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Geochemistry of Shale Groundwaters: Results of Preliminary Laboratory Leaching Experiments

K. L. Von Damm
K. O. Johnson

Environmental Sciences Division
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ENVIRONMENTAL SCIENCES DIVISION

GEOCHEMISTRY OF SHALE GROUNDWATERS: RESULTS OF
PRELIMINARY LABORATORY LEACHING EXPERIMENTS

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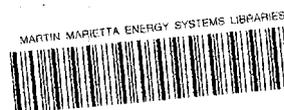
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ABSTRACT

Twelve shales were reacted with distilled water at 20°C and 100°C; the composition of the waters and the mineralogy were determined before and after reaction. The experiments were conducted in a batch mode over a period of approximately 40 days. Major changes occurred in the solution chemistry; in most cases sulfate became the dominant anion while either sodium or calcium was the major cation. The high sulfate is most likely a result of the oxidation of pyrite in the samples. In the 100°C experiments some of the solutions became quite acidic. Examination of the observed mineralogy and comparison to the mineral assemblage calculated to be in equilibrium with the experimentally determined waters, suggests that the acidic waters are generated when no carbonate minerals remain to buffer the groundwaters to a more neutral pH. The pH of shale waters will be determined by the balance between the oxidation of pyrite and organic matter and the dissolution of carbonate minerals. The experimental data are helping to elucidate the chemical reactions that control the pH of shale groundwaters, a critical parameter in determining other water-rock and waste-water-rock interactions and ultimate solute mobility. An experimental approach also provides a means of obtaining data for shales for which no groundwater data are available as well as data on chemical species which are not usually determined or reported.

INTRODUCTION

The Sedimentary Rock Program (SERP) is part of the U. S. Department of Energy's (DOE) Repository Technology Program. The purpose of SERP is to examine sedimentary rocks as possible hosts for a second high level nuclear waste (HLW) repository. In an earlier study (Croff et al. 1987), shales were identified as the sedimentary rock type having the best overall characteristics for hosting an HLW repository.

Brookins and Stow (1986), in the Proceedings of the First Geochemical Workshop on Shale, identified the determination of the organic and inorganic composition of shale groundwaters as a high priority task. Within a repository setting, the chemistry of the groundwater is critical to the repository's performance as it is an important factor in determining canister corrosion behavior and waste form dissolution. Mobility and transport of the radionuclides will also be related to reactions occurring between the groundwater and the waste form, and between the groundwater and the enclosing rock. Temperature increases expected within a repository after emplacement of nuclear waste are expected to induce changes in the groundwater chemistry and rock mineralogy.

The overall objective of this study is to determine the composition of shale groundwaters and to relate the observed differences in chemistries to physical and chemical characteristics of the shales. A variety of methods are being used to achieve this objective. A previous report (Von Damm 1987) provides a data base of shale groundwater chemistries for various shale formations in the United States. The data were

obtained primarily from the U.S. Geological Survey WATSTORE data base, which contains groundwater data on a formation specific basis for the United States. Data were available for a limited number of formations and the chemical data were not always complete. This report details the preliminary results of another approach that is being used to obtain additional data - the experimental reaction of various shales with water in the laboratory. The experiments have the potential for providing information on groundwater chemistry for formations for which no data were available, and data on aqueous species, including dissolved organics, which were not included in WATSTORE. The experimental approach also provides a way to obtain data on changes that may occur in shale groundwater chemistry and mineralogy as a result of changes in temperature that are expected in a repository setting. The experimental leaching of shales has applications for a national survey of shales and their groundwaters, when no WATSTORE or other field data are available. The experiments reported herein are preliminary in nature and were undertaken to determine if the experimental approach is a viable one for providing data on shale groundwater chemistry. Results and additional discussion are also presented in Johnson (1986).

METHODS

Twelve shale samples, including nine from various members of the Pierre Formation, were reacted with distilled water at room temperature (-20°C) and -100°C and the changes in the solution chemistry and mineralogy were determined. The shale samples were chosen to include the wide compositional and mineralogical range observed for this rock type. The shales that were reacted include samples from the Green River Formation (a carbonaceous shale), the Pumpkin Valley Shale of the Conasauga Group (an illitic shale), two Devonian shales which are rich in organic carbon (West Virginia Rhinestreet and Upper Dowlletown Member of the Chattanooga Shale), and the Pierre Shale (a smectitic shale). The Pierre Shale samples were from the DeGrey Member, the Elk Butte Member (two samples), the Mobridge Member (two samples), the Verendrye Member, and the Virgin Creek Member (two samples). All samples were obtained from drill core rather than outcrop to minimize alteration and to obtain a more representative sample of the formation at depth. Prior to the start of the leaching experiments, the samples were ground to a maximum grain size of 0.15 mm using a shatterbox and mortar and pestle.

