equivalent. With one exception (CM_20), all of the micro-thermometry and LA-ICP-MS measurements agree well.

Table A.1: Compilation of fluid inclusion analyses by LA-ICP-MS. Sodium was used as the internal standard. All signals are matrix corrected and the standard deviation is given as 2 sigma. Rows in bold are fluid inclusions with suspected solid minerals (see text and Fig. 9).

	Size µm	Depth µm	Spot ø µm	Na µg/g	Mg µg/g	Cl µg/g	K µg/g	Ca µg/g	Mn µg/g	Fe µg/g	Cu µg/g	Br µg/g	Pb µg/g	Cl/Br [m]*	Na/Br [m]	Na/Ca [m]	Na/Cl [m]
LD (Lucky Dog)																	
LD_1	**40**	**10**	**44**	**87334**	**1635**	**186085**	**2642**	**21929**	**1.3**	**<25**	**<1.7**	**589**	**54**	**712**	**516**	**7.7**	**0.72**
LD_3	42	15	44	88120	1985	163777	2348	17106	2.3	<70	25	645	52	572	475	10	0.83
LD_4	40	15	44	88120	1862	188532	2898	22444	2.3	154	22	586	52	725	523	7.6	0.72
LD_6	**40**	**18**	**44**	**87800**	**1807**	**181820**	**2757**	**16880**	**1.6**	**<57**	**<3.6**	**564**	**43**	**727**	**541**	**10**	**0.74**
LD_7	**32**	**20**	**44**	**87800**	**1841**	**185341**	**2624**	**18875**	**2.1**	**<46**	**9.4**	**612**	**35**	**682**	**498**	**9.1**	**0.73**
LD_8	38	24	44	87800	1884	185104	2996	20867	1.6	60	12	663	21	629	460	8.2	0.73
LD_10	40	20	44	87800	1911	210233	3188	25348	2.2	<57	<6.0	737	52	643	414	6.8	0.64
LD_12	**20**	**20**	**32**	**87334**	**1692**	**173121**	**2118**	**17559**	**4.6**	**83**	**<7.4**	**527**	**178**	**740**	**576**	**9.8**	**0.78**
LD_13	35	30	44	88120	1899	189003	2838	21388	2.1	<31	20	634	60	672	483	8.2	0.72
LD_14	**40**	**28**	**44**	**87800**	**1736**	**203882**	**2745**	**17906**	**2.0**	**48**	**21**	**559**	**61**	**822**	**546**	**9.7**	**0.66**
LD_15	**30**	**20**	**44**	**87334**	**2065**	**195135**	**2816**	**25700**	**5.0**	**296**	**<10**	**579**	**<1.1**	**759**	**524**	**6.8**	**0.69**
LD_16	25	20	32	87334	1950	203892	3235	23471	7.9	206	<16	612	51	751	496	7.4	0.66
LD_17	**25**	**30**	**32**	**88120**	**1846**	**206596**	**3049**	**22429**	**<6.3**	**<246**	**<14**	**580**	**176**	**802**	**528**	**7.8**	**0.66**
LD_18	44	10	44	88514	1564	191035	2720	22825	2.5	43	<2.4	588	63	732	523	7.8	0.71
LD_19	**42**	**10**	**44**	**88120**	**1866**	**173680**	**2144**	**18474**	**2.5**	**48**	**<1.6**	**581**	**70**	**674**	**527**	**9.5**	**0.78**
LD_20	25	10	32	87727	1954	180671	2235	20331	2.8	<82	<4.7	627	41	650	487	8.7	0.75
LD_21	**28**	**20**	**32**	**87334**	**1744**	**176893**	**2434**	**20072**	**<2.2**	**<88**	**65**	**566**	**56**	**705**	**537**	**8.7**	**0.76**
