

Origin of hydrothermal sulphide and dolomite mineralizing fluids in southern Northwest Territories and northern Alberta

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Abstract: Bulk fluid-inclusion analyses were carried out on matrix dolomite, sulphides, coarse-grained dolomite and late-stage calcite from Great Slave Reef, Hay West, Windy Point and Qito mineral properties in Northwest Territories and selected areas in northern Alberta. The study shows that there is no systematic difference in the major solute sources in any phase from early to late in the paragenesis or spatially throughout the study area. The halogen compositions of all the samples indicate that the bulk of the fluids originated as highly evaporated seawater. However, some of the coarse dolomite and all the late-stage calcite samples show evidence for mixing between this saline fluid and a dilute, probably meteoric, water.

Résumé : Nous avons effectué des analyses d'inclusions fluides totales dans de la dolomite matricielle, des sulfures, de la dolomite à grain grossier et de la calcite de phase tardive provenant des propriétés minières de Great Slave Reef, de Hay West, de Windy Point et de Qito, dans les Territoires du Nord-Ouest, et d'endroits choisis dans le nord de l'Alberta. L'étude révèle qu'il n'existe aucune différence systématique dans les principales sources de solutés à n'importe quelle phase du début à la fin de la paragenèse ou spatialement dans l'ensemble de la région à l'étude. Les compositions des éléments halogènes de tous les échantillons indiquent que la plus grande partie des fluides sont dérivés d'eau de mer hautement évaporée. Toutefois, quelques-uns des échantillons de dolomite à grain grossier et tous les échantillons de calcite de phase tardive montrent des indices de mélange entre ce fluide salin et de l'eau diluée, d'origine probablement météorique.

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INTRODUCTION

This study is part of a Targeted Geoscience Initiative entitled “Potential for carbonate-hosted Pb-Zn (MVT) deposits in northern Alberta and southern NWT”, a collaborative project between the Geological Survey of Canada, the C.S. Lord Northern Geoscience Centre and the Alberta Geological Survey (Hannigan 2001, 2002; Hannigan et al., 2002). The primary aim of this study was to characterize the chemistry of brines responsible for base metal mineralization and dolomite precipitation in Alberta and the southern Northwest Territories by carrying out crush-leach analyses of fluid inclusions in sulphide and carbonate samples on a regional scale. These data were then used to constrain the origin of the fluids, and to constrain (where possible) the nature of water-rock interactions that occurred along the flow path to the site of mineral precipitation.

PARAGENESIS

The carbonate and ore mineral assemblages in the Pine Point ore district and more regionally in the Western Canadian Sedimentary Basin region have been documented by many authors including Skall (1975), Kyle (1977, 1981), Krebs and MacQueen (1984), Rhodes et al. (1984), Qing (1991), and Qing and Mountjoy (1994), among others. It is beyond the scope of this study to discuss the regional paragenetic relationships in any depth and such studies are documented elsewhere in this volume (e.g. Coniglio, et al., 2006; Rice and Lonnee, 2006; Turner, 2006).

In summary, in the Pine Point area, the paragenesis of the alteration assemblage is characterized in terms of the relationship to ore, and is separated into three stages (pre-ore, main event of ore deposition, and post-ore). The pre-ore stage is characterized by an early diagenetic dolomitization resulting in the recrystallization of the host limestone. This was followed by the formation of the coarser “Presqu’île dolomite” facies, which in some places is succeeded by coarse-crystalline white “saddle” dolomite. The ore stage typically involves the precipitation of marcasite, pyrite, sphalerite and galena (Krebs and MacQueen, 1984). The sulphides are associated with syngenetic saddle dolomite and some bitumen occurrences. Following ore deposition, further fracturing, dissolution, and saddle dolomitization occurred. The latest mineral phases observed in this study are fracture- and vug-fills of coarse calcite, native sulphur and bitumen (e.g. Kyle, 1981).

Sample classification and selection

The crush-leach technique uses approximately 1–2 g of clean mineral separate and ideally is carried out on samples that have been characterized by microthermometry. One of the limitations of the study was being able to confidently relate the sampled mineral phases to any of the published paragenetic schemes. For example, the Krebs and MacQueen

(1984) paragenesis strongly depends on the relationship between the different dolomite phases and sulphides in the ore deposits. In much of the core sampled in this study, no sulphides were identified, and therefore, we could not categorically place our data into their paragenetic sequence. As a result, and in view of the large sample volumes used in the study, we divided the dolomite samples in terms of their grain size, resulting in fine-grained early “matrix” dolomite hosting the mineralization and later coarse-grained dolomite including samples of saddle dolomite. In some of the coarse dolomite samples that had ample sample material and contained different coloured dolomite, an effort was made to pick separate dolomite phases. These samples are referred to as #1 etc. in Table 1.

In total 15 samples of the fine-grained “matrix” dolomite were analyzed from the Great Slave Reef (GSR), Hay West, and northern Alberta areas; 32 coarse-grained dolomite samples were analyzed from GSR, Hay West, and Windy Point areas; 12 sulphide analyses were completed from GSR; and 14 analyses of medium- to coarse-grained calcite from the northern Alberta, GSR, Windy Point, and Qito areas were completed. The general sample areas in the Northwest Territories are shown in Figure 1 and the reader is referred to Turner (2006) for the detailed locations of the drill core and outcrop samples. The locations of the samples from northern Alberta are shown in Figure 2 (*after* Rice and Lonnee, 2006).

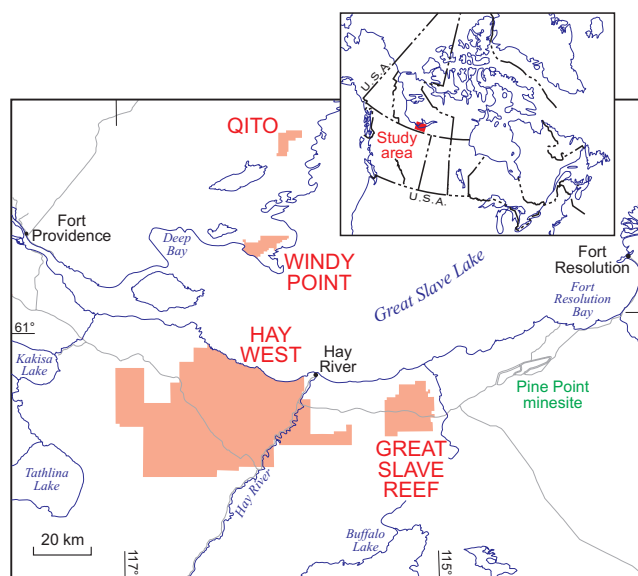


Figure 1. The area near Great Slave Lake, Northwest Territories, showing the Pine Point mining camp and the Great Slave Reef (GSR), Hay West, Qito, and Windy Point sampling sites (*after* Turner, 2006). Detailed location information on individual samples within these sampled areas may be found in Turner (2006).

Table 1. The total data set for samples from Windy Point, GSR, Hay West, Qito, and northern Alberta