Twenty-five grams of shale and 100 ml of distilled water were reacted in linear polyethylene bottles at 20°C and in teflon bottles at 100°C , resulting in a water-to-rock ratio of 4:1 on a mass basis. The headspace in the bottles was purged with nitrogen gas prior to the start of the reaction, but oxygen was able to diffuse across the polyethylene and teflon as a result of the concentration gradient during the course of the experiment. The experiments were run in a batch mode for a total

of 43 days for the 20°C experiments and 38 days for the 100°C experiments. Because a batch mode was used, it cannot be determined if the reactions reached equilibrium or steady-state. The 20°C samples were agitated for a total of 29 hours and the 100°C samples were agitated for a total of 23 hours spread over the course of the experiment.

The mineralogy of the samples was determined by quantitative x-ray diffraction. Unreacted shale samples as well as samples collected at the termination of the low and high temperature experiments were x-rayed. The x-ray diffraction work was done at the South Dakota School of Mines by B. Davis and the results have approximately a 10% error for the major mineral components and a higher error for minerals with very low abundances (Davis and Johnson 1982). The mineralogic data for the unreacted shale samples is given in Table 1, those for the low temperature reaction in Table 2, and those for the high temperature reaction in Table 3. Duplicates were run for several of the shale samples, but in some cases a large variation is observed in the quartz content between the unreacted and high and low temperature reacted samples. This may imply initial inhomogeneities among the various sample splits.

The chemical composition of the shales was determined on the starting materials, but not on the reacted shales (Table 4). These analyses were done by Travis Laboratory in Rapid City, South Dakota. The metals were analyzed by atomic absorption, bicarbonate was by alkalinity titration, and chloride and sulfate were by gravimetric titration. Total carbon was by weight loss upon high temperature oxidation and total sulfur by oxidation and sulfate determination. Generally each elemental analysis has a precision of $\leq 10\%$.

Table 1. Mineralogy of shale (in percent) before leaching.

	DeGrey	Elk Butte 1	Elk Butte 2	Mobridge 1	Mobridge 2	Verendrye	Virgin Creek 1	Virgin Creek 2	Green River	Pumpkin Valley	W. Va. Rhinstreet	Chatta
Analcite									8.3			
Bassanite		1.5					0.63		1.2			
Calcite		17	9.1	19	56	1.7	6.4		6			
Chlorite	1.5				2.3					20	20	
Dolomite									44			
Glauconite												
Gypsum	1.1		1.2		2.5							
Illite	5.5	14	11	14	3.5	27	35	12	3.9	53	31	21
Jarosite			0.71									
Kaolinite		7.7	4.1	8.7	1.9	2.1	0.67	1.5				1.4
Limonite	5.1											
Montmorillonite	31	26	32	25	13	33	41	42				20
Oligoclase	4.9	4.5	5.3	3.9	2.3	4.9	3.6	3.4	7.9	3.5		4.6
Orthoclase	4.3	4.6	4.8	4.1	1.8	4.5	4.8	3.8	5.9			5.8
Pyrite	1.1	0.72	0.9	0.59	1.1	0.74	1	1.1		2.2	0.43	6.5
Quartz	45	24	26	25	11	25	14	35	18	21	21	41
Siderite			1.2	0.48			0.31	0.47		19		
Stilbite			3.8									

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Table 2. Mineralogy of shale (in percent) after low temperature leaching.

	DeGrey	Elk Butte 1	Elk Butte 2	Hobridge 1	Hobridge 2	Verendrye	Virgin Creek 1	Virgin Creek 2	Green River	Pumpkin Valley	W. Va. Rhinstreet	Chattanooga
Analcite	+1	+	+	+		+	•	•	9.1•	+	•	+
Bassanite						1.1						
Calcite	+	17+	9.6+	16+	57+	1.3+		+	6.4+		6.1+	+
Chlorite	1.7+	+	+			+			+	18+	20+	+
Dolomite	1.6+	+	+	+	+	+		+	46+	+	+	+
Glauconite										5	5	
Gypsum		+	+	+	0.43+			+			+	
Illite	6.4+	6.9+	10+	5.9+	2.1+	8.8•	6.7+	8.8+	1.7•	31+	28+	23+
Jarosite			0.64									
Kaolinite	+	6.9+	3.6+	7.4+	2.4+	2.7+		3.8+	+	+	•	1.4+
Limonite	5.6											
Montmorillonite	25+	28+	26+	31+	16+	34+	+55	29+	3.2+	27+	+	22+
Oligoclase	6.3+	5.1+	6.8+	5.3+	2.7	5.3+	2.4+	1.9+	9.1+	3.5+	+	5.1+
Orthoclase	5.2+	3+	4.1+	3.7+	1.7+	5+	+	3.9+	5.1+	0.55+	2.4+	6.8+
Pyrite	0.85+	1.1+	1.3+	0.81+	1.9+	1+	2.4+	2.8+	+	1.1+	0.28+	7+
Quartz	45+	32+	27+	30+	15	41+	33+	50+	19+	14+	22+	34+
Siderite			1.2	0.5					+	+	21+	
Stilbite	1.9		8.7									

1 + = shale leachate water from experiment is calculated to be saturated or supersaturated with mineral indicated.