LD_22	24	20	32	87800	1938	304419	4106	32381	<5.2	<206	<12	930	183	738	328	5.5	0.44
LD_23	**26**	**10**	**32**	**87334**	**1736**	**192485**	**2785**	**20783**	**<2.2**	**230**	**<5.1**	**594**	**97**	**730**	**511**	**8.5**	**0.70**
LD_24	40	10	44	87334	2391	206949	2869	21082	3.7	737	22	616	147	757	493	8.4	0.65
LD_25	**28**	**15**	**32**	**87334**	**1802**	**203012**	**2930**	**21687**	**<8.5**	**<341**	**133**	**598**	**145**	**765**	**508**	**8.1**	**0.66**
LD_26	**28**	**15**	**32**	**89301**	**1958**	**205017**	**2887**	**24813**	**<4.2**	**<167**	**135**	**662**	**413**	**698**	**469**	**7.3**	**0.67**
LD_27	**32**	**10**	**44**	**88907**	**1965**	**186718**	**3455**	**18569**	**<1.1**	**<43**	**48**	**608**	**60**	**693**	**509**	**9.7**	**0.73**
Average					*1871*	*195365*	*2818*	*21431*				*620*	*96*	*712*	*499*	*8.3*	*0.70*
Standard deviation					*324*	*52511*	*857*	*6822*				*157*	*170*	*111*	*98*	*2.3*	*0.14*
ET (East Tennessee)																	
ET_1	**16**	**15**	**24**	**92840**	**1611**	**219955**	**19378**	**54796**	**<21**	**<1069**	**87**	**2551**	**622**	**194**	**126**	**3.0**	**0.65**
ET_2	17	17	24	92840	1929	223046	14508	42145	<5.5	743	166	3430	64	147	94	3.8	0.64
ET_3	**17**	**14**	**24**	**92840**	**2082**	**285771**	**18611**	**71105**	**<7.7**	**2338**	**101**	**3844**	**110**	**168**	**84**	**2.3**	**0.50**
ET_4	20	20	24	92840	1733	339208	17936	66493	<6.1	<322	<22	4187	328	183	77	2.4	0.42
ET_6	22	20	32	92840	2827	370955	14444	94369	11	2233	<29	4231	305	198	76	1.7	0.39
ET_7	**18**	**20**	**24**	**92840**	**2076**	**367902**	**20456**	**63395**	**10**	**8497**	**974**	**4597**	**236**	**180**	**70**	**2.6**	**0.39**
ET_9	20	20	24	92840	2034	307012	18886	51611	<26	9821	237	4086	225	169	79	3.1	0.47
ET_10	18	20	24	92840	2248	261728	13091	45629	<6.4	<356	<23	3474	58	170	93	3.5	0.55
ET_11	**16**	**20**	**24**	**92840**	**1552**	**325919**	**18264**	**58091**	**<24**	**<1351**	**<88**	**2651**	**142**	**277**	**122**	**2.8**	**0.44**
ET_12	17	5	24	92840	2079	292669	11505	54116	27	5165	49	4012	1486	164	80	3.0	0.49
ET_13	**18**	**10**	**24**	**92840**	**1858**	**292611**	**18281**	**49006**	**<11**	**5246**	**108**	**3767**	**227**	**175**	**86**	**3.3**	**0.49**
ET_14	**16**	**20**	**24**	**92840**	**2085**	**312374**	**18444**	**63909**	**19**	**3116**	**<74**	**3934**	**420**	**179**	**82**	**2.5**	**0.46**
ET_15	17	10	24	92840	2248	323800	17608	59099	<17	<992	<66	4432	536	165	73	2.7	0.44
Average					*2028*	*301765*	*17032*	*59520*				*3784*	*366*	*182*	*88*	*2.8*	*0.49*