GSC sample	Field sample number	Location	Min.	IC	Br	F	SO ₄	Na	AAS	K	Ca	Mg	Na	K	Fe	Mn	S	Ba	B	Cd	Co	Pb	Li	Ni	Sr	Zn	Charge Balance
C-421227	WP-Z25-16	Windy Point	dol#1	156.46	0.64	<0.02	5.42	41.64	0.72	Host	Host	Host	Host	1.5	0.026	0.018	<0.00005	<0.0005	<0.0005	<0.0005	<0.0005	<0.0005	0.005	<0.0025	0.681	0.048	0.4
C-421225	WP-Z27-11	Windy Point	dol#1	180.32	1.32	<0.02	2.00	35.49	1.61	Host	Host	Host	Host	6.5	<0.05	0.621	0.77	0.028	0.022	0.00005	<0.0005	0.0023	<0.005	<0.003	1.2	0.036	0.3
C-421223	WP-Z20-06	Windy Point	dol#2	134.65	1.20	<0.02	1.25	26	1.15	Host	Host	Host	Host	<2	3.39	0.424	8.9	<0.005	<0.01	0.0105	0.0006	1.76	<0.005	<0.003	0.125	93.8	0.3
C-421224	WP-Z21-10	Windy Point	dol#2	146.25	1.27	<0.02	4.90	31.2	1.3	Host	Host	Host	Host	6.5	<0.05	0.591	2.4	0.019	0.012	0.00014	0.0016	0.004	<0.005	0.0588	0.77	0.222	0.3
C-421222	WP-Z23-04	Windy Point	dol#2	415.32	3.48	<0.02	6.12	6.9	0.34	Host	Host	Host	Host	<2	0.32	0.16	58.2	<0.005	0.015	0.00037	<0.0005	0.0511	<0.005	0.0079	150	0.127	
C-421011	01-Z155-223-327-7	GSR	cal	11.23	0.05	<0.02	4.51	5.57	0.39	Host	Host	Host	Host	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	0.2
C-421011	01-Z155-223-327-7	GSR	cal	2.27	<0.02	<0.02	0.60	<0.002	<0.03	Host	Host	Host	Host	<2	<0.05	0.16	0.99	0.126	<0.01	0.00005	<0.0005	<0.0005	<0.005	<0.0025	0.159	0.012	
C-421012	01-Z155-223-332-8	GSR	cal	6.20	<0.02	0.02	9.87	2.55	n.a.	Host	Host	Host	Host	<2	<0.05	0.11	0.99	<0.005	0.015	<0.00005	<0.0005	<0.005	<0.005	<0.0025	0.497	0.015	0.3
C-421013B	01-Z155-223(525-35)9	GSR	cal	12.02	0.05	<0.02	203.20	6.43	0.25	Host	Host	Host	Host	<2	<0.05	0.088	60.9	<0.005	0.012	<0.00005	<0.0005	0.0009	<0.005	<0.0025	130	0.044	0.1
C-421013B	01-Z155-223(525-35)9	GSR	cal	5.07	0.84	<0.02	186.33	3.6	0.14	Host	Host	Host	Host	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	
C-421018	01-X25-77-475-5	GSR	cal	7.19	1.00	<0.02	45.98	2.45	n.a.	Host	Host	Host	Host	<2	<0.05	0.063	12.9	0.023	0.012	<0.00005	<0.0005	<0.005	<0.005	<0.003	26.6	0.009	0.1
C-421033	01-R190-749-515-7	GSR	cal	14.81	0.35	<0.02	92.65	6.24	0.91	Host	Host	Host	Host	<2	0.22	<0.02	53.4	<0.005	0.015	0.00041	<0.0005	0.123	<0.005	0.016	125	0.148	0.1
C-421039	01-O556-754-499-1	GSR	cal	1.60	<0.02	<0.02	<0.05	1.53	n.a.	Host	Host	Host	Host	<2	<0.05	<0.02	0.82	0.001	0.015	<0.00005	<0.0005	<0.0005	<0.005	<0.0025	0.884	0.005	1.5
C-421053	01-P499-783-398	GSR	cal	26.31	0.10	0.02	7.45	<0.002	<0.03	Host	Host	Host	Host	4.9	<0.05	<0.02	1.6	<0.005	0.035	<0.00005	<0.0005	0.0081	<0.005	<0.0025	0.673	0.036	0.0
C-421053	01-P499-783-398	GSR	cal	87.32	<0.02	<0.02	<0.05	45.68	3.32	Host	Host	Host	Host	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	0.9
C-421042	01-O556-754-509-4	GSR	dol	63.09	<0.02	<0.02	38.31	25.11	2.75	Host	Host	Host	Host	4.1	<0.05	0.14	9.48	<0.005	<0.01	0.00025	<0.0005	0.0048	<0.005	<0.0025	0.464	0.708	0.5
C-421062	01-W19-219(465-470)-5	GSR	dol	202.96	1.50	<0.02	33.76	51.15	7.71	Host	Host	Host	Host	17	3.7	<0.05	0.408	0.016	0.029	<0.00005	<0.0005	0.0019	0.01	<0.0025	0.871	0.014	
C-421060	01-W19-219-460-3	GSR	dol	41.63	0.51	<0.02	>500	20.59	2.64	Host	Host	Host	Host	13	<2	0.66	0.412	1.5	0.009	0.041	0.00014	<0.0005	0.013	<0.0025	0.604	0.07	
C-421059	01-W19-219(450-455)-2	GSR	dol	86.24	0.64	<0.02	30.03	20.44	3.1	Host	Host	Host	Host	14	2.2	1.18	0.365	7.59	0.006	0.018	0.00047	<0.0005	0.0066	<0.0025	0.488	0.173	
C-421041	01-O556-754-507-3	GSR	dol	152.60	1.20	<0.02	21.95	48.5	4.79	Host	Host	Host	Host	6.8	<2	<0.05	0.53	4.42	0.007	<0.01	0.00014	<0.0005	0.0509	<0.0025	0.474	0.216	
C-421038	01-R190-749-532-12	GSR	dol	69.36	0.47	<0.02	60.29	23.016	3.28	Host	Host	Host	Host	3.5	<2	<0.05	0.562	52.7	0.178	<0.01	0.00042	<0.0005	0.354	<0.005	95.1	0.311	0.4

All the data are in ppm; n.a. indicates that the sample was not analyzed for those elements; "<" detection limit value" indicates samples that were analyzed but yielded data below the detection limits of the techniques. Calcium and Mg data are not reported for the fluid inclusions hosted by carbonate, S, Zn, and Pb data are likewise not reported from the appropriate sulphides. The charge balance calculation is discussed in the text. IC= ion chromatography, AAS= atomic absorption spectroscopy, ICP = inductively-coupled plasma techniques, dol=doomite, m.dol=matrix dolomite, cal=calcite, gr=galena, sph=sphalerite.

Table 1. (cont.)

GSC sample	Field sample number	Location	IC		Br	F	SO ₄	AAS		ICP			K	Ca	Mg	Na	K	Fe	Mn	S	Ba	B	Cd	Co	Pb	Li	Ni	Sr	Zn	Charge Balance
			Min.	Cl				Na	SO ₄	Na	Ca	Mg																		
C-421025	01-R190-750-425-1	GSR	dol	352.80	<0.02	<0.02	75.40	90.1	13.17	Host	Host	15	2.9	<0.05	0.21	9.96	0.008	0.049	<0.00005	<0.0005	0.0087	0.009	<0.0025	0.544	0.211	0.4				
C-421021	01-V46-239-401-3	GSR	dol	124.07	0.28	<0.02	nd	26.62	4.83	Host	Host	23.7	2.7	0.84	0.5	9.15	0.007	0.031	0.00039	<0.0005	0.0045	0.012	<0.003	0.638	0.392					
C-421019	01-V46-239-392-1	GSR	dol	158.82	0.94	<0.02	35.22	55.53	5	Host	Host	9.9	<2	<0.05	0.05	9.94	<0.005	0.043	<0.00005	<0.0005	<0.0005	0.006	<0.0025	0.442	<0.005	0.5				
C-421017	01-X25-77(465-475)-4	GSR	dol	260.80	2.03	<0.02	63.90	68.61	8.4	Host	Host	21.4	3.2	<0.05	0.509	13.3	0.017	0.037	<0.00005	<0.0005	0.0006	0.014	<0.0025	1.56	0.036	0.4				
C-421013A	01-Z155-223(525-535)9	GSR	dol	283.60	1.89	<0.02	136.30	63.89	10.23	Host	Host	17	2.6	<0.05	0.347	22.5	0.012	0.041	<0.00005	<0.0005	<0.0005	0.013	<0.0025	0.998	0.012	0.3				
C-421047	01-P499-783-343	GSR	dol#1	16.92	0.12	0.07	30.02	4.71	0.59	Host	Host	4.5	<2	0.15	0.19	7.71	<0.005	<0.01	0.00018	<0.0005	0.0033	<0.0025	<0.0025	0.291	0.061	0.2				
C-421018	01-X25-77-475-5	GSR	dol#1	70.29	0.77	<0.02	6.46	15.97	2.66	Host	Host	18	2.5	0.28	0.278	3.9	0.011	0.042	0.00016	0.0014	0.0079	0.009	<0.003	0.578	0.045					
C-421014	01-X25-77-(444-448)-1	GSR	dol#1	39.74	0.20	<0.02	34.43	15.74	1.08	Host	Host	20.6	<2	<0.05	0.08	22	<0.005	0.055	<0.00005	<0.0005	0.0968	0.014	<0.0025	0.522	0.019					
C-421047	01-P499-783-343	GSR	dol#2	6.78	0.09	0.18	12.91	3.75	3.85	Host	Host	3.8	3.9	0.12	0.24	6.44	0.009	0.011	0.0001	0.0008	0.0044	0.005	0.0081	0.261	0.192	0.3				
C-421018	01-X25-77-475-5	GSR	dol#2	78.90	0.62	<0.02	6.48	19.94	2.92	Host	Host	11	2.1	<0.05	0.24	2.3	0.008	0.059	0.00013	0.0052	0.0044	0.007	0.0036	0.336	0.036					
C-421014	01-X25-77-(444-448)-1	GSR	dol#2	67.45	0.73	0.09	24.01	16.17	2.74	Host	Host	18	<2	0.19	0.262	10.3	0.006	0.039	0.00005	0.0006	0.0153	0.012	<0.0025	0.641	0.098	0.4				
C-421014	01-X25-77-(444-448)-1	GSR	gn	6.19	0.05	<0.02	Host	2.27	<0.03	150	73.8	4.3	<2	1.93	0.285	Host	<0.005	<0.02	0.00095	<0.001	Host	<0.01	0.0062	0.15	0.364	0.1				
C-421022	01-V46-239-404-4	GSR	gn	<0.02	<0.02	<0.02	Host	n.a.	n.a.	131	33.3	<2	<2	0.66	0.14	Host	<0.005	<0.01	0.00668	<0.0005	Host	<0.005	0.011	0.077	3.05					
C-421041	01-O556-754-507-3	GSR	gn	11.60	0.09	<0.02	Host	2.89	<0.03	548	7.3	<2	<2	0.21	0.05	Host	<0.005	<0.01	0.0362	<0.0005	Host	<0.005	<0.0025	0.219	19	0.1				
C-421049	01-P499-783-375	GSR	gn	8.97	0.08	<0.02	Host	1.61	n.a.	284	60.2	<2	<2	6.25	0.47	Host	<0.01	<0.02	0.211	<0.001	Host	<0.01	<0.005	0.14	147	0.1				
C-421011	01-Z155-223-327-7	GSR	m. dol	1.11	<0.02	0.08	2.37	0.72	n.a.	Host	Host	<2	<2	1.07	0.848	1.5	<0.005	<0.01	0.00015	0.0012	0.0067	<0.005	<0.003	0.074	0.337	0.8				
C-421012	01-Z155-223-332-8	GSR	m. dol	2.17	<0.02	0.36	2.86	1.5	n.a.	Host	Host	<2	4.7	0.22	0.649	3.35	0.01	0.014	0.0004	0.0018	1.29	0.006	0.0041	0.159	3.46					
C-421039	01-O556-754-499-1	GSR	m. dol	44.04	2.06	0.16	13.47	15.49	2.67	Host	Host	13	3.3	1.91	0.539	4.56	0.007	0.013	<0.00005	<0.0005	0.0094	0.008	<0.003	1.35	0.185	0.6				
C-421054	01-P499-783-404	GSR	m. dol	4.94	0.04	0.11	6.71	2.01	1.31	Host	Host	<2	2.3	3.12	0.807	5.77	0.01	<0.01	0.00107	0.0014	3.28	<0.005	0.0097	0.082	8.66					
C-421006	01-Z155-223-287-2	GSR	sph	5.78	0.07	0.03	Host	2.66	0.045	564	3.9	4.7	<2	0.52	4.7	Host	<0.005	0.083	0.0001	0.0009	1.57	<0.005	<0.0025	0.252	<0.005	0.1				
C-421022	01-V46-239-404-4	GSR	sph	11.73	0.11	<0.02	Host	4.56	0.22	508	52.6	<2	<2	9.13	0.581	Host	<0.005	<0.01	0.00134	0.0005	8.02	<0.005	<0.0025	0.142	Host	0.2				
C-421028	01-R190-749-490-2	GSR	sph	<0.02	<0.02	<0.02	Host	n.a.	n.a.	435	1.9	<2	<2	0.14	0.303	Host	0.006	<0.01	0.0006	0.0044	2.56	<0.005	0.0753	0.254	Host					