Table 3. Mineralogy of shale (in percent) after high temperature leaching.

Mineral	DeGrey	Elk Butte 1	Elk Butte 2	Mobridge 1	Mobridge 2	Verendrye	Virgin Creek 1	Virgin Creek 2	Green River	Pumpkin Valley	W. Va. Rhinestreet	Chattanooga
Analcite	+ ¹	+				+			7.5			
Bassanite		+	+	+	+	+		*			+	+
Calcite	+	13+	5.4+	9.3+	54+	0.54+			6.2+		*	
Chlorite	1.1+	+	+	*	+	+			+	3.2	1.6+	
Dolomite	1.9+	+	+	+	*	+			46+		+	
Glauconite										0.83	5.3	
Gypsum	+	+	0.4+	+	1.7+	+	*	*			+	*
Illite	12+	6.2+	11+	6.5+	3.2+	7.4+	7.8	7.5+	2.5+	26+	24+	43+
Jarosite			0.25									0.28
Kaolinite	+	7.7+	5.0+	6.7+	2.0+	2.9+	*	+	+	4.0+	15+	+
Limonite		2.6	2.6			3.6				4.3	4.1	
Montmorillonite	36+	24+	36+	31+	19+	37+	51+	33+	3.7+	37+	+	+
Oligoclase	5.8+	4.4+	7.9+	6.5	3	6.3+	8.2	4.6	7.7	3.1	4.4	7.7
Orthoclase	3.8+	2.8+	4.6+	3.8+	2.0+	4.0+		3.5+	9.7+	0.31+	2.6+	6.0
Pyrite	+	0.78+	0.41+	0.53+	0.75+	+	0.53+	0.84+	+	1.2+	+	5.5+
Quartz	39+	38	26	33	13	37+	33+	50+	17+	15+	41	37+
Siderite	+	+	0.65+	+	+	0.66+					1.6+	
Stilbite												

¹ + = shale leachate water from experiment is calculated to be saturated or supersaturated with mineral indicated.

Table 4. Chemical composition of unreacted shale.

	CO ₃	SO ₄	Ca	Mg	K	Na	Al	Fe	Mn	SiO ₂	S ¹	TOC ²
	mol/kg	mol/kg	mol/kg	mol/kg	mol/kg	mol/kg	mol/kg	mol/kg	mol/kg	mol/kg	mol/kg	mol/kg
DeGrey	0.0692	0.00344	0.0357	0.00206	0.00639	0.0126	0.268	0.0546	0.00928	1.02	0.103	0.157
Elk Butte 1	0.114	0.00583	0.109	0.00329	0.0159	0.104	0.322	0.0707	0.000127	0.929	0.178	0.0791
Elk Butte 2	0.0845	0.0120	0.0876	0.0325	0.0146	0.0457	0.314	0.0784	0.000873	1.00	0.184	0.179
Hobridge 1	0.312	0.00635	0.125	0.00658	0.0128	0.0422	0.298	0.0654	0.000728	0.947	0.235	0.0549
Hobridge 2	0.0699	0.0263	0.444	0.000123	0.0102	0.000043	0.176	0.0820	0.000036	0.593	0.105	0.316
Verendrye	0.0732	0.00406	0.0504	0.00453	0.00870	0.0239	0.314	0.0663	0.00619	1.29	0.129	0.0849
Virgin Creek 1	0.0153	0.0144	0.0549	0.269	0.0256	0.126	0.314	0.0546	0.000200	0.975	0.0958	0.0716
Virgin Creek 2	0.0459	0.0178	0.0389	0.114	0.0320	0.135	0.268	0.0704	0.00273	1.06	0.135	0.0674
Green River	0.266	0.00156	0.304	0.00535	0.0161	0.0826	0.177	0.0363	0.000364	0.771	0.129	0.757
Pumpkin Valley	0.0549	0.00750	0.0274	0.0119	0.0174	0.0565	0.482	0.109	0.000182	1.16	0.154	0.0516
W. Va. Rhinestreet	0.0719	0.00552	0.0117	0.00864	0.0151	0.0652	0.371	0.101	0.00109	0.932	0.180	0.0500
Chattanooga	0.0559	0.00448	0.00649	0.000288	0.0141	0.0478	0.239	0.0775	0.000018	1.09	0.236	0.522

¹ Total sulfur minus sulfate.

² Total organic carbon.

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The composition of the leachate solutions was determined at the termination of the experiments. Distilled water was used as the starting fluid in these experiments and no attempt was made to buffer the pH. Although distilled water is geologically unrealistic, many shale waters are relatively dilute, and the essentially zero ionic strength starting solutions made it easier to observe changes in the solution chemistries. The composition of the solutions was determined by the same methods as were used on the shales, with the same precision. Results for iron, manganese, and aluminum were, in most cases, close to the detection limit of the method and should be viewed as upper limits. The composition of the fluids is given in Table 5 for the low temperature experiments and in Table 6 for the high temperature experiments, along with the calculated charge balances.