Standard deviation					*626*	*90617*	*5219*	*25740*				*1195*	*726*	*60*	*34*	*1.1*	*0.16*
CM (Coy Mine)																	
CM_1	20	5	24	62398	1858	153068	6957	23319	<4.7	1819	<11	1332	30	259	163	4.7	0.63
CM_2	**23**	**8**	**24**	**61635**	**1030**	**222915**	**16914**	**35959**	**126**	**32721**	**<13**	**2626**	**8892**	**191**	**82**	**3.0**	**0.43**
CM_3	30	10	32	62000	<46	192331	14164	<408	<4.8	<198	<11	3268	70	133	66		0.50
CM_4	**20**	**10**	**24**	**62000**	**1103**	**206152**	**16374**	**33385**	**4.5**	**1208**	**5.6**	**2310**	**82**	**201**	**94**	**3.2**	**0.47**
CM_5	20	20	24	62000	661	191935	14378	22917	<16	<624	<35	1852	17	234	117	4.7	0.50
CM_6	**20**	**20**	**24**	**62000**	**1194**	**149127**	**12825**	**21982**	**13**	**<294**	**<17**	**2617**	**44**	**128**	**83**	**4.9**	**0.64**
CM_7	25	20	24	62000	1027	199767	17515	31567	<16	3079	44	3093	291	146	70	3.4	0.48
CM_7.1	25	30	24	62000	1291	182781	14148	28198	<5.7	<222	<13	2430	<0.2	170	89	3.8	0.52
CM_8	28	20	32	62000	1303	180141	14376	33905	16	3763	24	2592	<0.8	157	83	3.2	0.53
CM_9	17	15	24	62000	1198	211664	12868	28410	20	2427	48	3238	127	147	67	3.8	0.45
CM_10	22	20	32	62000	1037	187575	16557	31716	40	6764	<7.7	2622	976	161	82	3.4	0.51
CM_11	28	10	32	60865	1226	182533	15133	30812	31	8845	<6.8	2287	1107	180	93	3.4	0.51
CM_12	20	10	24	59694	1401	163958	13906	31846	3.7	<130	<7.7	2511	41	147	83	3.3	0.56
CM_14	**18**	**10**	**24**	**62398**	**1151**	**199509**	**16495**	**34435**	**<6.2**	**<253**	**<15**	**2414**	**10**	**186**	**90**	**3.2**	**0.48**
CM_17	**17**	**10**	**24**	**63901**	**1196**	**181829**	**15585**	**30847**	**13**	**4503**	**31**	**2817**	**258**	**145**	**79**	**3.6**	**0.54**
CM_18	**19**	**15**	**24**	**62000**	**1306**	**268217**	**14974**	**58116**	**103**	**27459**	**46**	**3061**	**3364**	**197**	**71**	**1.9**	**0.36**
CM_19	**18**	**12**	**24**	**62000**	**764**	**147293**	**7800**	**17587**	**<14**	**2416**	**<35**	**2331**	**183**	**142**	**93**	**6.2**	**0.65**
CM_20	20	10	24	64641	1395	135405	3864	25948	<226	13040	254	2413	<2.5	126	93	4.3	0.74
CM_21	28	15	32	62000	1605	183410	14263	<462	5.7	2193	<7.8	2523	<0.2	164	88		0.54
CM_22	**20**	**10**	**24**	**62398**	**479**	**264972**	**14536**	**72590**	**39**	**5962**	**<8.2**	**3200**	**340**	**187**	**68**	**1.5**	**0.36**
Average					*1170*	*190229*	*13682*	*32974*				*2577*	*989*	*170*	*88*	*3.6*	*0.52*
Standard deviation					*613*	*67208*	*6872*	*25266*				*921*	*4394*	*68*	*42*	*2.1*	*0.18*