Table 1. (cont.)

GSC sample	Field sample number	Location	Min.	IC	Cl	Br	F	SO ₄	AAS	Ca	ICP	Mg	Na	K	Fe	Mn	S	Ba	B	Cd	Co	Pb	Li	Ni	Sr	Zn	Charge Balance
C-421041	01-0556754-507-3	GSR	sph	14.31	0.10	<0.02	<0.02	Host	3.28	n.a.	436	7.7	<2	<2	0.77	0.11	Host	0.012	<0.01	0.00006	<0.0005	0.395	<0.005	0.025	0.407	Host	
C-421048	01-P499-783-369	GSR	sph	<0.02	<0.02	<0.02	<0.02	Host	<0.002	n.a.	271	174	<2	<2	3.46	0.606	Host	0.198	<0.01	0.00032	<0.0005	0.14	<0.005	<0.003	2.45	Host	
C-421049	01-P499-783-375	GSR	sph	6.99	0.04	<0.02	<0.02	Host	4	0.69	354	218	6.1	<2	<0.05	0.24	Host	0.16	<0.01	<0.00005	0.001	0.0008	<0.005	0.012	5.15	Host	0.4
C-421051	01-P499-783-395	GSR	sph	7.36	<0.02	<0.02	<0.02	Host	2.93	n.a.	464	81.9	<2	<2	6.04	0.673	Host	<0.005	<0.01	0.00214	<0.0005	7.74	0.187	<0.0025	0.187	Host	
C-421229	Qlto-Q5-27	Qlto	cal	27.91	0.17	<0.02	<0.02	1.81	8.68	0.17	Host	Host	<2	<2	<0.05	0.22	0.85	0.005	<0.01	<0.00005	<0.0005	0.0081	<0.005	<0.0025	0.234	0.019	0.5
C-421246	HW-81-41-12	Hay West	cal	107.65	0.93	<0.02	<0.02	2.15	26.21	5.59	Host	Host	5.5	<2	<0.05	0.13	0.74	0.014	0.014	0.00011	0.0014	0.0094	<0.005	0.021	0.232	0.362	0.5
C-421239	HW-79-11-33	Hay West	dol#1	252.70	2.36	<0.02	<0.02	6.53	<0.002	n.a.	Host	Host	6.9	2.1	<0.05	0.22	18.4	0.025	0.012	0.00038	0.0097	0.0081	<0.005	0.0371	0.419	3.45	
C-421231	HW-80-29-46	Hay West	dol#1	320.70	2.10	<0.02	<0.02	32.40	98.5	11	Host	Host	9.2	<2	<0.05	0.537	5.3	0.041	0.013	0.00006	<0.0005	0.001	<0.005	<0.0025	0.436	0.042	0.5
C-421237	HW-80-31-31	Hay West	dol#1	249.62	1.84	<0.02	<0.02	6.19	54.48	10.01	Host	Host	7.7	2.1	<0.05	0.254	12.4	0.019	0.019	0.00024	0.0072	0.0056	<0.005	0.0346	1.46	1.57	0.4
C-421244	HW-81-45-17	Hay West	dol#1	174.85	1.12	<0.02	<0.02	19.95	49.98	4.45	Host	Host	6.8	<2	<0.05	0.466	9.25	0.012	0.015	0.00011	0.0018	0.0761	0.005	0.0692	0.301	0.0289	0.5
C-421245	HW-81-47-3	Hay West	dol#1	262.96	1.84	<0.02	<0.02	11.440	68.28	10.37	Host	Host	12	2.4	<0.05	0.526	12.7	0.007	0.015	0.00005	<0.0005	0.016	0.006	0.0324	0.529	0.094	0.4
C-421239	HW-79-11-33	Hay West	dol#2	368.60	2.93	<0.02	<0.02	15.30	82.2	14.6	Host	Host	13	2.4	<0.05	0.457	3.93	0.037	0.027	0.00014	<0.0005	0.0047	0.008	<0.003	0.671	0.081	0.4
C-421238	HW-80-14-29	Hay West	dol#2	220.48	1.21	<0.02	<0.02	35.00	60.83	7.31	Host	Host	16	2.7	<0.05	0.16	6.98	0.008	0.03	<0.00005	0.0012	0.0021	0.009	0.0499	0.604	0.056	0.5
C-421231	HW-80-29-46	Hay West	dol#2	271.30	1.48	<0.02	<0.02	49.41	88.4	7.9	Host	Host	13	<2	<0.05	0.33	9.33	0.013	0.038	<0.00005	<0.0005	<0.0005	0.01	<0.0025	0.577	0.005	0.5
C-421246	HW-81-41-12	Hay West	dol#2	231.70	1.60	<0.02	<0.02	10.00	49.3	10.55	Host	Host	9.2	2.9	<0.05	0.14	1.4	0.009	0.011	0.00015	0.0013	0.0112	0.006	0.0399	0.35	0.173	0.4
C-421245	HW-81-47-3	Hay West	dol#2	151.80	0.94	<0.02	<0.02	50.35	43.54	6.2	Host	Host	9.7	<2	<0.05	0.1	2.88	0.006	0.012	<0.00005	0.0012	0.005	<0.005	0.0999	0.572	0.005	0.4
C-421235	HW-81-50-10	Hay West	dol#2	91.81	0.52	<0.02	<0.02	4.47	29.07	3.33	Host	Host	6.9	<2	<0.05	0.618	0.76	0.032	0.013	0.00008	<0.0005	0.001	<0.005	<0.0025	0.517	0.056	0.6
C-421234	HW-79-9-20	Hay West	dol#3	<0.02	<0.02	<0.02	<0.02	<0.05	<0.002	<0.03	Host	Host	6.3	<2	<0.05	0.074	131	0.005	0.021	<0.00005	<0.0005	0.0013	<0.005	<0.0025	1.1	0.048	
C-421238	HW-80-14-29	Hay West	m. dol	107.20	0.60	<0.02	<0.02	2.89	37.37	3.78	Host	Host	8.3	<2	<0.05	0.17	1.6	0.005	0.021	0.00005	0.0017	0.0888	0.006	0.0443	0.224	0.046	0.6
C-421236	HW-80-31-14	Hay West	m. dol	216.88	1.69	<0.02	<0.02	132.08	54.39	10.29	Host	Host	13	2.2	<0.05	0.22	2	0.022	0.035	<0.00005	<0.0005	0.006	0.009	<0.0025	0.655	<0.005	0.4
C-421246	HW-81-41-12	Hay West	m. dol	101.65	0.63	<0.02	<0.02	3.35	21.06	4.96	Host	Host	6.5	<2	<0.05	0.14	1.6	0.01	0.011	0.00009	0.008	0.0362	<0.005	0.173	0.268	0.146	0.4
C-421247	RR3800	Alberta	cal	12.30	<0.02	<0.02	<0.02	18.0	5.62	0.6	Host	Host	3.2	<2	<0.05	0.054	5.7	1.28	<0.01	<0.00005	0.0019	0.0035	<0.005	0.014	9.89	<0.005	0.4
C-421247	RR3800	Alberta	m. dol	18.48	0.164	0.30	<0.02	18.1	5.76	12.85	Host	Host	2.6	8.2	<0.05	0.15	12.5	0.064	0.116	<0.00005	0.0124	0.0021	0.01	0.018	0.511	0.096	1.4
C-421248	RR3805	Alberta	cal	<0.02	<0.02	<0.02	<0.02	<0.02	<0.002	<0.03	Host	Host	<2	<2	<0.05	0.091	1.4	1.16	<0.01	<0.00005	0.0279	0.0081	<0.005	0.0827	0.163	<0.005	
C-421248	RR3805	Alberta	m. dol	22.91	<0.02	<0.02	<0.02	0.39	21.4	7.99	Host	Host	2.6	7.2	<0.05	0.18	10.6	0.049	0.101	0.00043	0.012	0.0014	0.007	0.019	0.415	<0.005	1.4
C-406494	RR1099	Alberta	m. dol	86.28	1.04	<0.02	<0.02	6.0	4.01	2.5	Host	Host	<2	<2	<0.05	0.925	1.5	0.065	0.045	0.00007	0.0006	0.0012	0.006	<0.0025	0.542	0.074	0.1
C-406495	RR1100	Alberta	m. dol	7.23	0.08	0.031	0.031	0.5	1.46	<0.03	Host	Host	<2	<2	<0.12	0.272	0.55	0.054	0.02	<0.00005	0.0006	<0.0005	0.007	<0.0025	0.323	0.008	0.3
C-406496	RR3751	Alberta	m. dol	6.94	0.09	0.10	0.10	0.2	1.25	<0.03	Host	Host	<2	<2	<0.05	0.476	<0.3	0.049	0.021	0.0001	0.0016	<0.0005	0.005	<0.0025	0.299	0.022	0.3
C-406499	RR3754	Alberta	m. dol	5.63	<0.02	<0.02	<0.02	3.9	1.87	<0.03	Host	Host	<2	<2	<0.05	0.446	1.9	0.73	0.011	<0.00005	0.0035	0.0006	<0.005	<0.0025	0.454	0.008	0.3
C-406500	RR3755	Alberta	m. dol	3.68	<0.02	<0.02	<0.02	9.9	1.34	<0.03	Host	Host	<2	<2	<0.05	0.08	1	0.061	<0.01	<0.00005	<0.0005	<0.0005	<0.005	<0.0025	0.256	<0.005	0.2
C-406461	RR3801	Alberta	m. dol	21.73	0.378	<0.02	<0.02	1.9	<0.002	<0.03	Host	Host	<2	<2	<0.05	0.287	1.2	0.087	<0.01	<0.00005	<0.0005	<0.0005	<0.005	<0.0025	0.398	<0.005	