Table 5. Chemical composition of low temperature shale leachate waters.

Data Label	HCO ₃ mmol/kg	Cl mmol/kg	SO ₄ mmol/kg	Ca mmol/kg	Mg mmol/kg	K mmol/kg	Na mmol/kg	Al mmol/kg	Fe mmol/kg	Mn mmol/kg	SiO ₂ mmol/kg	pH	Tot. Cat meq/kg	Tot. An. meq/kg	Tot.Cat./ Tot. An.	
DeGrey	1	6.97	2.12	9.27	0.873	0.411	0.895	2.17	0.0556	0.00448	0.0109	0.0832	7.4	5.84	27.61	0.211
Elk Butte 1	2	4.42	0.705	18.9	12.4	2.72	2.17	6.52	0.0556	0.00448	0.0582	0.0832	7.4	39.12	43.02	0.909
Elk Butte 2	3	4.18	0.987	20.3	13.2	2.72	1.66	8.05	0.0556	0.00448	0.0609	0.0832	7.4	41.89	45.77	0.915
Mobridge 1	4	4.92	1.41	17.6	12.4	2.72	2.17	6.52	0.0556	0.00448	0.0618	0.0832	7.5	39.13	41.31	0.943
Mobridge 2	5	5.82	1.41	31.2	25.1	3.39	2.05	8.05	0.0556	0.00448	0.00818	0.0832	7.4	67.30	69.69	0.966
Verendrye	6	5.49	1.69	11.3	1.25	0.432	1.02	2.17	0.0741	0.00448	0.0136	0.108	7.4	6.82	29.88	0.228
Virgin Creek 1	7	1.72	1.41	23.3	3.56	1.54	2.05	3.91	0.0556	0.0179	0.0236	0.381	6.5	16.41	49.77	0.330
Virgin Creek 2	8	4.02	1.55	27.7	12.4	4.07	4.48	3.70	0.0556	0.00448	1.40	0.381	6.6	44.00	60.95	0.722
Green River	9	9.18	0.987	0.729	1.06	1.71	0.384	4.35	0.0556	0.00448	0.00273	0.0832	8.2	10.45	11.62	0.899
Pumpkin Valley	0	4.59	5.64	0.989	0.125	0.638	2.69	8.48	6.71	0.371	0.00273	5.48	7.8	33.56	12.21	2.749
W. Va. Rhinestreet A		5.16	1.69	0.208	1.50	0.720	1.15	4.57	0.0741	0.00448	0.00273	0.108	7.9	10.39	7.27	1.429
Chattanooga	8	5.00	2.68	0.312	0.873	0.411	1.53	6.96	0.0741	0.00448	0.00273	0.221	7.1	11.30	8.30	1.361

Table 6. Chemical composition of high temperature shale leachate waters.

Data Label	HCO ₃ mmol/kg	Cl ₁ mmol/kg	SO ₄ mmol/kg	Ca mmol/kg	Mg mmol/kg	K mmol/kg	Na mmol/kg	Al mmol/kg	Fe mmol/kg	Mn mmol/kg	SiO ₂ mmol/kg	pH	
DeGrey	1	5.16	0.846	20.4	8.36	1.85	3.07	29.4	0.102	0.00985	0.596	0.724	7.1
Elk Butte 1	2	5.98	0.564	23.5	20.7	4.53	3.32	8.26	0.130	0.00806	0.0564	0.340	7.5
Elk Butte 2	3	5.16	0.776	22.5	19.2	2.47	4.60	10.4	0.0352	0.00448	0.0646	0.340	7.5
Hobridge 1	4	5.00	0.635	19.4	17.6	2.67	2.81	8.26	0.0537	0.00448	0.0273	0.340	7.6
Hobridge 2	5	7.21	0.846	30.9	26.2	2.47	2.17	8.70	0.0185	0.00448	0.00273	0.275	7.7
Verendrye	6	5.00	0.564	20.5	11.5	1.65	3.07	30.7	0.0352	0.00806	0.139	0.549	7.3
Virgin Creek 1	7	0.164	0.395	29.6	7.24	4.53	3.32	31.3	0.315	1.40	0.0537	2.17	3.4
Virgin Creek 2	8	1.07	0.423	38.9	12.4	7.61	6.65	33.1	0.185	0.492	2.11	1.12	4.5
Green River	9	0.164	0.564	7.18	2.12	0.823	0.639	16.1	0.0185	0.00448	0.00273	0.474	7.7
Pumpkin Valley	0	0.819	6.21	24.3	3.99	13.0	5.88	19.6	0.130	0.215	0.264	1.12	4.6
W. Va. Rhinestreet A	A	5.57	0.987	17.3	14.1	5.14	2.30	6.96	0.0185	0.00448	0.0618	0.275	7.5
Chattanooga	B	0.164	1.35	30.5	12.7	6.17	4.60	8.70	0.797	7.18	0.146	2.17	3.4