*[m] molar ratio **bold = suspected galena daughter phases**

Na is used as the internal standard

Table A.2: Calculated NaCl wt.% based on anion/cation coupling and Cl measured by LA-ICP-MS using Na as an internal standard ($NaCl_{LAICPMS}$). Salinities calculated according to Bodnar (1993) based on final ice melting temperatures are given in $NaCl_{equi.}$ wt.%.

Sample	Na [mol]	Cl [mol]	Ca [mol]	K [mol]	Mg [mol]	Fe [mol]	[1]$NaCl_{LAICPMS}$ [wt.%]	[2]$NaCl_{equi}$ [wt.%]
Lucky Dog								
LD_1	3.80	5.31	0.55	0.07	0.07	<0.001	23.5	22.2
LD_3	3.83	4.68	0.43	0.06	0.08	<0.001	21.0	22.4
LD_4	3.83	5.38	0.56	0.07	0.08	0.003	23.5	22.4
LD_6	3.82	5.18	0.42	0.07	0.07	<0.001	24.1	
LD_7	3.82	5.27	0.47	0.07	0.08	<0.001	24.0	
LD_8	3.82	5.27	0.52	0.08	0.08	0.001	23.3	
LD_10	3.82	5.97	0.63	0.08	0.08	<0.001	26.1	
LD_12	3.80	4.90	0.44	0.05	0.07	0.001	22.4	22.2
LD_13	3.83	5.35	0.53	0.07	0.08	<0.001	23.7	22.4
LD_14	3.82	5.76	0.45	0.07	0.07	<0.004	27.2	
LD_15	3.80	5.51	0.64	0.07	0.08	0.005	23.3	22.2
LD_16	3.80	5.76	0.59	0.08	0.08	0.004	25.4	22.2
LD_17	3.83	5.83	0.56	0.08	0.08	<0.001	26.2	22.4
LD_18	3.85	5.38	0.57	0.07	0.06	<0.001	23.6	22.5
LD_19	3.83	4.89	0.46	0.06	0.08	0.001	22.0	22.4
LD_20	3.82	5.08	0.51	0.06	0.08	<0.001	22.5	22.3
LD_21	3.80	4.98	0.50	0.06	0.07	<0.002	22.0	22.2
LD_22	3.82	8.56	0.81	0.11	0.08	<0.004	39.0*	
LD_23	3.80	5.41	0.52	0.07	0.07	0.004	24.3	22.2
LD_24	3.80	5.81	0.53	0.07	0.10	0.013	26.2	22.2
LD_25	3.80	5.70	0.54	0.08	0.07	<0.006	25.7	22.2
LD_26	3.88	5.76	0.62	0.08	0.08	<0.003	25.0	22.7
LD_27	3.87	5.24	0.46	0.09	0.08	<0.001	23.7	22.6
Average		*5.52*	*0.53*	*0.07*	*0.08*		*24.0*	*22.3*
Standard Deviation		*0.73*	*0.09*	*0.01*	*0.01*		*1.6*	*0.2*
Coy Mine								
CM_1	2.71	4.33	0.63	0.18	0.08	0.03	15.6	15.9
CM_2	2.68	6.30	0.98	0.43	0.04	0.59	15.5	15.7
CM_3	2.71	5.43	<0.01	0.36	<0.002	<0.004	29.6*	
CM_4	2.71	5.82	0.91	0.41	0.05	0.02	20.2	
CM_5	2.71	5.42	0.62	0.36	0.03	<0.011	21.8	
CM_6	2.71	4.21	0.60	0.32	0.05	<0.005	15.1	
CM_7	2.71	5.63	0.86	0.44	0.04	0.06	19.2	
CM_7.1	2.71	5.15	0.77	0.36	0.05	<0.004	18.4	
CM_8	2.71	5.08	0.92	0.36	0.05	0.07	15.4	
CM_9	2.71	5.96	0.77	0.32	0.05	0.04	22.9	
CM_10	2.71	5.28	0.86	0.42	0.04	0.12	16.5	
CM_11	2.65	5.14	0.83	0.38	0.05	0.16	15.6	15.5
CM_12	2.60	4.61	0.86	0.35	0.06	<0.002	14.1	15.2
CM_14	2.71	5.61	0.93	0.42	0.05	<0.005	18.9	15.9
CM_17	2.78	5.11	0.83	0.39	0.05	0.08	16.3	16.2
CM_18	2.71	7.53	1.57	0.38	0.05	0.49	17.1	
CM_19	2.71	4.13	0.47	0.20	0.03	0.04	16.6	
CM_20	2.81	3.80	0.70	0.10	0.06	0.23	10.0	16.4
CM_21	2.71	5.14	<0.01	0.36	0.07	0.04	26.7*	
CM_22	2.71	7.42	1.95	0.37	0.02	0.11	18.2	15.9
Average		*5.35*	*0.89*	*0.35*	*0.05*		*17.1*	15.8
Standard Deviation		*0.94*	*0.34*	*0.09*	*0.01*		*2.9*	0.4

[1] calculated based on Cl values from LA-ICP-MS analyses with Na as an internal standard

[2] determined by microthermometry and calculated after Bodnar (1993)

* treated as outliers and not considered in average values (value is outside 3 x SD of average)