All the data are in ppm; n.a. indicates that the sample was not analyzed for those elements; "< detection limit value" indicates samples that were analyzed but yielded data below the detection limits of the techniques. Calcium and Mg data are not reported for the fluid inclusions hosted by carbonate. S, Zn, and Pb data are likewise not reported from the appropriate sulphides. The charge balance calculation is discussed in the text. IC= ion chromatography, AAS= atomic adsorption spectroscopy, ICP = inductively-coupled plasma techniques, dol=dolomite, m. dol=matrix dolomite, cal=calcite, gr=galena, sph=sphalerite.

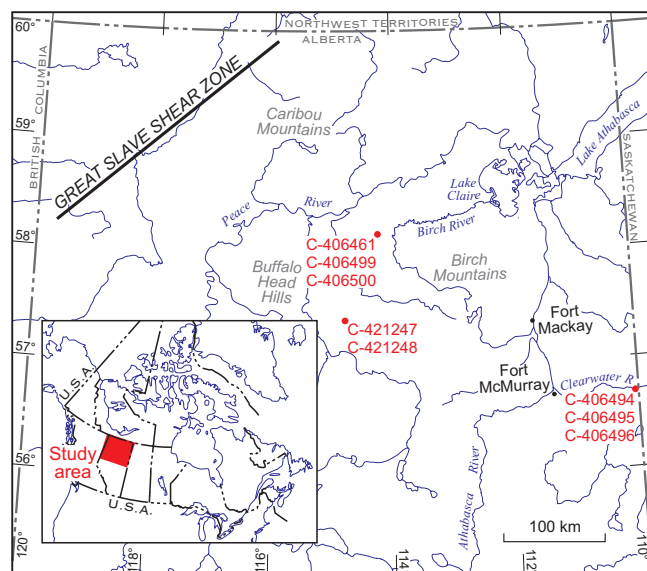


Figure 2. Sample location map, northern Alberta (after Rice and Lonnee, 2006).

Methodology

Sample preparation and analytical technique

Specific sample phases were carefully cut from core or hand sample using a trim rock saw. The samples were crushed and sieved to a 1–2 mm size fraction and hand picked under a binocular microscope to obtain 2 g of a clean mineral separate. In some cases, where the amount of available sample was limited, it was necessary to analyze impure mineral separates. In this instance, the compositions and relative proportions of the sample and the contaminant phases were recorded. Following crushing, sieving, and cleaning, all samples were then washed in ultra-clean water and heated overnight on a hot plate, then dried in an oven. A portion of the sample (1–2 g) was ground to a fine powder in an agate mortar and pestle in a clean and controlled environment. Half the powder was transferred to an unreactive vial and 5 ml of clean water was added. These samples were shaken, and filtered through 0.2 micron filters to give a clean leachate. Anions (Cl, Br, F and sulphate) were analyzed using a Dionex DX600 ion chromatograph (IC) at the University of Alberta. Sodium and K were analyzed on the same leachate using atomic adsorption spectroscopy (AAS). Ten ml of an acidified La-solution was added to the remainder of the crushed sample, this solution was centrifuged and the cations were analyzed by Norwest Labs in Edmonton by Inductively Coupled Plasma – Atomic Emission Spectrometry (ICP–AES) for the major cations (Na, K, Mg, Mn, Fe, and Ca) and Inductively Coupled Plasma–Mass Spectrometry (ICP–MS) for the minor and trace elements (e.g. S, Ba, B, Cd, Co, Pb, Li, Ni, Sr, As, Be, Bi, Cd, Cr, Cu, Mo, Ag, Th, Sn, Ti, and Zn). The data for the 73 crush-leach samples that were analyzed are presented in Table 1. In many samples, Cl, Br, total SO_4 , Na,

K, Ca, Li, Mg, Fe, Mn, Si, Ba, B, Pb, Sr, and Zn were detected. Fluoride, Co, and Ni were detected in a small number of samples. Anions and cations of significance to this study are presented in this section.

Results

It is important to note that the results in Table 1 do not represent the concentrations of the elements in the mineralizing fluids, because the number and total volume of inclusions in each sample is unknown; rather, these are the concentrations measured in the leachates. In order to calculate full fluid chemical analyses, detailed microthermometric data from each sample are needed. This data was only available for a small number of samples, therefore, the data are discussed below in terms of molar element ratios in the mineralizing fluids.

Anion geochemistry

Fine-grained “matrix” dolomite

Chlorine and sulphate were identified in all fine-grained “matrix” dolomite samples and concentrations vary from 1.11 to 216.88 ppm and 0.2 to 132.08 ppm, respectively. Bromide was detected in all but five dilute samples, and ranged from 0.04 to 2.06 ppm. The maximum fluoride concentration in the leachates was 0.39 ppm, however, it was not detected in three of the Hay West and three of the northern Alberta samples (Table 1).

The Cl/Br (molar) ratios for the fine-grained “matrix” dolomite range from 48 to 402 (Fig. 3). The lowest ratio comes from the GSR property, whereas ratios from Hay West samples range from 289 to 402, and those from northern Alberta have values between 129 and 254 (Table 2).

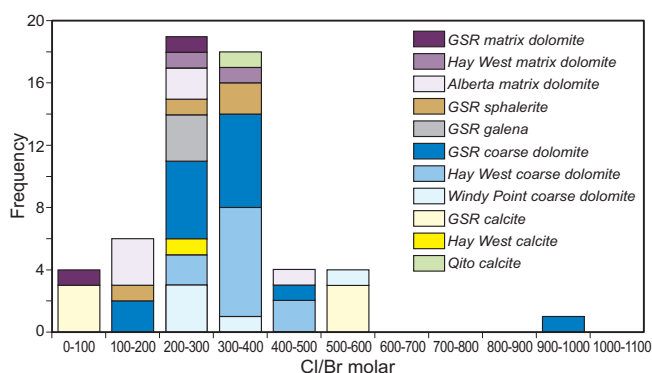


Figure 3. Histogram of the molar Cl/Br ratio of fluid inclusions hosted by fine-grained “matrix” dolomite, sulphides, coarse-grained dolomite and calcite from all five study areas. The Cl/Br molar ratio of seawater is approximately 565 (Fontes and Matray, 1993). Values less than seawater represent Br-enriched brines, and values greater than seawater may have a halite dissolution component to the fluids.