RESULTS AND DISCUSSION

Change in Chemistry of the Waters

The change in the chemistry of the waters from the low temperature experiments (Table 5) shows that major changes have occurred from the starting solution of distilled water. Maximum concentrations of the dissolved species from the low temperature experiments are as follows: $\text{HCO}_3 = 9.18$ mmoles/kg; $\text{Cl} = 5.64$ mmoles/kg; $\text{SO}_4 = 31.2$ mmoles/kg; $\text{Ca} = 25.1$ mmoles/kg; $\text{Mg} = 4.07$ mmoles/kg; $\text{K} = 4.48$ mmoles/kg; $\text{Na} = 8.48$ mmoles/kg; $\text{Al} = 6.7$ mmoles/kg; $\text{Fe} = 0.37$ mmoles/kg; $\text{Mn} = 1.40$ mmoles/kg and $\text{SiO}_2 = 5.48$ mmoles/kg. As noted above the Al, Fe and Mn data should be used with caution. The pH of these solutions remained close to neutral. These solutions fall within the observed concentration ranges for shale groundwaters (Von Damm 1987). In many of the waters from the low temperature experiments SO_4 is the most abundant anion (Table 5 and Fig. 1), while SO_4 is rarely the most abundant anion in actual shale groundwaters based on WATSTORE data (Von Damm 1987). As in the shale groundwaters, either Na or Ca is the major cation.

In the high temperature experiments (Table 6) the following maximum concentrations of the dissolved species are observed: $\text{HCO}_3 = 7.21$ mmoles/kg; $\text{Cl} = 6.21$ mmoles/kg; $\text{SO}_4 = 38.9$ mmoles/kg; $\text{Ca} = 26.2$ mmoles/kg; $\text{Mg} = 13.0$ mmoles/kg; $\text{K} = 6.65$ mmoles/kg; $\text{Na} = 33.1$ mmoles/kg; $\text{Al} = 0.79$ mmoles/kg; $\text{Fe} = 7.2$ mmoles/kg; $\text{Mn} = 2.1$ mmoles/kg; and $\text{SiO}_2 = 2.17$ mmoles/kg. These values are, in general, somewhat higher than those values observed in the lower temperature experiments, except in the

Table 7. Relative ion abundances in low and high temperature shale leachate waters.

	20°C Experiments	100°C Experiments
DeGrey	SiO ₂ >SO ₄ >HCO ₃ >Cl>Na SO ₄ >HCO ₃ >Cl;Na>K>Ca>Mg	Na>SO ₄ >HCO ₃ SO ₄ HCO ₃ >Cl;Na>Ca>K>Mg
Elk Butte 1	SO ₄ >Ca>Na SO ₄ >HCO ₃ >Cl;Ca>Na>K>Mg	SO ₄ >Ca>Na SO ₄ >HCO ₃ >Cl;Ca>Na>K>Mg
Elk Butte 2	SO ₄ >Ca>Na SO ₄ >HCO ₃ >Cl;Ca>Na>Mg>K	SO ₄ >Na>Ca SO ₄ >HCO ₃ >Cl;Na>Ca>K>Mg
Mobridge 1	SO ₄ >Ca>Na SO ₄ >HCO ₃ >Cl;Ca>Na>K>Mg	SO ₄ >Ca>Na SO ₄ >HCO ₃ >Cl;Ca>Na>K>Mg
Mobridge 2	SO ₄ >Ca>Na SO ₄ >HCO ₃ >Cl;Ca>Na>Mg>K	SO ₄ >Ca>Na SO ₄ >HCO ₃ >Cl;Ca>Na>K>Mg
Verendrye	SO ₄ >HCO ₃ >Na SO ₄ >HCO ₃ >Cl;Na>K>Ca>Mg	Na>SO ₄ >Ca SO ₄ >HCO ₃ >Cl;Na>Ca>K>Mg
Virgin Creek 1	SO ₄ >Na>K SO ₄ >Cl>HCO ₃ ;Na>K>Ca>Mg	Na>SO ₄ >Cl SO ₄ >Cl>HCO ₃ ;Na>Ca>K>Mg
Virgin Creek 2	SO ₄ >Ca>K SO ₄ >HCO ₃ >Cl;Ca>K>Na>Mg	Na>SO ₄ >K SO ₄ >HCO ₃ >Cl;Na>K>Ca>Mg
Green River	HCO ₃ >Na>Mg HCO ₃ >Cl>SO ₄ ;Na>Mg>Ca>K	Na>SO ₄ >Ca SO ₄ >Cl>HCO ₃ ;Na>Ca>K>Mg
Pumpkin Valley	Na>Cl>SiO ₂ >HCO ₃ Cl>HCO ₃ >SO ₄ ;Na>K>Mg>Ca	Na>SO ₄ >Mg SO ₄ >Cl>HCO ₃ ;Na>Mg>K>Ca
W. Va. Rhinestreet	HCO ₃ >Na>Cl HCO ₃ >Cl>SO ₄ ;Na>Ca>K>Mg	SO ₄ >Ca>Na SO ₄ >HCO ₃ >Cl;Ca>Na>Mg>K
Chattanooga	Na>HCO ₃ >Cl HCO ₃ >Cl>SO ₄ ;Na>K>Ca>Mg	SO ₄ >Na>Ca SO ₄ >Cl>HCO ₃ ;Na>Ca>Fe>K>Mg

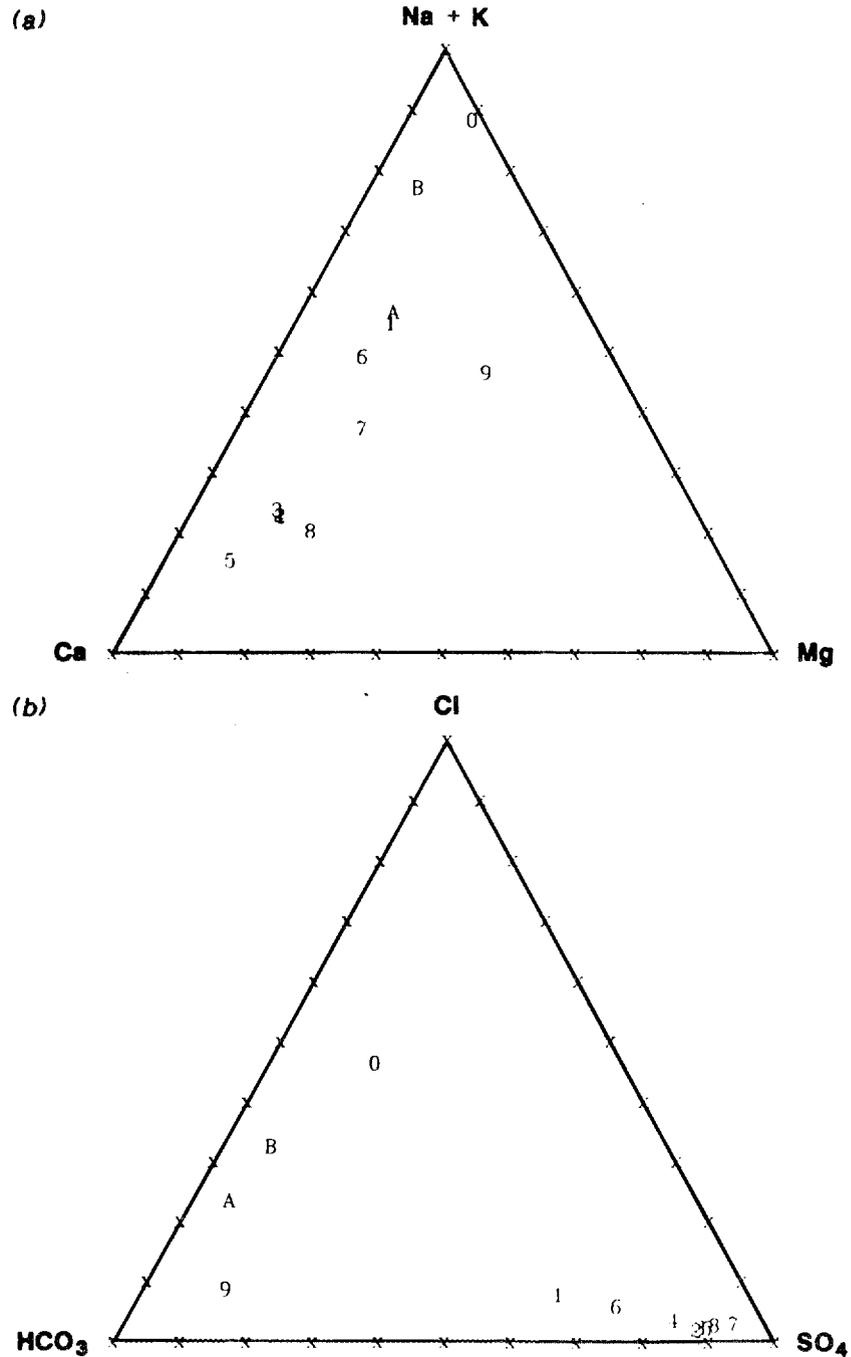


Fig. 1. Ternary plots for the low temperature leachate shale waters; (a) cations, (b) anions. Plot symbols are the formation data labels as listed in Table 5.

case of HCO_3 . A major change has occurred in the pH of several of these waters and they are quite acid, with a minimum pH = 3.4, while others remain close to neutral. There appears to be a correlation between the dissolved SiO_2 content and the pH; those waters with the lowest pH values have the highest dissolved SiO_2 concentrations. Sulfate is the major anion in every case (Table 6 and Fig. 2), while Na or Ca may be the major cation. In many of the waters, K is a more abundant cation than under the lower temperature conditions. The Green River Shale leachate contains the lowest concentration of K, which is in good agreement with the lower abundance of clays, a source of K in this shale. It may also be noted that it is the Pumpkin Valley Shale which, in both the low and high temperature experiments, has released the most Cl to solution. This is in good agreement with the high chlorinity solutions found within this formation in the area in which the core was taken.