Table 2. Summary of the range of molar ratio data for the minerals sampled from the study area

Location	Host mineral	Cl/Br (molar)	Cl/SO ₄ (molar)	K/Na (molar)	Li/Na (molar)	Zn/Na (molar)	Pb/Na (molar)	Sr/Na (molar)	Ca/Na (molar)	Na/Br (molar)	SO ₄ /Br (molar)	K/Br (molar)	Ba/Na (molar)	B/Na (molar)
GSR	Matrix dolomite	48, 278	1–9	0.102, 0.384	0.002	0.00501	0.00008	0.027	Host	26,175	5,140	3,67	0.00009	0.002
	Sphalerite	186–393	Host	0.01–0.102	-	Host	Host	0.014, 0.221	33.4, 69.0	114–347	-	1–35	0.004	0.04
	Galena	253–290	Host	-	-	Host	Host	0.009	20.01	70–158	-	-	-	-
	Coarse-grained dolomite	170–999	1–33	0.040–0.605	0.002–0.004	0.0003–0.0607	0.000003–0.01122	0.007–7.129	Host	72–330	7–208	7–87	0.00005–0.009	0.003–0.01
	Calcite	14–592	0.07–10	0.023–0.086	-	0.0026	0.00018	0.036	Host	9–447	38–3380	0.3–16	-	0.015
Hay West	Matrix dolomite	289–402	4–100	0.059–0.139	0.002, 0.002	0.0020, 0.0079	0.00005–0.0012	0.007–0.013	Host	112–216	4–65	12–16	0.0001–0.0003	0.004–0.006
	Coarse-grained dolomite	241–413	6–109	0.053–0.126	0.002–0.003	0.00014–0.1758	0.00001–0.00124	0.010–0.050	Host	97–207	2–52	8–14	0.00008–0.0008	0.003–0.006
	Calcite	261	135	0.126	-	0.023	0.00019	0.011	Host	98	2	12	0.0004	0.005
Windy Point	Coarse-grained dolomite	253–550	78–291	0.01–0.029	0.002	0.0017–0.012	0.00004, 0.00007	0.018–0.048	Host	7–226	1–7	0.2–2	0.0004–0.0007	0.004–0.007
Qito	Calcite	370	42	0.012	-	-	-	-	Host	177	9	2	-	-
Alberta	Matrix dolomite	129–254	1–94	0.368–1.312	0.009, 0.013	0.01299	0.00006, 0.00009	0.042, 0.051	Host	13–122	2–92	5,160	0.003, 0.004	0.08, 0.09
	Calcite	-	2	0.063	-	-	0.00012	0.811	Host	-	-	-	0.07	-
Single numbers indicate that only one ratio could be calculated.														

Sulphides

Chlorine and Br concentrations in the leachates from sphalerite and galena from the GSR property range from 5.78 to 14.31 ppm, and 0.04 to 0.11 ppm, respectively (Table 1). Fluoride was present at low levels in two GSR samples (0.01 and 0.03 ppm). The sulphate data is not reported, as the degree of contamination by the sulphide host minerals cannot be assessed.

Galena and sphalerite samples cannot be differentiated in terms of their Cl/Br ratios in the fluids (Fig. 3). Cl/Br ratios for galena and sphalerite from the GSR area range from 186 to 393 (Table 2).

Coarse-grained dolomite

In general, the coarse-grained dolomite samples analyzed in the study contain large numbers of fluid inclusions and consequently have high solute concentrations in the leachates.

Anion concentrations of the GSR leachates (determined for 17 samples) have Cl values ranging from 6.78 to 352.80 ppm, Br values from 0.09 to 2.03 ppm (with the exception of two leachate analyses (C-421042 and C-421025) for which no results could be obtained), and F concentrations from 0.07 to 0.18 ppm (detected in three samples). Sulphate data was acquired from 16 samples, with one of these samples (C-421060), having an anomalously high SO_4 value of >500 ppm. With the exception of samples C-421060 and C-421047-dol#2, all samples have SO_4 values that are less than their associated chloride values, suggesting that Cl is the dominant anion in the fluids.

The leachates from 11 Hay West samples consistently have high Cl values (ranging from 91.81 ppm to 368.60 ppm), high Br values (0.52–2.93 ppm) and F below the detection limits of the technique. The sulphate values are variable (4.47–114.40 ppm) but are consistently lower than the associated Cl concentrations in the leachates.

The Cl and Br values from the five Windy Point samples (134.65–415.32 ppm and 0.64–3.48 ppm, respectively) are comparable with those from Hay West and, similarly, F is not detected. The SO_4 values in the leachates, however, are much less variable and range from 1.25 to 6.12 ppm (Table 1).

The samples from GSR have a relatively wide range of Cl/Br ratios (170–999). Two samples (C-421025 and C-421042) have high concentrations of Cl in the leachates but Br was not detected, suggesting that these two samples also have Cl/Br ratios in excess of 999. The samples from Hay West and Windy Point have Cl/Br ratios in the range 241 to 413 and 253 to 550, respectively (Fig. 3).

GSR samples have variable SO_4/Br molar ratios that range from 7 to 208, whereas the values from the Hay West samples vary from 2 to 52. The five samples from Windy Point have a much more restricted range (1–7).

Calcite

Fluid inclusions in the late-stage calcite samples have lower salinities and are less abundant than those observed in the other phases sampled. Therefore, the total salinity of the leachates is lower and in many cases it was not possible to detect Br. Chloride, which was detected in all the calcite leachates from GSR, varies from 1.60 to 87.32 ppm, Br from 0.05 to 1.00 ppm (detected in six samples), and SO_4 ranging from 0.60 to 203.20 ppm (detected in eight samples). A single leachate from the Hay West area had Cl, Br, and SO_4 values of 107.65 ppm, 0.93 ppm, and 2.15 ppm, whereas a single leachate from the Qito area had Cl, Br and SO_4 values of 27.91 ppm, 0.17 ppm, and 1.81 ppm, respectively. Although Cl was detected in one of the two calcites sampled from northern Alberta, Br and F were not detected in any of the samples. Sulphate concentration was detected in one Alberta calcite sample, giving a value of 18 ppm.

Fluid inclusions in samples from GSR had Cl/Br ratios from 14 to 592 (Fig. 3). The Qito and Hay West samples had values of 370 and 261, respectively. The SO_4/Br ratios over all three areas were highly variable and ranged from 2 at Hay West and 9 at Qito to 3380 at GSR (Table 2).

Cation chemistry

Fine-grained “matrix” dolomite

Sodium and K concentrations were commonly below the detection limit of the ICP–AES for most samples, however, when they were detected, Na (detected in six samples) ranged from 2.6 to 13 ppm, whereas K (detected in six samples) ranged from 2.2 to 8.2 ppm (Table 1). Sodium and K, measured by AAS, give leachate values of 0.72 to 54.39 ppm and 1.31 to 16.31 ppm, respectively. Calcium and Mg data were not reported, as contamination by the host mineral will have affected the concentration of these elements. Strontium was detected in all the fine-grained “matrix” dolomite leachates and had values ranging from 0.074 to 1.35 ppm, but may also have a contribution from the host mineral. Iron, which was detected in the GSR samples and one sample from northern Alberta (C-406495), ranged from 0.12 to 3.12 ppm, whereas Mn, which was detected in all fine-grained “matrix” dolomite leachates, ranged from 0.08 to 0.925 ppm. Barium and B were detected in most samples and had values ranging from 0.005 to 0.73, and 0.011 and 0.116, respectively. Lead was detected in all leachates: Zn was detected in all but one leachate from the Northwest Territories, and their concentrations were as high as 3.28 ppm and 8.66 ppm, respectively (both of which are determined from leachates from the GSR samples). Lithium, Cd, Co, and Ni were also detected in some of the fine-grained “matrix” dolomite leachates but these elements showed no systematic spatial variation.

The K/Na and Li/Na molar ratios in fine-grained “matrix” dolomite inclusions varied from 0.053 to 1.316 and 0.002 to 0.013, respectively (Table 2). The highest K/Na and Li/Na

values come from one of the northern Alberta samples (C-421247). This sample and another northern Alberta sample in the same location (C-421247 and C-421248, see Fig. 2) have the highest Sr/Na ratio values (0.051 and 0.042, respectively). Lower Sr/Na values occur at GSR and Hay West (0.007–0.027). The Zn/Na molar ratios of the matrix dolomite samples have values ranging from 0.0020–0.01299 (Table 2). Unlike the Ba/Na molar ratios, the B/Na ratios are relatively consistent in all the sample areas and have a modal value of about 0.005 (Table 2).

Sulphides

Sodium was not detected in many of the sulphide leachates using ICP–AES so the number of ratios calculated is limited. Potassium was consistently below the detection limit of this technique and was only detected in three samples using AAS (Table 1). All samples yielded high Ca concentrations, ranging from 131 to 564 ppm ($n=11$) in the GSR leachates (Table 1). Calcium concentrations in all samples were significantly higher than Na. Magnesium values were also highly variable, with a range of 1.9 to 218 ppm. Zinc, Pb, Fe, Mn, and Cd had highly variable concentrations depending on the host mineral. Boron and Li were rarely detected in the sulphide leachates and Ba was also less common; this may be due to a smaller number of inclusions in the samples.