Although no major difference is observed in the range of absolute abundances of various ions between the experimental and WATSTORE results, a major difference is seen in the relative abundances. Many of the experimental waters have $\text{SO}_4 \gg \text{Cl}$ and $\text{Ca} \gg \text{Na}$, while Cl and Na are often the most abundant species observed in groundwaters, and SO_4 is rarely more abundant than both HCO_3 and Cl. Previous experimental studies have also found SO_4 to be the most abundant anion in "shale" waters (Schmidt 1973; Weaver and Beck 1971; Dickey and Baharlou 1973) but the available field data do not support this (Von Damm 1987). The SO_4 is most likely formed as an experimental artifact as the result of oxidation of pyrite in the shale, possibly prior to and during the

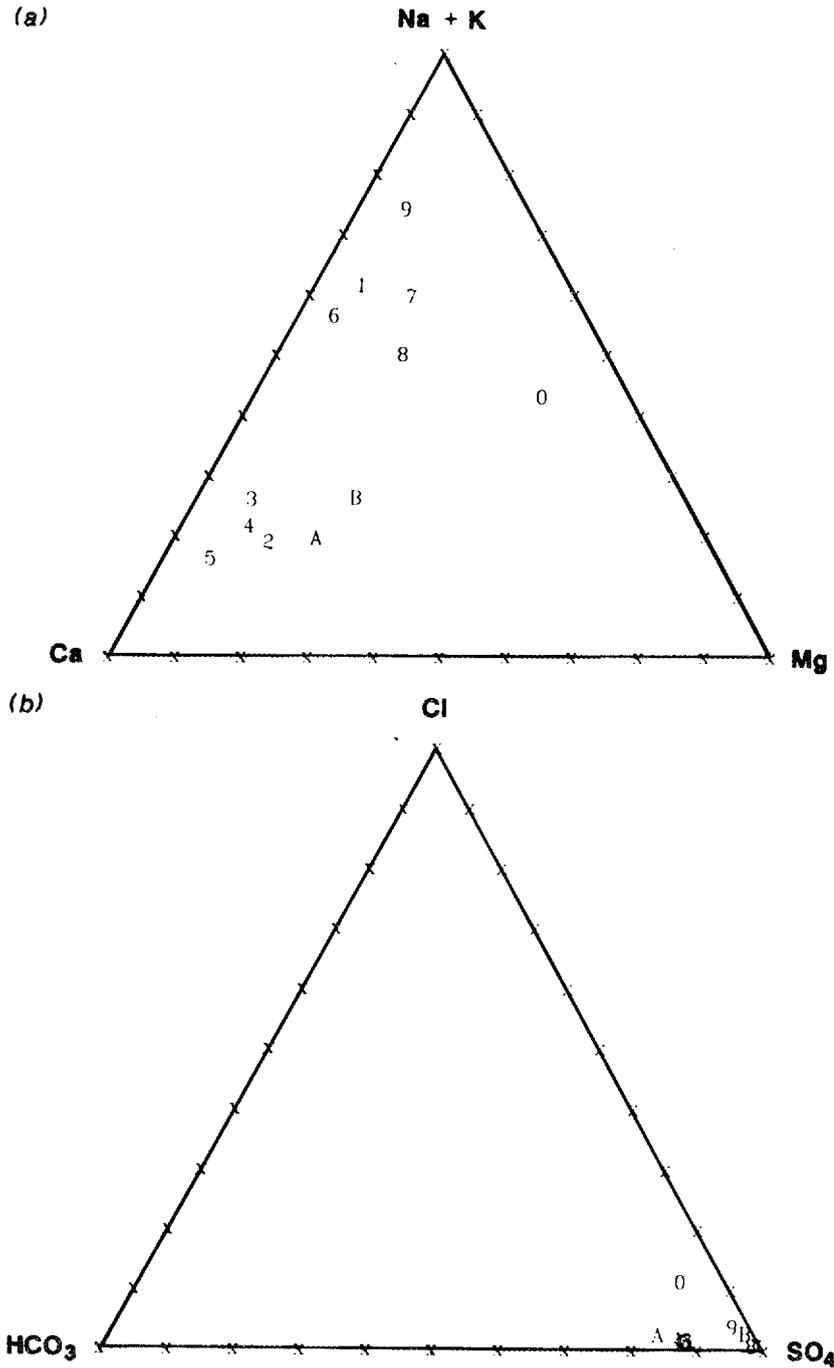


Fig. 2. Ternary plots for the high temperature leachate shale waters; (a) cations, (b) anions. Plot symbols are the formation data labels as listed in Table 6.

experiment. It can be seen that the leachates from the Green River Shale experiments contain the lowest SO_4 values, in agreement with the virtual absence of pyrite in this formation. Although an effort was made to fill the headspace in the experimental bottles with nitrogen, it is obvious from these results that more stringent methods need to be taken to exclude oxygen from the experiments if a more representative water is to be produced. Alternatively, it may be argued that an experiment into which oxygen has been introduced may be more representative of the conditions that would occur in a shale repository where oxygen would be introduced during the construction and pre-closure period.