The K/Na ratios from the GSR area range from 0.010 to 0.102 (Table 2). The Ca/Na ratios range from 20.0 to 69.0 and Sr/Na ratios from 0.009 and 0.221. On the basis of the small data set there is no systematic relationship between the two elements; i.e. the sample with the highest Ca/Na ratio does not also have the highest Sr/Na ratio.

Coarse-grained dolomite

The concentrations of Na and K in the leachates analyzed by AAS from GSR, Hay West, and Windy Point were similar, ranging from 3.75 to 98.5 ppm ($n=32$) and 0.34 to 14.6 ppm ($n=32$). Manganese, which was identified in all the leachates, ranged from 0.05 to 0.621 ppm, whereas Fe (detected in nine leachates) ranged from 0.12 to 3.39 ppm, most of those being from the GSR area. Strontium, which was present in all the leachates, had variable concentrations, from 0.125 to 150 ppm (Table 1). Barium, B, Li, Pb, and Zn were detected in many samples but there appeared to be no systematic variation between sample sites.

The fluids in the coarse-grained dolomite samples from GSR have K/Na molar ratios from 0.040 to 0.605, values from Hay West varied from 0.053 to 0.126, and Windy Point samples ranged from 0.010 to 0.029 (Table 2). In total there was no significant variation in the K/Na molar ratio between samples from GSR and Hay West, although the K/Na ratios from Windy Point are in general lower than in the other areas.

Most of the Sr/Na ratios from GSR data fall within a reasonably narrow range (0.007–0.03) with the exception of one sample that had an anomalously large ratio of 7.102. Two samples from Hay West (both 0.05) and one from Windy Point (0.048) had Sr/Na molar ratios that were slightly higher than the GSR data.

The bulk of the Li/Na data from GSR have values around 0.002 but there was a single elevated value at 0.004 in sample C-421047. This sample also had an elevated K value. The Li/Na molar ratios from Hay West varied from 0.002 to 0.003 and the single ratio obtained from the Windy Point area had a value of 0.002.

The Zn/Na and Pb/Na molar ratios were quite variable, although commonly Zn concentrations in the fluids were at least an order of magnitude greater than Pb. The Pb/Na ratios for GSR samples were as high as 0.01124 and the Zn/Na values varied between 0.0003 and 0.0607. The Hay West and Windy Point data for both ratios were comparable with the GSR fluids.

Calcite

The calcite leachates are quite dilute and Na, K, and Li are generally below the detection limits of the ICP–AES with the exception of three Na values of 3.2, 4.9, and 5.5 ppm. Sodium and K values acquired by AAS, range from 1.53 to 45.68 ppm and 0.14 to 5.59 ppm, respectively. Iron was detected in only one GSR sample (0.22 ppm), and values for B, Pb, and Zn are comparable with those from the Hay West and Qito samples. The calcite samples from northern Alberta (C-421247 and C-421248) have elevated Ba values (see Table 1). The Sr concentrations of the leachates are detectable in all samples, ranging from 0.159 to 130 ppm.

Only one K/Na molar ratio is measured in the northern Alberta samples (Table 2); this ratio has a value of 0.063 and is comparable to the ratios of the GSR fluids (0.023–0.086) and the single Qito sample (0.012), but is lower than the Hay West sample (0.126).

DISCUSSION

Charge balance and contamination issues

Once the data have been acquired, an assessment of the quality of the data is carried out. In particular, one of the major concerns is whether the data generated truly represent the composition of the fluid inclusions or have been contaminated by the host mineral. One of the first steps in assessing the quality of the data is a charge balance calculation, since in most hydrothermal fluids the overall charge is neutral. Such a calculation is only possible if you have both anion and cation

data on the fluids. If the units of the analyses are not molar, charge balance is carried out using the following equation (Shepherd et al., 1985):

$$\frac{\sum \text{Charge} * (\text{Concentration} / \text{Atomic mass})_{\text{cation}}}{\sum \text{Charge} * (\text{Concentration} / \text{Atomic mass})_{\text{anion}}} \quad (1)$$

Ideally, the charge balance should be within about 10 % of unity. In this study a charge balance calculation was carried out where possible on the samples analyzed by IC and AAS. This calculation, therefore, is based on the Cl, Br, F, Na, and K values measured in the sulphides and the Cl, Br, F, SO₄, Na, and K compositions of the carbonate minerals; that is, all the fluids analyzed are missing at least one major solute from the charge balance calculations. The charge balance for the carbonate and sulphide minerals range from 0.1 to 1.5, with the majority of the fluids having a charge balance of 0.4 to 0.5. This suggests that there is an excess of anions in the fluids and is consistent with the lack of Ca and Mg data for the leachates. The fluids will also contain carbonate species, which cannot be analyzed using the IC technique so in reality, the anion excess is even greater than suggested by the charge balance.

The problem of contamination by mineral inclusions will also affect some of the other analyses. Several of the calcite samples have anomalously high Sr and sulphate concentrations, suggesting that there are small inclusions of celestite (SrSO₄) present in the samples. Equally, some of the coarse-grained dolomite samples have high Zn, Pb, S or sulphate concentrations, which may indicate the presence of small sulphide inclusions in the host mineral. Two of the northern Alberta samples likewise have anomalous compositions. C-421247 and C-421248 have high sulphate values and all the elemental ratios to Na seem anomalously high, suggesting that the samples are depleted in Na. At the time of writing this report there are no microthermometric data available for these samples, so it is difficult to judge whether this is truly representative of the fluids in these samples.

Origins of the fluids and water-rock interaction

The bulk of the fluids analyzed in this study have Cl/Br ratios that are lower than seawater (Cl/Br molar ratio of 565; Fontes and Matray, 1993); that is, these fluids are relatively Br-enriched brines (Fig. 3). They are found in fine-grained "matrix" dolomite, sulphides, coarse-grained dolomite, and calcite from all the sample areas. This suggests that the fluids originated as seawater, which evaporated past the point of precipitation of halite, and for some samples, past K-Mg salt saturation. This suggestion is in agreement with a previous fluid inclusion halogen study on the Pine Point deposits (Tesler, 1999).

There are some variations in the data from the predicted behaviour of evaporated seawater in terms of Na-Cl-Br concentrations. Some of the data plot on or close to the seawater evaporation trajectory (SET; Fig. 4). Most of the data,

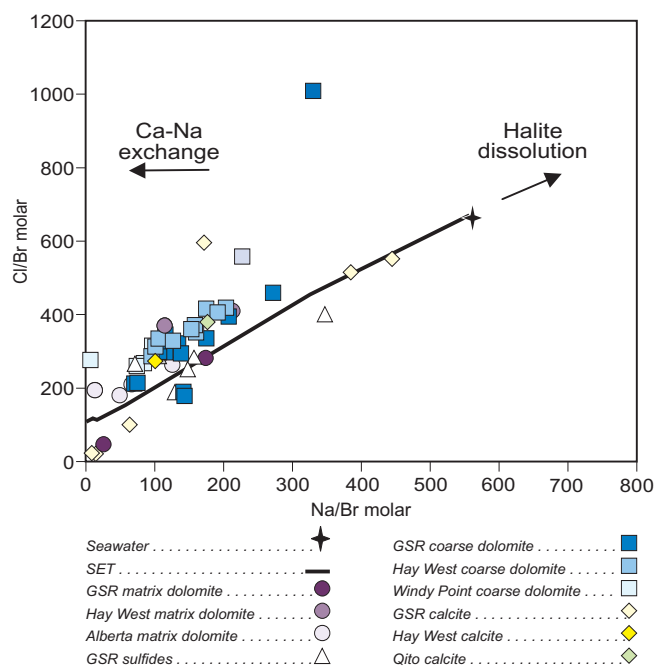


Figure 4. Data for all Br-enriched samples plotted on Na-Cl-Br diagram (after Kesler et al., 1995). There is no systematic variation in composition between sample localities or across the paragenesis. Many of the samples sit to the left of the seawater evaporation trajectory (SET) suggesting that there has been some modification of the Na content of the fluids on the flow path. The source for the data for the SET is Fontes and Matray (1993).

however, lie to the left of this line, suggesting that there has been some loss of Na or gain of Cl in the fluids relative to evaporated seawater compositions.

Chlorine and Br are thought to be relatively conservative in most geological environments and, therefore, such shifts are commonly interpreted to be the result of the loss of Na during water-rock interaction. If these samples did indeed originate as evaporated seawater, the bulk of them have lost up to a maximum of half their Na to account for the shift to the left of the evaporated seawater line. One of the samples from Windy Point (C-421222) has an extremely low Na/Br ratio of 7. In this sample, a large amount of Na has been lost (approx. 90%).

One coarse-grained dolomite and one calcite sample (C-421021 and C-421053 from GSR) have elevated Cl/Br ratios, suggesting that these fluids have acquired Cl relative to Br. However, neither sample has a Na/Br ratio significantly higher than seawater values. This relationship may suggest that if the Cl excess is being produced from the dissolution of halite, then these two samples have lost significant Na. Alternatively, the Cl could have been acquired from a Cl-bearing mineral that does not contain much Na, such as sylvite, but neither sample has elevated K (see below).

A third, more enigmatic group of samples has also been identified in this study. The samples (n = 4) of this group are characterized by very low Cl/Br and Na/Br ratios that lie off

the SET (Fig. 4) and are found only in matrix dolomite and calcite from the GSR study area. One possible explanation is that these fluids have anomalously high levels of Br, as a result of dissolution of Br-rich evaporites.

Recognizing fluid mixing and identifying end-members can be problematic using the Na-Cl-Br molar ratio diagram. In order to assess potential end members, absolute Cl and Br data have been calculated for the small number of samples that have sufficient microthermometric salinity data (Turner, 2006). These data are then plotted on a log-log plot (Fig. 5; Carpenter, 1978). Even with a small amount of well-constrained data, several conclusions can be drawn. The diagram highlights the large spread of Br for relatively constant Cl concentrations in the GSR dolomite samples. One sample lies to the left of the seawater evaporation curve, suggesting there may be a component of a halite dissolution fluid. The matrix dolomite sample is highly Br-enriched, and sits off the seawater evaporation curve, suggesting that normal evaporative processes are unlikely to produce this signature. The bulk of the coarse-grained dolomite samples in the study do plot on or close to the SET, and, thus can be interpreted as having formed from evaporated seawater. It should be noted however, that mixing the Br-enriched matrix dolomite fluid and the somewhat Cl-enriched end-member could also produce this spread of data. Another feature emphasized by the diagram is that although some of the coarse-grained dolomite and calcite have similar halogen ratios, their salinity is less than most of the coarse-grained dolomite and the sulphides. This suggests that these samples may represent a mixture of the coarse-grained dolomite-forming fluids and a dilute fluid, possibly meteoric water.

In terms of the alkali metal ratios of the fluids, the K/Na and Li/Na ratios of the fluids are comparable in the coarse-grained dolomite samples from the Hay West and GSR areas. The compositions of the fluids, however, have been modified from an evaporated seawater composition and may have been enriched in either K or Li, or a combination of both elements (Fig. 6), since Figure 4 suggests that Na depletion cannot fully account for the variation. In order to assess whether K has been significantly modified, the data have been plotted on a K-Cl-Br diagram (Fig. 7). The matrix dolomite samples have highly variable K/Br ratios. The bulk of the coarse-grained dolomite samples from GSR and Hay West plot on the evaporative path for normal seawater, suggesting that if this is the origin for these fluids, their K concentrations have not been strongly modified along their flow path. All the Windy Point coarse-grained dolomite samples show a marked depletion in K, suggesting that their dolomitizing fluids had a different water-rock interaction history. Some of the late-stage calcite samples have low apparent K/Br ratios, but since many of these samples are bromine-enriched, it is likely that they may actually be slightly enriched in K.

Most of the coarse-grained dolomite samples from Hay West and GSR should have K/Na ratios on or close to the seawater evaporation curve, past the point of halite precipitation but before the precipitation of K-Mg salts. This suggests that

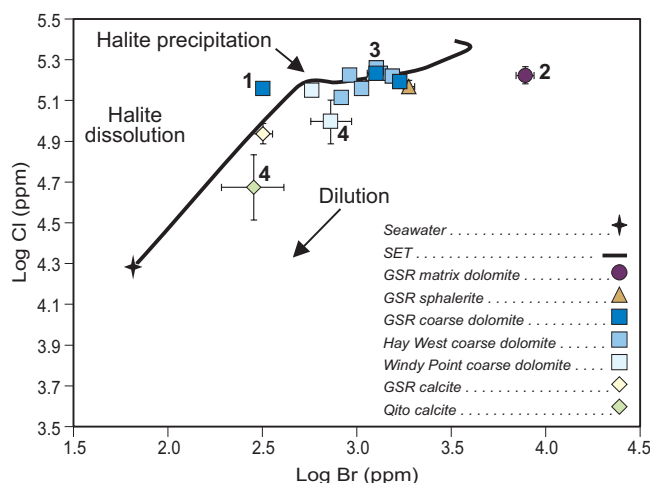


Figure 5. Log-log plot of absolute Cl concentrations (ppm) against Br (ppm). Absolute concentrations are derived using the mean salinity calculated from microthermometric data (from Turner, 2006). The error bars represent the full spread of the microthermometric data. This plot outlines the end-member compositions encountered in this project: 1. a Cl-rich fluid possibility indicating some input from halite dissolution fluids; 2. a Br-rich fluid, here found in one matrix dolomite sample from the GSR property; 3. the bulk of the data sits on or near the seawater evaporation trajectory past the point of halite dissolution. The possibility that these fluids may represent a mixing of fluids 1 and 2 is unlikely but cannot be ruled out without a more detailed petrographic and microthermometric study; 4. the calcite samples and one of the dolomite samples may have undergone some mixing with a more dilute fluid, such as meteoric water.

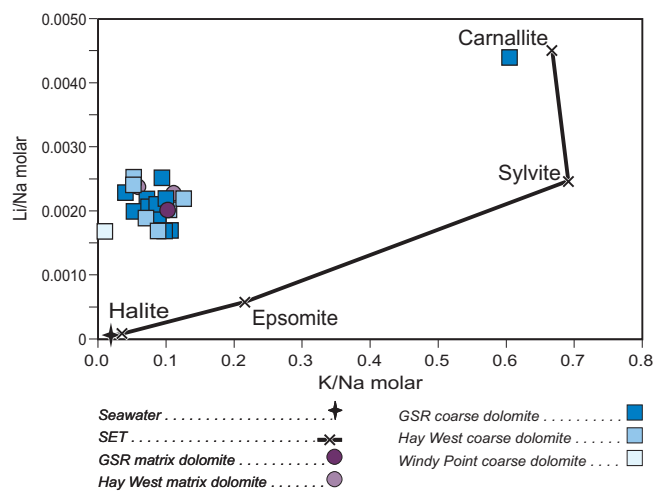


Figure 6. Plot of Li/Na vs. K/Na in fluid inclusions from coarse-grained dolomite and fine-grained "matrix" dolomite. The alkali elements in the fluids have compositions that have been modified from those of evaporated seawater (Fontes and Matray, 1993). All the fluids have elevated Li contents, but K contents are consistent with evaporated seawater. This suggests that the fluids did not acquire K along their flow path by interaction with feldspathic sequences. However, the slight elevation in Li may indicate some interaction with clay- or mica-bearing sequences. The two very high K-bearing samples from the Grosmont Formation in northern Alberta are not plotted on this diagram.

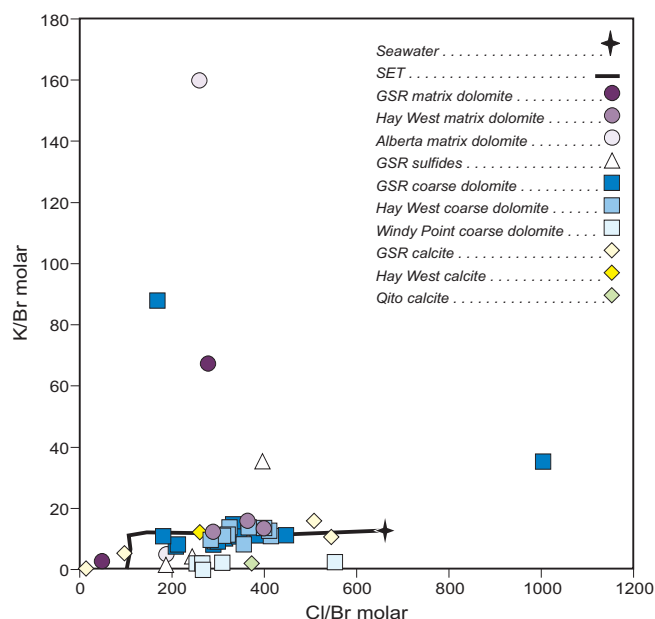


Figure 7. The data plotted in K-Cl-Br space. Although many of the matrix dolomite samples have comparable Cl/Br ratios, they have highly variable K/Br molar ratios, which may suggest the presence of multiple fluids in these samples. The bulk of the coarse-grained dolomite from GSR and Hay West sits on the seawater evaporation trajectory, indicating that the K content of these fluids has not been modified by water-rock interaction subsequent to their formation. A notable exception to this are the dolomite samples from the Windy Point area, which have lost significant K, suggesting that these fluids may have had a different fluid-flow history.

the deviation from SET seen in Figure 6 is due to an enrichment of Li in these samples. Indeed, the Cl/Br ratio of the GSR sample with high apparent K/Na (C-421047dol#2) is 171, close to the Cl/Br ratio of evaporated seawater to sylvite saturation. Thus, normal evaporative processes could explain the high K/Na ratio. The two matrix dolomite samples from Alberta have compositions that are not compatible with the SET. However, as discussed above, without the results of a petrographic and microthermometric study on these samples, it is not clear whether these data reflect contamination or represent a real K-rich fluid composition.