The water samples obtained from these experiments, both low and high temperature, were also examined for organic acids and preliminary results suggested that some acetate (at the $100 \text{ } \mu\text{moles/kg}$ level) may be produced during the higher temperature experiments from some of the more organic rich shales. These results are very preliminary and need to be confirmed with further work. They do suggest that dissolved organic ions, which could be important to radionuclide transport, may be produced from the interaction of shales and water under elevated temperature conditions.

Change in Mineralogy of the Solids

The starting mineralogy, and the mineralogy of the low and high temperature reactants are given in Tables 1, 2 and 3, respectively. The most consistent change that occurs is the loss of calcite and the formation of limonite in the high temperature experiments. Results from the x-ray diffraction analyses are compared to the mineralogy predicted

to be in equilibrium with the solutions using the geochemical modeling code EQ3NR (Wolery 1983). Minerals with which the solutions are calculated to be saturated or supersaturated are noted by a "+" in Tables 2 and 3. As no redox data were available, the EQ3NR code was run twice for each sample - one run assuming that the solution was in equilibrium with air at the relevant temperature and a second run assuming that the concentration of H₂S in the solutions was equal to 0.001 times the measured SO₄ value. This is similar to the ratio of these two species observed in several shale groundwaters. It also suggests a total H₂S concentration in line with the observation that no H₂S was smelled at the termination of the experiments. The major difference between the results of the two calculations is the saturation or supersaturation of pyrite in the reducing case. The results of the reducing case are given in the Tables 2 and 3. Many additional aluminosilicates were found to be saturated or supersaturated in the calculations than were observed in the x-ray data as a result of three factors: (1) poor quality of aluminum and aluminosilicate thermodynamic data, (2) poor quality of aluminum data for the solutions due to high detection limits, and (3) possible low abundance or poor crystallinity of some of these minerals, making them undetectable by x-ray diffraction. Only results for those minerals also found in the x-ray analyses are included in the Tables 2 and 3. Limonite and glauconite are not in the EQ3NR mineral data base and hence could not be compared, although they were observed with x-ray diffraction. Although the x-ray data suggest a decrease in the abundance of illite and pyrite in the higher temperature experiments, the thermodynamic calculations suggest that these minerals should still

be present and are several orders of magnitude supersaturated in the solutions.

It has already been stated that there is a relationship between the SO_4 contents of the experimental solutions and the pyrite contents of the shales. A major result is the observation of an important relationship between the pH of the solutions and the presence or absence of calcite and/or dolomite in the shales. As a result of the high temperature experimental conditions, those shales which have calcite and/or dolomite present, as observed in either x-ray diffraction or predicted thermodynamically, have produced solutions with a pH close to neutral. Solutions that have a very acid pH come from shales in which carbonate minerals are no longer present. Although those shales that have produced acidic leachates all contain pyrite, most of the shales that did not produce acidic leachates also contain pyrite, suggesting that the presence or absence of pyrite is not the most critical parameter in determining the acidity of the solutions. Hence it is the presence or absence of carbonate minerals that is critical to buffering the pH of the coexisting waters. Although it cannot be quantitatively observed in this data set, the oxidation of pyrite or organic matter will produce protons and will lead to acid solutions; hence, there is a balance to be obtained or maintained between these oxidation reactions and the buffering ability of carbonate minerals that will ultimately determine the pH of the solutions.

CONCLUSIONS AND SUGGESTIONS FOR FURTHER WORK

The results from these preliminary leaching experiments have shown that solutions can be produced from laboratory interactions between shales and water that are close in composition to those observed in shales. The major difference that exists between the laboratory and field data is the high levels of SO_4 observed in the experimental results. This suggests that much care is needed in controlling the availability of oxygen during the course of the experiment if representative data are to be obtained. The experimental data are helping to elucidate controls on the pH of shale waters, which will be a critical parameter in determining other water-rock and waste-water-rock interactions and ultimately, solute mobility. The experiments provide a way to obtain data for formations for which no field data are available and could be used for qualitative survey studies. These experiments also provide data for inorganic and organic species, which are not routinely determined or reported for field analyses but which may be of importance in a repository setting. If major changes in solution chemistry are anticipated for whatever reason in a repository setting, experimental studies also permit the reaction of the rock, shales in this case, with various solutions chemistries at ambient and elevated temperatures and the observation of the change in the rock composition and mineralogy, as well as the change in solution chemistry.

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