One of the common processes that can lower the Na content of basinal fluids is the albitization of Ca or K-bearing feldspars. Many basinal fluids have a characteristic 2:1 relationship between Ca and Na concentrations. This is not observed in the fluids analyzed in this study; however, such a relationship may be masked by the subsequent addition of Ca to the fluids by another process. Equally, the lack of enrichment in K and the relative depletion in Na may indicate the mineralizing fluids have not significantly interacted with K-feldspar bearing sequences. The Li concentrations of the fluids have also been altered somewhat. Neither limestone nor feldspars contain significant amounts of Li and are unlikely to explain the enrichment. Banks et al. (2002)

suggested that micas and some clay minerals are the major reservoir for Li in crustal rocks and it may be that the fluids in this study have interacted with mica or clay-bearing units. The levels of Li in these fluids however, are not high enough to indicate significant interaction with crystalline basement rocks (e.g. Banks et al., 2002), although minor interaction with basement rocks and/or clastic sediments likely did occur.

One of the unusual features of the fluids analyzed is the high concentration of Ca and Mg. The microthermometric data suggest that the ratio of Ca to Na of the type 1 fluid is at least 10:1 (Turner, 2006). The concentrations of the divalent cations (Ca, Mg, Sr, and Ba) in these fluids are significantly higher than those predicted for seawater evaporation. It would seem then, that these elements have been added to the fluids on the flow path. Two major processes can add Ca to a basinal fluid. The first is dolomitization and should be accompanied by an associated decrease in Mg concentrations of the fluids resulting in a Ca/Mg ratio of approximately 10 (Carpenter, 1978). The Ca/Mg ratios of the fluids do vary significantly, however, there is not enough data to assess whether there is a negative correlation between the two elements. The second possibility is that at some point along the flow path the fluid encountered and dissolved gypsum (e.g. Muskeg Formation). Such a process should be associated with an increase in sulphate. Unfortunately, no single mineral phase could be analyzed for both Ca and SO_4 , however, many of the dolomite samples do have elevated SO_4 contents relative to evaporated seawater and this may be a source for at least some of the Ca.

CONCLUSIONS

In terms of the major solutes composition of the fluid inclusions, it is not possible to identify any systematic chemical variations spatially or on the basis of the paragenesis, for most of the study area. The major exception to this is the fluids in the coarse-grained dolomite from the Windy Point area, which have a consistent depletion in K relative to the other samples. It is also important to note that in terms of solute molar ratios, the data from the late-stage calcite phases are comparable to the data from the earlier sulphide and coarse-grained dolomite phases, suggesting that they had a similar origin. However, the late-stage calcite fluids are less saline (also see Turner, 2006), which suggests that the calcite-forming fluids were modified, likely by dilution by a component of meteoric water.

The halogen compositions of the mineralizing fluids indicate that the bulk of the fluids are likely to have originated from highly evaporated seawater. However, two GSR samples are relatively Cl-enriched and may have acquired their salinities from the dissolution of evaporite deposits. Some of the GSR late-stage calcite samples and one matrix dolomite

sample contain a very Br-enriched fluid of enigmatic origin. Some degree of mixing between these end members cannot be ruled out and needs further investigation.

If the bulk of the fluids originated as evaporated seawater, then the Na and Li compositions of the fluids have been modified on the flow path. A loss of Na without a significant gain in K may suggest that if the fluids had interacted with feldspar-bearing sequences, they likely reacted to a small degree with Ca-feldspars rather than K-feldspars. The Li compositions of the fluids may be interpreted as indicating limited interaction with mica or clay-bearing sequences.

The Ca, Sr, and Ba compositions of the fluids are significantly higher than the concentrations expected for evaporated seawater. Ca has been added to the fluids either by dolomitization or by the dissolution of gypsum on the flow path. Currently, it is not possible to distinguish between these possibilities.

REFERENCES

- Banks, D.A., Boyce, A.J. and Samson, I.M.**
2002: Constraints on the origins of fluids forming Irish Zn-Pb-Ba deposits: Evidence from the composition of fluid inclusions; *Economic Geology*, v. 97, p. 471–480.
- Carpenter, A.B.**
1978: Origin and chemical evolution of brines in sedimentary basins; Thirteenth Annual Forum on the Geology of Industrial Minerals, K.S. Johnson and J.A. Russell (eds.); Oklahoma Geological Survey Circular 79, p. 60–77.
- Coniglio, M., Morrow, D.W., and Wilson, N.**
2006: Reassessment of Middle Devonian dolomite, Presqu'île Barrier, Northwest Territories; in *Potential for Carbonate-hosted Lead-zinc Mississippi Valley-type Mineralization in Northern Alberta and Southern Northwest Territories: Geoscience Contributions, Targeted Geoscience Initiative*, (ed.) P.K. Hannigan; Geological Survey of Canada, Bulletin 591.
- Fontes J.C. and Matray J.M.**
1993: Geochemistry and origin of formation brines from the Paris basin, France, 1. Brines associated with Triassic salts; *Chemical Geology*, v. 109, p. 149–175.
- Hannigan, P.K.**
2001: Potential for carbonate-hosted MVT deposits in northern Alberta and southern NWT – A Targeted Geoscience Initiative; in *Program and Abstracts of Talks and Posters, 29th Yellowknife Geoscience Forum, 21–23 November 2001*, p. 22–23.
2002: Potential for carbonate-hosted MVT deposits in northern Alberta and southern NWT – A Targeted Geoscience Initiative; in *Calgary Mineral Exploration Group 11th Annual Calgary Mining Forum, April 24–25, 2002*, p. 25–26.
- Hannigan, P.K., Morrow, D.W., Miles, W.F., Paradis, S., Wilson, N., Grasby, S., and MacLean, B.C.**
2002: Potential for carbonate-hosted MVT deposits in northern Alberta and southern NWT: New data from the Targeted Geoscience Initiative project; in *Program and Abstracts of Talks and Posters, 30th Yellowknife Geoscience Forum, 20–22 November 2002*, p. 23–24.
- Kesler, S.E., Appold, M.S., Martini, A.M., Walter, L.M., Huston, T.J., and Kyle, J.R.**
1995: Na-Cl-Br systematics of mineralizing brines in Mississippi Valley-type deposits; *Geology*, v. 23, p. 641–644.
- Krebs, W. and Macqueen, R.**
1984: Sequence of diagenetic and mineralization events, Pine Point lead-zinc property, Northwest Territories, Canada; *Bulletin of Canadian Petroleum Geology*, v. 32, p. 434–464.
- Kyle, J.R.**
1977: Development of sulfide-hosted structures and mineralization, Pine Point, Northwest Territories; PhD thesis, University of Western Ontario, London.
1981: Geology of the Pine Point lead-zinc district; in *Handbook of Strata-Bound and Stratiform Ore Deposits*, (ed.) K.H. Wolf, Elsevier Publishing Co., Amsterdam, New York, v. 9, p. 643–741.
- Qing H.**
1991: Diagenesis of Middle Devonian Presqu'île dolomite, Pine Point, NWT and adjacent subsurface; Ph.D. thesis, McGill University, 292 p.
- Qing H., and Mountjoy, E.W.**
1994: Origin of dissolution vugs, caverns, and breccias in the Middle Devonian Presqu'île Barrier, host of Pine Point Mississippi Valley-type deposits; *Economic Geology*, v. 89, p. 858–876.
- Rhodes, D., Lantos, E.A., Lantos, J.A., Webb, R.J., and Owens, D.C.**
1984: Pine Point orebodies and their relationship to the stratigraphy, structure, dolomitization and karstification of the Middle Devonian barrier complex; *Economic Geology*, v. 79, p. 991–1055.
- Rice, R.J. and Lonnee, J.**
2006: Mississippi Valley-type (MVT) Pb-Zn potential in Middle and Upper Devonian carbonate deposits of northeastern Alberta, and implications for future exploration based on diagenesis and isotope geochemistry; in *Potential for Carbonate-hosted Lead-zinc Mississippi Valley-type Mineralization in Northern Alberta and Southern Northwest Territories: Geoscience Contributions, Targeted Geoscience Initiative*, (ed.) P.K. Hannigan; Geological Survey of Canada, Bulletin 591.
- Shepherd, T.J., Rankin, A.H., and Alderton, D.H.M.**
1985: *Practical Guide to Fluid Inclusion Studies*; Blackie, Glasgow and London, 239 p.
- Skall, H.**
1975: The paleoenvironment of the Pine Point lead-zinc district; *Economic Geology*, v. 70, p. 22–47.
- Tesler, H.**
1999: Significance of inclusion fluid chemistry for the origin of the Pine Point mineralization, NWT; M.Sc. thesis, University of Leoben, Leoben, Austria.
- Turner, W.A.**
2006: Microthermometric study of fluids associated with Pb-Zn mineralization in the vicinity of the Pine Point mining camp; in *Potential for Carbonate-hosted Lead-zinc Mississippi Valley-type Mineralization in Northern Alberta and Southern Northwest Territories: Geoscience Contributions, Targeted Geoscience Initiative*, (ed.) P.K. Hannigan; Geological Survey of Canada, Bulletin 591.